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Environmental Research & Technology

Research Article

Ionic status of ground and surface water at Madaripur in Bangladesh for drinking and agricultural uses

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ABSTRACT

Water is essential for livestock consumption, drinking, agriculture, and aquaculture. Pond and river are considered to be self-contained, landlocked ecosystems that are often teeming with rich vegetation and diverse organismal life. Groundwater is also involved with drinking and irrigation. Water contains different organic and inorganic components. The water samples were investigated for Mg, pH, Na, EC, Ca, K, S, and P ion at Rajoir Upazila on Madaripur district in Bangladesh to know the water quality of this Upazila for various uses from November 2020 to October 2022. During the study period, Surface water (pond water) had an average pH higher than that of river and tube-well water. The average pH of Pond water was 7.54 at Bajitpur and Raajoir Union. The present research also showed the Electrical Conductivity (EC) ranged from 280 to 1451.67 µScm-1. For irrigation, the Sodium Absorption Ratio (SAR) is the key feature. River water had the lowest SAR (0.567) and Groundwater had the highest (8.67 MeL-1). Groundwater had the highest SSP value (88.9%), while river water had the lowest (24.8%). Almost all the ground and surface (pond and river) water samples were slightly alkaline and appropriate for drinking, irrigation, livestock farming, and aquaculture.

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INTRODUCTION

Quality water is essential for saving lives, and agricultural production as well as to build up a healthy nation. The earth's surface is covered in water to a degree of about 80%. Merely 33,400 m^3 of the predictable 1,011 million km^3 of entire water on Earth are suitable for home, industrial, agricultural, and drinking purposes [1]. In Bangladesh, there are roughly 1.3 million ponds spread across 147000 hectares. With careful excavation and use, these ponds can be transformed into possible miniature reservoirs for fish farming or irrigation [2]. Rivers, streams, and lakes conveniently contain freshwater, which up to only 0.01% of the earth's total water [3]. The amount of fresh water decreased

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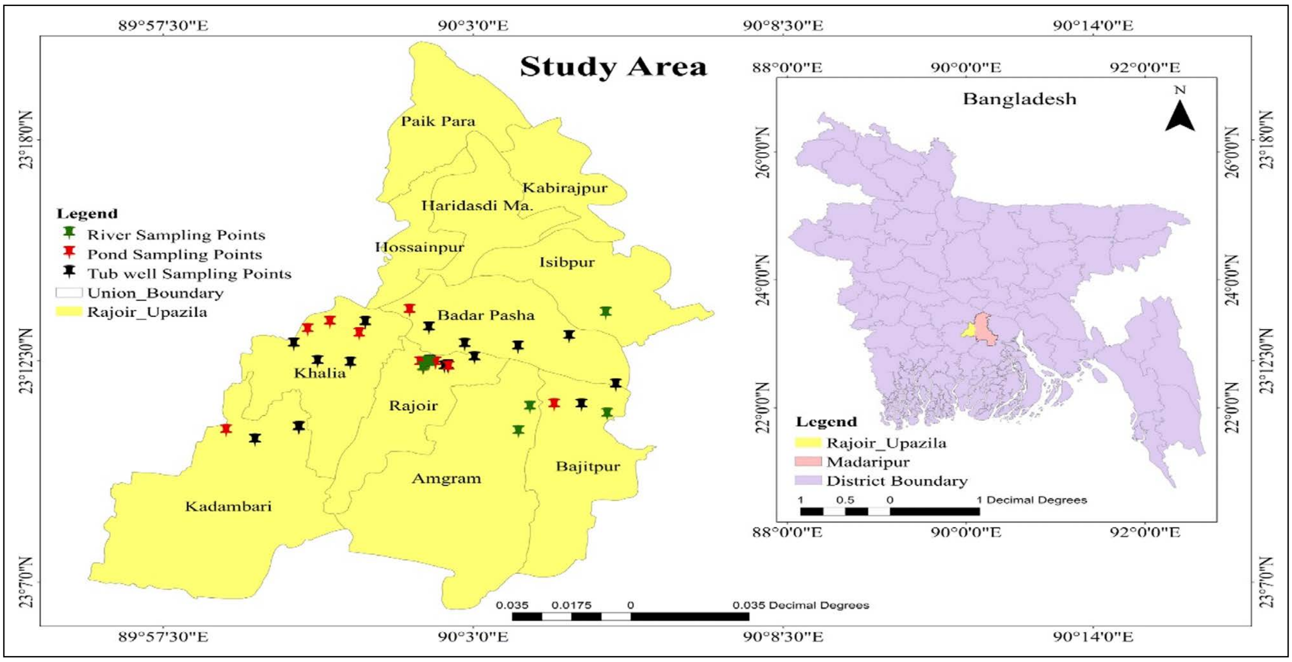

Figure 1. Map of sampling location of Rajoir Upazila.

and the amount of undrinkable water increased due to rising sea levels. Bangladesh is a riverine and plane country with large inland aquatic bodies, containing some of the largest rivers in the world. Due to its peculiar geographic features, Bangladesh is highly vulnerable [2]. Both humans and other animals are harmed by poor quality or contaminated water. Nonetheless, there are trace amounts of organic matter and ions of a few other elements, including Li, B, Ba, Si, Zr, Ti, V, Cr, Mn, Pb, F, Mo, Co, Se Ru, Br, I, Cu, Be, Ni, Ce, As, Bi, P, and Sb [4]. The chemical composition of water is one of the primary factors influencing its quality [5]. Ionic toxicity can arise from using poor quality water for drinking, irrigation, aquatic culture, livestock and poultry consumption, and other uses [6]. In the aforementioned conditions, studies were carried out in Rajoir Upazila of the Madaripur district to evaluate the water quality for agriculture and to compare the ionic status of river, groundwater, and pond water. In addition, to evaluate water sources are suitable for livestock feed, aquaculture, drinking, and irrigation. No comprehensive study was performed in this locality related to the Ionic status of drinking and irrigation water, which is essential for this area.

MATERIALS AND METHODS

According to data from 2016 to 2024, Madaripur district has a maximum temperature of 91°F and a minimum temperature of 80°F with an average rainfall of 65% at summer. On the other hand, the maximum and minimum temperatures during the fall season are 89°F and 63°F, respectively while the average rainfall is 34.5% (source: weather spark).The chemical analyses included Total Dissolved Solids (TDS), Electrical Conductivity (EC), Total Permanent Hardness (TPH), Residual Sodium Carbonate (RSC), pH, Sodium Adsorption Ratio (SAR), Soluble Sodium Percentage (SSP), calcium (Ca), sodium (Na), potassium (K), phosphorous (P), magnesium (Mg), sulphur (S) etc.

Collection of Water Samples

Twenty one (21) ground water samples, eleven (11) pond water and eight (8) river water samples were taken from various points of Rajoir Upazila at Madaripur district in Bangladesh (Fig. 1) and to know the water quality of this Upazila for various uses during November 2020 to October 2022 following the water sampling methods as defined [7]. Water samples were collected in 500 ml plastic bottles. These bottles were cleaned with dilute hydrochloric acid, and washed with tap water and distilled water. Before sampling, containers were again rinsed 3 to 4 times with the water to be sampled. In the case of the river, water samples were drawn from the mid-stream and a few centimeters below the surface. The collected samples were tightly sealed immediately to avoid exposure to air. After proper marking and labeling, the water samples were carried to the Laboratory of the Department of Agricultural Chemistry, PSTU for testing and kept in a clean, cool, and dry place. Samples were filtered through Whatman No. l filter paper to remove undesirable solid and suspended materials. The analysis was conducted as soon as possible on arrival at the laboratory

Analytical Methods of Water Analyses

The pH value of water samples was evaluated using a pH meter (Brand: WTW pH 522) according to Singh & Parwana [8]. A conductivity meter (Brand: WTW LF 521) was used to measure the EC of a sample of water [9]. TDS was measured using the Chopra and Kanwar [10] method. The samples of pond water were tested for calcium content using the EDTA Titrimetric method. The authors of this analytical method were Singh and Parwana (1999) [8] and

Table 1. Maximum recommended concentrations of various chemical ions for irrigation and drinking water

Name of elements	Drinking		Irrigation
pH	Existing average limits	Recommended maximum limits	Maximum limits
EC	6.50–7.50	6.5–9.0	6.5–8.4
Ca	50–600 µScm-1 (Suitable), more than 600 µScm^{-1}, (Harmful)		50–500 µScm^{-1} (Suitable)
Mg	Less than 2.50 meL^{-1}	Less than 3.75 meL^{-1}	800 mgL^{-1}
Na	Less than 3.50 meL^{-1}	Less than 3.75 meL^{-1}	121.50 mgL^{-1}
K	More than 1.5 meL^{-1}	1.50 - 15.50 meL^{-1}	121.50 mgL^{-1} (4.5 meL^{-1}), suitable
S	Less than 2.50 meL^{-1}	0.30 – 0.80 meL^{-1}	2 mgL^{-1}
P	400 mgL^{-1}	200 mgL^{-1}	20 mgL^{-1}
	1 mgL^{-1}	5 mgL^{-1}	2 mgL^{-1}

Source: WHO, [18] [Dringking Water]; Ayers and Westcott, [17] [Irrigation].

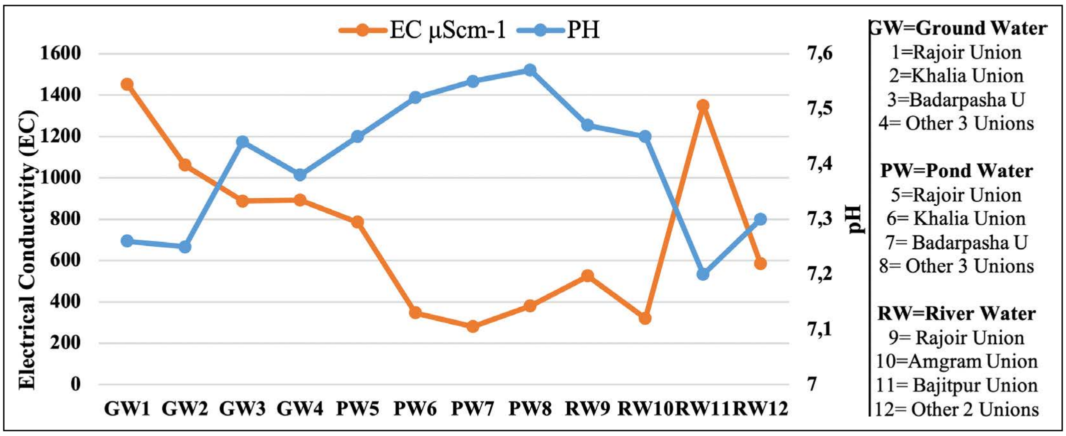

Figure 2. pH and EC profiles during the study period.

Page et al. [11]. Potassium and sodium concentrations were measured from individual water samples, and the percentage of emissions was noted using the procedure defined by Golterman [12] and Ghosh et al. [9]. The concentration of phosphate in water samples were determined by the process of spectrophotometric as per Jackson [13]. Sulphate was determined by Tandon (terbidimetric method) [14]. The Carbonate and bicarbonate content of water samples were examined by acidimetric method of Ghosh et al. [9] and Tandon [14].

Statistical Analysis

The analytical data from the water sample analyses were statistically analyzed (Gomez and Gomez) [15]. Additionally, correlation studies were conducted using MS Excel, a standard computer program.

RESULTS AND DISCUSSION

The major ionic constituent of surface water samples collected from different sources and locations at Rajoir Upazila under Madaripur District were analyzed and the results obtained from chemical analyses have been delineated in this chapter. In the study area, vital ionic constituents such as Ca, SO_4, Mg, Na, K, PO_4, were analyzed and elements were present in variable amounts in the surface water samples.

pH and Electrical Conductivity (EC) Values of Water

The average pH value of surface water (pond water) was comparatively higher than tube wells and river water (Fig. 2). Two pond water samples collected from pond showed pH 7.57 and 7.51 in Bajitpur and Rajoir union. It might be due to the application of liming materials to the pond water to control pH value and fish diseases. These results were partially similar to Zaman et al. [16] where pH ranged from 7.26 to 9.67 in surface water. For agriculture purpose, Ayers and Westcot [17] state that the pH value between 6.5 and 8.4 is acceptable. Permitting to FAO standards, almost all the water samples were appropriate for irrigation. For livestock consumption and drinking purposes, recommended range of pH is 6.5 to 9.2 (Table 1) [18].

According to this recommendation collected water samples from rivers, cannals and ponds (surface water) were acceptable for livestock farming. The average value of EC indicate that the EC of groundwater was comparatively higher than pond and river water (Fig. 2). Based on EC, the agricultural waters were classified into four groups such as low salinity (EC=0–250 µScm^{-1}), moderate salinity (EC=250–750 µScm^{-1}), high salinity (EC=750–2250 µScm^{-1}) and extreme salinity (EC>2250 µScm^{-1}) following Richards [19]. These results are lower than the report on EC 219.0 to 748.0 µScm^{-1}, conducted by Uddin et al. [20] pointed out the EC value of 18 surface water samples of Dumki upazila and have little similarity with the report on EC 348 to 497 µScm^{-1} and 255 to

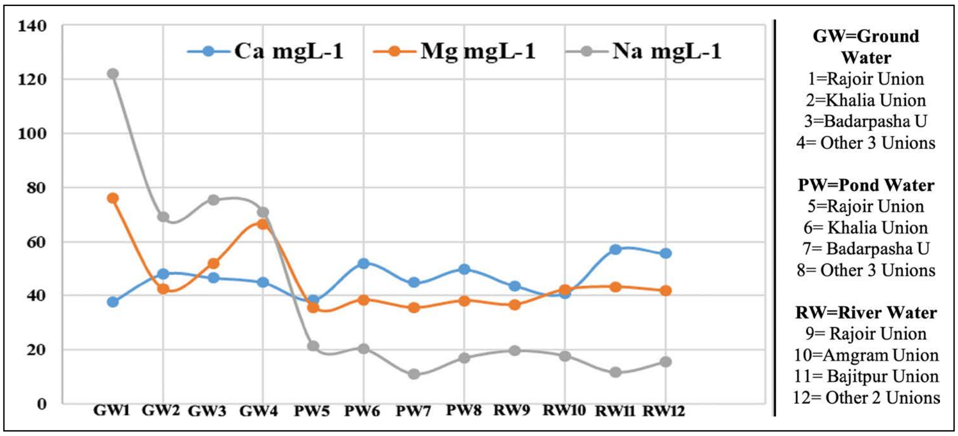

Figure 3. Ca, Mg and Na profiles during the study period (mgL^{-1}).

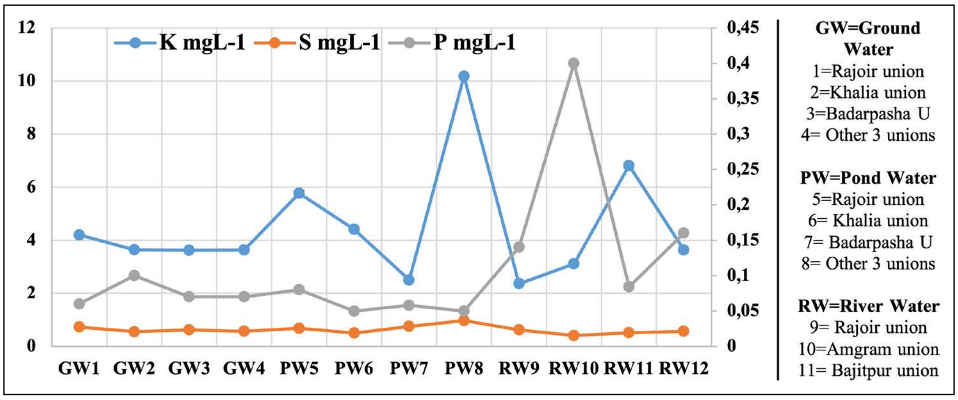

Figure 4. K, S and P profiles during the study period (mgL^{-1}).

387 μScm^{-1} of dry and wet season by Halim [21]. High EC indicated a higher concentration of salt, which has an impact on the salinity hazard and irrigation water quality [22].

Ionic Constituents of Water

The average value of Ca in tube wells, ponds and river water were 44.126, 45.181 and 49.599 mgL^{-1} (Fig. 3). The presence of higher Ca content in some samples might be due to the solubility of $CaCO_3$, $CaSO_4$ and $CaCl_2$. Some of the samples were similar to the findings of Uddin et al. [20] in Dumki different from 16.5 to 34.62 mgL^{-1}. Agricultural water containing less than 20 meL^{-1} (400.8 mgL^{-1}) Ca is appropriate for irrigating crop (Table 1) [17]. According to content of Ca, all water samples could safely be used for irrigation.

Considering fresh water quality for drinking purpose, almost 100% of the samples were found suitable, where the acceptable range of Ca for this aspect is 0.75 to 200 mgL^{-1} as mentioned in (Table 1) WHO, [18].

The results are almost similar to Karim et al. [23] reported that Mg content of 50 surface water were varied from 1.94 to 40.85 mgL^{-1} of 3 Upazilas of Bhola district. For drinking water, the highest suitable limit is 30 mgL^{-1} and maximum acceptable limit is 150 mgL^{-1} [18]. Based on WHO standards, all collected water samples were suitable for drinking purposes. It can be said that all the samples of Mg are appropriate for livestock consumption.

The average value of sodium indicate that Na ion content of groundwater was comparatively higher than pond and river water. The main causes of higher Na ion content in surface water are the presence of evaporated sediments, sewage and wastes, using soaps and detergents etc. Findings in this study showing a little similarity to Karim et al. [23], sodium (Na) content varied from 4.11 to 36.13 mgL^{-1} of 3 Upazila of Bhola. Water generally holding less than 920.00 mgL^{-1} Na is not harmful for long-term irrigation [17]. The acceptable content of Na in water samples for aquaculture is 121.50 mgL^{-1} [24]. All about collected samples of surface water were "suitable" for agricultural uses (Table 1). The average value of potassium indicate that K ion content of pond water was comparatively higher than pond and river water (Fig. 4). The existence of higher level of K in surface water (pond and river) might be due to the surface runoff of irrigation wastes, farm refuses, untreated manure sludge etc. The average value of Sulphur indicates that the S content of pond water was comparatively higher than tube well water and river water. The higher amounts of SO_4 ion in some samples were mainly due to the presence of sulfur reducing bacteria in water, which chemically change natural sulphates in water to hydrogen sulphide.

Similar results were also observed by Zaman et al. [16]. The suitable range of SO_4 ion in agricultural water is less than 20 mgL^{-1}, according to Ayers and Westcot [17]. All the surface water samples (river and pond) being examined were determined to be suitable for irrigation based on this limit. These samples were also healthy for drinking purposes because the expected range of SO_4 ion for these purpose is 200–600 mgL^{-1} according to WHO, 1971 [18] (Table 1). The average value of phosphorus indicates that the P content of tube well water was comparatively higher than pond and river water (Fig. 4). Taslima [25] also studied that this PO_4 content was similar in Gouripur and Muktagacha Upazila (PO_4 ion varied from 0.16 to 2.51 mgL^{-1}). According to Phosphorus content, all the samples were acceptable for aquaculture and irrigation. The expected range of Phosphorus content for livestock consumption is 0–1 mgL^{-1}. Therefore, all the samples were positive for livestock consumption. The Suitable range of phosphorus is 0.00–70 [18]. According to WHO, all taken samples were satisfactory for drinking purposes.

WATER QUALITY DETERMINING INDICES

Sodium Adsorption Ratio (SAR)

Richards [19] stated that water samples with SAR values of less than 10 are suitable for irrigation, 10 to 18 are good, 18 to 26 are fair, and more than 26 are not suitable for agriculture. The calculated SAR obtained from the chemical analyses of 19 surface water samples fluctuated from 0.600 to 2.356 MeL^{-1} in pond water with the average of 1.075 MeL^{-1} and 0.567 to 1.335 MeL^{-1} in river water with an average value of 0.915 MeL^{-1}. The highest SAR (8.674 MeL^{-1}) was found in groundwater and the lowest SAR (0.567) was found in river water. Crops may not be harmed by agricultural water with a SAR of less than 10.00 [26]. Alkalinity hazard was another factor taken into consideration when classifying all of the irrigation water samples. Based on the SAR value, 100% of the samples were classified as excellent for irrigation.

Soluble Sodium Percentage (SSP)

Another important metric that is frequently used to assess the suitability of groundwater for irrigation is the SSP. Furthermore, high sodium contents in relation to Ca and Mg ions decrease soil absorptivity because Na ions are drawn to clay particles and displace Ca and Mg ions, impairing soil permeability and causing deflocculation [27]. The highest SSP value (88.9%) was showed in groundwater and the lowest (24.8%) was observed in river water. In case of ground water, this ranged varied from 24.4% to 88.9% with the mean value of 63.7%. This outcome was slightly similar to Taslima [25] who studied in Gouripur and Muktagacha Upazila where the SSP varied from 9.11 to 31.28% but contradictory to Uddin et al. [20] in Dumki upazila (SSP 0.19 to 0.97%).

Total Permanent Hardness (TPH)

The total hardness (HT) or total permanent hardness (TPH) of groundwater ranged from 216 to 555 mgL^{-1} with an average value of 352 mgL^{-1}. Nine of the twenty-one groundwater samples had TPH values above the mean, while the remaining twelve samples had TPH values below the mean. The highest TPH value (553 mgL^{-1}) was monitored in groundwater and it was tube well water and the lowest value (191 mgL^{-1}) was also observed in pond water. On the other hand, the highest value of 343 mgL^{-1} was found in pond water. In case of surface water (pond and river), the TPH value of river water ranged from 208 to 366 mgL^{-1} and the mean value was 215 MeL^{-1}. Based on hardness, irrigation water was classified as "soft" (0–75 mg L^{-1}), "moderately hard" (75–150 mgL^{-1}), "hard" (150–300 mgL^{-1}) and "very hard" (>300 mgL^{-1}) [28]. According to their classification, out of 19 surface water samples, all the samples were hard to very hard. The higher values of TPH indicated the presence of higher amounts of Mg [27]. Divalent cations, such as Ca and Mg ions were abundant in the water samples, which led to their hardness [26].

CONCLUSION

Although there have been many studies on the ionic content of water in the past, this is significant as updated information for Madaripur district as well as Bangladesh as a whole. According to the World Health Organization, drinking water should contain no more than 70 mgL^{-1} of K, while 19.2 mgL^{-1} of K is acceptable for irrigation. Based on its K content, all of the collected water samples were suitable for drinking and irrigation. Pond and river water were perfect for drinking, agricultural purposes, and livestock use depending on the content found in tube wells. Water from ponds, rivers, and tube wells had acceptable P levels for irrigation, aquaculture, and drinking. All of the water samples were classified as excellent class (SAR<10) for irrigation purposes, with SAR values ranging from 0.567 to 8.377. In case of SSP 12 samples of surface water out of 19 were in "excellent" class, 6 samples were permissible and 1 sample was not permissible in class, whereas 15 groundwater samples were in "not-permissible" class, 4 samples were in "good" class, and the remaining two samples were in "permissible" class for irrigation in the studied area. According to hardness, out of 19 surface water samples, all the samples were hard to very hard in class. Furthermore, regular monitoring of water quality should be needed for the residents of this locality to access safe drinkable water to avoid health-related risks as well as determination of ionic status for irrigation purposes in a seasonal context for successful crop growth according to season which helps rational irrigation scheduling and water budget.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Anaerobic treatment of N-(phosphonometyl) glycine using mixed culture in batch reactor

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ABSTRACT

Pesticides are chemicals and preparations used in agricultural control practice and research. They are used to prevent and control pests. Pesticides are toxic and biocidal substances. The unconscious and uncontrolled use of pesticides in order to provide high yields in agricultural areas is an important problem for human health and the environment. For this reason, biodegredation of pesticides was gained importance in recent years. N-(phosphonomethyl) glycine formulated as isopropylamine salt, is a broad spectrum herbicide with high activity and effective destruction. In this study, the optimization of anaerobic treatment of N-(phosphonomethyl) glycine was investigated by applying a statistical-based experimental design. Full factorial experiments with different initial pesticide concentrations and cosubstrate types were established and 9 different experimental setup were established. The experiments carried out in 2 replicates. The experiments were carried out in Oxitop C flasks in a working volume of 200 mL with stirring. The pH was adjusted to 7±0.2. The experiments carried out at 35 °C for 30 days. At the end of the process, the removal of inlet and outlet COD and pesticide values were analyzed. As a result, the most efficient COD removal was obtained with 99% at a pesticide concentration of 5 mg L^{-1} and glucose as cosubstrate. The highest pesticide removal was found to be 75% at a pesticide concentration of 25 mg L^{-1} and glucose as cosubstrate. 5 mg. L^{-1} pesticide containing inlet concentration had toxic effect over 19% of the Vibrio fischeria before treatment, while no toxic effect was observed after treatment. This shows that the toxic value of wastewater containing pesticides decreased.

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This study was produced from Çağla Uygun's master's thesis titled "Investigation of Anaerobic Digestibility of Different Pesticide Groups" which was carried out under the supervision of Prof. Dr. Cansu Filik Iscen.

INTRODUCTION

Agriculture is the most important source of nutrition for the whole world and the need for nutrition is increasing with the increasing population, so it is aimed to obtain more agricultural products. For this purpose, all kinds of harmful weeds, plants and insects that will damage the agricultural product and affect the productivity of the product are tried to be prevented from damaging the product. Agricultural drugs developed to combat these weeds, plants, and insects are generally called pesticides. Pesticides are grouped as insecticides, herbicides, fungicides, acaricides, rodenticides, nematicides, avicides, tree protectants and defoliants according to their intended use [1]. Pesticides are further defined as aniline derivatives, carbamates, chlorophenoxy compounds, organochlorinated compounds, organophosphorus compounds, pyridine and pyridine derivatives, triazines, urea-containing compounds and unclassified compounds according to their active ingredients [2].

Agricultural production is one of the most important factors in Turkish economy. For this reason, a significant amount of pesticide are produced and consumed in our country. However, increasing urbanization has increased the use of pesticides for other purposes in addition to agricultural purposes. Türkiye is an agricultural country and it is known that agricultural areas cover about 50% of the country's surface area and the amount of pesticides used per hectare is proportional to the surface area of agricultural areas. However, pesticide consumption per hectare in countries such as the USA, Germany, the Netherlands and Italy, which have around 50% agricultural land, is much higher than in Türkiye [3]. The main problem for Türkiye is that the amount of pesticide use is high in some regions and excess pesticides are detected in agricultural products in these regions. For example, in Antalya province where fruit and vegetable production is high and these products are exported, the amount of pesticides used per hectare in arable agriculture areas is 26.85 kg. ha^{-1}, while this value is 10.9 kg. ha^{-1} in the Netherlands, the country with the highest pesticides use in Europe [3].

Pesticide contaminated wastewaters cause environmental pollution problems because they contain toxic substances, have high chemical oxygen demand (6000–10000 mg. L^{-1}), high biological oxygen demand (2000–5000 mg. L^{-1}), and high total dissolved solids (12000–13000 mg. L^{-1}) concentrations and have basic properties [4].

Pesticides applied to agricultural areas, are transferred and transformed in air, water and soil, and from there to other organisms living in these environments. Glyphosate (N-(phosphonomethyl)glycine) was developed in the early 1970s and at present is used as a herbicide to kill broadleaf weeds and grass. Glyphosate [N-phosphonomethyl glycine] is a broad-spectrum herbicide formulated as an isopropylamine salt with high activity and effective knockdown. It is an organophosphate and non-selective herbicide applied to the leaves of plants to kill both broad-leaved plants and grasses. The widely occurring degradation product aminomethylphosphonic acid (AMPA) is a result of glyphosate and amino-polyphosphonate degradation [5, 6].

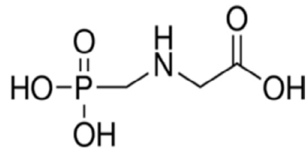

Figure 1. N- (phosphonomethyl) glycine.

Table 1. Characteristics of anaerobic sludge (AS) used in batch studies

Parameter	AS content
pH	7.4
TS (g. L^{-1})	36.4
TSS (g. L^{-1})	30.8
VSS (g. L^{-1})	14.6

The EPA divided the toxicity of Glyphosate (N-phosphonomethyl) glycine into slight toxicity with concentrations ranging from 10 to 100 mg/L and almost nontoxicity with concentration higher than 100 mg/L to fish species with acute LC50 values from >10 to >1000 mg/L. Lethal concentrations are various for 24, 48, and 96 h ranging from 0.295 to 645 mg/L for fish species; from 6.5 to 115 mg/L for amphibian's species; and from 35 to 461.54 mg/L for invertebrate species [6].

Complete and rapid degradation of glyphosate occurs microbiologically in soil and/or water, not chemically occurs. This study aim was to investigate the removal of N-(phosphonomethyl)glycine pesticide under anaerobic conditions in a batch study regardinf the effect of various operating conditions, such as concentration of pesticide and co-substrate type. The full factorial (3^2) experimental design was adopted to determine the statistical significance of each parameter on treatment performance.

MATERIALS AND METHODS

Pesticide Solution

In this study, N- (phosphonomethyl) glycine ($C_3H_8NO_5P$) (Fig. 1), which is a type pesticide that is widely used in agricultural areas. Commercial pesticide solutions containing these active ingredients were obtained from Eskişehir Green Agricultural Products, Pesticides, and Tools Company in order to be both economical in pesticide removal experiments in the batch reactors and to test the form commonly used in agricultural activities in Eskişehir province. The pesticide was stored in a refrigerator at +4 °C

Anaerobic Sludge

Anaerobic sludge (AS) used in the batch reactor was obtained from Eskişehir Sugar Factory Anaerobic Treatment Unit. Before use, the sludge was homogenized by thorough mixing and filtered through a filter with a pore diameter of 1 mm. The important properties of AS in terms of treatment, such as pH, total suspended solids (TSS),total solids (TS) and volatile suspendedn solids were determined (Table 1) [7].

Figure 2. Batch reactor (Oxitop C bottles).

Basal Medium

The composition of the basal medium used in the experiments is as follows (Concentrations of the components are given as mg. L^{-1}): NH_4Cl (1200), $MgSO_4.7H_2O$ (400), KCl (400), $Na_2S.9H_2O$ (300), $CaCl_2.2H_2O$ (50), $(NH_4)_2HPO_4$ (80), $FeCl_2.4H_2O$ (40), $CoCl_2.6H_2O$ (10), KI (10.0), $MnCl_2.4H_2O$ (0.5), $CuCl_2.2H_2O$ (0.5), $ZnCl_2$ (0.5), $AlCl_3.6H_2O$ (0.5), $NaMoO_4.2H_2O$ (0.5), H_3BO_3 (0.5), $NiCl_2.6H_2O$ (0.5), $NaWO_4.2H_2O$ (0.5), Na_2SeO_3 (0.5), and cysteine (10.0). This basal medium contains all the micro and macronutrients necessary for an optimum anaerobic microbial growth [8–10].

Factorial Experimental Design

Factorial experimental designs are widely used in experiments involving several factors to investigate the common effects of factors on the outcome [11]. Factorial (3^2) experimental designs were used to minimize the number of experiments. In this factorial design, 9 different experimental setups were established by matching three factors and three levels. In this study, a 3^2 factorial experimental design was used to investigate the effects of pesticide containing wastewater and co-substrate on COD and pesticide removal. The experiments were conducted in two parallel runs. Statistical analysis and interpretations were performed using IBM SPSS Statistics 22 software program.

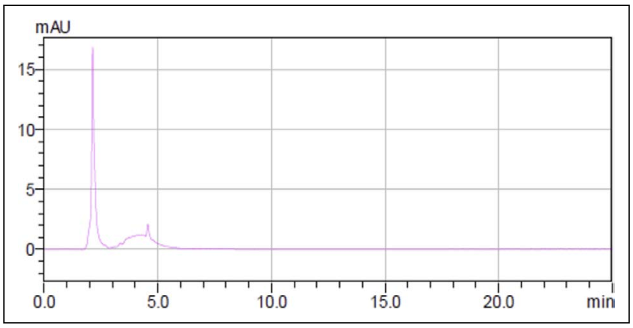

Figure 3. Chromatogram obtained for N phosphonomethyl glycine in HPLC.

Anaerobic Batch Reactor

The optimization of anaerobic treatment of synthetic wastewater containing pesticides was studied by applying statistical-based experimental design in batch studies. The batch studies were performed in 200 mLworking volume in 250 ml glass Oxitop C bottles (OxiTop® Control AN12, WTW, Weilheim, Germany) (Fig. 2). In the full factorial experimental design nine different experimental setups were investigated including the effects of different parameters such as different pesticide initial concentrations (5 mg. L^{-1}, 25 mg. L^{-1}, 45 mg. L^{-1}) and co-substrates (a-glucose (2000 mg L^{-1}, b-propionic acid (1000 mg L^{-1}), c-acetic- propionic-butyric acid mixture (ABP) (1500, 350, 350 mg L^{-1} respectively).

In all studies, a mineral medium containing substances necessary for the growth of anaerobic microorganisms was also used. pH stability was ensured by addition of $NaHCO_3$ and dissolved oxygen removal by $Na_2S.9H_2O$. pH was adjusted to 7±0.1. All experiments were carried out at 35 °C for 30 days. At the end of the period, COD and pesticide removal rates were determined [12].

The HPLC Analysis of N-Phosphonomethyl Glycine

Shimadzu UFLCXR model High-Pressure Liquid Chromatography System (HPLC) device was used for determining pesticide removal in a batch reactor. Chromatographic instructions of HPLC device with DAD detector for the determination of N- (phosphonomethyl) glycine: [13]

Column: C18 (inner diameter: 250 mm x 4.6 mm, particle size: 5 mm)

Mobile Phase: 0.05 M sodium phosphate buffer

Flow Rate: mL / min

Wavelength: 265 nm

The chromatogram obtained for the analysis of N phosphonomethyl glycine in HPLC is given in Figure 3. The calibration curves were created for all pesticides with the analysis made on the HPLC device. These curves include

Table 2. Batch reactor COD results obtained with full factorial (3^2) experimental design of synthetic wastewater containing N phosphonomethyl glycine and co-substrates (a-glucose (2000 mg L^{-1}, b-propionic acid (1000 mg L^{-1}), c-acetic- propionic-butyric acid mixture (ABP) (1500, 350, 350 mg L^{-1} respectively)

Experiment no	Pesticide concentration (A)		Co-substrate type (B)		Average COD removal (%)
	Real	Code	Real	Code	
1	**5 mg. L^{-1}**	**-1**	**Glucose**	**-1**	**99**
2	5 mg. L^{-1}	-1	Propionic acid	0	96
3	5 mg. L^{-1}	-1	ABP	1	98
4	25 mg. L^{-1}	0	Glucose	-1	96
5	25 mg. L^{-1}	0	Propionic acid	0	96
6	25 mg. L^{-1}	0	ABP	1	97
7	45 mg. L^{-1}	1	Glucose	-1	97
8	45 mg. L^{-1}	1	Propionic acid	0	95
9	45 mg. L^{-1}	1	ABP	1	97

ABP: C-acetic- propionic-butyric acid mixture.

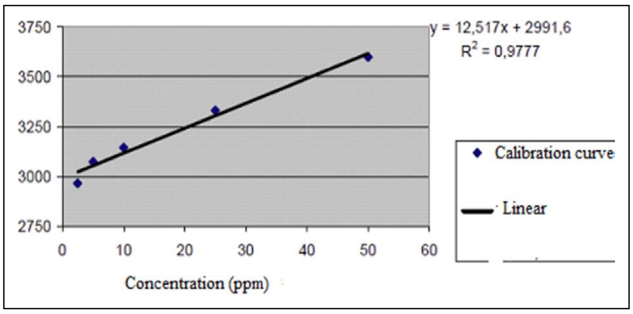

Figure 4. Calibration graph for N phosphonomethyl glycine in HPLC.

from 2.5 to 50 mg. L^{-1}. Standard solutions of N- (phosphonomethyl) glycine (Sigma) are used and the obtained calibration chart is given in Figure 4.

Toxicity Tests

Toxicity Test Using Vibrio Fischeri

The effect of wastewater containing pesticides on prokaryotic organisms before and after treatment was determined by the *Vibrio fischeri* toxicity test. The experiment was performed on SDI (United States) M500 Microtox® instrument. The determination of toxicity is based on the principle that the ability of the marine bacterium *Vibrio fischeri* culture decreases luminescence properties in the presence of toxic substances. The experiments were carried out in 2% NaCl solution at 15 °C. Luminescence was measured at 490 nm. The results were expressed as the concentration at which 50% of the luminescence was lost at 5 and 15 minutes (EC_{50}) [14].

Toxicity Test Using Lepidium Sativum

The toxic effect of pesticide-containing wastewater on eukaryotic plant cells before and after treatment was evaluated by its effect on the germination of *Lepidium sativum* seed. The experiment was carried out in 10 cm petri dishes on 2 Whatman No: 1 papers sterilised paper and 10 seeds were placed in each petri dish. The petri dishes were with 5 ml each of the pre and post-treatment samples to wet the entire Whatman No: 1 paper. Afterwards, the seeds were placed with equal distance between them. After 7 days of incubation, measurements were made. The number of germination and root elongation for each concentration were used to determine the toxic effect [15]. Experiments were carried out in 2 replicates.

RESULTS AND DISCUSSION

Determine the Properties of Anaerobic Sludge

Some characteristics of anaerobic sludge used in batch reactor studies are given in Table 1.

Batch Reactor Studies of Synthetic Wastewater Containing N-(phosphonomethyl) glycine

In this work, a statistical approach was chosen based on a factorial experimental design that would allow us to infer about the effect of the variables with a relatively small number of experiments. The independent variables of the experimental design are presented in Table 2. Each one of the three variables received three values, a high value (indicated by the plus sign), a medium value (indicated by the zero sign) and a low value (indicated by the minus sign) [8].

COD Removal Results

Batch reactor experimental setups were prepared using different concentrations of N phosphonomethyl glycine and different types of cosubstrate and the average COD removal rates obtained from each experiment are given in Table 2.

In line with these results, variance analyses, single and pairwise interaction analyses of factors were performed. Experimental design results were calculated with IBM SPSS Statistics 22 software. The analysis of variance obtained in terms of COD removal as a result of the statistically based study is given in Table 3.

Table 3. Variance analysis table for COD removal

Source	Sum of squares	df	Average of squares	F	Sig.
Corrected model	19.240[a]	8	2.405	12.013	0.001
Interrupter	168428.211	1	168428.211	841253.064	0.000
Concentration	6.642	2	3.321	16.587	0.001
Co-substrate	5.828	2	2.914	14.555	0.002
Concentration * Co-substrate	6.770	4	1.693	8.454	0.004
Error	1.802	9	0.200		
Grand Total	168449.253	18			
Adjusted Total	21.042	17			

a R^2=0.914 (Adjusted R^2=0.838) df: Degree of freedom; F: Frequency; Sig: Significance level.

When Table 3 is analysed, it is seen that the significance value calculated for the model is less than 0.05 and pesticide concentration and 3 different levels of cosubstrate have a statistically significant effect on COD removal ($p<0.05$). It is seen that the single interactions and pairwise interactions of the factors in the experiments are also statistically significant at 0.05 significance level. In addition, it was determined that the established model explained 83.8% of the COD removal.

The relationship between pesticide concentration difference and COD removal is given in the homogeneous subset in Table 4.

Table 4. Relationship between pesticide concentration and COD removal

Concentration	N	Subset	
		1	2
45 mg L^{-1}	6	96	
25 mg L^{-1}	6	97	
5 mg L^{-1}	6		97
Sig.		0.060	1.000

Sig: Significance level.

When Table 4 was examined, it is seen that the best COD removal is at 5 mg L^{-1} and 25 mg L^{-1} pesticide concentration. The significance value calculated for the model is greater than 0.05 and there is no statistically significant effect between pesticide concentration and COD removal ($p>0.05$).

According to the statistical data, the comparison of pesticide concentrations in COD removal is given in Table 5.

According to Table 5, COD removal was enhanced by 1.49%, on average, when the pesticide concentration decreased from 45 mg L^{-1} (high level) to 5 mg L^{-1} (low level). When 25 mg L^{-1} pesticide concentration was used instead of 5 mg.L^{-1} pesticide concentration, COD removal decreased by 0.79%. When 25 mg L^{-1} pesticide concentration was used instead of 45 mg.L^{-1} pesticide concentration, COD removal increased by 0.69%. As a result of the significance test made regarding whether this difference is statistically significant, sig. the value was obtained as 0.06. It was found that the difference in COD removal between the use of 25 mg. L^{-1} and 45 mg L^{-1} concentrations were not statistically significant.

The relationship between co-substrate and COD removal was given in Table 6. When Table 6 was examined, it is seen that the best COD removal is in glucose use. In batch reactor studies, using propionic acid instead of ABP as a cosubstrate type increases COD removal by 1.13%, while the use of glucose increases COD removal by 1.27%. There is no statistically significant difference in the comparison of propionic acid and glucose use as co-substrate.

A comparison of different co-substrates in COD removal according to statistical data is given in Table 7. According

Table 5. Effect of pesticide concentrations on COD removal

(I) Concentration	(J) Concentration	Average difference (I-J)	Std. error	Sig.	95% Confidence interval	
					Lower limit	Upper limit
5 mg. L-1	25 mg. L^{-1}	0.7967*	0.25834	0.032	0.0754	1.5179
	45 mg. L^{-1}	1.4867*	0.25834	0.001	0.7654	2.2079
25 mg. L-1	5 mg. L^{-1}	-0.7967*	0.25834	0.032	-1.5179	-0.0754
	45 mg. L^{-1}	0.6900	0.25834	0.060	-0.0313	1.4113
45 mg. L-1	5 mg. L^{-1}	-1.4867*	0.25834	0.001	-2.2079	-0.7654
	25 mg. L^{-1}	-0.6900	0.25834	0.060	-1.4113	0.0313

Sig: Significance level.

Table 6. Relationship between co-substrate and COD removal

Co-substrate	N	Subset	
		1	2
ABP	6	96	
Propionic acid	6		97
Glucose	6		97
Sig.		1.000	0.850

ABP: C-acetic- propionic-butyric acid mixture; Sig: Significance level.

to Table 7, the use of glucose as a co-substrate increased the COD removal rate by 1.27% compared to the use of propionic acid. When using ABP instead of glucose, the COD removal rate increased by 0.14%. As a result of the significance test made regarding whether this difference is statistically significant, sig. the value was obtained as 0.850. Since this value is higher than the significance level of 0.05, it was determined that the difference in COD removal between glucose and ABP use was not statistically significant. The use of propionic acid as a co-substrate reduces COD removal by 1.27% compared to glucose use and by 1.13% compared to ABP use.

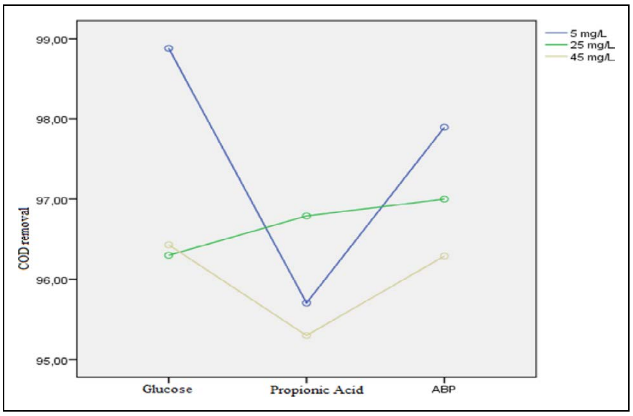

Figure 5. Profile graph of concentration and cosubstrate interaction for COD removal.

The profile graph of the pesticide concentration and cosubstrate interaction is given in Figure 5. When Figure 5 is analyzed, 5 mg L^{-1} pesticide concentration and glucose as cosubstrate, maximum COD removal was obtained.

Pesticide Removal Results

The N-(phosphonomethyl) glycine removal with different times and different co-substrate test setups and the average pesticide removal rates are given in Table 8.

Table 7. Effect of co-substrate on COD removal

(I) Co-substrate	(J) Co-substrate	Average difference (I-J)	Std. error	Sig.	95% Confidence interval	
					Lower limit	Upper limit
Glucose	Propionic acid	1.2717*	0.25834	0.002	0.5504	1.9929
	ABP	0.1417	0.25834	0.850	-0.5796	0.8629
Propionic acid	Glucose	-1.2717*	0.25834	0.002	-1.9929	-0.5504
	ABP	-1.1300*	0.25834	0.005	-1.8513	-0.4087
ABP	Glucose	-0.1417	0.25834	0.850	-0.8629	0.5796
	Propionic acid	1.1300*	0.25834	0.005	0.4087	1.8513

ABP: C-acetic- propionic-butyric acid mixture; Sig: Significance level.

Table 8. Pesticide removal results by batch reactor obtained with full factorial design of synthetic wastewater containing N phosphonomethyl glycine

Experiment no	Pesticide concentration (A)		Co-substrate type (B)		Average pesticide removal (%)
	Real	Code	Real	Code	
1	5 mg. L^{-1}	-1	Glucose	-1	73
2	5 mg. L^{-1}	-1	Propionic acid	0	52
3	5 mg. L^{-1}	-1	ABP	1	71
4	**25 mg. L^{-1}**	**0**	**Glucose**	**-1**	**75**
5	25 mg. L^{-1}	0	Propionic acid	0	49
6	25 mg. L^{-1}	0	ABP	1	51
7	45 mg. L^{-1}	1	Glucose	-1	74
8	45 mg. L^{-1}	1	Propionic acid	0	69
9	45 mg. L^{-1}	1	ABP	1	54

ABP: C-acetic- propionic-butyric acid mixture.

Table 9. Variance analysis table for results of pesticide removal rates

Source	Sum of squares	df	Average of squares	F	Sig.
Corrected model	2007.987[a]	8	250.998	2086.630	0.000
Interrupter	71029.318	1	71029.318	590489.432	0.000
Concentration	191.264	2	95.632	795.021	0.000
Co-substrate	1097.180	2	548.590	4560.605	0.000
Concentration * Co-substrate	719.542	4	179.886	1495.446	0.000
Error	1.083	9	0.120		
Grand total	73038.387	18			
Adjusted total	2009.070	17			

a R2=0.999 (Adjusted R2=0.999) df: Degree of freedom; F: Frequency; Sig: Significance level.

In line with these results, analyses of variance, single and pairwise interaction analysis of the factors were performed. The results of the experimental design were calculated with IBM SPSS Statistics 22 software and the analysis of variance obtained in terms of pesticide removal as a result of the statistically based study is given in Table 9.

Table 9 shows that the significance value calculated for the model is less than 0.05. Then, the significance tests for the model coefficients were examined. It is seen that the single and pairwise interactions of the factors in the experiment are statistically significant at 0.05 significance level. In addition, it was determined that the established model explained 99.9% of the pesticide removal. As a result, 3 different levels of concentration and cosubstrate were considered and their effects were statistically significant.

The relationship between concentration difference and pesticide removal is given in the homogeneous subset table in Table 10.

When Table 10 was examined, it is seen that the best pesticide removal is at 5 mg L^{-1} and 45 mg L^{-1} pesticide concentration. The significance value calculated for the model is greater than 0.05 and there is no statistically significant effect between pesticide concentration and COD removal ($p>0.05$).

Comparison of the concentrations for pesticide removal according to statistical data is given in Table 11.

Table 10. Relationship between pesticide concentration and pesticide removal

Concentration	N	Subset	
		1	2
25 mg. L^{-1}	6	58	
5 mg. L^{-1}	6		65
45 mg. L^{-1}	6		65
Sig.		1.000	0.181

Sig: Significance level.

According to Table 11, when the pesticide removal rates obtained at 5 mg L^{-1} and 25 mg L^{-1} concentrations were analyzed, it was found that the pesticide concentration of 5 mg L^{-1} instead of 25 mg L^{-1} increased the pesticide removal by 6.71%. The removal rate decreased by 0.39% at 5 mg L^{-1} compared to 45 mg L^{-1}. As a result of the significance test for statistical significance of this difference, the sig. value was 0.181. Since this value is higher than 0.05 significance level, it is determined that the difference in pesticide removal between the use of 5 mg L^{-1} and 45 mg L^{-1} concentrations is not statistically significant.

The relationship between cosubstrate and pesticide removal is given in the homogeneous subset table in Table 12.

According to Table 12, it is seen that the best pesticide removal is in the use of glucose. In batch reactor studies, the

Table 11. Effect of pesticide concentration on pesticide removal

(I) Concentration	(J) Concentration	Average difference (I-J)	Std. error	Sig.	95% Confidence interval	
					Lower limit	Upper limit
5 mg. L^{-1}	25 mg. L^{-1}	6.7117*	0.20024	0.000	6.1526	7.2707
	45 mg. L^{-1}	-0.3900	0.20024	0.181	-0.9491	0.1691
25 mg. L^{-1}	5 mg. L^{-1}	-6.7117*	0.20024	0.000	-7.2707	-6.1526
	45 mg. L^{-1}	-7.1017*	0.20024	0.000	-7.6607	-6.5426
45 mg. L^{-1}	5 mg. L^{-1}	0.3900	0.20024	0.181	-0.1691	0.9491
	25 mg. L^{-1}	7.1017*	0.20024	0.000	6.5426	7.6607

Std: Standart; Sig: Significance level.

Table 12. Relationship between cosubstrate and pesticide removal

Co-substrate	N	Subset		
		1	2	3
Propionic acid	6	56		
ABP	6		58	
Glucose	6			74
Sig.		1.000	1.000	1.000

ABP: C-acetic- propionic-butyric acid mixture; Sig: Significance level.

use of ABP instead of propionic acid as co-substrate increases pesticide removal by 1.67%, while the use of glucose increases pesticide removal by 17.33%. The use of glucose instead of ABP increases pesticide removal by 15.66%. These values are statistically significant. Recently, Feng et al. (2020) [16] reported that most of the organisms utilized glyphosate as a phosphorus source.

Comparison of different cosubstrates for pesticide removal according to statistical data is given in Table 13.

According to Table 13, the use of glucose increases the pesticide removal by 17.33% compared to the use of propionic acid and provides 15.66% more pesticide removal than the use of ABP. When propionic acid was used instead of glucose as a cosubstrate, pesticide removal decreased by 17.33%, while removal decreased by 1.67% when ABP was used. When ABP was preferred to glucose and propionic acid, pesticide removal decreased by 15.66% and increased by 1.67%, respectively. These values are statistically significant.

The profile plot of concentration and cosubstrate interaction is given in Figure 6. When Figure 6 is analysed, 25 mg. L^{-1} pesticide concentration and glucose as cosubstrate, maximum pesticide removal was obtained.

Most of the recent studies focused on the degradation of glyphosate pesticides in soil and water by aerobic microorganisms and reported successful degradation performances [16, 17]. However, there aren't any papers that show the degradation of this pesticide by anaerobic organisms. According to our present knowledge, this is the first paper that investigated the degradation of pesticides by anaerobic conditions.

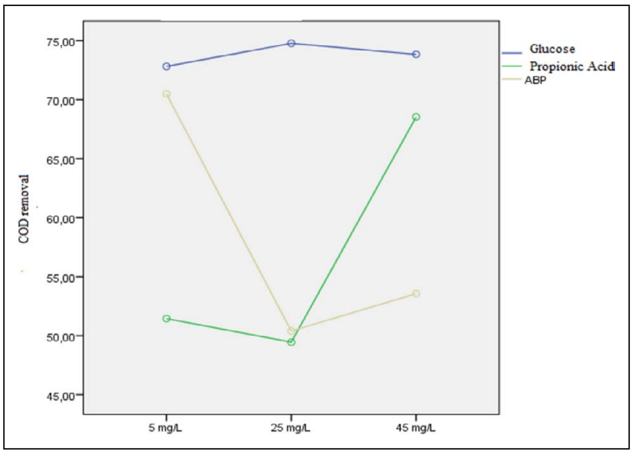

Figure 6. Profile graph of concentration and cosubstrate interaction for pesticide removal.

Ecotoxicological Studies

Toxicity Results with Prokaryotic Cells

In Tables 14 and 15, *Vibrio fischeri* toxicity test results of samples taken before and after the batch reactor using 5 mg L^{-1} as the concentration and glucose as co-substrate with the best efficiency in COD removal were given.

5 mg L^{-1}pesticide containing inlet concentration had toxic effect over 19% of the Vibrio fischeria before treatment, while no toxic effect was observed after treatment. This shows that the toxic value of wastewater containing pesticides decreased.

Toxicity Results with Eukaryotic Cells

Table 16 shows the results of Lepidium sativum toxicity test of the samples taken before and after the batch reactor with 5 mg L^{-1} pesticide concentration and glucose as cosubstrate.

The tested concentration 5 mg. L^{-1} pesticide showed toxic effect on root and stem growth *Lepidium sativum* before anaerobic treatment. After the anaerobic treatment in the batch reactor, root germination increased at a certain rate (15.2 mm) and stem germination decreased (18.4 mm). This indicates that the toxic effect of wastewater on root germination decreased after treatment. However, it is seen that the pressure on root and stem germination continues after treatment compared to control petri dishes.

Table 13. The effect of cosubstrate on pesticide removal

(I) Co-substrate	(J) Co-substrate	Average difference (I-J)	Std. error	Sig.	95% Confidence interval	
					Lower limit	Upper limit
Glucose	Propiyonic acid	17.3350*	0.20024	0.000	16.7759	17.8941
	ABP	15.6617*	0.20024	0.000	15.1026	16.2207
Propionic acid	Glucose	-17.3350*	0.20024	0.000	-17.8941	-16.7759
	ABP	-1.6733*	0.20024	0.000	-2.2324	-1.1143
ABP	Glucose	-15.6617*	0.20024	0.000	-16.2207	-15.1026
	Propiyonic acid	1.6733*	0.20024	0.000	1.1143	2.2324

ABP: C-acetic- propionic-butyric acid mixture; Sig: Significance level.

Table 14. *Vibrio fischeri* toxicity test results of 5 mg L^{-1} concentration before anaerobic treatment

			5 Mins data			15 Mins data		
Sample	**Concentration (mg. L^{-1})**	**I_0**	**I_t**	**Gamma**	**% Effect**	**I_t**	**Gamma**	**% Effect**
Control	0.000	97.00	145.29	1.000#		178.39	1.000#	
1	0.019	89.40	150.25	0.0000#	-12.00%	178.42	-7.000*	-8.000%
2	0.039	90.93	139.58	-2.000*	-2.000%	176.42	-5.000*	-5.000%
3	0.078	83.28	136.31	-8.000*	-9.000%	173.30	0.0000*	-13.00%
4	0.156	90.15	147.85	-8.000*	-9.000%	178.42	-7.000*	-7.000%
5	0.312	96.37	148.60	-2.000*	-2.000%	178.42	-6.000*	0.0000%
6	0.625	92.10	149.11	-7.000*	-8.000%	177.32	-4.000*	-4.000%
7	1,250	89,91	133,87	5,000*	0,0000%	162,13	1,000*	1,000%
8	2,500	86,30	121,66	6,000#	5,000%	145,91	0,0000#	8,000%
9	5,000	81,47	102,60	0,0000*	15,00%	120,82	0,0000#	19,00%

Table 15. *Vibrio ficsheri* toxicity test results after anaerobic treatment of a concentration of 5 mg L^{-1}

			5 Mins data			15 Mins data		
Sample	**Concentration (mg. L^{-1})**		**I_t**	**Gamma**	**% Effect**	**I_t**	**Gamma**	**% Effect**
Control	0.000	95.44	112.49	1.000#		130.06	1.000#	
1	0.019	89.67	109.89	-3.000*	-3.000%	130.71	-6.000*	-6.000%
2	0.039	92.53	103.89	4.000*	4.000%	119.57	5.000	5.000%
3	0.078	87.46	105.84	-2.000*	-2.000%	125.80	-5.000*	-5.000%
4	0.156	90.66	111.53	-4.000*	-4.000%	130.62	-5.000*	-5.000%
5	0.312	92.11	121.95	0.0000*	-12.00%	144.54	0.0000*	-15.00%
6	0.625	90.72	122.56	0.0000*	-14.00%	150.42	0.0000*	-21.00%
7	1.250	81.86	103.00	-6.000#	-6.000%	118.84	-6.000*	-6.000%
8	2.500	75.90	122.88	0.0000*	-37.00%	133.19	0.0000*	-28.00%
9	5.000	74.79	122.28	0.0000*	-38.00%	152.05	0.0000*	-49.00%

Table 16. Lepidium sativum toxicity root and stem growths

Root (average)			Stem (average)		
Control	**Before batch reactor**	**After batch reactor**	**Control**	**Before batch reactor**	**After batch reactor**
21.85 mm	13.35 mm	15.2 mm	30.05 mm	22.95 mm	18.40 mm

Recently, de Castilhos Ghisi et al. (2020) [18] showed that glyphosate had toxic effects on living organisms. Similarly, in the results of ecotoxicology studies, the presence of this pesticide affected procaryotic and eucaryotic organisms, but the water treated with the anaerobic system contained less amount of pesticide and showed less toxicity to the test organisms.

CONCLUSION

Pesticides are plant protection drugs that are becoming more and more widespread day by day, although their damages to human and environmental health have been revealed by many scientific studies all over the world and in our country. The use of pesticides, which are used to protect plants against the negative effects of diseases and pests, has been shown by many scientific to be harmful to human and environmental health, ecological balance and agricultural products, especially cancer.

One of the most important sources of pesticide contamination is the discharge pesticide-containing domestic and industrial wastewater into receiving environments. In this context, the treatment process of pesticides is ecologically important. However, due to their complex chemical structure and synthetic origin, the treatment of pesticides is very difficult. Depending on the need, the structures of pesticides change and the removal process becomes more difficult.

In this study, the treatment potential of wastewater with different pesticide concentrations prepared with N- (phosphonomethyl) glycine in a laboratory environment was determined in a batch anaerobic reactor. When the analysis of variance obtained in terms of COD removal as a result of the statistically based study is examined, it is seen that the significance value calculated for the model is less than 0.05. This shows that the established model is statistically significant. Then, the significance tests for the model coefficients were examined. It is seen that the individual effects and the interaction effects of the factors in the experiment are statistically significant at the 0.05 significance level. In addition, it was determined that the established model explained 83.8% of the COD removal.

According to the results of the experimental design of anaerobic batch reactor studies, it was found that the best COD removal in the experimental set prepared with N-(phosphonomethyl) glycine was 99% when pesticide concentration was 5 mg L^{-1} and glucose was used as cosubstrate and the best pesticide removal was 75% when pesticide concentration was 25 mg L^{-1} and glucose was used as cosubstrate. In terms of binary interaction, it was determined that pesticide concentration and co-substrate type were not statistically significant on COD and pesticide removal.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Enhancing climate change resilience: Assessing adaptation needs, and significance of monitoring and evaluation systems

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ABSTRACT

Losses and damages from climate change-related extreme weather events and disasters require the development of adaptation measures to increase resilience to the adverse impacts of climate change. In line with the United Nations Framework Convention on Climate Change (UNFCCC) and the Paris Agreement's Global Goal on Adaptation, Parties have developed strategies that include adaptation actions, but there are significant gaps in the identification of adaptation needs and the monitoring and evaluation (M&E) of actions to address them. Adaptation M&E systems are critical for measuring the success of adaptation actions, providing feedback from the implementation process, and identifying new actions. There is no global methodology for adaptation M&E. At international climate change negotiations in 2023, it was agreed that countries should operationalize their national adaptation M&E systems by 2030. The study aims to evaluate adaptation M&E methodologies developed by countries at different development levels and to present future policy recommendations for the adaptation M&E system planned to be established in Türkiye. The study reveals the necessity of up-to-date socio-economic data as well as climate data in determining adaptation needs and adaptation M&E systems. In Türkiye, which is vulnerable to the impacts of climate change, for the success of adaptation actions, besides the rapid operationalization of the adaptation M&E system, the establishment of the system with an approach that includes all stakeholders in the process and considers adaptation actions as integrated with disaster risk management actions is an important requirement in the context of Türkiye's international commitments, national security, and development.

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INTRODUCTION

The two key strategies identified by the United Nations (UN) for combating climate change today are mitigation of greenhouse gas emissions and adaptation to the adverse effects of climate change. Adaptation to climate change is becoming increasingly important in today's conditions, where climate-related extreme weather events are increasing. Adapting to climate change is defined by the Intergovernmental Panel on Climate Change (IPCC) as "In human systems, the process of adjustment to actual or expected climate and its effects, in order to moderate harm or exploit beneficial opportunities" [1]. In addition to determining the needs that require adaptation to climate change and the actions taken towards them, conducting monitoring and evaluation (M&E) that will make it possible to evaluate the effectiveness of these actions and learn from the results is very important in determining forward-looking adaptation strategies [2].

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Climate change adaptation efforts, actively pursued through the UNFCCC and the Paris Agreement, specifically aim to achieve the Global Goal on Adaptation (GGA). The main components of the GGA, which are detailed under Article 7 of the Paris Agreement and form the basis of adaptation efforts, include the following [3–5]:

- Enhancing adaptive capacity,
- Reinforcing resilience,
- Mitigating vulnerability to climate change.

The importance of the GGA and its components lies in the escalating frequency, severity, and global scale of climate change impacts, resulting in widespread loss and damage worldwide [1]. Even if countries aim for net-zero emissions, the lasting effects of historical emissions will persist for centuries. This underscores the urgency of conducting studies on adapting to climate change, enhancing climate resilience, and reducing vulnerabilities across sectors to achieve the GGA targets [1, 6].

In this context, there is a growing body of research dedicated to ensuring sustainable and climate-resilient development in economic sectors [7, 8], establishing efficient and flexible heating, cooling, and energy systems [9–12], climate-sensitive urban planning and design [13–15], local climate action [16, 17], public health protection [18], disaster risk management [19, 20], capacity building in legal, human, and administrative systems [21, 22], ecosystem protection, and using nature-based solutions to combat climate change [23, 24], constructing climate-resilient infrastructure [25, 26], ensuring water and food security [27–29], and combating drought [30, 31]. A plethora of studies have demonstrated that the implementation of adaptation actions in order to achieve the GGA objectives not only enhances resilience but also yields considerable environmental, economic, and social benefits by reducing vulnerability [1].

However, assessing the success of adaptation actions involves some difficulties in itself. This is because, while M&E methodologies that show the success of actions to reduce greenhouse gas emissions on a global scale in terms of carbon dioxide (CO_2) equivalents have already been established, there is not yet a global M&E (and Learning-MEL[1]) system or methodology that would enable the monitoring of the adequacy and effectiveness of global efforts to adapt to climate change to achieve the goals of the GGA or that would link national M&E systems. Although efforts are underway to establish such a system, there is a need to improve these efforts [3, 4, 32–34]. The Annual Report of the UNFCCC Adaptation Committee published on 26 October 2023 also emphasized the need for studies and adaptation M&E systems to guide planning for adaptation to climate change. Among these efforts, it was stated that work is underway to prepare a technical document for establishing an M&E system and to support Parties' adaptation actions within the framework of National Adaptation Plans (NAPs) [35].

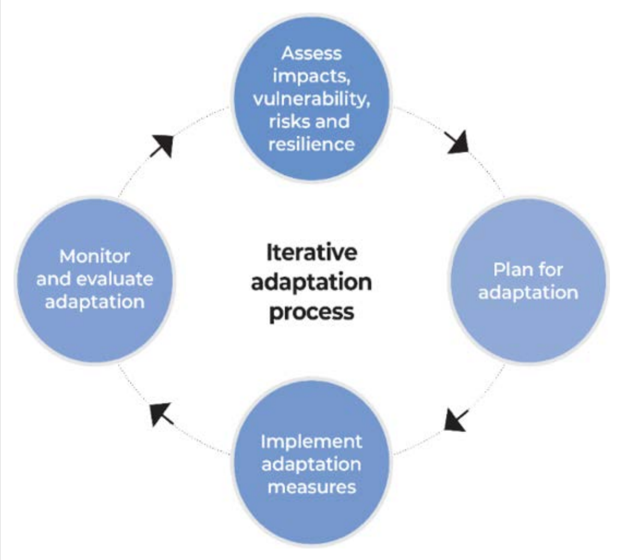

Figure 1. UN adaptation cycle [41].

Establishing adaptation M&E systems was also one of the main subjects of the Adaptation Gap Report published by the UN Environment Program (UNEP) in 2023. The Report emphasized that adaptation M&E systems are relatively underdeveloped due to difficulties in developing systems and methodologies for understanding the effectiveness of planning and implementation of adaptation actions. However, today, the pressure in legal and financial processes that require proving the effectiveness and success of adaptation actions, especially in international climate change negotiations, is increasing, further increasing the importance of adaptation M&E systems [36].

During the 28th Conference of the Parties (COP 28) to the UNFCCC held in Dubai from November 30th to December 13th, 2023, the taken decisions reflected the necessity for M&E systems for adaptation actions. COP28 was the first of the Global Stocktakes (GST), which will now take place every five years. Under the GST, Parties to the UNFCCC and the Paris Agreement are urged to demonstrate their national mitigation and adaptation actions clearly. Hence, the M&E of adaptation actions has become as crucial as their planning. At COP28, the GST Decision-CMA5 document, which outlines the decisions, specifies a timeline for a roadmap defining the adaptation actions that countries need to undertake within the adaptation cycle (Fig. 1) established by the UN [37]. The COP28 decision text encompasses the completion of planning and policy development processes regarding adaptation by all countries by 2025, ensuring their implementation until 2030, and the consolidation of adaptation-related information submitted by Parties in their biennial transparency reports within a synthesis report by the Secretariat (Articles 59 and 60) [38].

1 In the context of adaptation M&E, integrating insights from action outcomes and experiences enhances the system, integrating the notion of 'Learning' into M&E frameworks. Some sources in the literature refer to these systems as MEL (Monitoring, Evaluation and Learning) [33].

Therefore, transparent reporting of the steps taken on adaptation has become very important. This means that the contribution levels of national actions to global efforts will be determined by developing national M&E systems for adaptation actions reported through National Communications (NCs), Nationally Determined Contributions (NDCs) and/or NAPs to the UNFCCC Secretariat [1, 33, 39, 40]. This is emphasized in the Adaptation section (Article 48) of the COP28 CMA5 document with the following statement: "Notes that there are gaps in implementation of, support for and collective assessment of the adequacy and effectiveness of adaptation, and that M&E of outcomes is critical for tracking the progress and improving the quality and awareness of adaptation action" [38].

Besides the above-mentioned documents, at UNFCCC COP28, as part of the United Arab Emirates Framework for Global Climate Resilience, within the adaptation cycle's defined objectives, the necessity for UNFCCC, and Paris Agreement parties, including Türkiye, to develop national MEL systems for adaptation by 2030 was highlighted. This is stated in the Glasgow–Sharm el-Sheikh Work Programme on the GGA referred to in decision 7/CMA.3 text (paragraph 10/d) as "Monitoring, evaluation and learning: by 2030 all Parties have designed, established and operationalized a system for monitoring, evaluation and learning for their national adaptation efforts and have built the required institutional capacity to fully implement the system" [37].

Another dimension of the need for adaptation M&E/MEL systems is undoubtedly related to adaptation financing. The delay in observing the outcomes of adaptation actions compared to mitigation actions raises discussions about how funds provided by developed countries for adaptation actions in developing countries are utilized, in other words, whether they are effectively used for adaptation actions in developing countries [34, 40, 42–44]. Therefore, the importance of adaptation M&E systems has also increased in the future to collect data for the necessary assessments to use the Loss and Damage Fund established at COP28 to compensate for losses and damage caused by extreme weather events and slow onset events in developing countries, as well as other existing sources of adaptation finance [39, 45].

As mentioned above, efforts to measure the effectiveness of adaptation actions through M&E have been ongoing for some time, mainly under the leadership of the UNFCCC Adaptation Committee. As a result, various approaches have been developed [46]. For example, there are indicators for assessing climate adaptation projects that apply to benefit from the Green Climate Fund, one of the funds under the UNFCCC and the Paris Agreement. However, these indicators are independent of the characteristics of the beneficiaries and are based on numerical results [34]. Most country-based indicator-driven adaptation M&E systems use different methods, with assessments based on fewer than 15 or more than 100 indicators. There is no standardized approach for collecting the data required for these indicators; surveys, workshops, interviews, and literature reviews are often used. In the assessment of adaptation actions, most developing countries do not have the basic data required for adaptation M&E, or there are problems with the quality and reliability of existing data. Another challenge in M&E of adaptation actions is the relationship of some actions with GHG mitigation actions. This situation adds uncertainties to adaptation M&E [1, 47, 48]. Nevertheless, the ongoing evolution of and insights gained from existing M&E methodologies are crucial for both national M&E/MEL systems, and the UNFCCC Secretariat in developing a methodology/system for M&E of global adaptation efforts. In addition, understanding the types of data used in the adaptation cycle and the existing methodologies developed by some countries for the M&E of adaptation actions is also of great importance in the context of reporting the national adaptation M&E methodology/systems requested from the Parties in line with the COP28 decision and the outputs to be obtained from them to the UNFCCC Secretariat.

In this framework, the study seeks answers to the following research questions:

1. What kind of data are used in determining the need for adaptation to climate risks and then determining adaptation actions, is only climate data sufficient?
2. What are the methodologies developed by countries at different levels of development for M&E of the effectiveness and adequacy of climate change adaptation actions and what is the situation in adaptation M&E in Türkiye?

MATERIAL AND METHODS

This study aims to evaluate the adaptation M&E methodologies developed by countries at different levels of development and to provide future policy recommendations for the adaptation M&E system planned to be established in Türkiye.

The study employed a relational research model to address the research questions and examined the relationship between climate change adaptation actions and the methodologies for adaptation M&E efforts (Fig. 2). Various international institutions such as the UN, UNFCCC, IPCC, along with publications, reports, websites related to climate change adaptation from Türkiye and other countries, were utilized as data sources, in addition to academic literature.

This study examines different M&E systems and approaches to climate change adaptation, revealing that this issue has not yet been comprehensively researched in Türkiye and many other countries, and contributes to the literature. The methodologies summarized here cover the elements of the systems and methodologies that the UNFCCC Secretariat requests from Türkiye and other countries to be established by 2030 regarding adaptation in international climate change negotiations. Therefore, Türkiye and other countries can benefit from the content of this study in the processes of developing policies on adaptation to climate change and establishing an M&E system for adaptation actions. The study aims to guide the revisions to be made to Türkiye's National Climate Change Adaptation Strategy and Action Plan (NCCASAP) in the future. In addition, the study aims to lay the groundwork for the establishment of

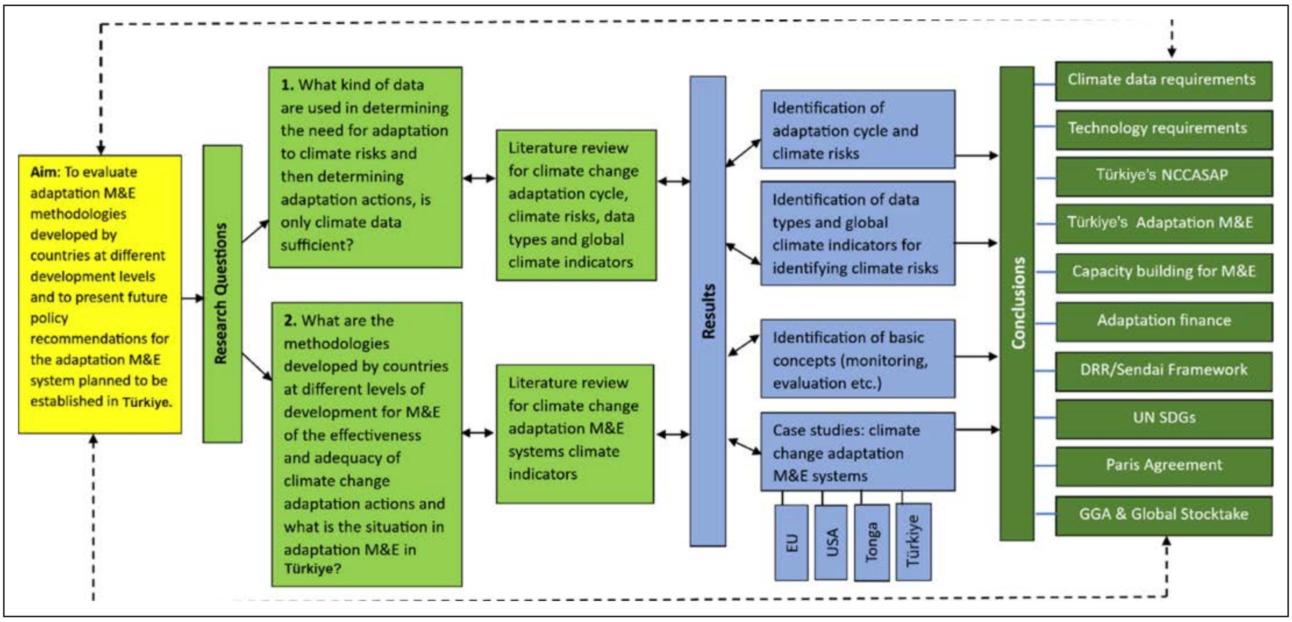

Figure 2. Conceptual method flowchart.

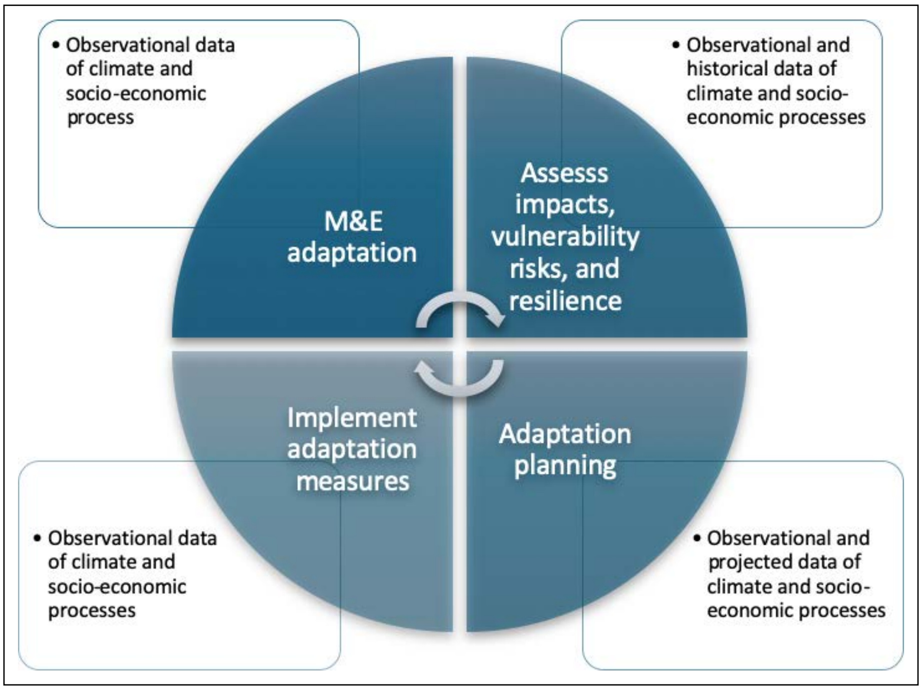

Figure 3. Data requirements in adaptation cycle [39].

an M&E/MEL system for NCCASAP in Türkiye and to facilitate academics to conduct further research in this field.

RESULTS AND DISCUSSION

Types of Data Necessary for Assessing Climate Risks and Adaptation Needs

The need for M&E systems to assess the effectiveness of climate change adaptation is growing. Therefore, data on adaptation is crucial. Article 7 of the Paris Agreement calls on Parties to use the best available science for adaptation. GSTs will assess global progress on adaptation and support the review process. The Cancun Framework for Adaptation provides the basis for strengthening data systems and making climate data available to decision-makers. Research and systematic observation are on the Subsidiary Body for Scientific and Technological Advice (SBSTA) agenda in international climate negotiations [5, 49, 50].

Preparation of adaptation-related communications for the UNFCCC Secretariat involves the use of tools such as NAP, NDC and NC, which highlight the need for different types of data across the four stages of the adaptation cycle (Fig. 3). The actions taken and the data used at each stage can be linked to M&E. The steps in this process are as follows [39, 47, 48]:

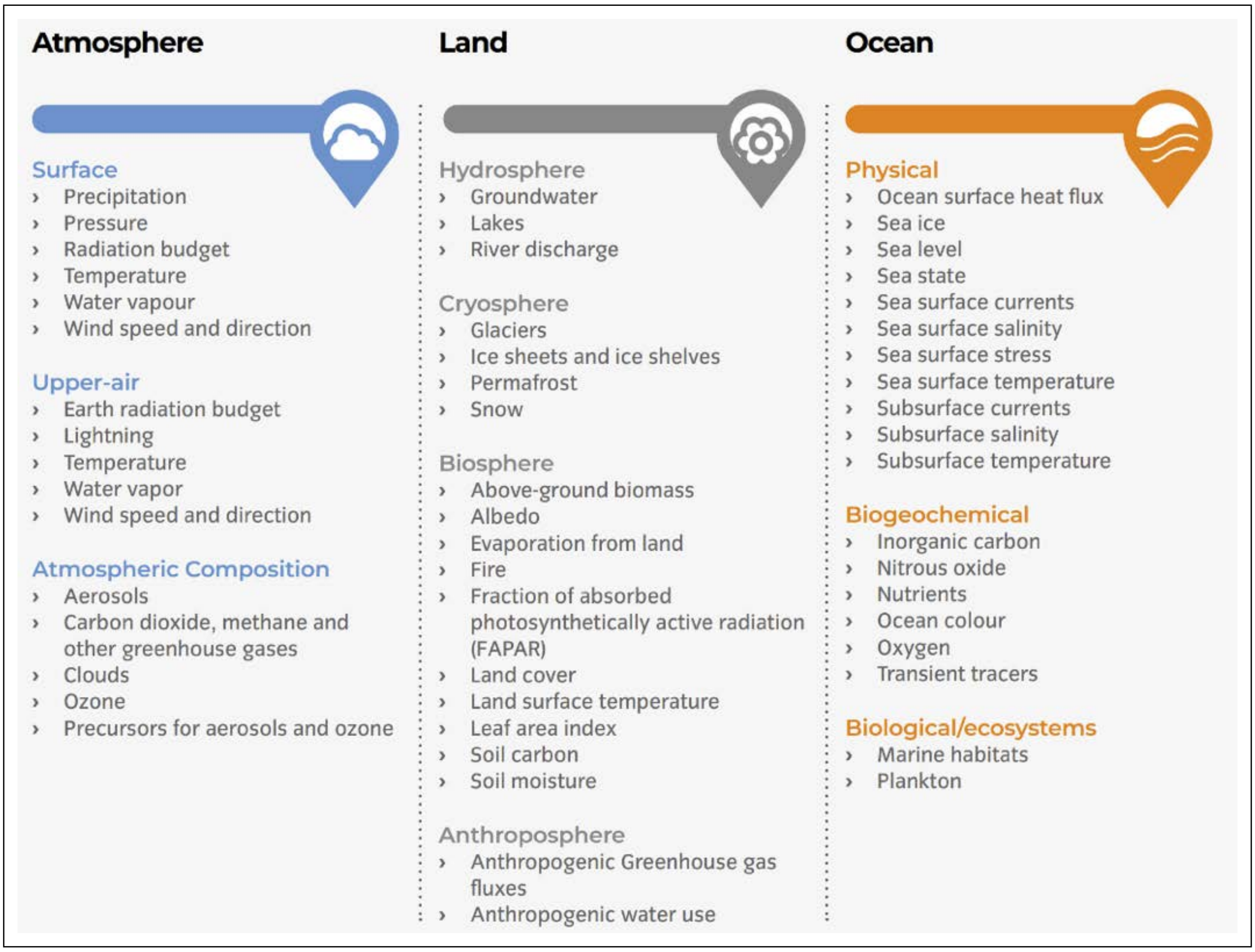

Figure 4. Global climate indicators [39, 52].

1. Assessment of impacts, vulnerability, climate risks and resilience (this initial step will also determine the measures to be used for M&E in step 4),
2. Adaptation planning (this step requires the identification of an appropriate set of adaptation measures, considering financial, administrative, and legal aspects. This process will help define other measures for the M&E stage),
3. Implementation of adaptation measures (this stage indicates whether the stages of the cycle are well designed and provides lessons learned from the established M&E system),
4. M&E of adaptation actions (conducting M&E at each stage of the cycle, not just at the end, will positively support the process).

In the IPCC 6th Assessment Report (AR6) Working Group II (WGII) on Impacts, Adaptation and Vulnerability report provides important insights into climate risks and adaptation data. It highlights the interconnected nature of climate risks, which arise from the interplay between climate-related hazards and the exposure and vulnerability of human and natural systems. These risks are shaped by both climate and socio-economic processes, underscoring the need for adaptation strategies to incorporate data from both domains to mitigate climate risks effectively [1].

The Global Climate Observing System (GCOS), supported by key organizations such as UNESCO's Intergovernmental Oceanographic Commission, World Meteorological Organization, UNEP, and the International Science Council, plays a critical role in collecting climate data. GCOS monitors atmospheric, terrestrial, and oceanic conditions and provides critical guidance for improving global climate conditions [51]. The global climate indicators that are essential to support mitigation and adaptation efforts are listed in Figure 4.

Economic and social data, as well as historical climate data, should be considered when conducting analyses at different scales within the four-stage adaptation cycle described above. However, it is only when these data are combined with climate data that consistent projections for adaptation can be developed. In other words, it is essential to make not only observations of the atmosphere, soil and ocean, but also observations of socio-economic processes to obtain the data necessary for the analyses to be carried out to determine adaptation needs. In this way short-, medium- and long-term adaptation plans can be made using the data obtained. Examples of socio-economic data that can be considered in this context are [39],

- Population data (e.g., total population, density, urban population, age and gender distribution, inequalities),
- Economic data (e.g., GDP, annual GDP growth rate, income from sectors such as climate-sensitive industry, agriculture),
- Land cover and land use (e.g., total land area, amount of cropland, rangeland, forest and other land and land uses),
- Water resources and water data (e.g., amount of water per capita, annual water withdrawals for different uses)
- Agriculture and food data reflecting the socio-economic situation (e.g., amount of irrigated land, amount of agricultural employment, total labor force, livestock, economic value of the agricultural sector).

The concept of adaptation needs refers to "the actions and resources required to complete all stages of the adaptation process, from assessing risks and vulnerabilities to planning, implementing, and monitoring and evaluating adaptation measures". The first step in the adaptation cycle is to identify adaptation needs in response to climate change impacts [47, 53].

The availability and accuracy of data is essential for consistent forecasting and adaptation planning. Based on these data, climate models help to make projections of weather, climate and socio-economic conditions. However, there are global challenges to the data used in these studies, such as the lack of observing systems in some regions and/or the unavailability of data in digital formats. Although it is possible to scale global data to local levels, the unpredictable nature of climate change poses some challenges in determining climate impacts. These challenges affect the identification and implementation of adaptation measures, particularly in the areas of food and water security, resilience, and disaster risk management [39]. These challenges arise from the following characteristics of adaptation actions [54, 55]:

- The results of adaptation measures can unfold over a long time period, sometimes several decades.
- While adaptation actions are determined based on local conditions, the unpredictable dimensions of climate change can further complicate local impacts. Measuring these uncertain conditions can be difficult and sometimes impossible.
- The existence, collection and assessment of data related to adaptation sectors can also be challenging and may require the measurement and assessment of events that have not yet occurred.
- There isn't a globally accepted methodology for conducting adaptation M&E, making it difficult to assess the impact of adaptation actions on a global scale.
- At local and national levels, terminology related to adaptation may be used in different contexts.
- There are also shortcomings in linking locally identified adaptation needs and actions to national programs.

Different climate and socio-economic data from observations and forecasts from different stakeholders around the world require standardization by institutions such as national meteorological and water management agencies. These data, supported by local input, are used to meet the data needs of adaptation planning, including the use of high-tech tools such as artificial intelligence and big data. In this context, climate services facilitate the use of scientifically produced data by facilitating collaboration between data producers and decision-makers [1, 2, 33, 39].

Methodologies Focused on the Adaptation M&E

It's critical to conduct M&E of implemented adaptation actions, which marks the fourth step in the adaptation cycle [5, 43]. IPCC's AR6 WGII Report highlights the importance of linking adaptation planning and M&E processes, especially in addressing the limits of adaptation and developing effective responses to climate change risks. According to the IPCC, M&E in adaptation includes activities to track progress, improve effectiveness, and iteratively manage risks. It's critical at all stages to identify effective interventions and manage risks at multiple scales. Adaptation M&E systems are still under development and are not yet fully adequate [1]. Three fundamental aspects that need to be considered in M&E systems for adaptation actions at all scales [56]:

1. Evolving vulnerabilities and risks,
2. Identified adaptation goals and objectives,
3. Adaptation actions implemented.

From the actions within the scope of M&E [1, 33, 57];

- Monitoring aims to track progress in achieving objectives, including using financial resources, during implementing of climate change adaptation measures. It allows for comparison of results achieved with expected results and, if necessary, prompts improvements.
- Evaluation systematically determines the effectiveness of an action. It can be conducted before, during, or after implementation to assess goal achievement and identify success factors. It covers productivity, accountability, results, capacity, impact on groups, lessons learned, and parallels with similar interventions.

Transforming adaptation M&E into a MEL system facilitates leveraging insights from M&E to enhance adaptation actions. This approach aids in detecting the adverse effects of wrong adaptation choices (maladaptation) and identifying new vulnerabilities needing adaptation [44, 48, 58, 59].

Adaptation M&E/MEL systems are notably absent from NAPs worldwide, with only 24% implemented and 19% under development. Existing systems focus primarily on monitoring and neglect the crucial evaluation phase, which is essential for NAP updates. Results-Based Monitoring (RBM), which uses the Logical Framework approach to evaluate indicators, is preferred by many countries and organizations. There are also other methods, such as participatory M&E, and impact assessment, each with its advantages and disadvantages [33, 36, 60, 61].

Key initial priorities for the development of adaptation MEL systems include [48, 62]:

- Policy development and implementation at all levels of decision-making for effective operation of MEL systems.
- Addressing challenges in establishing these systems, including indicator development, long-term uncertainties, data gaps, capacity limitations, financial constraints, and implementation barriers.
- Selecting indicators and criteria that are appropriate for all levels of government to avoid incentivizing inappropriate adaptation actions.
- Establishing MEL systems incrementally, starting at the baseline level and improving over time with new indicators and criteria consistent with progress.
- Ensuring integration with diverse financial resources to sustain the functionality of the MEL system.

Following the decision taken at COP28 of the UNFCCC, efforts are underway, led by the Adaptation Committee, to establish systems to facilitate M&E of adaptation actions at the global level through collaborative work involving other relevant UN bodies and participants from the Parties to the UNFCCC [38, 57, 63]. Examples of adaptation M&E/MEL systems established by different countries at different levels of development have been examined as guiding models in the following titles.

United States (US) /Resilience Metrics (Climate Adaptation Toolkit)

The Resilience Metrics approach was developed over 10 years as a result of a collaborative effort of experts from various professions supported by the National Oceanic and Atmospheric Administration (NOAA) in the US. This approach is used in the M&E of climate change adaptation measures [64].

In this approach, the concepts of indicators and metrics are first explained [65]:

- An indicator is defined as 'a sign that shows the desired outcome of adaptation actions'.
- Metrics are defined as the expression of the relevant indicator with both qualitative and quantitative variables (for measurable indicators).

For example, if the indicator is an adaptation to flooding, the metric is the comparison of the monetary value of losses and damages before and after the implementation of these measures. Therefore, in this approach, the terms indicator and target are not used interchangeably. The target is considered only in terms of what is expected to be achieved at a given point in time. However, it was emphasized that the mentioned targets should be detailed through adaptation actions and expressed through indicators and metrics. In the Resilience Metrics approach, it is stated that the success of adaptation actions cannot be measured without M&E. Accordingly, it is stated that local needs, existing data, and the target audience of the implemented actions are important in the selection of adaptation indicators and metrics to be used in the M&E system. The general topics of the indicators and metrics discussed in the toolset of this method are listed below and examples of these are given in Table 1 [65]:

- Economic indicators and metrics
- Environmental indicators and metrics
- Governance indicators and metrics
- Infrastructure indicators and metrics
- Social indicators and metrics

The approach emphasizes the importance of human, financial, and technical capacity, as well as governance processes, in conducting M&E once these indicators have been identified. Within this framework, it's noted that M&E can also identify undesirable outcomes of adaptation actions [65].

Table 1 illustrates that while indicators and metrics exist for economic and environmental dimensions in the US's adaptation M&E approach, a more comprehensive assessment is conducted for the social dimension. This emphasis derived from the recognition that sustainable adaptation requires social ownership, and that socio-economic data are crucial for consistent evaluations. In this framework, while certain quantitative data such as population growth are monitored under headings like Social Aspects, Governance Aspects are integrated into the M&E system separately. Notably, indicators explicitly involving stakeholder participation in processes have been identified. An additional noteworthy aspect of the US's adaptation M&E methodology is the creation of a separate data layer for Infrastructure. This approach ensures that M&E is conducted dynamically and remains current, encompassing not only infrastructure sectors like transportation but also Emergency Action Plans.

European Union (EU)/Adaptation Support Tool (Climate-ADAPT)/M&E Component

The EU is stepping up its efforts to make adaptation efforts more efficient, guided by "smarter, faster and more systematic" approaches [66]. Adaptation policy studies from the Green Paper (2007) to the EU Climate Change Adaptation Strategy (CCAS) of 2013 show continuity in this area. The culmination of these efforts is the new EU CCAS, published in 2021 as part of the European Green Deal. The strategy aims to develop the Climate-ADAPT system, which is the EU's data/information exchange and decision support tool for adaptation, beyond an information tool to a monitoring and reporting mechanism for adaptation [67]. Climate-ADAPT outlines a six-step adaptation cycle [68]:

1. Ground preparation
2. Risk assessment
3. Identify adaptation options
4. Evaluate options
5. Planning for implementation
6. M&E

Table 1. Examples of indicators and metrics in $gy [65]

Adaptation strategy	Indicator	Metric	Process	Capacity	Barriers	Decision-making	Action	Outcome
Economic aspects								
Implement flood mitigation measures	Cost effectiveness	$ saved or $ in damages avoided/$ expenditure						X
Implement adaptation pathways	Cumulative damages	Damage totals/event or /year as triggers for moving to next set of adaptation strategies				X	X	X
Increase economic opportunities and resilience	Economic security/ wellbeing	# of childcare places/ year, employment rate, # of business start-ups/closures		X				X
Environmental aspects								
Improve/maintain water quality	Regulatory change	Width of stream channel buffer in ordinance			X		X	X
Preserve natural assets for flood resiliency	Protected (existing or restored) shorefront areas	Acres of natural shoreline area protected or restored						X
Increase use of green/NBSs	Open/green space	# acres of impervious surface converted to permeable surface; # of green infrastructure projects completed					X	X
Governance aspects								
Connecting short-term decisions with a long-term vision	Cohesive decision-making	Decisions integrate climate projections (yes/no/ partially); Short-term decisions are checked against the long-term vision (yes/no/partially); different government agencies work together on integrated adaptation plan (always/often/ sometimes/not enough/never)	X	X	X	X		
Improve compliance with existing flood mitigation standards	Compliance	% compliant structures within regulated flood risk zones; % houses above base flood elevation		X	X			X
Broaden climate change/adaptation conversation beyond existing stakeholders	Public interest in climate change	Requests for information (#/month or year)	X		X			
Infrastructure aspects								
Secure critical transportation routes	Adjusted/ relocated roads	Critical high-risk road sections elevated or relocated inland (planning/implementation phase); % of funding secured			X		X	X
Update emergency management plan	Up-to-date maps of emergency response routes	Mapping completed/ mapping not begun/ update in progress (regular updates, e.g., every 5–10 years)			X	X	X	
Maintain, elevate, restore and/or relocate (as needed) roads and trouble spots	Flood-related closures or disruptions	# of road or trail closures/year or flood event						X
Social aspects								
Adaptation efforts focus on the most vulnerable/disadvantaged	Improvement for disadvantaged	#of watermains fixed/year; #of trees planted; # of affordable housing unit (increasing over time); $ of investment in economic opportunities		X	X		X	X
Monitor and plan for expected population increase	Land use	Map/% of land use types, distribution, change in acreage over time; #of applications for development permits						X

Table 2. Examples of monitoring indicators for DAS [72]

Cluster	Action area	Impact-indicators-effects	Response-indicators-adaptations
Health	Human health	Heat exposure	Heat warning service
Water	Water management, water regime, coastal and marine protection	Groundwater levels	Water use index
Land	Soil	Soil moisture levels in agricultural soils	Humus content of arable land
Infrastructure	Building industry	Heat stress in urban environments	Recreation areas
Economy	Trade and industry	Heat-related loss in performance	The manufacturing sector's water consumption intensify
Spatial planning and civil protection	Civil protection	Man-hours required to manage damage from weather-related events	Disaster response information
Cross sectoral indicators			Adapting to climate change at the local administrations

In step 6, the EU focuses on generating learning and accountability results in adaptation M&E. This step ensures oversight and stakeholder coordination, learning from successes or failures to improve adaptation strategies and plans. The EU addresses the following subtopics in adaptation M&E [68]:

1 Understanding drivers and targets
2. Identifying stakeholders
3. Definition of monitoring, reporting, and evaluation (MRE) indicators and methods
4. Communicating results to decision-makers
5. M&E of adaptation actions.

Under these subtopics, the EEA's approach to indicator development, as outlined by Makinen et al. [69], includes three categories:

1. Climate change indicators to understand the impacts of climate change.
2. Climate change impact indicators to capture impacts.
3. Economic, social, environmental and health vulnerability indicators to identify vulnerability and monitor adaptation strategies.

EEA's methodology for selecting indicators considers how changes in the scope of adaptation actions at different levels, such as national and regional, will affect the approach. At the regional level, a new set of indicators on the impacts of climate change on society and environmental systems is introduced. At national and higher scales, these indicators are categorized within the EEA methodology as input, process, output and outcome indicators. Based on their scope, the indicators are grouped into exposure, adaptive capacity, sensitivity, composite vulnerability, and hazard indicators. Alignment with the Paris Agreement, the Sendai Framework for Disaster Risk Reduction (DRR) and the UN Sustainable Development Goals (SDGs) is a key criterion in the selection of indicators [69].

Despite this approach developed by the EEA, it should be noted that while the EU has an implemented M&E system for greenhouse gas emissions at the Union level, it has an approach for local identification and M&E of adaptation actions. This is detailed in Annex 1 of the Commission Implementing Regulation (EU) 2020/1208, Article 4 on National Adaptation Plans. In the section "Monitoring and evaluation of adaptation actions and processes" it is stated that "Member States shall report on their approaches, systems used, transparency and indicators when M&E relates to reducing climate impacts, vulnerabilities and risks and enhancing adaptive capacity" [70].

As a result of this approach towards local determination and M&E of adaptation actions, it is seen that the successful practices of the Union countries are included in Climate-ADAPT. One of the examples included in Climate-ADAPT is the M&E system created by Germany for its Climate Change Adaptation Strategy (DAS), which includes not only monitoring but also an evaluation system [71]. The indicators addressed in Germany's 2019 monitoring report are considered within different sector and thematic clusters (Table 2) in the context of impact and response [72].

In terms of evaluation, the evaluation of the German Adaptation Action Plan (APA II) covers both strategic and operational levels. While the products and outcomes of the DAS are evaluated at the strategic level, the impact of APA II measures on target groups is evaluated at the operational level. The strategic results cover the short-, medium- and long-term impact of the DAS, while the operational results measure the impact of APA II on the target groups. A three-stage evaluation system assesses the process, implementation status, and overall impact [71].

In line with the EU's policy on local determination of adaptation actions and adaptation M&E systems, it is seen that in the system created to carry out the M&E of Germany's DAS, which is taken as an example within the scope of this study, a sectoral approach is adopted and timeframes for the targets to be achieved are determined. Another feature of the German M&E approach is that a separate M&E layer has been created for horizontally cross-cutting issues and sectors regarding adaptation. In this regard, it is seen that adaptation activities especially in local governments are addressed and local climate action is also evaluated. In this way, it is also possible to carry out M&E of adaptation actions detailed down to the building scale. In this approach,

Table 3. Examples of indicators in the Tonga JNAP2 M&E System Guide [48]

Target area	Process indicators	Outcome indicators (proposed)	Impact indicators
Coasts	Vulnerability baselines developed for coastal sector	Total length of sewer and drainage network at risk from climate hazards	Percentage of wastewater with safe treatment (SDG 6.3.1)
Buildings	Developed a multi-hazard plan to prepare for, respond to, and recover from disasters affecting public and community infrastructure	Number and extent of building-related vulnerability problems perceived by disabled and marginalized groups by gender and age	Percentage of the population living in households with access to basic services (SDG 4.1)
Tourism	Development of resilience indicators (process, outcome and impact) for tourism	Water consumed by tourist facilities	Direct economic losses due to damage or destruction of cultural heritage as a result of disasters (Sendai)
Water	Monitoring system for water, soil and coastal erosion developed	Number of cases of water-borne disasters	Mortality due to unsafe water, sanitation, and hygiene
Community resilience	Development of standard resiliency guidelines forl community engagement activities	Number of people below poverty line living in flood-prone areas	Percentage of people living below the poverty lines, by gender and age (SDG 1.2.1)
Private sector	Developing a costed, gender and social inclusion resilient facility for the private sector	Reduced work productivity due to heat stress	Coverage of essential health services (SDG 3.8.1)

it is seen that the monitoring of disasters and emergencies is included in the adaptation M&E system.

Tonga/Joint Climate Change and Disaster Risk Management M&E System

In Tonga, an integrated approach to disaster risk management and climate change is supported by the Joint National Action Plan 2 on Climate Change and Disaster Risk Management 2018-2028 (JNAP2). An M&E system guide published in 2019 prioritizes learning, accountability, and adaptation management, and integrates local knowledge into adaptation planning. The selection of indicators aligns with Tonga's international reporting requirements, including the Paris Agreement, and emphasizes policy monitoring, implementation evaluation, and impact assessment across management levels. The selection was informed by the UN SDGs and the Sendai Framework for DRR, and Table 3 provides examples of indicators selected with stakeholder input. The system designates specific focal points for data entry, standardized entry procedures, and regular capacity building to ensure its functionality [73, 74].

The M&E system established by Tonga is a good example of tailoring adaptation actions and M&E systems to local needs. This is because the selection of target areas takes into account the sectors in the country and the issues that need to be addressed in adaptation. However, as in other countries' examples, a detailed sector analysis was not carried out. This may be because, as a developing country, Tonga, like many other developing countries, wants to focus scarce financial, technical and human resources and capacity on priority areas. What is striking about Tonga's M&E approach is that all of the adaptation target areas, especially the social resilience layer, are addressed in an integrated manner with the disaster issue mentioned above. In other words, adaptation measures are considered together with the co-benefits of DRR. This approach is in line with the approach of UN agencies, in particular the UNDRR [75], to address adaptation and DRR actions together in recent years, which is also reflected in the linking of impact indicators to the Sendai Framework for DRR and/or the UN SDGs.

Türkiye's NCCASAP and Future Prospects for Adaptation M&E

Türkiye's subtropical Mediterranean climate zone covers a significant portion of its territory, making it highly susceptible to the effects of climate change. As a result, the country is exposed to medium to high climate risks both now and in the future [76]. As one of the Parties to the Paris Agreement, Türkiye currently lacks an active M&E/MEL system specifically dedicated to tracking adaptation actions and the NCCASAP. The relevant ministries in Türkiye have prepared SAPs for various sectors related to climate change adaptation. These sectors include water, agriculture, drought, desertification, capacity building, air quality, waste management, pollutants, and energy. However, separate, and independent M&E systems have been established for each of these sectors, rather than a unified system [77]. In this context, relevant ministries are developing M&E tools specific to their respective sectors, particularly in the project- and investment-based areas related to the following topics [78]:

- Tracking technical progress: Monitoring intervention logic and indicators-Performance evaluation and thematic monitoring
- Physical monitoring, financial monitoring
- Risk management and monitoring
- Early warning systems

However, there is still no system that evaluates environmental parameters together with socio-economic parameters in the context of climate change adaptation. Türkiye's NCCASAP, prepared by the Ministry of Environment and Urbanization (MoEU) for the period 2011-2023, mainly covered the following thematic areas [79]:

1. Water resources management
2. Agriculture and food security
3. Ecosystem services, biological diversity, and forestry
4. Natural disaster risk management
5. Human health

NCCASAP has defined goals and objectives related to the thematic areas, together with outputs and performance indicators, responsible/coordinating bodies and relevant organizations (Table 4).

As can be seen from Table 4, many responsible institutions and organizations here have become abolished and NCCASAP has expired as of 2023. It is not possible to provide clear information about how many of the actions determined within the scope of NCCASAP have been carried out, because a system regarding M&E of NCCASAP has not been established. All these issues and the need to renew the scope of NCCASAP within the framework of current adaptation needs are also stated in the 8th National Communication of Türkiye submitted to the UNFCCC Secretariat in 2023 [76].

Studies have commenced to revise the NCCASAP as part of the Enhancing Adaptation Action in Türkiye Project. This project is supported by UNDP, with the Ministry of Environment, Urbanization, and Climate Change (MoEUCC) as the beneficiary [80]. It was announced by the Climate Change Presidency (CCP), a subsidiary of MoEUCC, that NCCASAP (2024–2030) was completed in 2023 and was submitted to the Climate Change and Adaptation Coordination Board for approval and accepted [81]. Strategic goals and adaptation actions have been determined in line with the results of vulnerability and risk analyses conducted for 11 sectors within the scope of the current NCCASAP document. Their scope has been explained briefly as follows [82];

1. City (technological actions; Nature-based Solutions (NBS); climate-sensitive urban planning),
2. Agriculture and food security (strengthening institutional capacity for a climate-resilient, technology-efficient, water-efficient and competitive agricultural sector; strengthening the legal framework; raising awareness, protection and sustainable use of natural resources in agricultural production),
3. Water resources management (basin-based water conservation studies; reuse of treated wastewater; access to safe drinking water; increasing the efficiency of agricultural irrigation; rainwater management),
4. Biodiversity and ecosystem services (increasing awareness and capacity on NBS, Ecosystem-based Adaptation issues, strengthening cooperation; reducing habitat fragmentation and overuse pressures; increasing protected areas and ecosystem restoration; researching, monitoring and assessment of climate change impacts on biodiversity and ecosystem services),
5. Public health (monitoring of climate-related diseases; strengthening capacity and cooperation in this area in national and local organizations; development of a list of climate-sensitive diseases; review of occupational health and safety legislation),
6. Tourism and cultural heritage (climate-resilient infrastructure in tourism investments and businesses; development of social infrastructure; ensuring cooperation between institutions by taking climate change adaptation into account in decisions related to tourism and cultural heritage),
7. Industry (conducting vulnerability and risk analyses for the industrial sector; identifying natural technological risks and facilities at risk of major industrial accidents; evaluating investment projects together with their climate impacts),
8. Energy (improving the policy and administrative framework, institutional capacity and cooperation for adaptation of the sector to climate change; strengthening the production, transmission, distribution and storage infrastructure);
9. Transport and communications (ensuring the resilience of critical infrastructure; reducing vulnerability; improving accessibility, communication, and evacuation in case of emergencies),
10. Social development (integrating climate change impacts on social life and actions into policies at all levels and processes in all sectors),
11. DRR (strengthening the understanding and information infrastructure on climate-related disaster risks; adopting a transformative approach to risk management; improving institutional capacity and awareness; making sustainable investments).

It is seen that Türkiye has adopted an approach of making detailed and comprehensive sectoral analysis on adaptation, as in the EU approach. Although it is important that Türkiye's updated NCCASAP has been prepared, what is at least as important is the establishment of an M&E/MEL system specific to NCCASAP. Because, as stated above; In line with the decisions taken at UNFCCC COP28, countries party to the UNFCCC and the Paris Agreement are required to develop national MEL systems for adaptation by 2030. Within the scope of CCP's 2024-2028 Strategic Plan [83], under the title "Goal 2: Increasing the capacity to adapt to climate change at the national and local scale", "H.2.3. "An online monitoring mechanism will be created to monitor the actions of the National Climate Change Adaptation Strategy and Action Plan (2024–2030) and the actions will be monitored." target is included.

The MEL systems can be used in the Biennial Transparency Reports to be submitted to the UNFCCC Secretariat and in the presentations on adaptation actions, and will bring

Table 4. Examples of sectoral objectives, targets, outputs, and performance indicators included in Türkiye's NCCASAP [79]

Actions	Period	Outputs and performance indicators	Responsible/coordinating organization	Relevant organizations
I. Water Resource Management Purpose US1. Integrate adaptation to climate change impacts into water resources management policies. Objective US1.1. Ensure adaptation to climate change is integrated into existing policies, plans and legislation.				
US1.1.7. Orientation of water user organizations by relevant institutions within the framework of irrigation businesses taking into account the impacts of climate change	2011–2014	Improvement of local capacity	General directorate of state hydraulic works (SHW)	Ministry of food, agriculture and livestock (mfal), special provincial administration, local Authorities, water user organizations, NGO's
II. Agriculture Sector and Food Security Purpose UT4. Protect soil and agricultural biodiversity from the impacts of climate change Objective UT4.1. Protect the physical, chemical and biological capacity of soils against the impacts of climate change				
UT4.1.3. Implementation of advanced harvesting systems, and development of agricultural forestr	2012– and onwards	Model practices	MFAL	
III. Ecosystem services, biodiversity and forests Purpose UO1. Integrate climate change adaptation into ecosystem services, biodiversity and forestry policies Objective UO1.1. Review existing policies for adaptation to climate change impacts				
UO1.1.3. Integrating and spreading adaptation to climate change into the existing planning for selected/priority protected areas	2011–2015	Plans for protected areas including adaptation to climate change	Ministry of forestry and water works (MFWW)	
IV. Natural Disaster Risk Management Purpose UA1. Identify threats and risks for managing natural disasters caused by climate change. Objective UA1.1. Identify risks of natural disasters caused by climate change, such as floods, overflows, avalanches, landslides, etc.				
UA1.1.2. Prepare implementation and audit guidance related to flood and landslide risk reduction and management plans.	2011–2015	Relevant plans and guidelines	MFWW, Disaster and emergency management presidency	SHW
V. Public Health Purpose UİS1. Identify existing and future impacts and risks of climate change on public health. Objective UİS1.1. Research on the impact of extreme weather events on public health				
UİS1.1.1. M&E the current and future impacts of extreme weather events such as heat waves, hurricanes, floods and droughts on public health based on climate projections.	2011–2020	Impact assessment reports and monitoring systems	Ministry of health	Governorships
VI. Cross-cutting issues in adaptation OBJECTIVE UYK1. Ensure cross-cutting adaptation to climate change Objective UYK1.3. Organize training, awareness-raising and information activities to develop the capacity to combat and adapt to climate change.				
UYK1.3.2 Ensure participation in the process of adaptation to climate change and prepare programs to raise awareness of the public.	2011–2014	Programs	Ministry of environment and urbanization	Climate change coordination board, universities

important gains that will enable Türkiye to understand and improve the realization and success of its adaptation actions. In addition, the information obtained from this adaptation MEL system will also contribute to the future justification of Türkiye's [84] request to benefit from the Loss and Damage Fund established at COP28.

Data is one of the main problems in Türkiye, as in many other countries. In order to determine adaptation needs and measures and to monitor and evaluate them, adequate, reliable and appropriate data in climatic and socio-economic fields should be kept by institutions and these data should be accessible. It is essential to develop policies on this issue and ensure the continuity of the process.

In assessing climate-induced disaster risks, providing sufficient financial resources to conduct impact and vulnerability analyses based on adequate and up-to-date climatic and socio-economic data is another essential issue for adaptation activities in Türkiye. While Türkiye, as a developing country, is already vulnerable to other disaster areas such as seismicity, its vulnerability to climatic disasters makes it necessary to develop policies that utilize resources effectively while allocating the country's financial resources to disaster-related issues. The most important way to achieve this is to shift from crisis management to risk management. A more effective strategy would be to invest in adaptation measures through proactive identification of potential losses and damages. This approach allows for informed decision-making and policy formulation that considers not only the financial implications of disasters but also their social and cultural impacts. This yields positive outcomes for development and national security.

In addition, determining the adaptation actions to be developed, using resources effectively in adaptation-related practices, investing in innovative technologies and supporting R&D studies in this context are very important for increasing the effectiveness of M&E systems. Ensuring regular capacity development of stakeholders who will be entering data is another critical strategy to ensure the sustainability and effectiveness of the adaptation M&E system. Even if appropriate and sufficient adaptation measures are identified and implemented, their correct data entry into the M&E system will directly affect the success of the process.

Adopting a multi-stakeholder approach in conducting studies on the above 11 sectors in the NCCASAP M&E system to be established is essential for the sustainability of the process and the accuracy of the results to be obtained. In this context, Türkiye should receive support and establish cooperation from EU countries with a similar approach to adaptation, as well as from the UNFCCC Adaptation Committee, which has been working on adaptation M&E for a long time. The lessons learned are important for the operation of the adaptation M&E system and benefiting from the experiences of other countries in this context can save time for Türkiye, which is a country vulnerable to climate impacts.

Furthermore, concerning DRR, which is discussed under a separate title in Türkiye's NCCASAP, it is very important to adopt an integrated approach within the framework of the adaptation M&E system to be established and to identify indicators related to disaster resilience in other adaptation sectors.

Considering the magnitude of losses and damages currently caused and projected to be caused by climate-related extreme weather events and disasters in Türkiye, the results obtained from the adaptation M&E system will also be able to provide the necessary information for the establishment of a national insurance system for losses and damages due to climate change.

CONCLUSIONS

Today, the magnitude of the adverse effects of climate change highlights the need for well-planned adaptation measures. This is also a fundamental aspect of the international climate change negotiations under the UNFCCC to realize the goals of the GGA as defined under the Paris Agreement, the Convention's implementing instrument. To ensure the success of current and future adaptation efforts, adaptation actions must be accurately identified and developed through regular review processes. To achieve this, M&E systems for adaptation actions within the UN adaptation cycle are of great importance. Lessons learned from the M&E step not only provide feedback on the adaptation process, but also enable the identification of areas or actions that are failing or working well in the process. In this way, it will be possible to increase the resilience of settlements and infrastructure of all types and levels, prevent disasters, and create opportunities for learning and development in various economic, social, and environmental fields.

The assessment of the research questions at the beginning of the study showed that it is critical to identify climate risks and adaptation needs before M&E of adaptation actions. In this way, the adaptation actions and related indicators for which M&E will be conducted can be accurately determined. This requires good quality and reliable climate and socio-economic data at each stage of the adaptation process.

The nature of climate change poses challenges for M&E in terms of adaptation actions, particularly as the quality of data needed for adaptation processes is limited, incomplete, or unavailable. Innovation in scaling down global data for local use and ensuring that these new technologies are accessible to all countries is crucial both for countries' NAP preparations and for M&E of identified adaptation actions. Although uncertainties may be difficult to eliminate, efforts should focus on developing adaptation actions based on the best available scientific data and on effectively managing uncertainties.

Inadequate M&E during the identification, planning, and implementation of adaptation actions prevents learning from the results of these phases. The provisions of the Paris Agreement, which aim to improve human capacity and achieve the adaptation cycle, call for a GST every five years starting in 2023. At UNFCCC COP28, the first GST, it was decided that all Parties would establish M&E/MEL systems for national adaptation actions by 2030.

Looking at the adaptation M&E systems and methodologies discussed in the study, it is seen that country priorities, level of development, and local conditions for adaptation to climate change affect the sectors covered by adaptation policies, strategies, and indicators in adaptation M&E systems. While developed countries emphasize indicator sets and detailed sector assessments that emphasize governance and infrastructure, developing countries focus on sectors that are prioritized due to scarce resources. In developing countries, there is also a clearer tendency to combine adaptation actions with DRR actions. However, regardless of the level of development, it is also observed that the adaptation M&E methodologies developed generally focus on the objectives of reducing vulnerability, increasing resilience, developing emergency action plans, and ensuring the effective use and sustainable management of financial and natural resources.

Adaptation M&E systems, once established, require continuous improvement. Lessons learned from the successes and shortcomings of adaptation efforts and changing climate conditions, should be used to improve these systems. In this context, the main priorities of M&E/MEL systems in the coming period should be to protect the health of individuals and all ecosystems and to protect and ensure the sustainability and development of all natural and man-made resources.

In Türkiye, one of the Parties to the Paris Agreement, there is no active M&E/MEL system to monitor adaptation actions or NAP. The 8th NC emphasized that efforts to establish such a system are continuing. However, floods and storms that occur especially in cities in Türkiye as a result of extreme weather events due to climate change cause significant loss of life and property, and adaptation measures need to be determined according to new climate norms, and M&E should be carried out especially considering these issues. Not only floods and storms, but also problems such as temperature increases and droughts show the urgency of M&E of adaptation measures in the context of water and food security.

As previously stated, in accordance with the COP28 decision, it is necessary to identify adaptation measures by 2030 and develop an M&E system for these measures. This system will help to understand the adequacy and effectiveness of adaptation measures in Türkiye, a developing country that is highly vulnerable to climate impacts. It will also facilitate the improvement of adaptation efforts, and also support accurate and consistent reporting of adaptation studies to the Secretariat and the contribution of the results of national efforts to global efforts.

In the context of Türkiye's NCCASAP framework, it is of the utmost importance to not only define policies and measures and establish an M&E system, but also to develop the institutional capacity to ensure the continuity of this system. In this regard, Türkiye should cooperate with other countries and the UNFCCC Secretariat.

Consequently, it can be said that adaptation M&E systems represent one of the most pivotal instruments for facilitating the transition from crisis management to risk management in the context of the adverse effects of climate change. Carrying out this last and crucial step of the UN adaptation cycle through established systems in all countries, including Türkiye, and ensuring the integration of M&E systems established by countries will help to understand the adequacy and success of global adaptation efforts, as well as it will make a significant contribution to achieving the goals of the UN SDGs, the Sendai Framework for DRR, and the Paris Agreement's GGA.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Combined treatment of domestic wastewater with landfill leachate using aerobic moving bed bioreactor (AeMBBR)

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ABSTRACT

In this study, the treatment of landfill leachate (LFL) and domestic wastewater using an aerobic moving bed biofilm reactor (AeMBBR) was investigated. AeMBBR was filled with 30% (v:v) biocarrier material (Kaldnes K1). The tested volumetric ratio of landfill leachate was 10%. The impact of varying hydraulic retention times (HRTs) (24–12-6 h) at a constant dissolved oxygen (DO) of 3.2 mg/L was investigated for system optimization. AeMBBR was successfully operated (HRT: 6h) for LFL and domestic wastewater treatment corresponding to 94%, and 78% ammonium nitrogen (NH4-N) and total organic carbon (TOC) removals, respectively. Additionally, *Proteobacteria* (66%) have been identified as the predominant culture in the biofilm layer, which plays a significant role in the co-treatment of domestic wastewater and LFL. Considering the results obtained; it was found that a significant amount of ammonium nitrogen was successfully removed.

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INTRODUCTION

Landfill leachate is the result of the percolation of water through waste deposits that have been subject to aerobic and anaerobic microbial decomposition [1–4]. Landfill leachate typically contains high levels of COD, heavy metals, ammonia—nitrogen, and inorganic salts [5–7]. The characteristics of this wastewater vary depending on factors such as the composition of the solid waste, landfill operation, hydrology, and climate. High ammonium nitrogen (NH_4^+-N) concentrations in LFL cause serious environmental problems such as eutrophication and ammonium toxicity, which inhibit photosynthesis via free ammonia (FA) under alkaline conditions (pH>8.0) [8, 9]. Therefore, NH_4^+-N must be removed from the LFL.

Co-treating landfill leachate with domestic wastewater can be a cost-effective solution that promotes the degradation of organic pollutants through dilution [10]. This treatment option has the added advantage of being able to utilize existing wastewater treatment plants, eliminating the need for new investments. Various physicochemical [11, 12] and biological treatment [13] methods are available to remove NH_4^+-N from LFL and domestic wastewater. Biological treatment methods have important advantages compared to physicochemical methods, such as being cost-effective, having low sludge production capacity, and being environmentally friendly [14, 15]. The treatment of domestic sewage wastewater mixed with landfill leachate poses a major challenge due to the high concentration of ammonium in the leachate, which requires effective biological nitrogen removal. Activated sludge [16], anammox [17], and nitrification-denitrification [18] processes are among the biological technologies that have been extensively used for LFL and domestic wastewater treatment. The nitrification process is a good option for achieving complete NH_4^+-N removal [19].

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Table 1. Previous studies in different reactors

Reactor type	Wastewater	Reactor volume (L)	Temperature (°C)	HRT (day)	Volumetric ratio (%)	Removal efficiency (%)	Ref
MBBR-MBR (Moving bed biofilm reactor and aerobic membrane reactor)	Leachate	5	32–25	48	–	COD: 74.2 NH_4^+-N: 99.7	[22]
MBHBR (Moving bed hybrid bioreactor)	Domestic sewage and leachate	7.9	25	6	4	COD: 77–80	[23]
SAFF (Submerged aerobic fixed film)	Domestic sewage and leachate			24	8	COD:	[24]
SBR (Sequencing batch reactors)	Domestic wastewater and leachate	2	25	0.43 1–10	5	COD: 73	[25]
Active sludge	Leachate	2	22	–	5–20	COD: 16–88	[13]
Active sludge	Domestic wastewater and leachate	6.1	–		5–25	–	[26]

HRT: Hydraulic retention times; Ref: References.

Many studies have focused on new treatment technologies for the co-treatment of LFL with domestic wastewater. The Moving Bed Biofilm Reactor (MBBR) is a rapidly developing technology for the treatment of wastewater [20]. MBBR is a biological treatment process based on conventional activated sludge and biofilter processes. The biomass present in the MBBR exists in two distinct structural forms: a suspended solid phase and a biofilm that is attached to the carrier. MBBR is more effective for nitrification than conventional activated sludge (CAS) systems due to the lower density and size of the CAS floc [21]. Table 1 shows previous studies using different reactors.

This study examines the nitrification process in an MBBR used for the simultaneous treatment of domestic wastewater and landfill leachate. The main research questions are as follows:

- What is the nitrification efficiency of the MBBR under different operating conditions?
- What factors can affect the nitrification efficiency of the MBBR?
- Which microbial communities are most prevalent in wastewater treatment?

MATERIALS AND METHODS

Characteristics of Domestic Wastewater and LFL

The LFL utilized in the AeMBBR studies was sourced from the Kahramanmaraş landfill in Türkiye. Domestic wastewater was collected from a treatment plant in Kahramanmaraş, Türkiye, and stored in a refrigerator at a temperature of +4°C to prevent microbial growth, following standard methods. The properties of the real wastewater used in this study are listed in Table 2. The aerobic reactor was inoculated with sludge from the activated sludge tank of the Kahramanmaraş Domestic Wastewater Treatment Plant.

Table 2. Properties of domestic wastewater and LFL

Parameters	Domestic wastewater	Landfill leachate (mg/L)	Parameters	Domestic wastewater	Landfill leachate (mg/L)
COD (mg/L)	645±100	7000–14000	TSS (mg/L)	–	1190±100
TOC (mg/L)	150±10	4000–11000	Sulfate (mg/L)	–	100±10
NH_4-N (mg/L)	40±10	1700-3600	Copper (mg/L)	–	2.572±0.6
NO_2 (mg/L)	–	330±10	Zinc (mg/L)	–	0.029±0.01
NO_3-N (mg/L)	9±2	2–50	Iron (mg/L)	–	2.575±0.5
Phosphorus (mg/L)	–	80±20	Cadmium (mg/L)	–	0.001
Sulfide (mg/L)	–	100±10	Total chromium (mg/L)	–	0.255±0.05
TN (mg/L)	–	1800±100	Lead (mg/L)	–	0.00025
BOD (mg/L)	327±100	1200±300	Mangan (mg/L)	–	0.1±0.05
pH	7.5-8.0	7.5–8.2	Nickel (mg/L)	–	0.625±0.1
Color (Pt-Co)	100±20	6380–9200	Phenol (mg/L)	–	20±2
Color (RES)			Calcium (Ca^{2+})	–	150±10
436		220±20	Free Chlorine (mg/L)	–	0.6±0.1
525		90±10	VSS (mg/L)	–	850±20
620		55±5			

Aerobic Moving Bed Bioreactor (AeMBBR) Operation

The schematic diagram of the AeMBBR used in this study is shown in Figure 1. The continuous flow AeMBBR consisted of a 5L tank with an effective working volume of 3L. In the AeMBBR, polyethylene Kaldnes K1 was used as a bio-carrier to retain the biomass. The Kaldnes K1 has a specific surface area of nearly 500 m^2/m^3 and a density of 0.95 g/cm^3. To account for the reactor volume and potential biofilm growth on the support material, the fill rate of the Kaldnes K1 supplement was chosen as 30%.

Landfill leachate was added to the domestic wastewater at a rate of 10% by volume. The reactor was operated continuously at a DO concentration of 3.2 mg/L. The initial concentration of mixed liquid-suspended solids (MLSS) in the AeMBBR was adjusted to approximately 4000 mg/L. Sludge was not withdrawn from the reactor which infers that theoretical SRT was infinity (HRT 24 and 12 h). However, at 6 h HRT, the sludge was maintained at an SRT of 15–20 days and with MLSS of 3500–4400 mg/L. The contents of the reactor were stirred at 250 rpm, and the operating temperature was maintained at room temperature. The DO, temperature, and pH of the reactor were measured with external probes and recorded daily. The pH of the AeMBBR was maintained at 7–7.5, with the use of H_2SO_4 and NaOH to correct the pH. The operating conditions of the AeMBBR are listed in Table 3.

The performance of AeMBBR was utilized under different HRTs. Initially, the HRT and dissolved oxygen (DO) concentrations in AeMBBR were maintained at 24 hours and 3.2 mg/L, respectively. Then, the HRT was reduced to 12 hours. Finally, the HRT was further reduced to 6 hours.

Analysis

Suspended solids in the mixed liquor (MLSS) were measured using standard methods [27]. A DO meter (YSI5000, YSI Company, USA) was used to measure dissolved oxygen (DO), and the pH value was measured with a pH meter (Thermo, Orion 4 Star, Indonesia). Each sample was centrifuged at 4000 rpm for 5 minutes (Eppendorf Centrifuge 5415R, Hamburg, Germany) and then filtered through a 0.45 µm pore size syringe filter (Sartorius AG, Göttingen, Germany) before analysis. The COD measurements were conducted using the dichromate-closed reflux Colorimetric Method as defined by Standard Methods (5220 D). The TOC-TN analyzer (Shimadzu TOC-VCPN/TNM-1, Kyoto, Japan) was used to analyze total dissolved organic carbon (TOC) and total carbon (TC). IonPac AS19-CS19 analytical and ion chromatography (Dionex ICS-3000, Sunnyvale, CA, USA) were used to determine ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) concentrations with IonPac AG19 guard columns. The eluent was prepared by dissolving 9 mM sodium carbonate (Na_2CO_3) and 20 mM methane sulfonic acid in water, and then pumping the solution at a flow rate of 1 mL/min. To measure the mass of the biofilms, the three carriers were dried at 105°C for 2 hours and weighed. Subsequently, the dried carriers were combined with a 0.1 mol/L hydrochloric acid solution for 24 hours at a temperature of 80°C. Following this, the mixture was subjected to ultrasonic treatment for one hour. They were then washed several times with distilled water until all biofilm was removed from the carrier. The carrier sample was subjected to a second drying process and then weighed. The biofilm mass was calculated according to Piculell et al. [28].

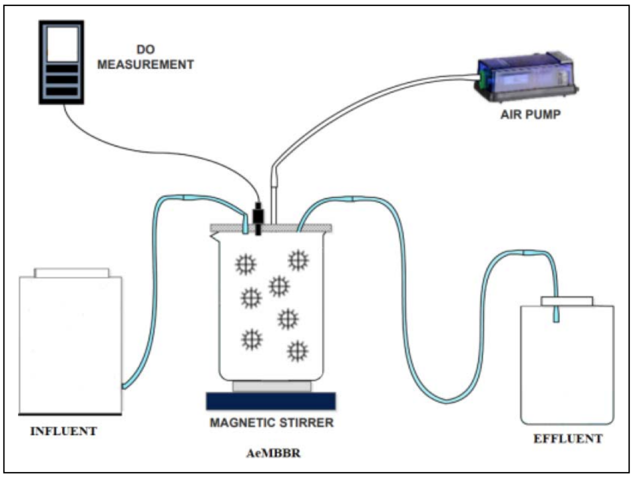

Figure 1. Experimental set-up of the AeMBBR.

Illumina MiSeq Sequencing Analysis

The Illumina MiSeq method was used to analyze bacteria on the contaminated Kalnes K1 surface (biofilm) and mixed liquor sample (supernatant). DNA was extracted from bacterial samples collected at 24 hours HRT in AeMBBR using the EurX Gene MATRIX Tissue & Bacterial DNA Purification Kit, according to the manufacturer's protocols. This sample was taken under the highest contamination operating conditions. The V3 and V4 domains of the bacterial 16S rRNA gene fragments were amplified using the forward primer 5'TCG TCGGCAGCGTCAGATGTGTATAAGAGACAGCCTACGGGN GGCWGCAG and reverse primer 5'GTCTCGTGGGTCCGGAGATGTGTATAAAGAGACAGAGGACTAC HVGGTATCTAATC, along with 12.5 µL of the reverse primer and 12.5 µL of 2X OFF Hot Start PCR mix. The temperature cycling conditions were as follows: initial denaturation at 95°C for 3 minutes, followed by 25 cycles at 95°C for 30 seconds, 55°C for 30 seconds, and 72°C for 30 seconds, with a final step at 72°C for 5 minutes.

Table 3. AeMBBR operational conditions

Reactor	Days	HRT (h)	Dissolved oxygen concentration (DO) (mg/L)	Kaldnes K1 (%)	LFL: DW (%)
	0–34	24			
AeMBBR	34–70	12	3.2	30	10
	70–107	6			

HRT: Hydraulic retention times; AeMBBR: Aerobic moving bed bioreactor; LFL: Landfill leachate.

RESULTS AND DISCUSSION

The Performance of the Aerobic Moving Bed Bioreactor (AeMBBR)

The variation of biofilm density and MLSS concentration during the study is shown in Figure 2. The MLSS concentration was kept stable at between 3500–4500 mg/L in AeMBBR during the whole operation. Initially, during the 24 h of HRT, the density of the biofilm in Kaldnes K1 remained constant at an average of 1000±100 mg/L for

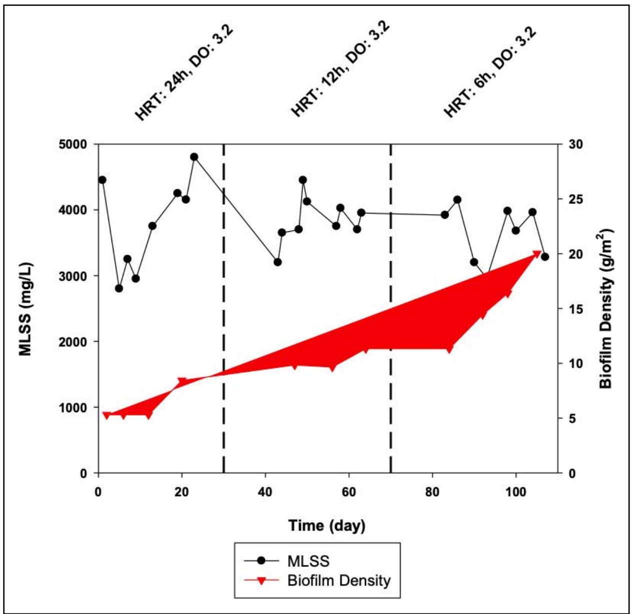

Figure 2. Evolution of MLSS concentration and biofilm density in the AeMBBR system.

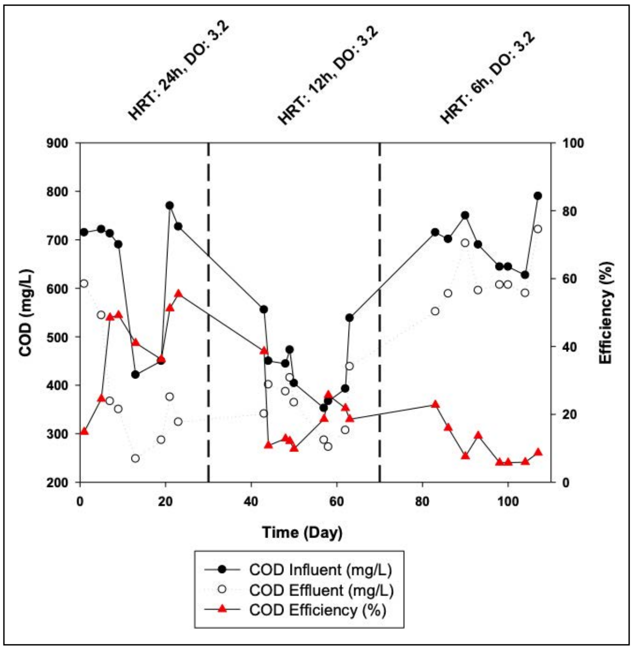

Figure 3. The COD removal performance of AeMBBR.

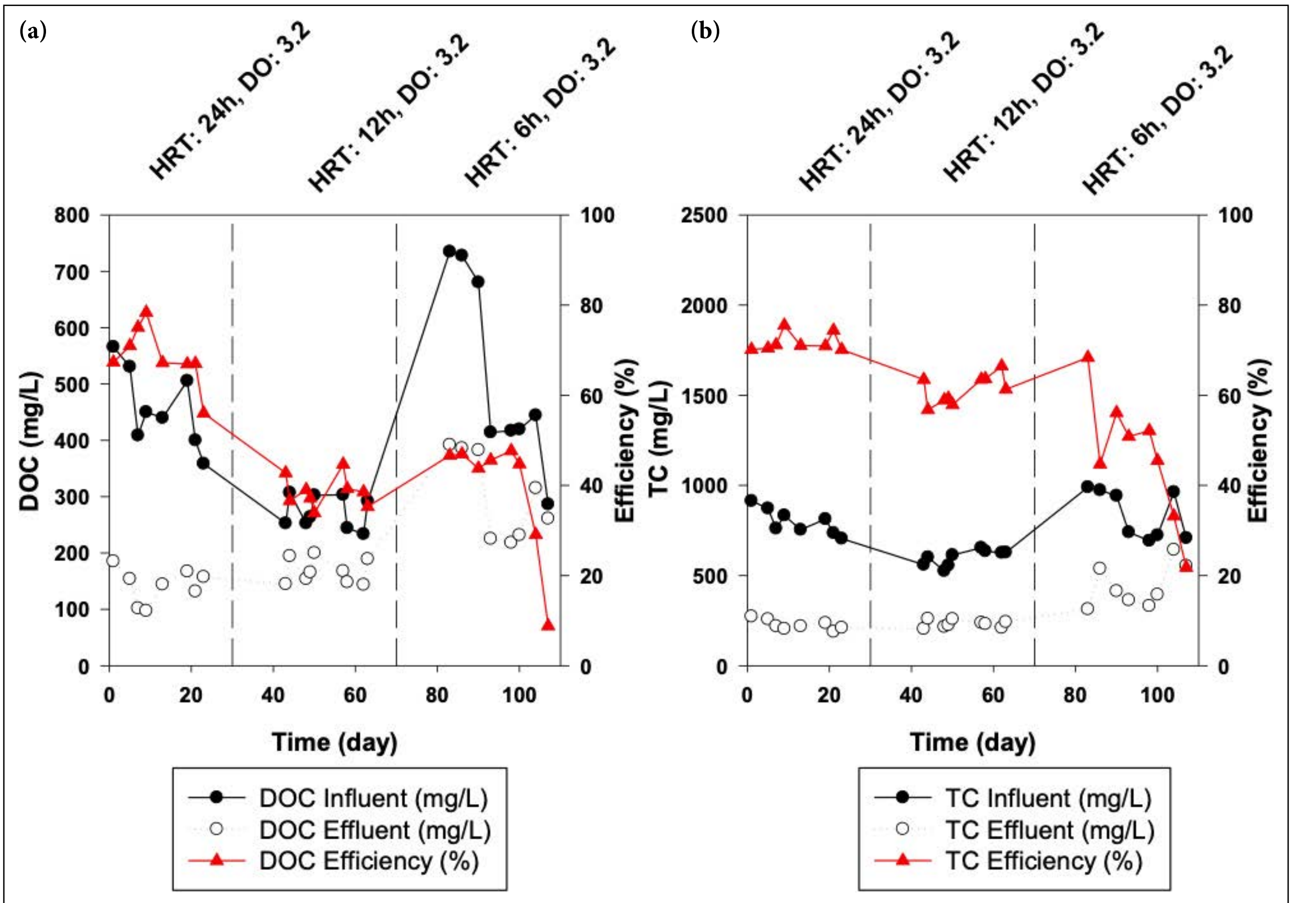

Figure 4. TOC **(a)** and TC **(b)** removal performance of AeMBBR.

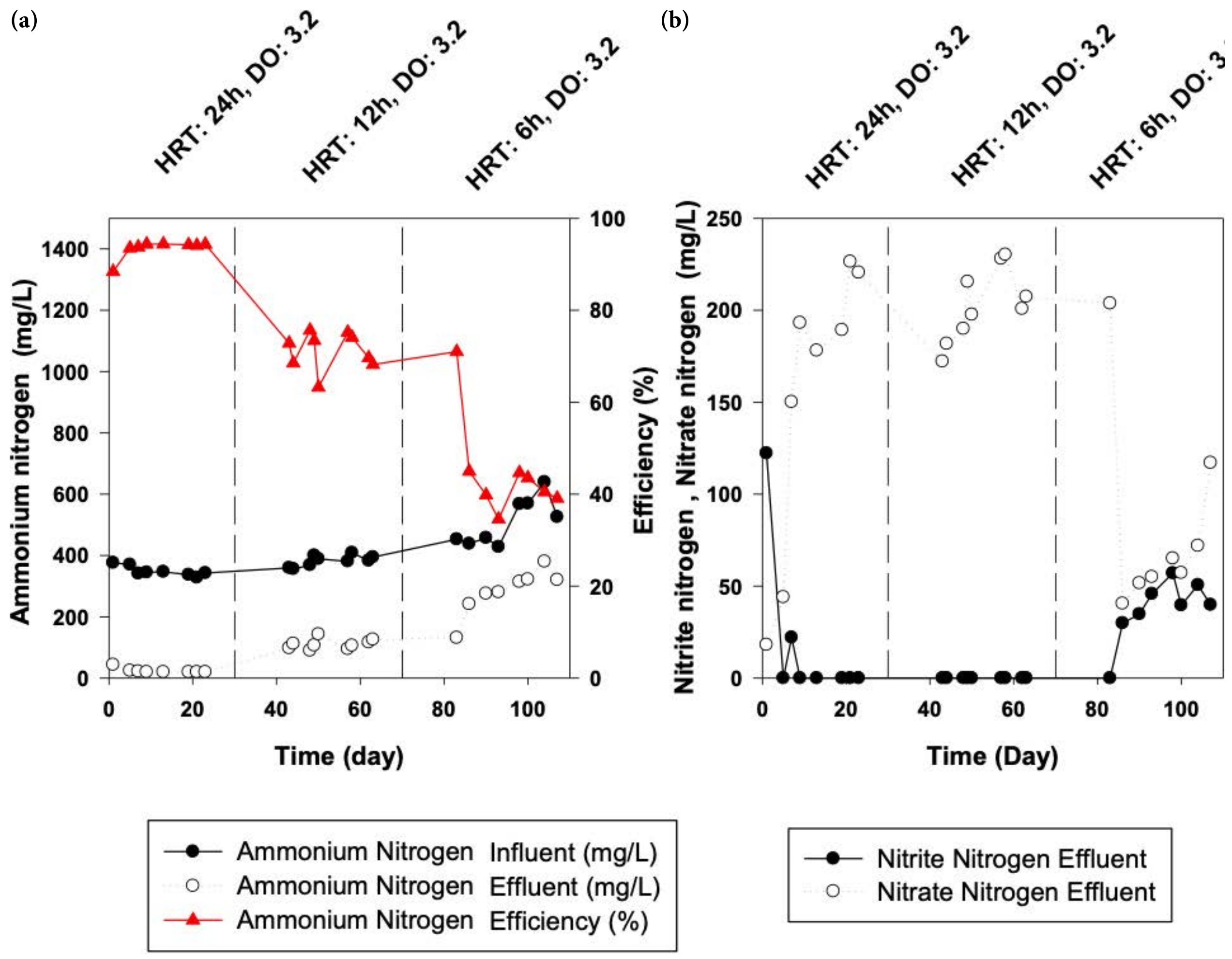

Figure 5. Performance of AeMBBR for NH4-N removal **(a)** and NO_2-N and NO_3-N accumulation **(b)**.

the first 12 days. After this day, the biofilm layer gradually increased. When HRT was reduced from 24 h to 12 h (days 34–70), a linear increase in biofilm density was observed. The average biofilm density at 12 h of HRT was 1542 mg/L. As seen in Figure 2, an increase in biofilm density was observed as HRT decreased. At 6 h of HRT, the average biofilm density increased to 3000 mg/L. Kozak et al. [29] observed that the biofilm-forming rate at 6 h was faster than that of 24 h and 12 h.

The effects of different HRTs on COD removal from combined LFL and domestic wastewater in the AeMBBR study are illustrated in Figure 3. The initial COD concentration varies between 350 and 800 mg/L depending on the characteristics of the landfill leachate. During the first 34 days of the study, the AeMBBR achieved a COD removal efficiency of 40%, resulting in an effluent COD concentration of 388 mg/L at 24 h. When HRT was reduced to 12 h (days 34–70), the COD removal efficiency was an average of 21%. Duyar et al. [22] reported that low HRT can negatively affect COD removal efficiency due to high loading rates and toxicity. Similarly, during days 70–107, reducing HRT from 12 h to 6 h resulted in decreased COD removal efficiency, corresponding to a 12% removal efficiency. It was difficult to compare our results with studies on COD removal efficiency in AeMBBR due to the highly challenging and variable concentrations of landfill leachate. Çeçen and Çakıroğlu [13] operated an activated sludge reactor for combined leachate and domestic wastewater treatment and achieved about 56% COD removal. Ferraz et al. [30] investigated the treatment of combined LFL and domestic wastewater using a submerged aerobic biofilter (SAB) system and achieved about 80% COD removal at 24 h HRT.

Figure 4 shows TOC and TC removal performance in the AeMBBR. Between days 0–34, average TOC and TC removal efficiency in AeMBBR were 68% and 71%, respectively, at 24 h HRT. When HRT was decreased to 12 h (days 34–70), the average TOC and TC removal efficiency was 40% and 61%, respectively. During days 70–107, the decreasing HRT from 12 h to 6 h resulted in decreasing TOC and TC removal efficiency, corresponding to 39% and 46% removal efficiency. According to Kozak et al. [29], this was probably due to the excessive biofilm production leading to mass transfer limitations.

The effect of HRT on ammonium nitrogen removal efficiency is shown in Figure 5a. During days 0 to 34, the average NH_4^+-N removal efficiency in the AeMBBR reactor

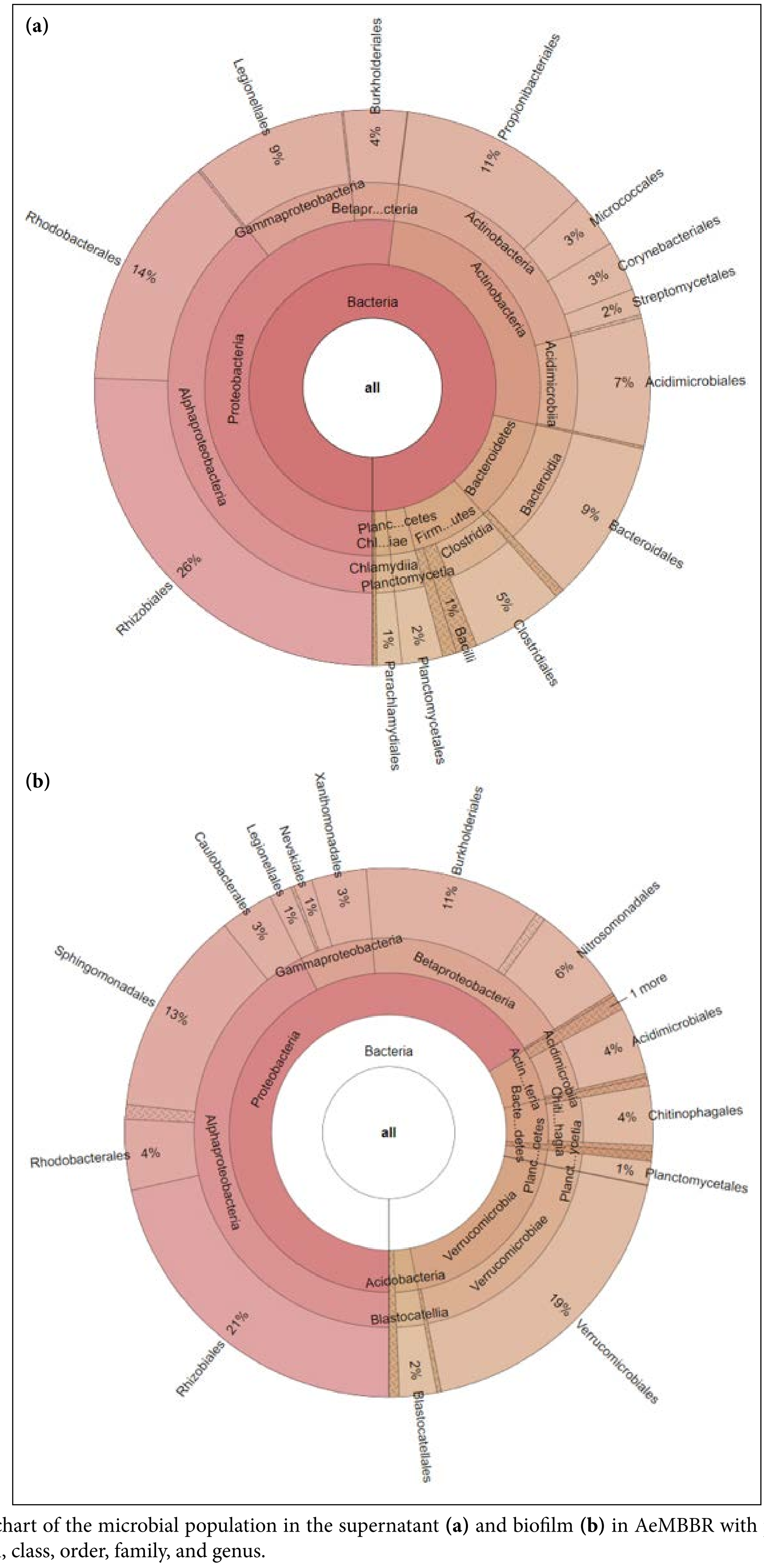

Figure 6. Krona chart of the microbial population in the supernatant **(a)** and biofilm **(b)** in AeMBBR with phylogenetic levels kingdom, phylum, class, order, family, and genus.

was 93%, corresponding to an effluent NH_4^+-N concentration of 23 mg/L at 24 h HRT. Chakraborty et al. [31], investigated the treatment of combined LFL and domestic wastewater using a sequenced batch reactor (SBR) system and achieved approximately 35% ammonium nitrogen removal at 2.5 days of HRT. NH_4^+-N removal efficiency decreased to 71% when HRT was reduced from 12 h to 6 h. Similarly, at 6 h HRT, reactor NH_4^+-N removal efficiency decreased significantly (47%). Nogueira et al. [32] reported that low HRT leads to increased loading rates, which negatively affects nitrifies as they compete with heterotrophic bacteria for substrates. Li et al. [33] reported that nitrification efficiency increased by 41% by reducing HRT from 10 h to 5 h, and the decrease in HRT increased ammonia oxidation activity.

As can be seen in Figure 5b, the accumulation of NO_2-N in the first 7 days was significantly high, but after this day, NO_2-N was not observed in the effluent and the NO_3-N accumulation was 152 mg/L NO_3-N. This was an indication that nitrification was taking place in the reactor. Similarly, no accumulation of NO_2-N was observed at 12 hours of HRT, and the accumulation of NO_3-N gradually increased, corresponding to 202 mg/L of NO_3-N. With the reduction of HRT to 6 hours, the NO_2-N accumulation decreased to 37 mg/L NO_2-N and the NO_3-N effluent concentration to 82 mg/L.

Microbial Community Structures

Microbial community analysis was examined using 16S rRNA gene amplicon sequencing for supernatant and biofilm samples collected from AeMBBR at 24 h HRT (Optimum condition). In AeMBBR, *Proteobacteria* predominated in the phylum group. As shown in Figures 6a and 6b, *Proteobacteria* were detected in 52% and 66% of the supernatant and biofilm, respectively. Many studies have shown that *Proteobacteria* always predominate in industrial wastewater treatment plants [34, 35]. In addition, the main bacterial group, *Proteobacteria*, includes facultative and aerobic bacteria that can remove nitrogen and organic matter [22, 36]. *Actinobacteria* (26%), *Bacteroidetes* (10%), *Firmicutes* (7%) and *Planctomycetes* (2%) are other phyla groups in the supernatant, while *Verrucomicrobia* (19%), *Actinobacteria* (5%), *Bacteroidetes* (5%), *Acidobacteria* (2%) were other groups of phyla in the biofilm. Matar et al. [37] reported that the Actinobacteria phylum is abundant in activated sludge. In addition, *Bacteroidetes* are commonly found in nitrogen removal systems [38, 39]. *Alphaproteobacteria* was dominant at the class level in the supernatant and biofilm which was 39% and 43%, respectively. *Actinobacteria* (19%), *Bacteroidia* (9%), *Gammaproteobacteria* (9%), *Acidimicrobiia* (7%), *Clostridia* (5%), *Betaproteobacteria* (4%), *Planctomycetia* (2%) were other class levels in the supernatant. Similarly, *Verrucomicrobiae* (19%), *Betaproteobacteria* (17%), *Gammaproteobacteria* (6%), *Acidimicrobiia* (4%), *Chitinophagia* (4%), and *Blastocatellia* (4%) were another class level in the biofilm.

CONCLUSION

In this study, the nitrification process was successfully carried out in the landfill leachate and domestic wastewater treatment using AeMBBR. Our findings revealed NH_4-N removal around 94% in 24h HRT. Microbial community structures showed that *Proteobacteria* were the dominant culture responsible for removing N and C in AeMBBR. This study showed that the co-treatment system could provide a desirable option for removing NH_4-N from wastewater. However, it was also determined that an additional denitrification system should be implemented to effectively remove the nitrate that was formed.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Environmental Research & Technology

Research Article

Which one is greener for the consumer? Product emission comparison between diesel and battery electric vehicles

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ABSTRACT

This study delves into a comparative analysis of electric vehicles (EVs) and diesel vehicles (DVs) across emissions, design, technology, and fuel consumption. One of the aims is to reveal the relationship between changes in form-based mass of the designed part, material selection influenced by production technologies, and the resulting production emissions and mass-based fuel consumption. The research aims to elucidate the environmental impact of EVs and DVs, particularly focusing on emissions stemming from raw materials of the production. Methodologically, the study employs theoretical analysis alongside practical assessments using Autodesk Fusion 360 and CCaLC2 software for mass determination and emissions calculation, respectively. Through an examination of key parameters such as vehicle design, material usage, and powertrain systems, the study sheds light on the nuances of emissions generated by each vehicle type's parts. The research contextualizes the growing importance of sustainable transportation solutions in the face of escalating environmental concerns, emphasizing the need for rigorous evaluation of alternative fuel vehicles. By comprehensively analyzing data on emissions, design, and fuel consumption, the study provides insights into the complexities of sustainability in the automotive industry. The findings underscore the critical role of industrial design in emissions reduction and offer recommendations for stakeholders to prioritize sustainability in vehicle production and consumption practices. Also, mentioning important notes for green consumers who are buying products according to environmental effects. The study contributes to advancing understanding in the field of sustainable transportation and underscores the importance of methodological rigor in evaluating environmental impacts.

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INTRODUCTION

In today's world, the transition to alternative fuel vehicles has accelerated due to the emissions created by fossil fuels. As it is known, production accelerated after the industrial revolution, and this acceleration increased the supply and demand [1]. The increase in supply also impacted population growth momentum. This growth in both supply and demand in production has also triggered resource use and emission problems. Today, the transportation and automotive sectors exemplify this supply and demand relationship. In parallel with the increasing population, vehicle demands are also increasing [2]. Consequently, emissions from vehicle fuels have become a significant issue. Alter-

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native fuel vehicle technologies were developed through research and development (R&D) to reduce emissions from fossil fuel vehicles. The most effective solutions today include hybrid, fully electric, and hydrogen-powered engines. Alternative fuel vehicles, called hybrids, contain electric propulsion systems along with fossil fuel. Thanks to this mixed resource use of the vehicle, fossil fuel usage is reduced. In fully electric vehicles, there are differences depending on the battery solutions [3]. As the name suggests, electric vehicles provide movement using electrical power. However, the battery technologies used in this technology have serious effects on the range and usage of the vehicle. Another technology is engines powered by hydrogen. These engines are still being developed to be more efficient [4]. Hydrogen engine vehicles use the energy produced by the combustion of hydrogen gas [5]. Extensive studies are being carried out on the release of oxygen to nature as a result of burning hydrogen due to its structure. R&D studies continue in this field within the scope of engine cost and commercial profit margin.

Apart from hybrid, electric vehicles that run entirely on alternative fuel sources are divided into battery electric vehicles and plug-in electric vehicles. Battery electric vehicles are considered to be very efficient in reducing emissions [6]. It is explained that environmentally friendly transportation can be achieved if the energy stored in the battery is used to reduce greenhouse gas emissions and the energy drawn from the lines to the battery is produced from renewable energy systems such as solar panels and wind turbines. In addition, the two biggest problems of battery electric vehicles are the product life cycle (lifespan of the vehicle) and the limited range of the batteries [7]. There are differences in terms of energy density between the technology used in the batteries of battery electric vehicles and the products made of different minerals. According to these differences; Lithium-ion battery is most suitable for use in vehicles, but rapid aging and decreased durability occur in fast charging situations. The use of LTO ($Li_4Ti_5O_{12}$) and LFP ($LiFePO_4$) cells within the scope of fast charging for high battery volumes is also common. In lithium-ion battery technologies, the battery type with the highest energy density compared to other lithium batteries is lithium nickel manganese cobalt oxide (NMC) [8]. Plug-in hybrid vehicles use a plug-in mechanism to charge their batteries, distinguishing them from conventional plug-in electric vehicles, which do not have a fossil fuel engine. It contains low-capacity batteries and uses electricity and fossil fuel effectively during long-term journeys, thanks to its systems that use fossil fuels [7]. Due to the reduction in fossil fuel consumption on long journeys and the efficiency of electricity in short-distance working situations, it is ensured that it operates with an optimum combined consumption.

In addition to optimum greenhouse gas emission and consumption studies provided commercially, one of the most important issues of today is sustainability, and achieving sustainability targets in both production and consumption have become a common goal for all stakeholders in society. The United Nations recognized that the world's resources are not unlimited and brought up the issues of sustainable production and consumption in 1972. In the meetings held in Rio de Janeiro in 1992, unsustainable production and consumption models were shown as the most important reason for the constant deterioration of the global environment. The definition of sustainable production and consumption was made at the meeting held in Oslo in 1994, and in 2015, a common decision was reached by the countries on the "2030 Agenda for Sustainable Development and 17 Sustainable Development Goals" in order to transform the world for the better [9–11]. According to Zuo et al. [12] in their study, likens sustainability to a structure consisting of three pillars: the environment, economy and society, and states that these three pillars must be balanced in order for sustainability to be built more solidly. However, it appears that these three dimensions are not treated equally in ensuring sustainable development. It seems that most of the sustainable efforts, especially in transformation processes, are directed towards issues related to environmental sustainability, such as energy efficiency, carbon emissions, resource consumption, ecology and waste management [12].

Günaslan et al. [13], in their study evaluating the life cycle of electric vehicles, state that the main factors causing greenhouse gas emissions emerge during the production process of these vehicles. They suggest that different technological developments are needed to improve the current situation. In another study investigating the relationship between circular economy and company performance, it was found that the circular economy has a significant and positive relationship with company performance. When the circular economy components are examined separately on a business basis, it is stated that businesses are turning to the production of sustainable products by taking measures such as reducing consumption or saving resources [14]. With the acceleration of studies in this direction after the sustainability criteria published by the European Union, green purchasing behavior has developed and attracted the attention of both academic and business circles. In order to encourage the adoption of green products, it has become important to identify moderators that can increase the consistency between attitude and behavior in the consumption of green products [15].

Setting aside any inherent contradictions in the concept, green consumerism is described as an accessible way for a significant portion of the Western industrial population to engage in pro-environmental and sustainable behavior. This includes purchasing energy star-labeled appliances, buying organic produce, conserving energy by turning off electrical appliances when not in use, and shortening shower times [16]. Green consumerism, defined as an accessible way to engage in pro-environmental and sustainable behavior for a significant part of the Western industrial population [16], and green products, defined as products produced in accordance with environmentally friendly and environmental sustainability [17], are now awareness

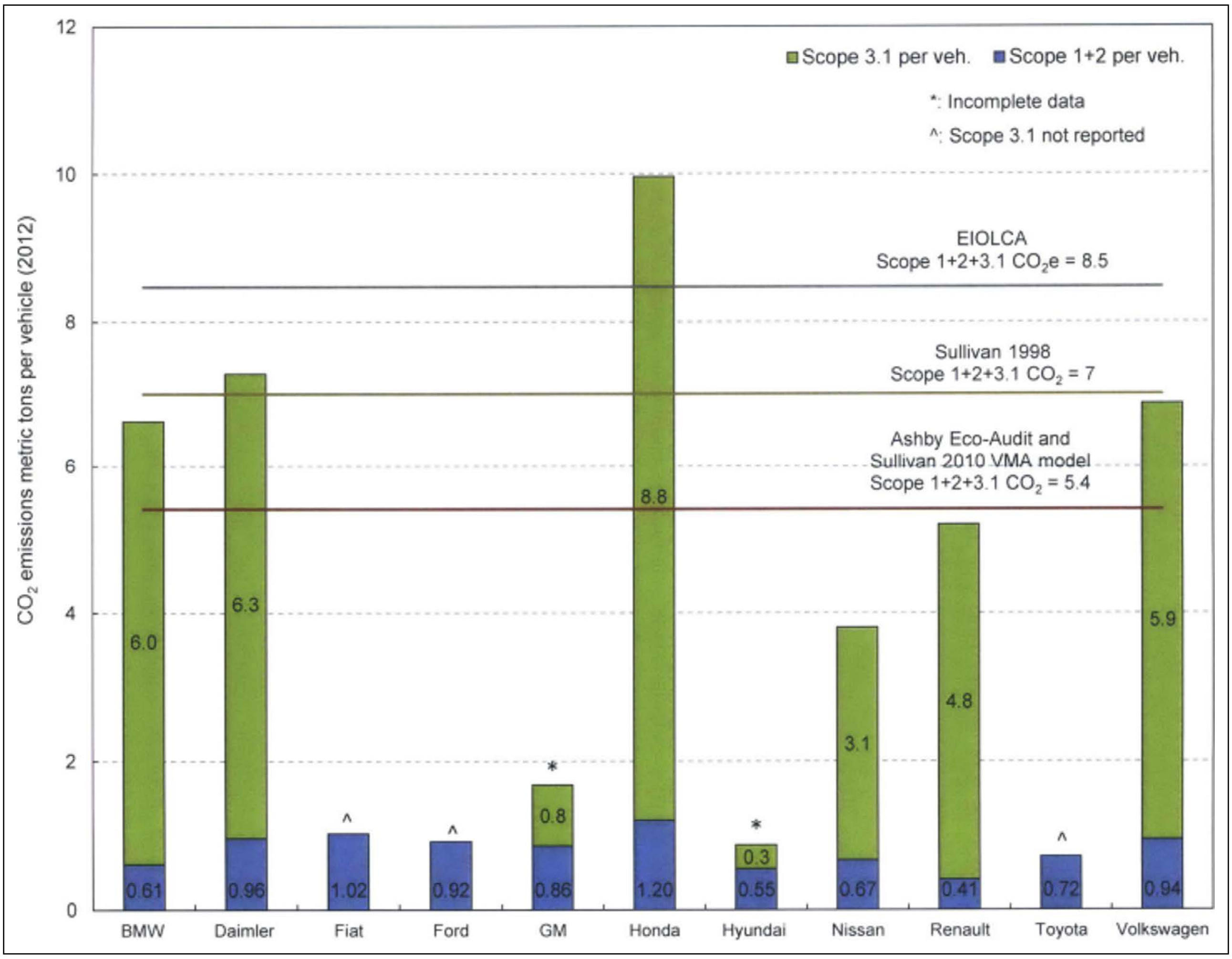

Figure 1. Scope 1, 2 and 3 emissions of vehicle manufacturers given in Raykar's thesis [19].

of consumers. Products that claim to be green or environmentally friendly are being researched more carefully by consumers before purchasing. Questions such as whether battery electric vehicles, which have become widespread because they are said to be economical and environmentally friendly, are really environmentally friendly or just reduce emissions caused by fuel consumption, are becoming more important day by day.

Regarding the reporting of emissions implemented by the European Union and how the reporting in vehicle production is done, the European Union examines emissions in three categories: scope 1, 2 and 3. In order to determine the positions of the parameters under the scopes in the calculations made; It refers to the direct emissions caused by the organization or its parts under scope -1 [18]. Scope -2 refers to indirect emissions such as purchased electricity and heat, which the organization does not produce directly but causes to be produced by purchasing what is produced. Scope -3 refers to the indirect emissions resulting from the activities of all the remaining organizations and their products. These emissions include emissions made by the company's stakeholders, transportation and distribution, purchased, rented parts, etc. They are called indirect emissions caused by the organization.

According to the research, the emissions shared by vehicle manufacturers globally are scope 1 and scope 2 emissions, and these are data related to emissions such as the processes used to shape the material in the factory, welding, and the energy used by the factory [19]. It has been understood that vehicle manufacturers also supply the metals and other parts they purchase for shaping under scope 3 because they do not produce them themselves but procure them from outside.

As seen in Figure 1, it is understood that the emissions caused by vehicle production are not only scope 1+2 emissions shared by the factories, but are the emissions caused by the vehicle manufacturers' own factories. Based on the values given in Figure 1, it has been seen that in order to understand how much emissions a vehicle causes, scope 3 data should also be looked at. According to the specified emissions, these values show radical changes to various parameters, such as the segment of the vehicles, the technologies used [20], the countries where the production and suppliers are located [21].

In the study, it was investigated which of these vehicles, Renault Clio as a diesel vehicle and Renault Zoe as a battery-electric vehicle, is more suitable for green consumer, considering the production and usage processes of these vehicles. Whether this green consumption depends only on the raw material of the vehicle will be examined in terms of other factors like fuel usage within the scope of the study. In the following sections, vehicle specifications including powertrain are provided. Each component is delineated in the methodology by a percentage, calculated in kilograms. Weight values for each material are multiplied by emissions to determine raw material emissions in this study. Furthermore, energy sources and their usage, along with emissions from various sources, are compared with the total raw material emissions of the vehicle.

In the following chapters, there are comprehensive analysis comparing diesel and electric vehicles, focusing on their environmental impact, design considerations, and technological aspects. The study employs advanced software tools to examine vehicle components, material composition, and associated emissions. There are detailed comparisons of emissions from raw materials, production processes, and fuel consumption for both vehicle types in Materials and Methods section. The research challenges common perceptions about electric vehicle sustainability, revealing how factors such as energy sources and geographical locations significantly influence their environmental impact, which is mentioned in the Results and Discussion section. The study also highlights the crucial role of designers in reducing emissions through thoughtful design choices in Conclusion section. Additionally, the analysis provides valuable insights into the relationship between vehicle design, material usage, and emissions which are also mentioned in the Recommendations section.

MATERIALS AND METHODS

This study aims to reveal the accuracy or inaccuracy of the hypothesis through theoretical analysis of the results. Autodesk Fusion 360, one of the computer-aided design software, is used to determine vehicle part masses. Then, the emission values of the parts will be calculated according to raw material usage rates using CCaLC 2 software [22]. Analysis will be carried out to compare the basic hypothesis of the study, examining how sustainable electric vehicles and diesel vehicles are in terms of parts and fuel consumption calculations. CCaLC 2 is an essential tool that uses one of the most important material database for sustainability, Ecoinvent. Consider revising for clarity: "The aim is to contribute to relevant scientific fields by detailing raw material usage emissions through vehicle parts and, consequently, Scope 3 emissions. The methodology of this article is explained in Figure 2 as flow chart diagram.

As mentioned in Figure 2, two types of vehicles were considered as constraints. Renault Clio as a diesel vehicle and Renault Zoe as a battery electric vehicle constitute these vehicles. [23]. While the features of the diesel vehicle are given in Table 1, the basic features of the battery electric vehicle are given in Table 2. The model of the Renault Clio vehicle with a diesel engine is 2012, and the model of Zoe is 2016 [24].

Table 1. Key specifications for Renault Clio [23]

Parameters	Specifications
Engine	Diesel 1.5 dci 51 kW
Total weight (kg)	1185 kg

Table 2. Key specifications for Renault Zoe [24]

Parameters	Specifications
Battery	Li-Ion NMC-41 kWh
Electric motor	AC 65 kW
Total weight (kg)	1480 kg

Table 3. Mass distribution of parts excluding powertrain systems for diesel vehicle [25]

Section name	Percent by mass (%)
Body in white	30
Closures/fenders	11
Suspension/chassis	28
Glazing	3
Lighting	1
Interior	19
Electrical	4
Thermal	2
Bumpers	2

In selecting the specified vehicle models, the parameter of accessibility to research data conducted in the global literature came to the fore. Such an approach was taken because companies will not share such detailed data. Therefore, the calculations do not reflect Renault data, but will show approximate data of any vehicle with similar design features. Vehicle segments are taken as economy segments due to material usage data. A reference source will be used that equates part weights as percentages based on the total mass of the vehicles. This reference will allow us to determine the amount of material used in various vehicle parts by mass.

As seen in Table 3, the percentage distribution by mass of the vehicle, excluding powertrain parts, is given. Using these percentages, it will be seen how much plastic or metal an economy segment vehicle uses, and the emissions within the scope of raw materials will be revealed.

Calculations for a diesel vehicle are based on the constraints of a 121.7 kg engine and 54.2 kg of transmission parts (including differentials, axles, and bearings) [26],

$$\sum W\,(kg) - 175.9\,(kg) = \sum NetW\,(kg) \quad (1)$$

By using the equation (1), the total net weight, excluding powertrain, in kg will be calculated using the mentioned symbol, $\sum NetW$. $\sum W$ symbol refers to total weight in kg, including powertrain. Data on the percentage mass distribution among vehicle parts will be obtained. When calculating the total mass of each part,

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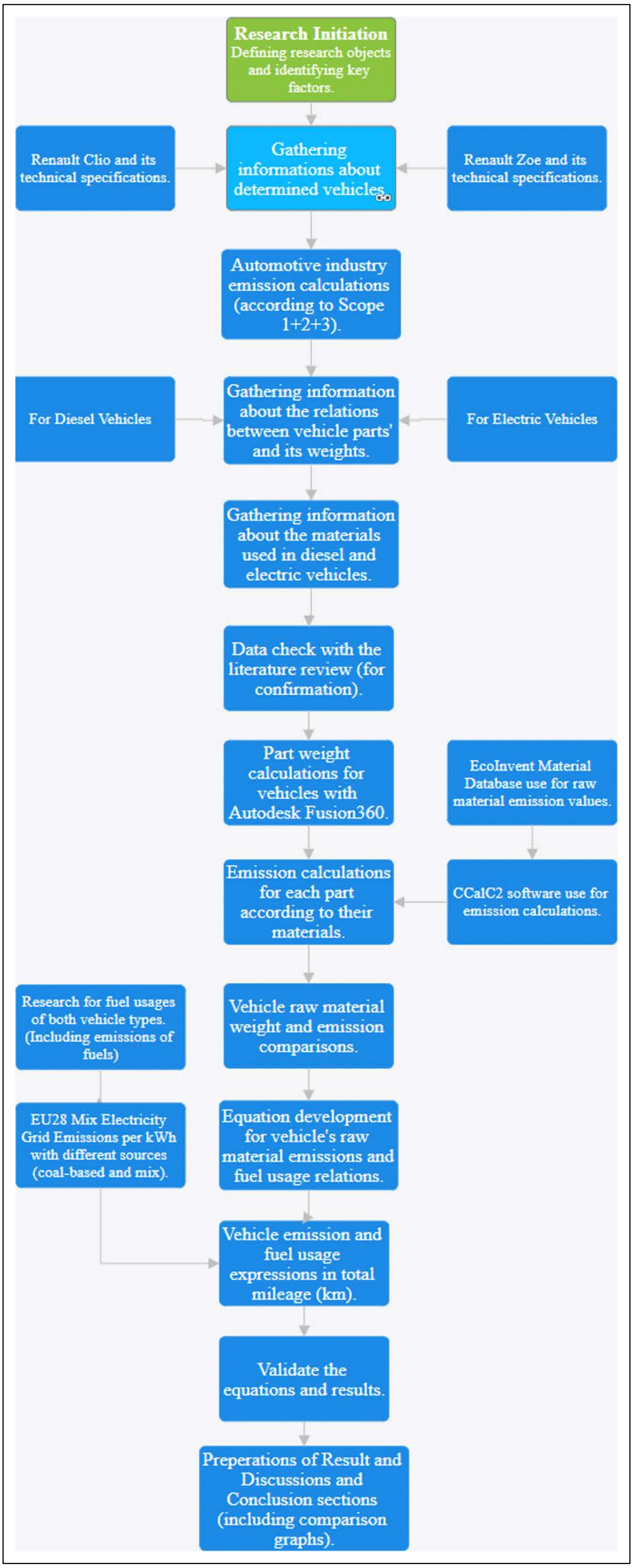

Figure 2. Flow chart diagram for the detailed explanation of methodology.

Table 4. Powertrain parts and masses for battery electric vehicle

Part name	Specifications	Net weight (kg)
Battery Pack 41 kWh Li-Ion	192 cells, 940 grams	305 kg [28]
Electric motor	65 kW	65 kg [29]
Transmission (shafts, differential, casings, bearings etc.)	–	18.1 kg [30]

Table 5. Percentage of materials excluding powertrain in general mass [25]

Section name	Material name	Percent by section's mass (%)	Percent by overall mass (%)
Body in white	Mild steel	88	26.4
Body in white	Low carbon steel	9	2.7
Body in white	Paint and isolation materials	3	0.9
Closures/fenders	Mild steel	97	10.67
Closures/fenders	Low carbon steel	3	0.33
Interior	Plastics	39% Plastics (90% Polypropylene, 6% Acrylonitrile Butadiene Styrene, 4% Polyurethane)	7.41
Interior	Low carbon steel	36	6.84
Interior	Wood fiber	1	0.19
Interior	Fabric	5	0.95
Interior	Carpets	14	2.66
Interior	Glass	5	0.95
Suspension/chassis	Mild Steel	46	13.08
Suspension/chassis	Low Carbon Steel	15	4
Suspension/chassis	Aluminium	18	5.04
Suspension/chassis	Others	21	5.88
Glazing	Glass	100	3
Lighting	Polycarbonate	100	1
Electrical	Others	100	4
Thermal	Plastics	100	2
Bumpers	Mild steel	100	2

$$\sum SW\ (kg) = \frac{Percent\ by\ Mass\ (\%)\ x\ \sum NetW\ (kg)}{100} \quad (2)$$

equation will be used. Section weights ($\sum SW$) will be calculated as mentioned (2). According to the research, the use of iron and steel in the powertrain systems of diesel vehicles averaged 57% for vehicles between 2011 and 2014. In cases where data is inaccessible while performing calculations, this ratio will be used to continue the calculations. [26].

Given the absence of a transmission in the powertrain systems of battery electric vehicles, it is crucial to know the masses of the battery pack and electric motor. According to this, the data given in Table 4 was accepted as a limitation in the research data obtained [27].

Based on the values given in Table 4, it can be seen that the powertrain for an electric vehicle has an average mass of 388.1 kg. Based on this, the equation applied to the diesel vehicle should be repeated, and the calculation should be made as,

$$\sum W\ (kg) - 388.1\ (kg) = \sum NetW\ (kg) \quad (3)$$

After separate calculations are made for each vehicle (3), detailed data in terms of material usage will emerge, so it is necessary to go into the material details of the sections under the section name.

It was aimed to obtain the net masses of the parts and materials used for both vehicles based on their ratio to the general mass, using constant coefficients taken from international automotive industry publications. The values are given in Table 5. CCaLC2 software is used to calculate raw material emissions. In these calculations, the term 'At plant' refers to emissions associated with the production of ready-to-use materials from raw materials.

(F.u. stands for Functional Unit) As seen in Table 6, the main cause of emissions is non-natural materials. The first highest emission value comes from industrial paints, followed by aluminum at 12.0 kg, and the lowest emission value is found in tempered glass at 0.235. Since there is no

Table 6. Emission values provided via CCaLC2 software

Raw material	Amount (kg/f.u.)	CO_2 eq. (kg/kg raw material)	CO_2 eq. (kg/f.u.)	Database section
1 hour painting and ısolation	1.00	268	268	
2 square meter – polyester (27.8 kg)	1.00	6.40	6.40	
Acrylonitrile butadiene styrene at plant	1000	4.40	4403	Ecoinvent / materials
Aluminium at plant	1000	12.0	1.20E+4	Ecoinvent / materials
Copper production, primary, EU	1000	1.91	1911	Ecoinvent / materials
Nylon 6 at plant	1000	9.29	9285	Ecoinvent / materials
Polycarbonate at plant	1000	7.79	7788	Ecoinvent / materials
Polypropylene granules at plant	1000	1.98	1983	Ecoinvent / materials
Polyurethane flexible foam at plant	1000	4.85	4845	Ecoinvent / materials
Polyvinylidenchloride granules at plant	1000	4.92	4916	Ecoinvent / materials
Synthetic rubber at plant	1000	2.66	2656	Ecoinvent / materials
Tempering, flat glass	1000	0.235	235	Ecoinvent / materials
Turning, steel, conventional, average	1000	3.34	3343	Ecoinvent / materials
Turning, steel, conventional, primary	1000	3.22	3219	Ecoinvent / materials
Total	**1.20E+4**	**Total:**	**5.69E+4**	

Table 7. Net weights of parts for diesel vehicle

Section name	Percent by mass (%)	Net weight (kg)
Body in white	30	302.73
Closures/fenders	11	111
Suspension/chassis	28	282.55
Glazing	3	30.27
Lighting	1	10.09
Interior	19	191.74
Electrical	4	40.36
Thermal	2	20.18
Bumpers	2	20.18

Table 8. Net weights of parts for battery electric vehicle

Section name	Percent by mass (%)	Net weight (kg)
Body in white	30	327.57
Closures/fenders	11	120.11
Suspension/chassis	28	305.74
Glazing	3	32.75
Lighting	1	10.92
Interior	19	207.47
Electrical	4	43.68
Thermal	2	21.83
Bumpers	2	21.83

recycling in the evaluations, pure values, which include the use of raw materials, were used. Studies can also be conducted that include factors such as production, transportation, wastewater resources, and other emissions. However, since it is not the focus of this study, this includes a comparison of electric vehicles and diesel vehicles and basic material usage emissions.

Data on fuel consumption per 100 km [23] for both vehicle types were found in the literature. When looking at the real-time fuel consumption of the vehicles, it was found that the electric vehicle consumed 16.6 kWh of electricity at a distance of 100 km, and the diesel vehicle consumed 4.9 L of fuel at a distance of 100 km. The greenhouse gas emission directly caused by 1 liter of diesel fuel is 2.64 kg CO_2. For the European Union EU28 mix (2016), 1 MWh of electrical energy corresponds to 295.8 kg of CO_2 emissions. If 1 MWh of electrical energy is produced from a coal-consuming power plant (according to EU28 mix source), it results in 850 kg of CO_2 emissions [31], which means 0.85 kg of CO_2 emissions per kWh.

It has been observed that the mass of the economic segment, diesel vehicle's mass is 1185 kg; it is 1009.1 kg, excluding the powertrain. When the percentage application was performed to determine the masses of the other parts, the results in Table 7 emerged.

It is seen that the powertrain systems in the battery electric vehicle with a mass of 1480 kg correspond to a value of 388.1 kg. It can be said that the mass excluding the powertrain is calculated as 1091.9 kg.

The values given in Table 8 also take into account the design-related emissions in the production of electric vehicles. The biggest reason why there are different values in both tables is that the design of both vehicles is different. The difference in powertrain systems accounts for the variation in overall vehicle mass.

Table 9. Materials massively used in diesel and battery electric vehicles

Section name	Material name	Percent by overall mass (%)	For diesel vehicle (kg)	For battery electric vehicle (kg)
Body in white	Mild steel	26.4	266.40	288.26
Body in white	Low carbon steel	2.7	27.24	29.48
Body in white	Paint and ısolation materials	0.9	9.08	9.83
Closures/fenders	Mild steel	10.67	107.67	116.51
Closures/fenders	Low carbon steel	0.33	3.33	3.60
Interior	Plastics (polypropylene) [32]	6.67	67.31	72.83
Interior	Plastics (ABS)	0.44	4.44	4.80
Interior	Plastics (polyurethane)	0.30	3.02	3.28
Interior	Low carbon steel	6.84	69.02	74.69
Interior	Wood fiber*	0.19	1.92	2.07
Interior	Fabric (polyester)	0.95	9.59	10.37
Interior	Carpets (nylon) [33]	2.66	26.85	29.04
Interior	Glass	0.95	9.59	10.37
Suspension/chassis	Mild steel	13.08	131.99	142.82
Suspension/chassis	Low carbon steel	4	40.36	43.68
Suspension/chassis	Aluminium	5.04	50.86	55.03
Suspension/chassis	Others (wheels - Rubber)	5.88	59.34	64.21
Glazing	Glass	3	30.28	32.75
Lighting	Polycarbonate	1	10.09	10.92
Electrical	Others (battery, wires, electronics etc.)*	4	40.36	43.68
Thermal	Plastics (polyvinyl chloride) [34]	2	20.18	21.84
Bumpers	Mild steel	2	20.18	21.84
Total	–	**100%**	**1009.1**	**1091.9**

Table 10. Emissions from powertrain parts of diesel and battery electric vehicles

Diesel vehicle powertrain parts	Emissions (CO_2 Eq. (kg/f.u.)	Battery electric vehicle powertrain parts	Emissions (CO_2 Eq. (kg/f.u.)
Engine	**406.47**	Electric Motor [35] (%42.37 mild steel, %12.89 low carbon steel, %17.32 aluminium, %8.88 copper, %18.54 others)	91.98 + 26.97 + 135.09 + 11.02 = **265.06**
Transmission (including shafts, differential, axles etc.)	**174.52**	Battery	**2160** [36]
		Power Inverter, Converter (**), Transmission (shafts, differential, casings, bearings etc.)	100 (**)+58.28 =
Sum of emissions (CO_2 Eq. (kg/f.u.)			**158.28**
580.99			**2583.34**

Table 9 shows the usage of diesel and battery electric vehicle materials in kilograms. Accordingly, the amount of usage on a material basis is shown. The amount of materials used by the vehicles and the changes in kilograms due to the design factor are also expressed in this table. Parameters marked * are not included in the emission calculations of both vehicles. Wood Fiber is not included in the emission calculations due to its low usage rate and the natural nature of the material.

In Table 10, emission values are calculated based on the raw materials used, based on the masses of the parts in the powertrain systems of battery electric vehicles and diesel vehicles. 18.54% of the electric motor could not be included in this cal-

Table 11. Material emission data for electric vehicles

Raw material	Amount (kg/f.u.)	CO_2 eq. (kg/kg raw material)	CO2 eq. (kg/f.u.)	Database section
*Others (including powertrain)	2583	1.00	2583	
1 hour painting and isolation	1.00	268	268	
2 square meter – polyester (27.8 kg)	0.373	6.40	2.39	
Acrylonitrile butadiene styrene at plant	4.80	4.40	21.1	Ecoinvent / materials
Aluminium at plant	55.0	12.0	663	Ecoinvent / materials
Nylon 6 at plant	29.0	9.29	270	Ecoinvent / materials
Polycarbonate at plant	10.9	7.79	85.0	Ecoinvent / materials
Polypropylene granules at plant	78.2	1.98	144	Ecoinvent / materials
Polyurethane flexible foam at plant	3.28	4.85	15.9	Ecoinvent / materials
Polyvinylidenchloride granules at plant	21.8	4.92	107	Ecoinvent / materials
Synthetic rubber at plant	64.2	2.66	171	Ecoinvent / materials
Tempering, flat glass	43.1	0.235	10.1	Ecoinvent / materials
Turning, steel, conventional, average	569	3.34	1904	Ecoinvent / materials
Turning, steel, conventional, primary	151	3.22	488	Ecoinvent / materials
Total	**3611**	**Total:**	**6732**	

Table 12. Material emission data for diesel vehicles

Raw material	Amount (kg/f.u.)	CO_2 eq. (kg/kg raw material)	CO_2 eq. (kg/f.u.)	Database section
*Others (including powertrain)	581	1.00	581	
1 hour painting and isolation	1.00	268	268	
2 square meter – polyester (27.8 kg)	0.345	6.40	2.21	
Acrylonitrile butadiene styrene at plant	4.44	4.40	19.5	Ecoinvent / materials
Aluminium at plant	50.9	12.0	612	Ecoinvent / materials
Nylon 6 at plant	26.9	9.29	249	Ecoinvent / materials
Polycarbonate at plant	10.1	7.79	78.6	Ecoinvent / materials
Polypropylene granules at plant	67.3	1.98	133	Ecoinvent / materials
Polyurethane flexible foam at plant	3.02	4.85	14.6	Ecoinvent / materials
Polyvinylidenchloride granules at plant	20.2	4.92	99.2	Ecoinvent / materials
Synthetic rubber at plant	59.3	2.66	158	Ecoinvent / materials
Tempering, flat glass	39.9	0.235	9.35	Ecoinvent / materials
Turning, steel, conventional, average	526	3.34	1759	Ecoinvent / materials
Turning, steel, conventional, primary	140	3.22	450	Ecoinvent / materials
Total	**1530**	**Total:**	**4435**	

culation due to the variety of sub-materials, and the constant coefficient in power inverters and converters was considered as 100 kg CO_2. The calculated CO_2 emissions were 2583.34 kg for battery electric vehicles and 580.99 kg for diesel vehicles.

The main focus of the study was the supply of materials from manufacturers' scope 3 emissions. The values given in Table 11 are the emission amounts caused by the specific raw materials used during the production of the vehicle. The machines used in the processes evaluated within the framework of scope 1 and 2 and their energy consumption are not included in the mentioned values. Additionally, calculations were conducted based on the total emissions of resulting parts, without distinguishing between scopes for parameters such as dyeing, powertrain, and polyester.

The parameters given in Table 12 are the emission values resulting from raw material consumption according to the raw material used during the production of a diesel vehicle. Within the scope of the study, the emissions resulting from the parts and materials required for the operation of the vehicles were found to be 6732 kg for electric vehicles and 4435 kg for diesel vehicles. Those values are results from Table 11 and Table 12.

$$\sum_{[Diesel]} R = \frac{4435\ kg\ CO2}{2.64\ kg\ CO2\ per\ Liter} \tag{4}$$

$$EM\ (km) = \frac{100\ km}{4.9\ Liter}\ x\ \sum_{[Diesel]} R \tag{5}$$

Total reps ($\Sigma_{[Diesel]}R$) values shows the total raw material emission's divided by energy emission per source (4,6). In the Expressed Mileage (EM) calculations (equivalent to km), the results are compared to the vehicle's raw material emissions and mileage emissions by energy source (5,7). When these values are compared with the fuel consumption of vehicles, diesel one will travel an average of 34270.63 km and will be equivalent to the emissions caused by the materials used. According to equations (4) and (5), higher fuel usage reduces mileage, while higher fuel emissions from the source also reduce mileage. Conversely, higher raw material emissions tend to increase mileage. However, it's important to note that higher raw material emissions typically lead to increased fuel usage. Therefore, the overall result is lower mileage for vehicles with higher raw material emissions. These calculations pertain specifically to automobiles. In electric vehicles, there is no stable value since the emissions resulting from the production of electricity are different in each country and each grid.

$$\sum_{[Electric]} R = \frac{6732\ kg\ CO2}{0.2958\ kg\ CO2\ per\ KWh} \tag{6}$$

$$EM\ (km) = \frac{100\ km}{16.6\ KWh}\ x \sum_{[Electric]} R \tag{7}$$

Accordingly, based on the EU28 mix (2016) value, it corresponds to the fuel consumption at an average distance of 137006.89 km. When you change the electrical energy source with its emissions (8), it will show the differences between energy sources in perspective of sustainable world (9).

$$\sum_{[CoalBasedElectric]} \boldsymbol{R} = \frac{\mathbf{6732\ kg\ CO2}}{\mathbf{0.85\ kg\ CO2\ per\ KWh}} \tag{8}$$

$$\boldsymbol{EM\ (km)} = \frac{\mathbf{100\ km}}{\mathbf{16.6\ KWh}}\ \boldsymbol{x}\ \sum_{[CoalBasedElectric]} \boldsymbol{R} \tag{9}$$

When electrical energy is provided from coal, the average distance reaches 47678.4 km. These findings indicate that before making claims about emission reductions from electric vehicles, the relevant parameters should be considered on a country, region, and power grid basis.

RESULTS AND DISCUSSION

This research study reveals the differences between electric vehicles and diesel vehicles in terms of emissions, design, technology, and fuel consumption. Even in design differences alone, changes in materials used and, consequently, emission increases have been highlighted. The aim was to understand whether electric vehicles or fossil fuel vehicles are less harmful to the environment in terms of emissions generated by design and product. Additionally, the effects of industrial design discipline on emissions were intended to be clearly demonstrated. As seen in the resulting tables, the segments of vehicles significantly affect emissions due to differences in design and material usage. Within this framework, an important example study has been presented for industrial designers and transportation vehicle designers to understand the sustainability and effectiveness of design on emissions. It has been understood that design activities conducted at the industrial level are not merely designs but can also lead to significant emissions, and designers can play a crucial role in reducing emissions. Given that green consumption and green production themes are deepening in today's conditions, it has been observed that the industry and consumers need to engage in production and consumption consciously.

As a result of the examination conducted on battery electric vehicles and diesel vehicles, it has emerged from the data that contrary to what is indicated in advertising campaigns, electric vehicle production results in more emissions, primarily due to battery-related factors. Diesel vehicles, on the other hand, do not cause additional emissions due to their use of more standardized technologies, while it has been understood that battery technologies are not part of a circular economy, both in their production and the minerals they use. Nowadays, the degree of "greenness" of the transition to electric vehicles under the banner of green transformation should be much more thoroughly debated. In today's context where electric vehicle emissions are produced with even more emissions compared to conventional vehicles, it can be observed that productions made under the concept of sustainability continue to harm the environment. Instead of converting as many vehicles as exist in the world to electric, a transformation journey has begun where vehicles are re-manufactured electrically in the same quantity as existing vehicles. This way, manufacturers continue their production with the potential for sales equivalent to the existing number of vehicles, rather than aiming to maintain or decrease the number of vehicles in the market.

In the research, not only material-based emission comparisons between electric vehicles and diesel vehicles were conducted, but also an attempt was made to calculate the distance equivalent of material emissions of vehicles through fuel consumption. As a result of the calculations, it was observed that while diesel vehicles provide a more consistent value, electric vehicles can have emissions from various fuel consumption sources through the grid they are connected to. For example, energy may be produced by wind turbines or solar panels on the grid where it is charged, while in another country or region, energy may come from power plants that consume coal. This diversity implies that electric vehicles can lead to significantly different fuel emissions regardless of the model or brand. While emissions per kilometer could be the same with diesel fuel on one hand, on the other hand, emissions per kilometer in electric vehicles could be 8 times, 9 times, or even higher differences with significantly lower emissions. In this context, whether electric vehicles are sustainable or not varies depending on the country, region, and grid they will be used in, and it would be more accurate to make an inference about their sustainability accordingly.

CONCLUSION

It is a fact that humanity faces various challenges in the face of changing and evolving technologies, with one of the foremost current issues being environmental disasters caused by the ease of mass production. In light of this reality, the desire of companies worldwide to implement sustainable economic growth with less environmental damage has become a prominent issue in today's industry. This study examines the transition to alternative fuel vehicles in the automotive industry in response to this situation, addressing how electric vehicles compare to fossil fuel vehicles in terms of their environmental impact, considering design and technological integration.

While factors such as the economic segment of the vehicle, materials used, and production capabilities concern the technological aspect, it has been determined how effective the design is in terms of emissions in the formation of the product, with parameters such as body in white, bumpers, trunk, windows, interior design, which are the parts where the design will be realized according to these capabilities. Especially in the automotive industry, it has been concluded that design should be done while considering technology, design, and carbon emissions.

The raw material emission section in Figure 3 is a significant aspect involving both technology and design considerations. It has been observed that even factors such as whether the vehicle is a hatchback or sedan greatly influence these emissions, and the adoption of alternative fuel technologies in vehicles leads to varying outcomes. While calculating emissions from usage and production is more feasible for diesel vehicles, electric vehicles yield different results depending on grid emissions. This challenges the notion that electric vehicles are inherently sustainable.

Figure 3 shows the overall raw material emissions of diesel and electric vehicles. From this, it can be understood that sustainability is holistic, requiring collaborative progress across all sectors and stakeholders to achieve sustainable outcomes. To determine whether electric vehicle users are making a sustainable choice, it is crucial to first investigate how far they can travel based on grid emissions in their country. Figure 4 shows the difference between EU28 Mix grid-based and coal-based electric grid emissions for an electric vehicle. According to this comparison, electric vehicle's raw material emissions are similar to Option 1 if the grid uses green/sustainable energy. Option 2 applies if the grid uses higher emission per kWh, which is shown in Figure 4 as a sharp decrease in expressed mileage (km).

According to Figure 4, in this study, equality is achieved if an electric vehicle travels on average 1.52 times farther per kilometer compared to a diesel vehicle, due to the raw material emissions ratio indicating this value. This average factor of 1.52 leads to a result of 52090 km, requiring grid emissions to be at least 0.7781 kg CO_2 per kWh. Under the conditions depicted in Figure 4, electric vehicles surpassing this emission value will create a less efficient environment compared to diesel vehicles in all scenarios. These conclusions are derived by reversing Equations (6) and (7).

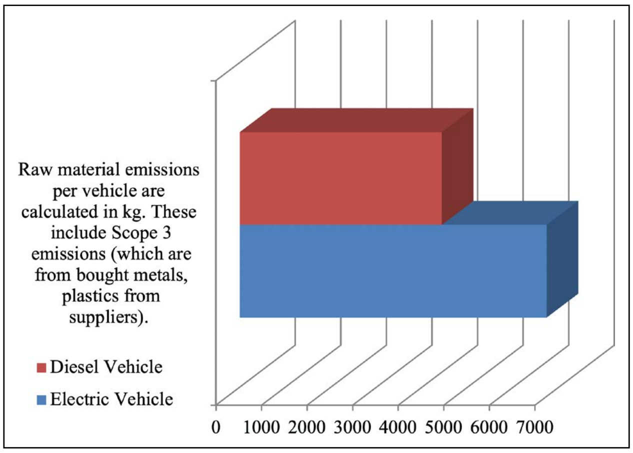

Figure 3. Comparison of raw material emissions for diesel and electric vehicles.

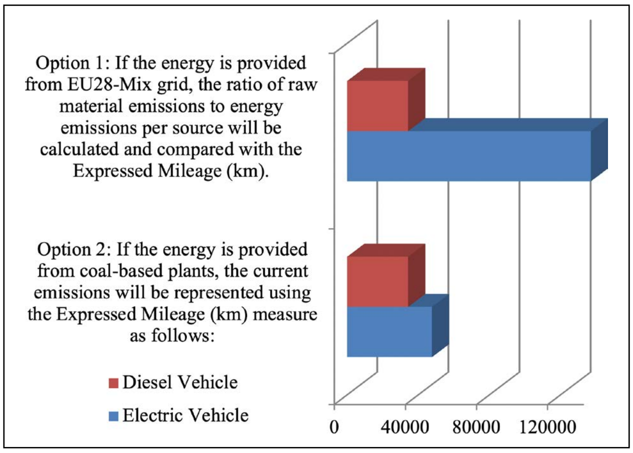

Figure 4. Expressed mileage comparisons for diesel and electric vehicles.

The study has uncovered important information for the global literature and consumers. From a literature perspective, data has been generated that can benefit individuals and institutions in the technical and social disciplines working in this field. It is of great importance for various scientific disciplines such as engineering, industrial design, and transportation vehicle design, which are involved in the design of vehicles in the industry, to understand to what extent their own contributions affect emissions. Specific data within the scope of the study includes which part designs can reduce emissions, the density of plastic or metals used in various parts, and how much emissions these parts cause. This information is crucial for understanding the primary impacts of different scientific disciplines such as engineering and design, on emissions.

RECOMMENDATIONS

The study highlights important perspectives for consumers, especially green consumers, to consider sustainability values when making purchases. It is emphasized that in every sector, Scope 1-2 emissions do not represent all emissions caused by a product, and it is important not to forget that material emissions caused under broad parameters such as

Scope 3 also exist. Therefore, it is recommended that consumption should continue with awareness of the material emissions caused under broad parameters like Scope 3, rather than solely relying on Scope 1-2 emissions.

For industries and manufacturers, the importance of emission calculations and reducing emission values is evident today. However, to understand the effectiveness of converting any item or vehicle to electric under the guise of sustainability, it is crucial to consider the amount of emissions per kWh in the connected grid. Otherwise, it should not be forgotten that conversions made may not reduce emissions but could even lead to an increase in emissions. If the emissions value in the connected grid is high, the optimum values of devices or items running on diesel or gasoline should be examined, and the conversion should be made accordingly. Otherwise, there could be an increase in emissions and a loss of resources as a result of the conversion. Since all the results are relevant and crucial for the respective scientific disciplines, consumers, and industries, an approach has been suggested that can be followed in studies related to these scientific disciplines.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Waste collection and transport optimization in accordance with zero waste principles of Karaman province in Türkiye

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ABSTRACT

The zero waste approach introduces a novel perspective on waste management, allowing for the categorization of waste at its origin. This enables each identified waste group to be assessed and optimized individually. One of these optimization studies focuses on the optimization of waste collection and transportation. The placement and number of containers, as well as the collection routes of vehicles, are crucial for optimizing these processes. In this study, the number of containers placed in Karaman, their placement, the distance between the containers, and the vehicle route optimization were analyzed. The results show that the current number of containers is not used efficiently, with an average distance of only 33 meters between them. Moreover, optimizing routes in five pilot areas resulted in an average efficiency gain of 32%, which saved 17 kilometers, 50 minutes, and 8 liters of fuel per route. Based on these findings, a 32% improvement is anticipated not only in economic and time efficiency but also in reducing the carbon footprint during the collection and transportation stages.

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INTRODUCTION

The amount of waste produced globally is increasing due to rapid population growth, industrialization, economic growth aspirations, the desire for a luxurious lifestyle, and technological advancements across various sectors. This rise in waste generation has necessitated the adoption of zero waste principles, making it essential to manage waste production and consumption effectively. Direct disposal of waste without any treatment, neglecting recycling, recovery, and optimization processes, creates significant resource problems in terms of both energy and raw materials [1–3].

In recent years, significant advancements have been made in the field of waste management in our country. To promote the zero waste philosophy, the Ministry of Environment, Urbanization, and Climate Change (MoEU) encourages people to consume only what they need, reduce their waste, and separate waste at the source. Detailed studies have been conducted to ensure the collection and recycling of waste separated at the source. On September 25, 2017, the "Zero Waste Project" was launched in the MoEU service building. This project aims to create awareness and provide a roadmap, involving citizens in waste management through public institutions, organizations, hospitals, uni-

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versities, schools, airports, shopping malls, and households. The "Zero Waste Project" aims to prevent wastefulness and foster both corporate and individual responsibility [3, 4].

Conceptually, integrated solid waste management (ISWM) can be defined as a systematic and scientific discipline that encompasses the minimization, collection, transportation, processing, and final disposal of all waste types with a holistic perspective. ISWM considers factors such as the supply and demand balances of the region's population, production and consumption habits, economic values, engineering solutions, protection of natural resources, aesthetic concerns, environmental and human health, and the preservation of natural assets like flora and fauna [5, 6]. This integrated approach ensures that all aspects of waste management are addressed, providing a comprehensive and sustainable solution [7].

Effective planning of waste management requires addressing various regional issues, including geography, physical elements, urban settlement patterns, building conditions, road conditions, livelihood, income levels, heating systems, and cultural habits. Understanding these factors helps in creating a tailored waste management plan that meets the specific needs of the region. Additionally, citizen support is crucial to reducing environmental impacts to near-zero levels with minimum cost and maximum benefit. Understanding the situation and expectations of the local population is vital for gaining their support. Projects and systems that lack citizen support are unlikely to be sustainable [8, 9].

Another critical aspect of integrated waste management is the selection and use of appropriate tools and equipment by local governments or private organizations. In the accumulation, collection, and transportation of waste, it is important to choose equipment and vehicles that are suitable for current technological standards and to evaluate them using technological capabilities. Well-planned selection, placement, and transportation of tools and materials can lead to significant savings in fuel, personnel, and equipment costs, while also reducing carbon emissions [10, 11].

In waste collection and transportation, various factors play a crucial role, including the structure and capacity of the containers, their placement, settlement frequency, the number of people per container, the condition of transport vehicles, the compression status and factor of vehicles, the distance of the disposal or recovery facility from the collection point, and the routing process. On average, 28 liters of fuel are consumed in an 8-hour operation depending on these factors. Additionally, the cost of collection and transportation ranges from 30$ to 70$ per ton of waste, making up 65–80% of total waste management costs. This highlights the importance of efficiently planning the collection and transportation systems to ensure sustainability [7, 12].

Another issue in integrated waste management is the collection and transportation of waste, which is the only point that individuals witness and experience directly in front of them. Dissatisfaction in these observations may lead to a decrease in the belief in waste management and zero waste by confronting the waste management and local administration with the perception of failure. Therefore, the integrated waste management system must be planned correctly and this plan must be strictly followed [6, 13–16].

This research aims to evaluate container locations and conduct an optimization study for waste collection and transportation systems in accordance with zero waste principles. By analyzing the current waste management practices in Karaman and optimizing the placement and routing of containers, this study seeks to enhance efficiency, reduce costs, and minimize the environmental impact of waste management processes.

MATERIALS AND METHODS

Current Situation of Karaman Province

Urban solid wastes in Karaman province are defined as wastes within the adjacent areas of Karaman Municipality and are collected by the Karaman Municipality Cleaning Affairs Directorate. The wastes of the district municipalities, those collected by the Special Provincial Administration, and the industrial wastes are not included in the urban solid wastes. Data on total urban solid waste, the number of containers, and location information of placed containers were obtained from the Cleaning Department of Karaman Municipality. Additionally, information on the types and numbers of vehicles involved in waste collection, waste collection route details, the number of containers on each route, vehicle tracking system data, current waste management practices, and other equipment details were also gathered.

Information on the amount of collected waste, the number of recycling containers placed, and the number of indoor boxes placed was obtained from Yunus Emre Cultural Foundation Economic Enterprise, which has a collection and separation facility license and an agreement with Karaman Municipality.

Information on the population of Karaman and the population of the neighborhoods was obtained from the official web page of the Karaman Governorship Provincial Directorate of Population and Citizenship.

The fuel consumption during the 8-hour operation of the compression vehicles used in the collection and transportation operations is taken as 28 liters [12].

Collection and Transport Optimization

The optimization process and maps of the vehicles used in the waste collection and transportation processes in Karaman were created using the ArcMap 10.5 program.

Finding Existing One-Day Routes of Collection Vehicles

The current route information reflects the daily movements of the Karaman Municipality Cleaning Affairs Directorate collection vehicles in the pilot areas. Coordinate data obtained from vehicle tracking systems of vehicles collecting in pilot areas was used. The coordinates received were transferred to the ArcMap 10.5 program. After the path

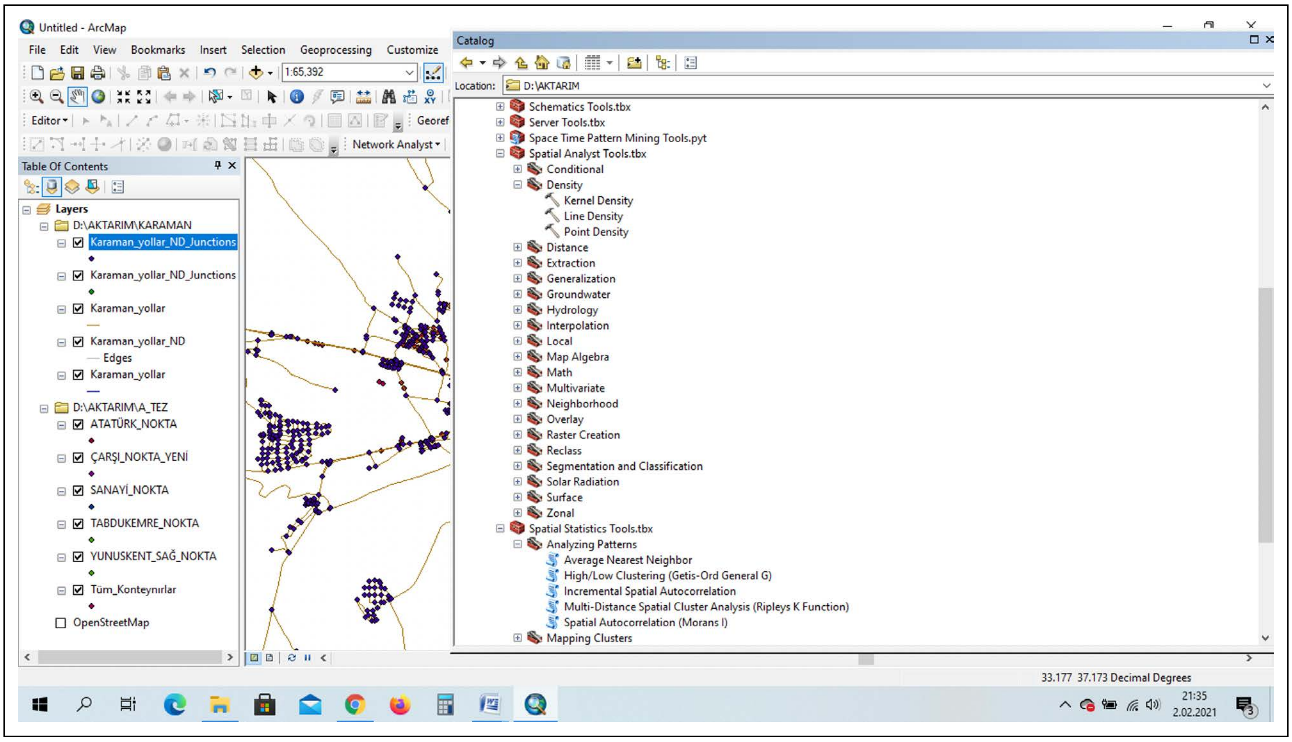

Figure 1. View of the density map rendering in ArcMap 10.5.

information was downloaded using OpenStreetMap, it was converted into a format that can be used in the ArcMap 10.5 program and roads were created. After creating the path and point data, routing was performed in the ArcMap 10.5 program with the Network Analyst tool to follow the sequential points (Fig. 1). Existing route drawings start with the movement of collection vehicles from the garage and end with their arrival at the disposal site. The distance from the disposal site to the garage is 7.7 km, and an average of 22 minutes is spent.

Container Data and Waste Density Map

The coordinates of the container locations were obtained from the Karaman Municipality Cleaning Affairs Directorate. These coordinates were input in the ArcMap 10.5 program according to the collection regions. By processing the road data using OpenStreetMap and the points, the container settlement map in Karaman and the container settlement status map in the pilot regions were obtained. Waste density maps were created using the Kernel Density toolbar in the Spatial Analyst Tool of the ArcMap 10.5 program by using the container point data and the container volume (800 L) in Karaman and in the pilot regions. The average nearest neighbor summary, showing the average distances between containers and their distances relative to the collection area, was obtained using the Average Nearest Neighbor toolbar in the spatial statistics tools of the ArcMap 10.5 program (Fig. 1).

Optimization of the Vehicle Routes

Route optimization was carried out considering the container layout in the existing 5 pilot regions, with the starting point being the Garage of the Cleaning Works Department and the ending point being the sanitary landfill. The Network Analyst module of the ArcMap 10.5 software was used for solid waste collection and optimum route determination. Working with the same logic as the smallest spanning tree method, this software enumerates the obtained solid waste coordinates on the road data by calculating the shortest distances between them and gives the optimum route between these points (Fig. 2) [15, 17–19].

RESULTS AND DISCUSSION

Current Situation of Karaman

The population for which waste collection service is provided by Karaman Municipality is 161,946 people. There are 63 neighborhoods in the center of Karaman. An average of 179,013 kg of waste is collected per day by Karaman Municipality. The amount of waste per capita in Karaman is 1.15 kg.

There are 4,750 containers placed on the site for the collection of urban solid waste (garbage collection). The volumes of the containers are 770 L, and there are 35 persons per container. The average waste volume per container is 0.25 m^3. The container utilization factor, which is the average occupancy rate when the containers are emptied, is 33%.

Urban solid wastes are collected by Karaman Municipality Cleaning Affairs Directorate with 9–13 m^3, 2–8 m^3, and 2–7 m^3 compression vehicles and disposed of in the sanitary landfill. No other process is applied for these wastes before disposal.

Detailed insights into the handling of oversized waste items, used cooking oils, and debris from building activities remain elusive. Information regarding hazardous waste materials, discarded mineral oils, depleted batteries, and out-

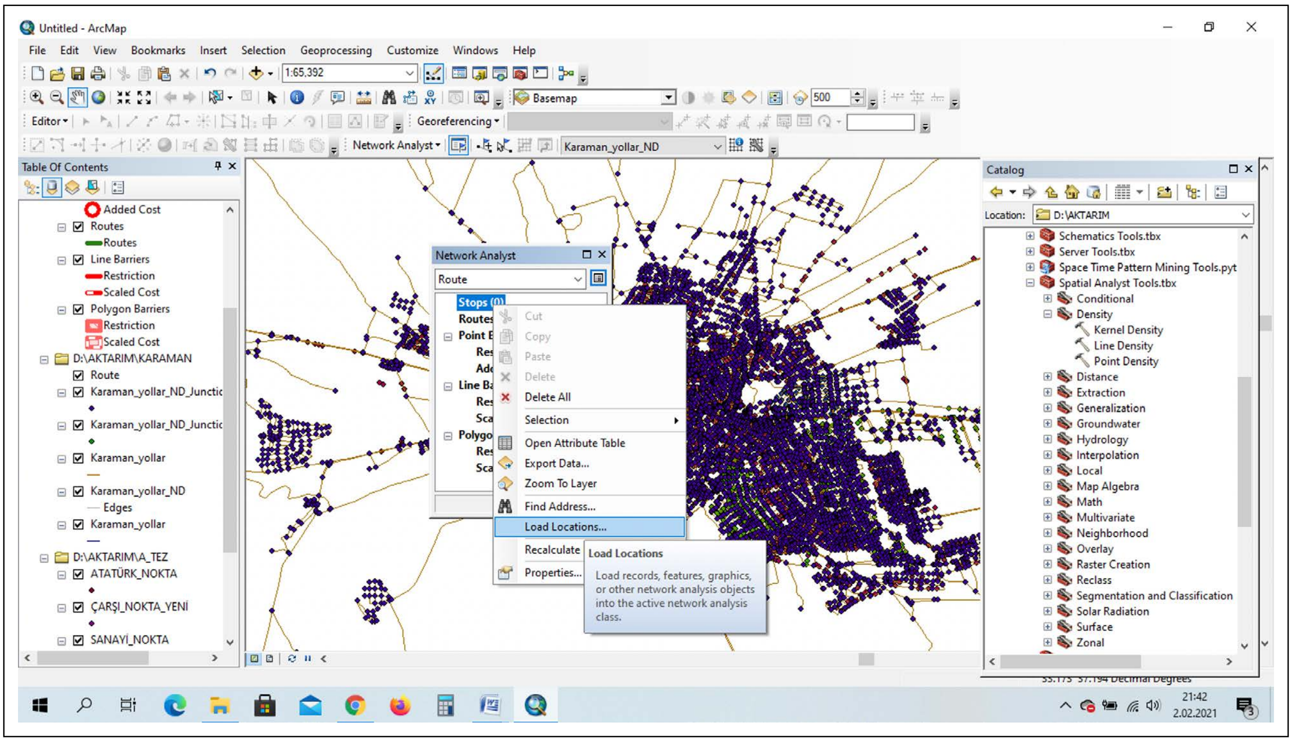

Figure 2. Network analyst data load view.

Table 1. Number of equipment installed and usage rates

Information of equipment placed in Karaman			
Total population (person)		**161946**	
Number of containers (pcs)	4750	Number of recycling containers	433
Container volume (m³)	0.77	Recycling container volume (m³)	2
Daily waste amount (kg/day)	179013	Number of indoor boxes	5950
Daily waste volume (m³/day)	1194	Waste retrieval center (7 compartments)	20
Karaman average waste density (kg/m³)	150	Daily amount of recyclable waste (kg/day)	63704
Number of people per container (person)	35	Daily recyclable waste volume (m3/day)	1118
Amount of waste per container (kg/day)	38	Karaman average recyclable waste density (kg/m³)	57
Waste volume per container (m³/day)	0.25	Number of persons per recycling container (person)	375
Container utilization factor	0,33	Amount of waste per recycling container (kg/day)	148
Number of containers required (piece)	2215	The volume of waste per recycling container (m³/day)	2,58
Average vehicle speed	18 km/h	Recycling container utilization factor	1,29
Compost unit	7 adet	Number of recycling containers required (pieces)	799
		Monthly amount of collected packaging waste (kg/month)	300000

dated tires is derived from industrial reports submitted to the Karaman Environmental and Urban Planning Authority. Additionally, the data on medical waste, as provided by this authority, is based on submissions from healthcare establishments in Karaman.

Packaging waste data can be divided in two ways: the first includes the packaging waste collected from industry and industrial organizations throughout Karaman, and the second includes the packaging waste information collected only from Karaman within the scope of the separation at source project. There are 433 recycling bins placed in Karaman by the licensed company. In addition, there are 5,950 indoor boxes distributed to households and workplaces. The volume of recycling containers is 2 m³ on average, and the number of people per container is 375. Considering the recyclable waste potential and the assumption that recycling containers are collected every day, the waste volume per container is 2.58 m³, and the container utilization factor is calculated to be 129%. In Karaman, the segregation processes for recycling yield an average daily collection of 10,380 kilograms of recyclable materials by authorized collection and sorting centers. The packaging waste gathered by the certified facility in Karaman accounts for 5.6% of the total

Table 2. Information on the amount of recyclable waste and equipment collected separately at source

Waste information collected separately at the source	
The amount of recyclable waste collected daily (kg/day)	10000
The volume of recyclable waste collected daily (m³/day)	176
Amount of waste per recycling container (kg)	24
The volume of waste per recycling container (m³)	0,41
Recycling container utilization factor	0,20

solid waste produced. Tables 1 and 2 provide a comprehensive breakdown of the waste types produced in Karaman.

Collection and Transport Optimization

Container Layout and Waste Density Map

Container density, container layout maps, and average distances of containers to each other were calculated by means of the ArcMap program within the framework of container coordinates obtained from Karaman Municipality Cleaning Affairs Directorate. In this framework, the average distance between the containers placed in Karaman is 33 meters, while the expected average distance is calculated to be 72 meters. The average distance between containers at the Atatürk location is 86 meters, with an expected average distance of 228 meters. The average distance between the containers at the Çarşı location is calculated as 73 meters, with an expected average distance of 132 meters. For the industrial site, the average distance between containers is 52 meters, with an expected average distance of 104 meters. For Tabduk Emre location, the average distance between containers is 58 meters, with an expected average distance of 146 meters. For Yunus Kent right location, the average distance between containers is calculated as 42 meters, with an expected average distance of 146 meters.

Finding Existing One-Day Routes of Collection Vehicles

The current route information reflects the daily movements of the Karaman Municipality Cleaning Affairs Directorate collection vehicles in the pilot areas. Coordinate data obtained from vehicle tracking systems of vehicles collecting in pilot areas was used. The coordinates received were transferred to the ArcMap 10.5 program. After the path information was downloaded using OpenStreetMap, it was converted into a format that can be used in the ArcMap 10.5 program and roads were created. The current route starts with the movement of the collection vehicles from the garage and ends with their arrival at the disposal site. The distance from the disposal site to the garage is 7.7 km, and an average of 22 minutes is spent (Fig. 3).

According to the vehicle tracking system data obtained from the Karaman Municipality Cleaning Affairs Directorate, the average speed of the waste collection vehicles is 18 km/h. While calculating the route in the ArcMap 10.5 program, the

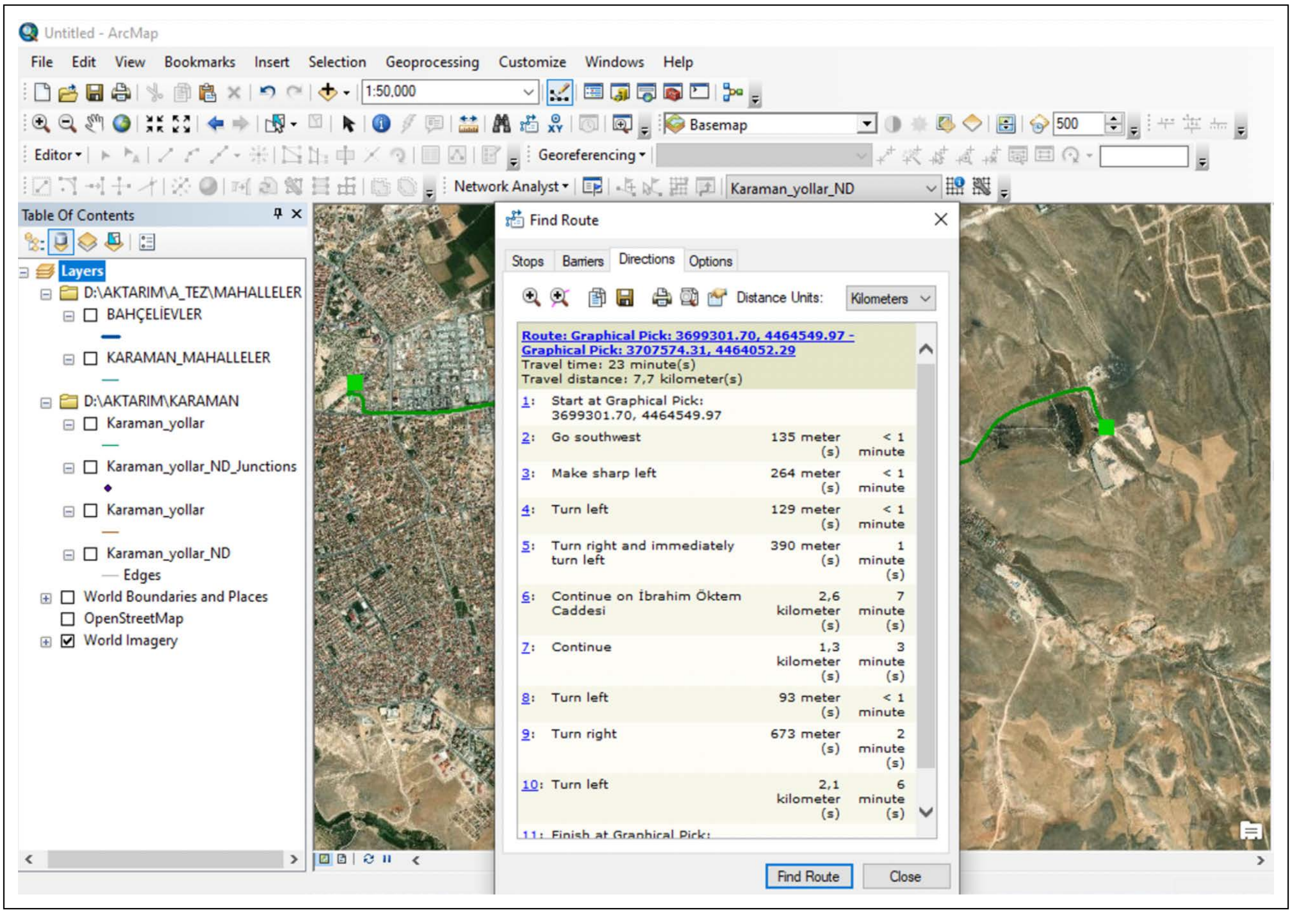

Figure 3. The distance from the landfill to the cleaning department garage.

Table 3. Optimization summary of the pilot regions

Route	Current route			Optimization			Earnings			%
	Distance (km/day)	Time (min/day)	Fuel (L/day)	Distance (km/day)	Time (min/day)	Fuel (L/day)	Distance (km/day)	Time (min/day)	Fuel (L/day)	
Atatürk	84	252	42	62	186	31	22	66	11	26
Çarşı	46	139	23	18.5	55	9	27.5	84	14	60
Sanayi	44	131	21	28	85	14	16	46	7	36
Tabduk emre	46	139	23	40	121	20	6	18	3	13
Yunus Kent sağ	43	130	21	32	97	16	11	33	5	26
Average	53	158	26	36	108	18	17	50	8	32

average speed of the vehicles was chosen as 20 km/h. The time spent at each location versus the length of the route was calculated based on this data. Atatürk locality has a route length of 84 km/day. After leaving the garage and completing its course on the route, the time to arrive at the landfill is 4 hours and 12 minutes. Çarşı location has a route length of 46 km/day. After leaving the garage and completing its course on the route, the time to reach the landfill is 2 hours and 19 minutes. The industrial site has a route length of 44 km/day. After leaving the garage and completing its course on the route, the time to reach the landfill is 2 hours and 11 minutes. Tabduk Emre locality has a route length of 46 km/day. After leaving the garage and completing its course on the route, the time to reach the landfill is 2 hours and 19 minutes. Yunus Kent Sag location has a 43 km/day route length. After leaving the garage and completing its course on the route, the time to reach the landfill is 2 hours and 10 minutes.

Optimization of Vehicle Routes

Considering the container layout in the existing 5 pilot regions, the route optimization is planned with the starting point being the Cleaning Works Directorate garage and the ending point being the sanitary landfill. The Network Analyst module of ArcMap 10.5 software was used for solid waste collection and optimum route determination. As a result of the optimization conducted in the light of this information, it seems possible to achieve an optimization of 26% for the Atatürk site, 60% for the Çarşı site, 36% for the Sanayi site, 13% for the Tabduk Emre site, and 26% for the Yunus Kent Right site. The optimization summary is provided in Table 3.

CONCLUSION

There are 4,750 containers placed on the site for the collection of urban solid waste (garbage collection) in Karaman. The number of people per container is 35. The average occupancy of the containers before they are emptied is 33%. Despite this, citizens sometimes complain about the overflow of the containers during meetings with the Karaman Municipality Cleaning Affairs Directorate. These results indicate two things: the number of containers is sufficient according to the container occupancy rate, and even more containers are placed than necessary. However, it is clear that the container layout lacks proper planning. This causes extra stops and starts for the vehicles, leading to some containers being overfilled while others remain empty. The placement of the containers on the streets should be re-planned based on the number of people per container, the population impact diameter of the container, or the optimum distance between containers [20–23].

There are 433 recycling bins placed in Karaman by a licensed company for packaging waste. Additionally, there are 5,950 indoor boxes distributed to households and workplaces. The waste volume per container is 2.58 m^3, and the container utilization factor is 129%. These results show that the existing recycling equipment is insufficient to collect the recyclable wastes in the city. Furthermore, the existing recycling containers are open, uncovered, and unprotected, making them susceptible to collection by people known as street collectors. This reduces the amount of waste that can be collected by the licensed company from the recycling containers and increases the company's costs. The number of recycling equipment in Karaman should be increased, and the containers should be modernized and protected from external interventions [22–28].

To enhance the efficiency of collecting recyclable materials, it is crucial to expand the availability of recycling bins and equipment, increase the distribution of indoor containers and recycling bags to public entities, organizations, and residential buildings, and ensure these are collected at designated times. Additionally, encouraging active involvement from individuals eager to contribute to recycling efforts is essential [29–31].

When the container density in Karaman is analyzed with the help of the ArcMap 10.5 program, the average distance between the containers is 33 meters, while the expected average distance is 73 meters. This analysis shows that the containers are too close to each other, which also explains the low container utilization factor. Container layout should be re-planned based on the population, using the container impact diameter or within the expected average distance range [7, 17].

Existing and optimized routes were created using the ArcMap 10.5 program for 5 pilot regions in Karaman. The route optimization studies have shown that an average of 32% optimization has been achieved, saving 17 km/day, 50 min/

day, and 8 L/day of fuel on average in the 5 pilot regions. In light of these results, it is possible to achieve a 32% gain in both economic and temporal aspects and in reducing the carbon footprint during the collection and transportation processes, which constitute the biggest expense item of waste management (in the range of 65–80%). Similarly, it is stated that a 27% gain in optimization studies can be achieved in the literature [7]. For the integrated waste management system to be created and progressed economically and systematically, after the container layout optimization is done, the route determination process should be carried out using systematic and scientific methods for the transportation of wastes by collecting the containers. Thus, the municipality will increase its economic gains with the Integrated Solid Waste Management system while minimizing the level of waste to be generated within the framework of zero waste [26, 29, 30].

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Removal of sodium isopropyl xanthate by capacitive deionization process

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ABSTRACT

This study investigated the removal of sodium isopropyl xanthate (SIPX) by capacitive deionization using an ion exchange resin/PVDF electrode. The electrode was prepared by coating a layer of ion exchange resin (Amberlite FPA54) and polyvinylidene fluoride (PVDF) on the carbon electrode. Batch experiments demonstrated that 96% of SIPX was removed through electrosorption and electrochemical advanced oxidation processes at 1 V. Carbon disulfide (CS_2) was generated as a by-product of the xanthate oxidation. Adsorption/desorption cycle tests revealed that the ion exchange resin/PVDF electrode has high adsorption capacity, and the maximum adsorption could not be achieved within 60 min of adsorption times. The total xanthate removed in the final adsorption stage of eight cycles was 323 mg/m^2, corresponding to 34.1% of xanthate from a 20 mg/L xanthate solution that flowed 0.4 mL per min at 1 V for 60 min of adsorption. At the end of the 30 min. desorption, 32.1% of the adsorbed xanthate was released back into the solution and oxidized to CS_2, which was adsorbed by the electrodes in the following adsorption stage. The percentage of the concentrate flow at the end of the desorption stage was 33%. The findings of the study suggest that CDI is a promising tool for the mining industry. However, further research is needed to evaluate its efficiency for specific mining applications.

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INTRODUCTION

Mineral processing operations consume significant amounts of water. Mining represents a small fraction of total water use worldwide but has a major effect on the quantity and quality of water resources at mine sites [1]. Environmental concerns have led to the need to reuse water to conserve freshwater resources [2].

Froth flotation is the most water intensive process in mining operations due to the significant water usage involved. However, among the other mineral processing methods it is the most affected by water quality [3]. Water reuse in flotation results in the accumulation of dissolved compounds that change the chemistry of the system and often have a detrimental effect on recovery and grade [4].

Xanthates are common collectors used in the flotation of sulphide minerals. They are not stable. Upon oxidation and hydrolysis, they form species such as perxanthate, monothiocarbonate, and dixanthogen, which affect the action of the collector [5]. In addition, the remaining xanthate and its degradation compounds in the process water can reduce the selectivity among minerals [4]. Although many flotation plants reuse tailings water at high levels, some discharge may occur. Without proper treatment, releases to the environment can result in contamination of water resources at the mine site. This study offers a novel and effective method for the removal of xanthate, aiming to reduce environmental impacts and conserve water resources.

In the last decade, xanthate removal via chemical oxidation using ozone [6], hydrogen peroxide, Fenton, and solar pho-

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tofenton processes [7], biodegradation [8], and adsorption by bentonite [9], montmorillonites [10], and activated carbon [11] have been extensively studied. The drawbacks of conventional methods, such as high reagent consumption, slow removal rate, and by-product formation, have led to the investigation of treatment methods that reduce xanthate to small molecules such as CO_2, H_2O, and SO_4^{2-}. For this purpose, the electrochemical advanced oxidation process, which utilizes very powerful oxidizing hydroxyl radicals (·OH), was employed to eliminate xanthate from flotation water. During the process, 95% of the xanthate was removed by producing carbon disulfide as an oxidation product, which was removed by the electrodes to some extent [12].

Electrosorption, also known as capacitive deionization (CDI), is a two-stage desalination process; the first stage is an ion electrosorption process that immobilizes ions on pairs of carbon electrodes to purify water. The second stage is the regeneration of the electrodes through the release of the adsorbed ions [13]. CDI has recently become an energy-efficient and cost-effective water treatment method as it requires lower operational voltages than other technologies such as reverse osmosis (RO), electrodialysis (ED), and distillation. Besides, unlike membrane-based methods such as RO and nanofiltration, CDI does not require the use of high-pressure pumps or membranes [14]. The energy demand of the CDI process is approximately 0.1–1.5 kWh/m^3, depending on the influent concentration and the effluent requirements. On the other hand, the typical energy requirement for RO treatment of feed water with a salinity of less than 5 g/L is about 0.8–2.5 kWh/m^3. Other emerging technologies, such as membrane CDI (MCDI) and flow-electrode CDI (FCDI), can further improve the energy efficiency of treatment compared to CDI [15].

Activated carbon (AC) is a viable electrode material due to its characteristic properties such as high pore volume, pore size, and pore connectivity, in addition to electronic conductivity and electrochemical stability. However, it has several limitations impeding its desalination capacity [16]. Various studies in the literature have shown that combining AC with other materials improves its desalination performance. For instance, adding ion exchange resin to the electrode improved performance by 35% due to increased hydrophilicity [17]. The anion exchange resin/QPVA coated carbon electrode removed sulfate selectively [18]. The AC electrode loaded with titanium dioxide improved the desalination performance by 62.7% [19]. Reduced graphene oxide and activated carbon composite (GAC) is a promising material with higher electrosorption capacity mainly based on the advantages of graphene acting as a bridge to form a conductive network, that prevents the aggregation of AC [20].

This study investigated the removal of SIPX by capacitive deionization. An electrochemical cell was fabricated using a carbon electrode coated with an ion exchange resin/PVDF layer as the anode and a cation exchange membrane attached to the carbon electrode as the cathode. The fabrication and characterization of the resin/PVDF electrode are presented here. The process efficiency was evaluated by batch and continuous flow experiments.

Table 1. Characteristics of the ion exchange resin*

	Amberlite FPA54
Copolymer	Crosslinked phenol-formaldehyde polycondensate
Matrix	Highly porous
Functional group	Tertiary amine
Physical form	Gray, opaque, granules
Ionic form as shipped	Free base
Total exchane capacity	≥1.8 Eq/L
Water retention capacity	60–65%
Particle size	470–740 µm

*Manufacturer supplied.

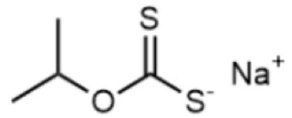

Figure 1. Structural formula of sodium isopropyl xanthate (SIPX).

MATERIALS AND METHODS

Powdered activated carbon (PAC; CEP-21K, PCT Co., surface area of 2040 m^2/g) was used to fabricate electrodes. A cation exchange membrane with an exchange capacity of 2.0 mol/kg was received from Shanghai Shanghua, LLC. A weak base anion exchange resin (Amberlite FPA-54) was purchased from DOW. Characteristics of the ion exchange resin are given in Table 1. Polyvinylidene fluoride (PVDF, molecular weight: 534,000 g/mol) and N, N-Dimethylformamide (DMF, ≥99.8%) were obtained from Sigma Aldrich. Sodium isopropyl xanthate (SIPX) was provided by a commercial supplier. The structural formula of SIPX is presented in Figure 1.

Preparation and Characterization of Electrodes

The carbon electrodes consisted of 90% PAC and 10% PVDF binder, based on the total electrode mass. The preparation of the electrodes consisted of three main steps: preparing the slurry, casting, and drying. To prepare the slurry, PVDF was dissolved in DMF (4%) by mixing for 1 hour. After complete dissolution, PAC was added to be 90% of the total mass. The resulting mixture (30% solids) was stirred overnight for homogenization. The carbon slurry was then cast onto the graphite sheet with a thickness of 300 µm using a flow coater (Newport, USA). The electrodes were dried at room temperature after deposition.

Ion exchange resin, AMBERLITE FPA54 was used to fabricate anode by casting a layer of PVDF and grounded resin on the carbon electrode surface. To prepare the slurry AMBERLITE FPA54 resin was grinded by mortar grinder (Retsch RM200, Retsch Gmbh, Germany). The ion exchange resin powder was mixed with 10% PVDF at a 1:1

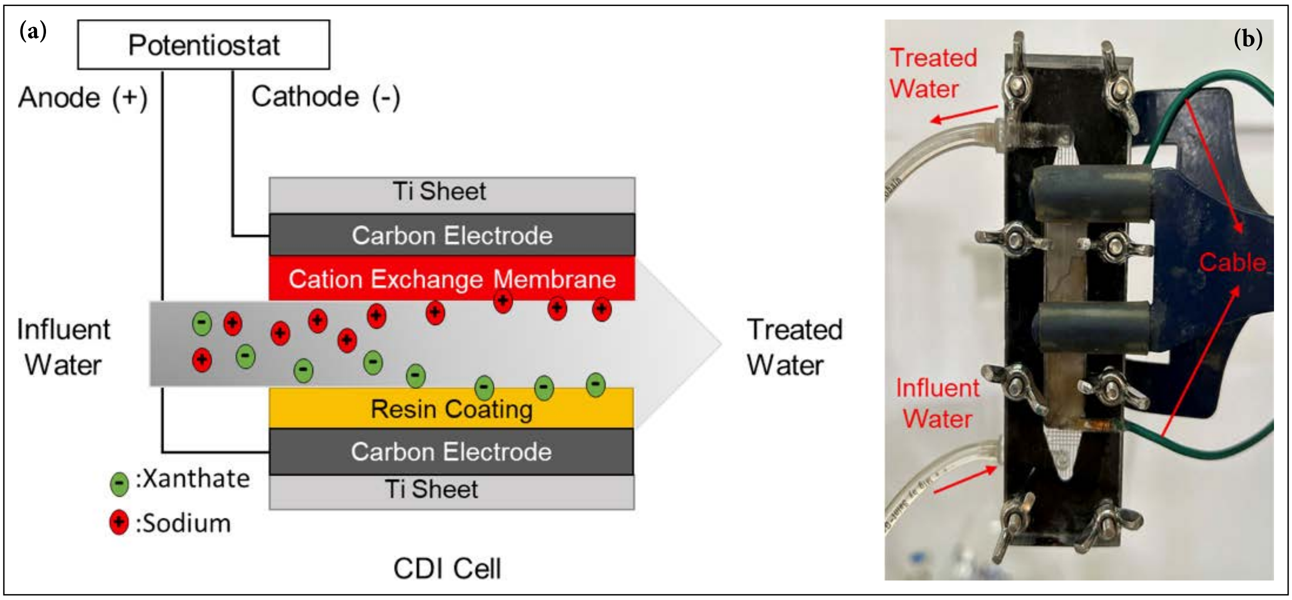

Figure 2. Schematic diagram of bench-scale desalination test setup [13] **(a)** and photograph of the CDI cell **(b)**.

resin to PVDF ratio. Ion exchange resin/PVDF slurry was deposited on the carbon electrode with a thickness of 30 µm and dried at room temperature.

The size of ground resin was measured by dynamic light scattering using a Zetasizer (Brookhaven, OMNI, USA). The surface and cross-sectional morphologies of the ion exchange resin/PVDF electrode were characterized by scanning electron microscopy (TESCAN, GAIA3, Triglav, Brno, Czech Republic).

Desalination Experiments

A schematic representation of the bench-scale capacitive deionization test setup is given in Figure 2. The feed solution was pumped with a peristaltic pump (Cole Parmer, Masterflex, LS Easy Load 7518–00, USA) through a flow by type capacitive deionization cell. A potential was applied by using a potentiostat (Gamry PCI-4750, Warminster, PA, USA) during the process. pH of the effluent solution was measured. The CDI cell consisted of two electrodes, an ion exchange resin/PVDF coated carbon electrode as the anode, and a cation exchange membrane placed on top of the carbon electrode as the cathode. The size of the electrode was 10X50 mm. The electrodes were separated from each other by a non-conductive nylon separator. In all experiments, the flow rate of the solution was 0.4 mL per minute.

Batch electrosorption tests were conducted to observe the xanthate removal efficiency by capacitive deionization. 20 ml SIPX solution at various concentrations; 10 mg/L, 50 mg/L, and 100 mg/L was cycled through the CDI test setup for 24 hours at 1 V. The final concentration of the solution was measured by UV-Vis spectrophotometer (Multispect 1501, Shimadzu, Kyoto, Japan) to determine the concentration of residual SIPX.

Continuous flow tests were performed for adsorption/desorption periods of 60 minutes and 30 minutes, respectively. The influent concentration of SIPX solution was 20 mg/L. The operating voltage was set to 1 V for adsorption and -10 V for desorption. A multi-step potential method was used to maintain a constant voltage during operation by potentiostat. Effluent samples were collected continuously at 10 min. intervals for adsorption and 3 min. intervals for desorption for the determination of SIPX by UV-Vis spectrophotometer. Four adsorption and desorption cycles were conducted before sampling, and then data collection began for four cycles after ensuring the system had reached a dynamic steady state.

Process efficiency was determined by the amount of total salt removed (SR, mg/m^2 (eq1)) and salt removal efficiency % (SRE %, (eq2)) during the adsorption stage.

$$SR = \frac{Q\int_0^t (C_i - C_f)dt}{A_e} \quad (1)$$

$$SRE[\%] = \frac{\int (C_i - C_f)d_t}{C_i t} x100\% \quad (2)$$

Q: flow rate (L/s); Ci: initial concentration (mg/L); Cf: final concentration (mg/L); t: time (s); Ae: effective frontal area of the anode (m^2).

Cost Analysis

The energy consumption for the adsorption and desorption steps was approximately determined using eq3 [21].

$$Energy\ Demand\ for\ Ads.and\ Des. = \left(\frac{kWh}{m^3}\right) = \left(a\frac{I_{ads.}V_{ads.}}{Q}\right) + \left(b\frac{I_{des.}V_{des.}}{Q}\right) \quad (3)$$

Iads: average current for adsorption (A); Vads: average voltage for adsorption (V); Ides: average current for desorption (A); Vdes: average voltage for desorption (V); Q: flow rate (m^3/h); a: water recovery rate; b: concentrate flow rate.

The unit price of electricity ($0.08/kWh in US Dollars) provided by the Turkish Electricity Distribution Corporation was used to convert energy consumption into cost [22].

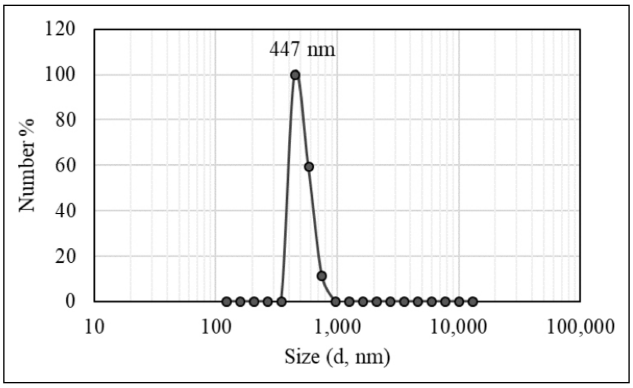

Figure 3. Size distribution of resin powder after grinding.

RESULTS AND DISCUSSION

Characteristics of the Resin/PVDF Electrode

Figure 3 illustrates the size distribution of the resin powder after grinding, with an average particle diameter of 447 nm. The SEM images of the resin/PVDF electrode surface and cross-section given in Figure 4 demonstrated a uniform distribution of resin nanoparticles. They showed that the thickness of the carbon layer was approximately 195 μm. Resin/PVDF coating resulted in a dense surface with a thickness of ~38 μm. The size of the resin particles varied between 0.2 μm and 0.6 μm (Fig. 4).

Desalination Experiments

20 ml of SIPX solution with three different concentrations of 10 mg/L, 50 mg/L, and 100 mg/L was recycled through the CDI cell at a flow rate of 0.4 mL/min and 1 V for 24 hours. The UV spectra of the effluent solutions are presented in Figure 5. Absorptions at 226 nm and 301 nm corresponded to residual xanthate in the effluent. The concentrations of SIPX in the effluent were 0.94 mg/L, 2.59 mg/L, and 4.46 mg/L for the 10 mg/L, 50 mg/L, and 100 mg/L influent solutions, respectively.

In acidic media, water discharges on the electrode, leading to the production of hydroxyl radicals (·OH) on the electrode surface (eq4). These radicals facilitate the electrochemical oxidation of organic compounds. The electrochemical oxidation of an organic compound by ·OH then occurs on the anode surface (eq 5) [23].

$$M+H_2O \rightarrow M(\cdot OH)+H^++e^- \quad (4)$$

$$M(\cdot OH)+R \rightarrow M+OxidationProducts+H^++e^- \quad (5)$$

M: the electrode, R: the organic compound.

A peak was detected at 206 nm in the UV spectra of 50 mg/L and 100 mg/L SIPX solutions (Fig. 5). It indicated the formation of carbon disulfide (CS_2) [24] by electrochemical oxidation of the -CSS- group of the xanthate by hydroxyl radicals during the process [6]. The CS_2 peak was not detected in the UV spectrum at an influent xanthate concentration of 10 mg/L due to the absorption of the released CS_2 by the electrode. As the initial xanthate concentration increased to 50 mg/L and 100 mg/L, the amount of carbon disulfide in the effluent increased since the resin/PVDF electrode reached its maximum absorption capacity.

Total xanthate removal was 3800 mg xanthate per m^2 of electrode in 20 mL of 100 mg/L SIPX solution. For solutions containing 10 mg/L, 50 mg/L, and 100 mg/L SIPX, 91%, 95%, and 96% of the xanthate was removed, respectively.

Adsorption/desorption cycle tests were performed with 60 min. adsorption and 30 min. desorption phases for eight cycles to investigate the removal efficiency of xanthate from

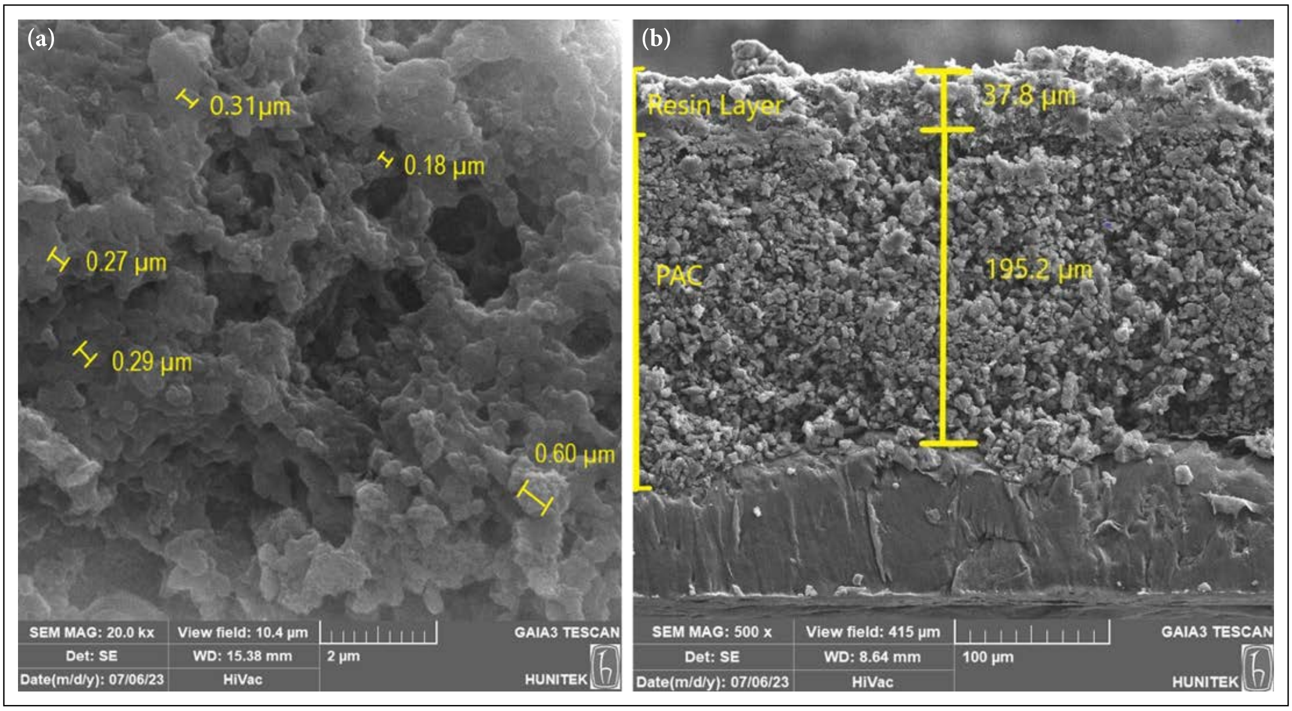

Figure 4. SEM images of surface **(a)** and cross-section **(b)** of resin/PVDF electrode.

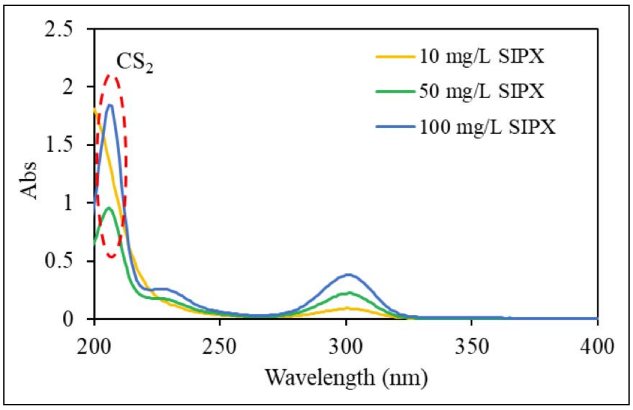

Figure 5. UV spectra for 20 mL SIPX solutions with the initial concentrations of 10 mg/L, 50 mg/L and 100 mg/L after batch electrosorption for 24 h at 1V.

the initial concentration of 20 mg/L SIPX solution. The applied voltage was set to 1 V for adsorption and -10 V for desorption stages. The xanthate solution was continuously passed through the system at a flow rate of 0.4 mL/min.

The UV spectra of the final adsorption/desorption cycle are illustrated in Figure 6. According to the results presented in Figure 6a, the xanthate peak at 301 nm decreased with time, indicating that SIPX was removed during the 60 min. adsorption step. The concentration of SIPX reduced from 20 mg/L to 12.5 mg/L at the end of the adsorption stage. An absorption peak at 206 nm was detected in the effluent sample collected during the first 10 min. of the adsorption stage (A-10 min.), which could be attributed to the formation of CS_2 during the desorption step in the previous cycle [12].

In the desorption stage, the compounds adsorbed by the electrodes were released back into the solution. It was clearly shown that the amount of xanthate and carbon disulfide increased during 30 min. of the desorption stage resulting in the regeneration of the electrode surface (Fig. 6b).

Changes in SIPX concentration during 60 min. adsorption and 30 min. desorption times for the last four adsorption/desorption cycles were given in Figure 7. Based on the results, it can be concluded that the resin/PVDF electrode had a high adsorption capacity and did not reach its maximum adsorption during 60 min. of adsorption step. Some of the xanthate adsorbed on the electrode surface during the adsorption stage was desorbed in the 30 min. desorption stage, but complete desorption could not be achieved.

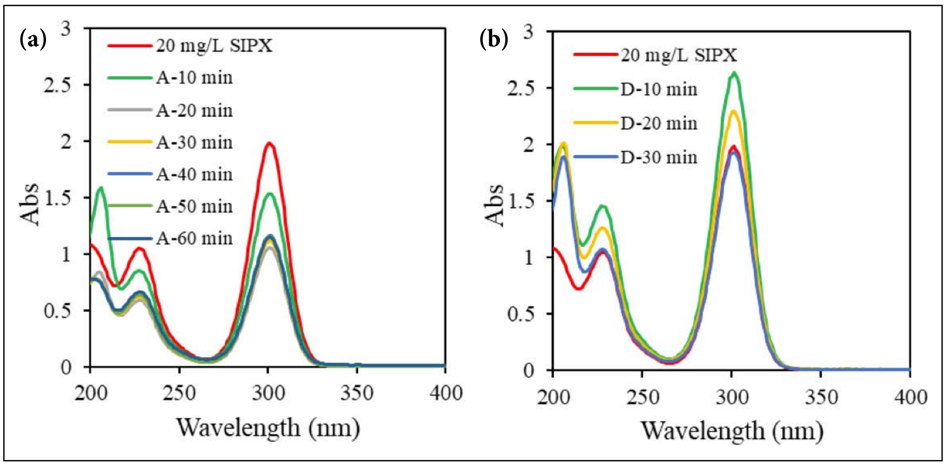

Figure 6. UV-spectra of the final adsorption/desorption cycle for the initial concentrations of 20 mg/L SIPX; a) 60 min. of adsorption times at 1 V and b) 30 min. of desorption times at -10 V

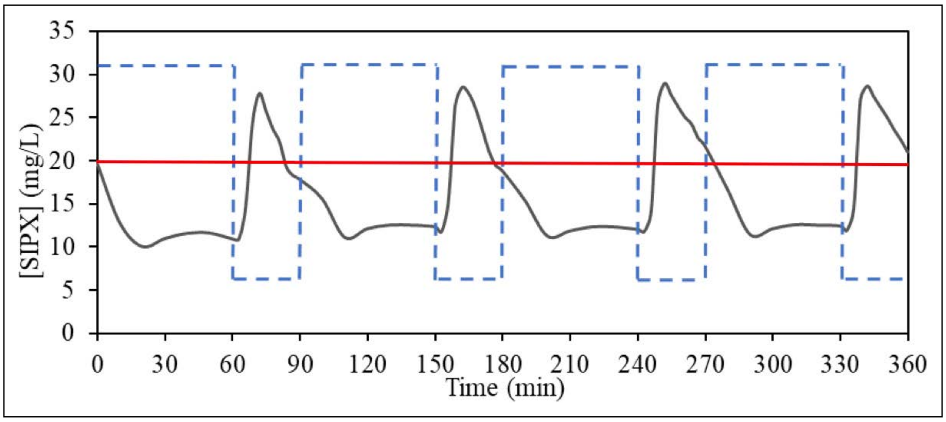

Figure 7. Changes in SIPX concentration during 60 min. adsorption and 30 min. desorption times for the last four adsorption/desorption cycles at an influent concentration of 20 mg/L.

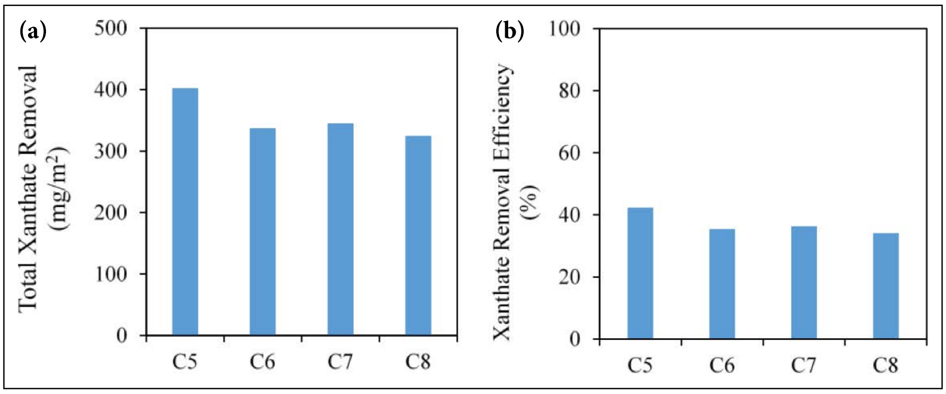

Figure 8. Desalination performance of the electrode; **(a)** total xanthate removal and **(b)** xanthate removal efficiency during 60 min. adsorption times for the last four adsorption cycles at an influent concentration of 20 mg/L SIPX.

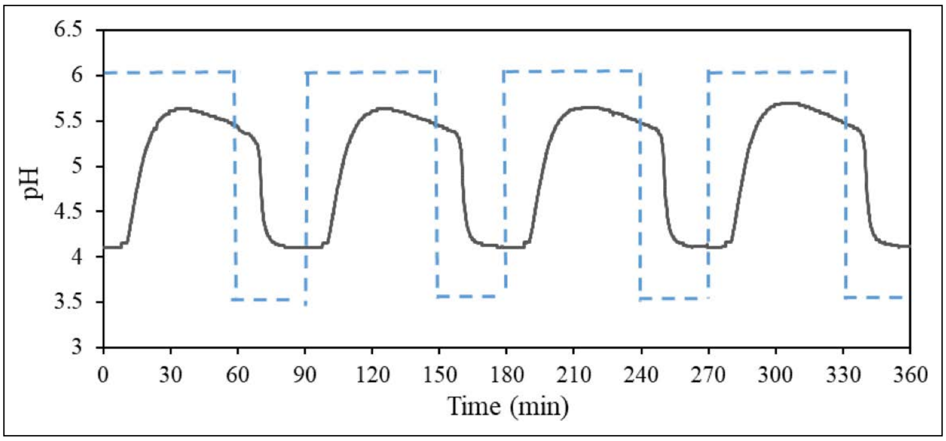

Figure 9. Changes in pH during 60 min. adsorption and 30 min. desorption times for the last four adsorption/desorption cycles at an influent concentration of 20 mg/L SIPX.

The desalination performance of the resin/PVDF coated electrode was assessed by the amount of total xanthate removal and xanthate removal efficiency % during the adsorption stage. Figure 8 illustrates the desalination performance of the electrode during the process. According to the results presented in Figure 8a, in the fifth adsorption cycle, 401 mg/m^2 of xanthate was removed, while in the last cycle, it decreased to 323 mg/m^2, corresponding to 42% to 34.1% of xanthate removal (Fig. 8b). The water recovery for the final adsorption stage was 67%. At the end of the 30 minutes of desorption in the last cycle, 103.9 mg/m^2 of the xanthate was recovered, corresponding to 32.1% xanthate recovery. The percentage of concentrate flow at the end of the final desorption stage was 33%.

Changes in pH during adsorption/desorption cycles were monitored online during the treatment and the results were presented in Figure 9. The pH of the initial solution was measured as 5.39. During the desorption stage, the pH decreased to 4.11, which was attributed to the production of hydroxyl radicals, resulting in the electrochemical oxidation of xanthate to CS_2 [25].

Cost Analysis

In this study, cost analysis was conducted by considering the energy consumption during both the adsorption and desorption stages. The average applied voltage and current were utilized to calculate the energy requirements for the process. During the adsorption phase, a voltage of 1.0 V and a current of 0.23 mA were observed. In the desorption phase, a voltage of -10 V and a current of 1.07 mA were measured.

The cost analysis indicated that the energy demand for the treatment was 0.154 kWh/m^3, corresponding to a cost of 0.013 \$/m^3. This demonstrates that capacitive deionization, known for its cost-effectiveness and low energy consumption in the range of 0.1 to 1.5 kWh/m^3 [15], is highly effective in removing xanthate.

CONCLUSION

The results obtained from this study are summarized below:

- Batch experiments showed that 96% of xanthate corresponded to the 3800 mg xanthate per m^2 of the electrode, which was removed from 20 mL of 100 mg/L xanthate solution that flowed 0.4 mL per minute at 1 V for 24 h via electrosorption and electrochemical advanced oxidation processes.
- Carbon disulfide (CS_2) was generated as a by-product of xanthate oxidation and was adsorbed to some extent by the electrode.

- Both batch and cycle tests demonstrated that the ion exchange resin/PVDF electrode possesses a high adsorption capacity. However, maximum adsorption was not reached within 60 minutes.
- The amount of xanthate removed over the last four adsorption cycles decreased from 401 mg/m^2 to 323 mg/m^2, which corresponds to 42% to 34.1% of xanthate removal.
- At the end of the desorption stage, 32.1% of the adsorbed xanthate was released back into the solution and oxidized to CS_2.
- The pH of the initial solution decreased due to the production of ·OH during the desorption stage.
- The impact of operating parameters such as adsorption/desorption cycle times, applied voltage, and flow rate on desalination performance should be further investigated to improve the process.
- CDI is promising for long-term desalination, but the electrodes may degrade over time. Therefore, the long-term performance of the resin/PVDF electrode should be monitored to determine the overall performance of the process.
- The study highlights CDI's potential for long-term desalination in the mining industry but also notes that the electrodes may degrade over time. Future research should focus on optimizing operating parameters such as adsorption/desorption cycle times, applied voltage, and flow rate to enhance process efficiency. Additionally, the long-term performance and stability of the resin/PVDF electrodes should be monitored to assess their overall efficacy in practical applications.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Environmental Research & Technology

Research Article

Experimental determination of mechanical properties and characterization of selected crop residues

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ABSTRACT

The management of huge waste generated from crop harvesting and processing has continued to create challenges and constitute an environmental nuisance. Inappropriate disposal and open-air burning of crop residues exacerbate environmental pollution, escalate bush burning and deforestation, and impact human health. Mixing, processing, and conversion of crop residues to form useful composites for various applications remain one of the economical, eco-friendly, and sustainable strategies for its management. The study constructed composites by mixing different ratios of unripe plantain peel (UPP) and coconut fibre (CCF) with an appropriate binder and hardener. The fabricated composites were subjected to mechanical, compositional, and morphological analyses. The outcomes of the tests show that the hardness, tensile strength, and impact strength only UPP is 97.8 RHN, 411 MPa, and 9 818 J/m^2, respectively while the CCF/UPP composite is 98.5 RHN, 538 MPa, and 12 273 J/m^2, respectively. The wear rate of UPP is 0.56 cm^3/m while that of the CFF/UPP composite is as high as 0.73 cm^3/m and increases with increased load. Silicon, oxygen, and aluminium are the major constituents of the composite samples as revealed by the compositional analysis. The tensile strength, hardness, impact, and wear rate of UPP can be boosted by the blending of CFF to form homogenous composites. The outcome of this study will deepen the literature and escalate research into the conversion and utilization of crop residues for diverse applications. The usage of innovative technologies and energy-efficient techniques should be adopted for the processing, modification, and conversion of crop residues.

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INTRODUCTION

Sustainable waste management is one of the challenges facing humanity in this generation. The problem of waste management has been exacerbated by increased waste generation across various sectors and countries. Due to escalating global population, increased food production and consumption, industrialization, and urbanization, global waste generation has continued to rise. From available data, the total waste generation which was 2 billion metric tons (BMT) in 2016 has been estimated rise to 2.6 BMT in 2030 and further to 3.4 BMT in 2050, globally [1]. The agricultural sector contributes significantly to global waste generation and the trend is expected to continue into the foreseeable future. Increased production, processing, and consumption of food to feed the human beings and animals and provide the needed raw materials for the industries are some of the contributors to increased waste from the agri-

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cultural sector. Crop residues form a significant part of the waste generated from the agricultural sector. The agricultural sector produces an average of 23.7 million tons of food daily, worldwide [2]. Food production from the agricultural sector has increased significantly over the last few decades due to accelerated population growth, the introduction of innovative agricultural practices, the development of high-yielding crops, and the introduction of technological and mechanized farming [3]. Crop residues are leftovers or remnant materials after agricultural products have been harvested, eaten, or processed. Common classifications of crop residues include peels, straws, husks, bagasse, shells, cobs, stovers, stubbles, etc. [4].

Plantain peel (PP) is the fleshy outer covering of a plantain fruit. It is bright green when unripe but becomes light yellow when ripe. Plantain is a major source of carbohydrates and is mostly consumed in Africa, the Caribbean, Latin America, Asia, and the Pacific. Plantains are usually cooked, roasted, boiled, and steamed, and can be processed into flours, snacks, and animal feed, and used as raw materials for food and beverage industries [5]. Nigeria, Cameroon, Ghana, and Uganda have dominated global plantain production in recent years with Nigeria producing 3.09 million metric tons (MMT), 3.08 MMT, and 3.8 MMT in 2016, 2020, and 2021, respectively (Fig. 1) [6–8]. Inappropriate disposal of plantain peels constitutes sanitation hazards, attracts flies, cockroaches, and other pathogens, and impacts human health. Plantain peel helps in wound healing, treatment of skin disorders, and hastens cell regeneration [4].

Coconut fiber (CCF) is a natural fiber extracted from the husk of a coconut. It is the outermost part of the coconut and directly shields the coconut shell. Coconut is one of the world's most versatile products and it is a drupe consisting of a fruit, seed, and nut. The fiber of an average coconut weighs about 0.80 kg and constitutes about 47.75% of the weight of the coconut [9]. The global production of coconut increased from 51. 66 MMT in 2000 to 59.85 in 2016 and further to 63.7 MMT in 2021 with over 84% coming from Asia [10]. India, the Philippines, and Indonesia have dominated global coconut production in recent years with 14.3 MMT, 14.7 MMT, and 17.2 MMT in 2021, respectively [11]. Over the past few years, Nigeria's coconut production has hovered around 0. 225 MMT (Fig. 2) [10]. CCF can be burned or converted to activated carbon, biochar, or made into briquettes for cooking. It can also be used as aggregate for concrete and road construction, as a natural filler in composites for thermal lagging, as production of phytochemicals and biofuels, as absorbents, and in automotive and construction applications [12].

In other to enhance the physicochemical, mechanical, thermal, electrical, structural, and compositional properties and behaviour of some materials or machine parts, other materials are added. Composite waste is a heterogeneous mixture of powder produced from some waste materials to advance the properties and enhance the applicability of the new materials. Various mechanical including tensile, hardness, wear, impact, etc., and compositional,

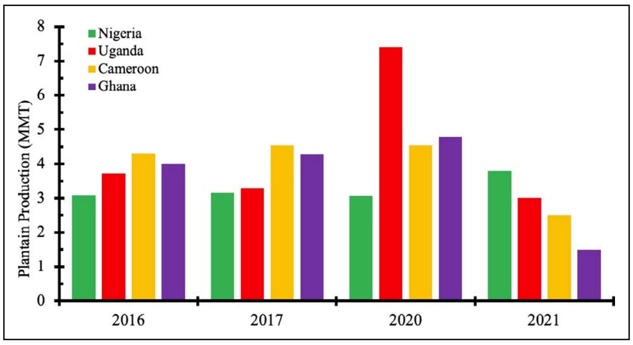

Figure 1. Top four plantain producing countries compiled from [6–8].

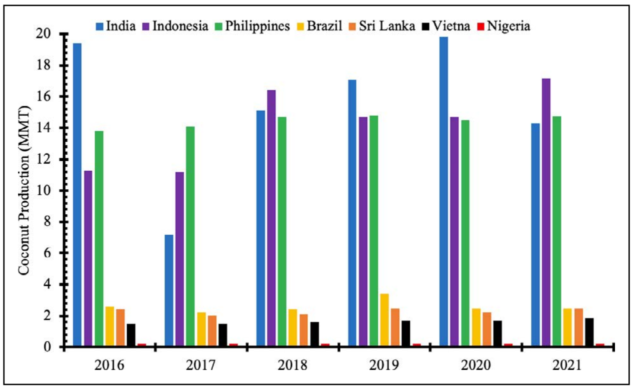

Figure 2. Coconut production in selected countries adapted from [10, 11].

morphological, and thermal techniques including scanning electron microscopy (SEM), thermos gravimetric analysis (TGA), Derivative Thermo gravimetry (DTG), Fourier transform infrared spectroscopy (FTIR), energy dispersive x-ray (EDX), x-ray diffraction (XRD), etc. have been deployed to characterize composites. Akash et al. [13] Mathew et al. [14], and Vinod et al. [15] carried out tensile, hardness, corrosion resistance, morphology, FTIR, XRD, SEM, TGA, etc. of some waste-derived composites. These tests and characterization technologies are performed to predict the features, behaviour, and potential application of composites. In a series of studies, Dwivedi et al. [16], Sujin Jose et al. [17], and Suresh Kumar and Mohanavel [18] demonstrated how the addition of CCF powder reinforced and improved the physical, mechanical, thermal, structural, and fire resistance properties of different materials for various applications. Similarly, Adeniyi et al. [19], Kilani et al. [20], and Akpan et al. [21] reported that the reinforcement of polyester and epoxy composites with PP powder enhanced the surface finish, workability, consistency, impact, compressive and tensile strengths, hardness, anti-corrosion, and other mechanical properties of the composites. The use of crop residues as composite materials are cost-effective, eco-friendly, biodegradable, renewable, sustainable, and recyclable. Also, the crop residues are readily available, easy to modify, and to ensures material recovery, and their applications contribute to circular economy [22–24].

Figure 3. Preparation of UPP sample **(a)** UPP as collected, **(b)** sundried UPP, **(c)** grinding process, **(d)** sieving of UPP sample.

Figure 4. Preparation of CCF sample **(a)** CCF as collected, **(b)** pulverized CCF sample.

Table 1. Details of samples composition

Sample notation	UPP (g)	CCF (g)	Epoxy resin (g)	Hardener (g)
A	30	20	100	50
B	35	15	100	50
C	40	10	100	50
D	50	0	100	50

UPP: Unripe plantain peel; CFF: Coconut fiber.

Despite the outcome of a plethora of research works on this subject matter, in the opinion of the authors, there are still not many investigations on the use of a blend of unripe plantain peel (UPP) and CCF as composites. This is the motivation for the present intervention. The study aims to investigate the mechanical properties of various blends of UPP and CCF as composite materials. Specifically, the composite generated from the blend of UPP and CCF is subjected to hardness, impact, tensile, and wear tests. The samples are also characterized by SEM and EDX. The scope of the current research is restricted to laboratory mechanical and characterization investigations of composites produced by the combination of UPP and CCF. The outcome of this laboratory investigation will update the information available on the mechanical, compositional, and morphological properties of the produced composites. The novelty of this work is in the determination of the effects of the mixing ratio of UPP and CCF on the mechanical properties and characterization of the fabricated composites.

MATERIALS AND METHODS

Materials Collection and Preparation

The UPP was collected from roadside plantain roasters and other consumers within Ado Ekiti metropolis and transported to the laboratory in a plastic bag. At the laboratory, the UPP was washed in running distilled water to eliminate any unwanted substance. The clean UPP were first sundried for 7 days, further dehydrated in an oven maintained at 70 ^oC for 5 h, crushed by mortar and pestle, pulverized into a fine powder with an electric coffee grinder, and sieved using a 75 µm mesh sifter. The powdered UPP was deposited in a dry airtight glass vial for analysis. Figure 3 shows the pictures of the UPP sample preparation process.

The CCF wastes were collected at the point of extraction in the coconut farms near the University campus and conveyed to the laboratory in a clean plastic bag. The UPP was washed in running distilled water to remove the dirts and other impurities, sundried for 10 days, dried at 70 ^oC for 10 h in an oven, crushed by mortar and pestle, pulverized into a fine powder with an electric coffee grinder, and sieved using a 75 µm mesh sifter. The CCF powder was stored in a dry airtight glass vial for analysis. Figure 4 shows the pictures of the CCF sample preparation process.

Epoxy resin and hardener, in analytical grade, were purchased from chemical store in Ado Ekiti. The UPP, CCF, epoxy resin, and hardener were carefully measured and weighed using a digital weight balance, thoroughly mixed together, poured into a prepared mould, and labelled as samples A – D as shown in Table 1.

Methodology

The prepared samples A – D were subjected to hardness, impact, tensile, wear, SEM, and EDX analysis. The reading for each sample was taken three time to improve the accuracy of the result. The average of the three value is recorded and tabulated.

Hardness Test

The hardness test was carried out using a Rockwell Hardness Tester (MVH03, Hardness gauge, China), as shown below using a 0.83325 mm diameter diamond indenter, as per the ASTM E384 standard. A 100 kgf load was applied for an average of 18 s. Following that, the readings were taken from the A scale while taking the appropriate precautions. The purpose of this test was to determine the specimen's Rockwell hardness number. The procedures include securing the clean sample on the anvil and ensure the load lever is in position A. Note the diameter of the ball and elevate the specimen so that it comes into contact with the indenter and ensure the deflecting meter on the small scale doesn't exceed the red point. The sample is put under a preliminary load by selecting 60 N on the load selector. The load lever was moved from position A to position B and left for at least 15 s as the load is gradually applied. The pointer is allowed to come to rest and reading on the hardness scale B is read. The sample was removed from the support table to allow for the identification of the indentation made using microscope and measurement of the indentation diameter 'd' through the attached micrometer. The process is repeated three times to ensure accuracy. The procedures are repeated for other samples.

Tensile Test

A computerized Instron Testing Machine (INSTRON 3365, Engstrom, United States) was used to carry out the tensile strength of the samples according to ASTME 8 standard at room temperature. Three identical test specimens were produced from each sample and were tested with a strain/loading rate of 5 mm/min. Load displacement plots were obtained on a X – Y recorder. The ultimate tensile strength, yield strength and percentage elongation values were calculated from this load displacement diagrams.

To start with, the required length of the sample was measured and inserted into the grips of the machine. The load and displacement on the digital indicator were set to zero and the load application was initiated by pressing unload (blue) button on the tensile machine and record load versus elongation data. The process is continued until the sample fractures. The length of the fracture specimen was measured to get the total elongation at fracture. The process was repeated for all the samples.

Impact Test

The samples were machined into the standard impact test specimen dimension (55 mm x 10 mm x 10 mm), a 2 mm deep V-notch was grooved into the center of the specimen A at 45 °, as shown in Figure 5. The impact test was carried out at room temperature using Charpy Impact Tester (PCICIT-1, Pacorr Testing Instruments Pvt. Ltd., India). During the process, the specimen is placed in the Charpy Impact Testing machine's vice in such a way that the notch backing the hammer and is positioned centrally on the vice and the hand brake for the pendulum was pulled and the pendulum returned to its locked position. The Impact Energy (IE) absolved was read out from the scale and recorded. The Impact Energy (IE) and Impact Strength (IS) of each sample were calculated using equations 1 and 2 and the procedure was repeated for all the samples.

$$Impact\ Energy\ (IE) = \frac{I_1+I_2}{2}\ (J) \quad (1)$$

$$Impact\ Strenght\ (IS) = \frac{E}{A}\left(J/_{m^2}\right) \quad (2)$$

Where: E= Energy required to fracture the sample (J) and A= Surface Area of the sample (m^2).

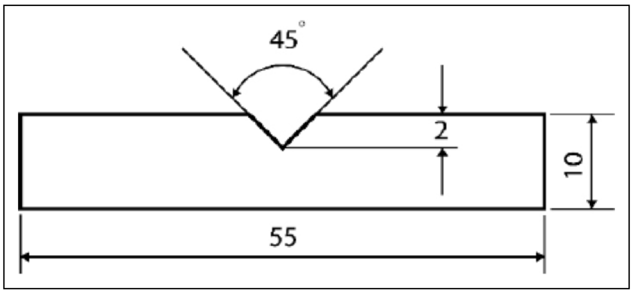

Figure 5. Impact test specimen.

Wear Test

The wear test was performed using Anton Paar GmbH (CSM Instruments Austria). During the process, the tribometer is connected to the computer system installed with the appropriate software. Key in the input parameters such as track diameter, linear speed (cm/s), speed (RPM), distance travelled/laps, and load. The test sample is mounted on the Jaw Chuck of the machine, while the tribometer arm that grips the ball is lowered on the sample. Initiate the test and at the end of the set distance, the tribometer stops automatically and the recorded result is saved. The procedure is repeated for other samples.

Scanning Electron Microscopy Analysis

The SEM analysis was performed on the samples using SEM (Phenom ProX, phenomWorld Einhoven, Netherlands). The sample was mounted on double adhesive on a sample stub and coated with 5 nm gold using a quorum technologies model Q150R sputter coater. It was then delivered to the SEM machine's chamber, where it was examined through NaVCaM for focusing and minor adjustments, then transferred to SEM mode, where it was focused and brightness contrasting was automatically changed, and the morphologies at a magnification of x9000 under vacuum condition were obtained. This process was repeated for other samples.

Energy Dispersive X-ray Analysis

The compositional analysis was performed on the samples using the EDX detector attached to the SEM (Phenom ProX, phenomWorld Einhoven, Netherland). The samples which were prepared under similar conditions described in Section 2.2.5 were loaded into the scanning electron microscopy system with a magnification of x9000 under vacuum condition. From the EDX scan of the loaded sample, the EDX spectra and the element percentage composition by weight were obtained.

Statistical Analysis

The data were subjected to descriptive statistical analysis. The descriptive statistical analysis involves the calculation of the mean, standard deviation (SD), coefficient of variation (CV %), and standard error of the mean (SEM) of the data obtained from the results.

$$\text{Where } SD = \sqrt{\frac{\sum(x_i - \mu)^2}{N}} \quad (3)$$

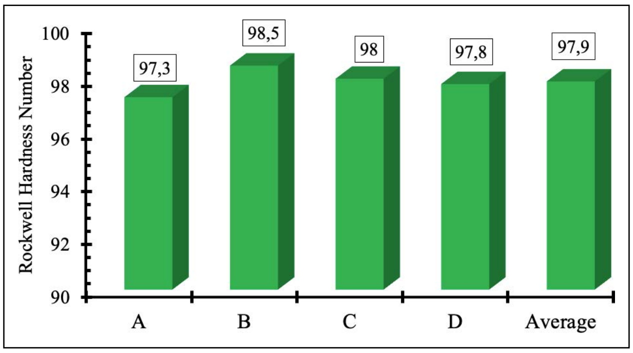

Figure 6. Hardness of samples.

$$CV\% = \frac{SD}{Mean} \times 100 \quad (4)$$

$$SEM = \frac{SD}{\sqrt{N}} \quad (5)$$

N= Population size, x_i = each value from the population, and μ= mean.

RESULTS AND DISCUSSION

Hardness

The result of the Rockwell hardness test shows that there is no substantial disparity in the values for the samples. Sample B presented the highest hardness of 98.5 while sample A hardness number was 97.3. The average hardness for samples was 97.9, as shown in Figure 6. These results show that the addition of CCF to UFP has a very slight impact on the hardness of the UPP. However, the addition of CCF to UPP to form a composite slightly increased the hardness value when compared with the hardness value for the UPP. These results are in harmony with earlier submission of Jacob et al. [25] and Akpan et al. [21]. The implication of this test is that mixing CCF with UPP does not significantly increase the hardness of the composite and supports its utilization as concrete admixture and other industrial applications.

Tensile

The tensile strength, breaking load, and stress of the samples are shown in Figure 7. The average tensile strength for the composite is 428 MPa while the average breaking load is 705 N. The addition of CCF increases the tensile strength, breaking load, and stress of the UPP. Sample A with the UPP and CCF mixture at a ratio of 3:2 presents the highest breaking load, tensile strength, and stress when compared with other samples and is higher than the average values. One of the ways to enhance the tensile strength and breaking load of UPP is to add some percentage of CCF or other agricultural waste powder to it. This will promote the composite tensile strength and empower it to withstand more load before breaking [21, 26].

Impact

The impact test results show that sample D which is wholly UPP and has no CCF has an impact energy of 216 J and impact strength of 9818 J/m² which is lower than the average value of 233 J for impact energy and 10625 J/m² for impact strength. The impact strength for samples A, B, and C is 10182 J/m², 10227 J/m², and 12273 J/m², respectively, as shown in Figure 8. The result implies that one feasible way to improve the impact strength and impact energy of UPP composite is to blend it with CCF [27, 28]. Composites with enhanced impact strength are used for various industrial products and other specialized purposes.

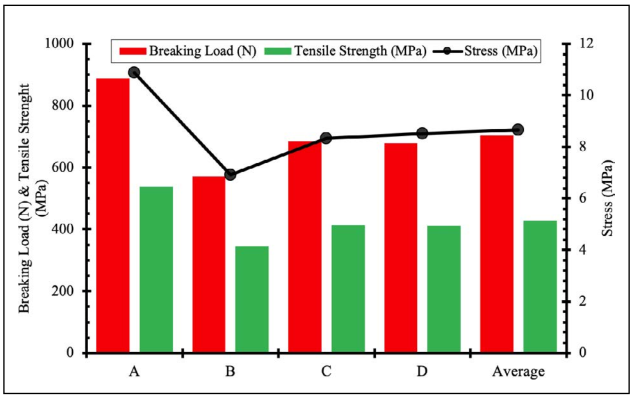

Figure 7. Breaking load, tensile strength, and stress of samples.

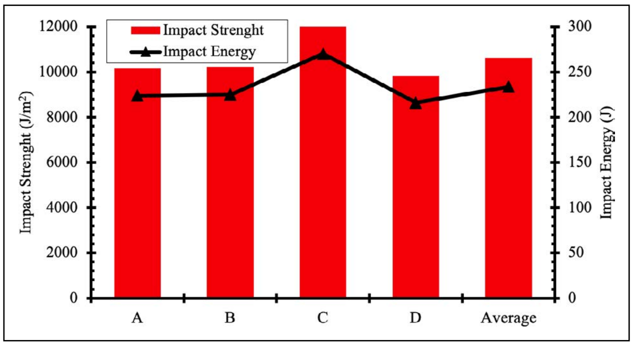

Figure 8. Impact strength and impact energy of samples.

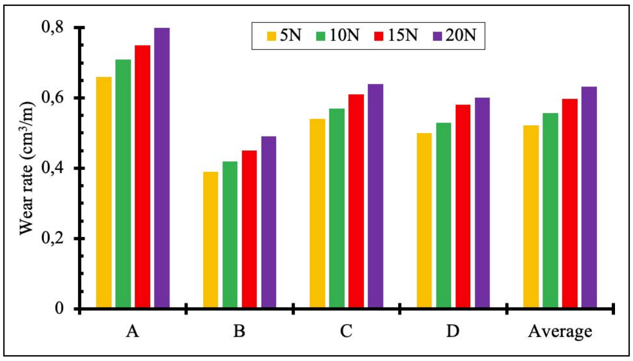

Figure 9. Wear rate of samples at different load.

Table 2. The wear rate of samples

Sample	Wear rate (cm³/m)
A	0.73
B	0.44
C	0.59
D	0.56

Table 3. Statistical analysis of the data

Parameters	Samples				Mean	SD	CV (%)	SEM
	A	B	C	D				
Hardness number	97.3	98.5	98	97.8	97.9	0.49	0.51	0.249
Tensile strength (Mpa)	538.6	345.9	414.2	411.5	427.6	80.49	18.82	40.243
Breaking load (N)	888.8	570.8	683.4	678.9	705.5	132.84	18.83	66.419
Stress (MPa)	10.9	6.9	8.3	8.5	8.7	1.66	19.08	0.831
Impact strength (J/m^2)	10182	10227	12273	9818	10625	1113.82	10.48	556.912
Impact energy (J)	224	225	270	216	233.7	24.5	10.48	12.25
Wear rate (cm^3/m)	0.73	0.44	0.59	0.56	0.58	0.12	20.55	0.059

SD: Standard deviation; CV: Coefficient of variation; SEM: Standard error of the mean.

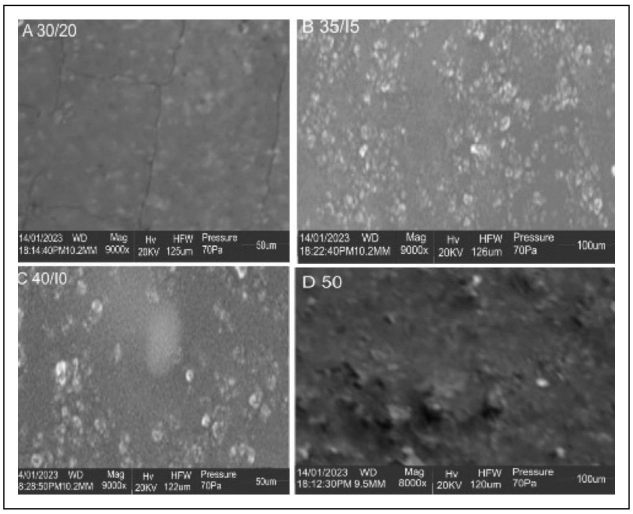

Figure 10. SEM images of samples.

Wear

As shown in Table 2, the wear rate of UPP (sample D) is 0.56 cm^3/m while that of the CFF/UPP composite is as high as 0.73 cm^3/m. The wear rate of the composite samples at different loads is shown in Figure 9. The wear rate increases as the applied load increases. Sample A displays the highest wear rate across the tested loads when compared with other samples and is higher than the average wear rate. The resistance to wear is highest in sample D and lowest in sample A. This shows that the addition of CCF increases the wear rate and reduces the resistance to wear of the composite of UPP. Sample B shows the lowest wear rate and consequently possesses the highest resistance to wear. The outcome of the wear rate conforms with previous results reported by Adeniyi et al. [26], Ohaga et al. [27], and Xie et al. [28].

SEM

The SEM micrograph of the samples are shown in Figure 10. It was observed that the addition of CCF to UPP distorted the homogenous nature of the base epoxy resin micrograph. Samples A, B, and C demonstrated a uniform coverage with a visible line crack on sample A. The observed crack might be due to the thermal stress during the formative stage of the epoxy resin substrate. Although the grain refinability of UPP

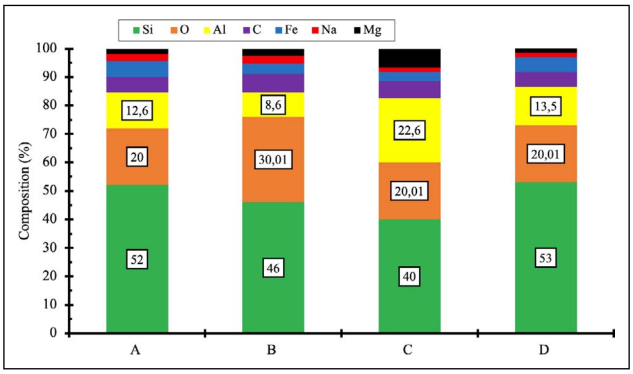

Figure 11. EDX results of samples.

nanoparticles is documented in the literature [21], continuous excessive addition. reduces the degree of homogeneity and surface coverage displayed by samples A, B, C, and D with the increasing presence of pores in the micrograph.

EDX

Silicon, oxygen, and aluminium are the major constituents of the samples. As shown in Figure 11, the concentration of silicon in sample D increased to 53% due to the addition of CCF. However, the addition of CCF to UPP increases the concentration of magnesium, sodium, and carbon in the composite. As shown in Figure 11, silicon, oxygen, and aluminium are the major constituents of the explored composite samples with traces of carbon, iron, sodium, and magnesium.

Results of the Statistical Analysis

Table 3 shows the outcome of the descriptive statistical analysis of the data. The low SD of hardness number, stress, impact energy, and wear rate shows the data for those parameters are not dispersed in relation to the mean while those of tensile strength, breaking load, and impact strength are well dispersed and scattered in relation to the mean. The CV (%) is a measure of the dispersion of the data around the mean. From the table, the CV% is generally low and ranges between 0.5% and 20.5%. The standard error of the mean measures the degree of discrepancy expected in the sample. The SEM is less than 1 in hardness number, stress, and wear rate while the SEM for impact strength is about 556.

CONCLUSION

Unregulated waste generation, inappropriate waste disposal, and ineffective waste management strategies result in poor sanitation, environmental pollution, and contamination of aquatic ecosystems. Burning of crop residues generates toxic smoke and unburnt hydrocarbon, reduces air quality, exacerbates bush burning and deforestation, and impacts human health. The fabrication of composites from crop residues and other agricultural wastes is one of the cost-effective and sustainable approaches for waste management. The mechanical properties of the composites fabricated from the blending of UPP and CCF show that the tensile strength, hardness, impact strength, impact energy, and wear rate of the composites are higher than that of UPP (sample D). Specifically, the hardness of UPP is 411 MPa compared with the value of 538 MPa for the CCF/UPP composite while the impact strength becomes 12 273 J/m^2 for the CCF/UPP composite compared with the value of 9 818 J/m^2 recorded for the UPP sample. The wear rate of UPP is 0.56 cm^3/m while 0.73 cm^3/m was reported for the CFF/UPP composite. Silicon, oxygen, and aluminium are the major constituents of the composite samples as revealed by the compositional analysis. The descriptive statistical analysis of the data shows a low coefficient of variation for each parameter.

The outcome of this study shows that blending UPP with CCF increases the tensile strength, hardness, impact strength, impact energy, and wear rate of the samples. The import of these is that the tensile strength, hardness, impact, wear rate, and other mechanical properties of a give crop residue can be modified by blending it with another crop residue. Scientific-based strategies for safe waste collection and handling should be introduced and adopted to ease the difficulty and encumbrances involved in waste handling, disposal, collection, and processing. Policies and financial incentives are needed to encourage more investments in waste conversion for resource recovery and industrial raw materials.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Environmental Research & Technology

Research Article

Narrowing band gap of ZnO codoping (Al+Mn) as a photocatalyst candidate for degraded textile dye wastewater

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ABSTRACT

Photocatalyst degradation is one method to reduce industrial textile dye pollution in water. In this study, ZnO material was synthesized by codoping Al and Mn using the chemical coprecipitation method to determine the structural and optical properties of the material. This research found that the structure of ZnO after codoping Al and Mn did not change the hexagonal wurtzite phase but changed in other lattice parameters. The addition of Mn and Al codoping is reported to affect the intensity of XRD peaks, especially on the 101 lattice. The higher the scattering peak, the more angular the shift, indicating the magnitude of oxygen vacancies. The addition of Mn with 0% concentration shows the smallest lattice parameter among the other four samples. This indicates that the oxygen vacancy of the sample without Mn is more significant than that with codoping Mn. The reflectance measurement results show that the energy gap value of ZnO (Al+Mn), with a 0% Mn percentage, reaches an immense value, which is 3.290 eV. The smallest energy gap is ZnO (Al+Mn) with 4% codopping Mn which is 3.258 eV. With this consideration, ZnO (Al+Mn) with 0% Mn percentage is suitable to be applied as a Congo Red photodegradation agent, and ZnO (Al+Mn) with 4% codoping Mn is appropriate to be used as a Methylene Green photodegradation agent.

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INTRODUCTION

The textile industry is increasing in all countries [1]. This is based on the fact that textiles are the primary needs of the people. Besides the magnitude of the textile industry, the negative impact on the environment produced is also significant. One of them is textile dye waste. Textile dye waste is an organic waste that is difficult to degrade. When this textile waste is disposed of in the river, it will cause water pollution [1–4]. Uncontrolled water pollution will affect the quality of water, the water ecosystem, and other problems. This problem needs to be solved in various ways. One uses photocatalysts to break down the bonds of textile dyes that have bonded with water molecules [3–5].

Textile dye waste that pollutes the environment will harm the environment and human health even in low concentrations. This happens because of the high composition of toxic textile dyes. In terms of the environment, this dye waste will increase Biochemical (BOD) and Chemical (COD) Oxygen Demand. This will directly inhibit further photosynthesis so aquatic plants will be disturbed. In addition, aquatic animals will stay away from the area because the aquatic environment is no longer healthy. Potential negative impacts also occur in humans. Like Azure B type textile dye waste, this type of dye waste has the potential to trigger gene mutation. This waste if contaminating the human body will be able to intercalate with the helical structure of DNA and RNA duplex [1]. Another potentially mutagenic dye is Disperse red.

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The behavior of this mutagen can increase the frequency of micronuclei which is key for cancer characterization. Disperse Orange also shows a similar pattern. The behavior of mutagens that induce DNA damage can cause base shifts that alter the reading of the genetic code [3].

Removing dye sewage is an action that must be taken because of its serious effects on the sustainability of living things. Various ways are done to overcome this including Adsorption, coagulation, and filtering. However, these methods are costly and inefficient. One of the other methods offered is the photocatalyst method. This method involves semiconductor materials such as ZnO [4, 5]. ZnO semiconductor material is one of the photocatalysts that is being intensively developed. It has the advantages of being cheap, widely available, non-toxic, and easily modified [6–9]. These advantages are considered suitable to answer the problems of the textile industry, especially as a dye pollution degradation agent. ZnO reacted with dye waste liquid will respond if it gets energy from outside. The energy used is photon energy. This mechanism is referred to as a photocatalyst [10, 11]. Photons exposed to the ZnO solution with textile dyes will stimulate electrons to excite from the valence band to the conduction band. This mechanism will form reactive oxygen species that are useful as photodegradation agents [12–14].

Pure ZnO has a reasonably wide energy gap value of 3.37 eV and an excitonic binding energy of 60 meV [6, 15–17]. In this condition, the UV spectrum is needed to regenerate electron-hole recombination. ZnO structure modification is one way to narrow the energy gap value. However, the limitations of ZnO are limited conductivity and low charge concentration carrier ability. This causes the low-efficiency value of ZnO material. Therefore, it is necessary to modify the two factors mentioned. One strategy that can be done is to make structural modifications that can improve electron transport capabilities. Researchers have intensively added doping with metal ions. Some use group III metal dopping such as Al, In, Ga, etc [18]. Of the many types of group III metals, aluminum (Al) is the most widely used for dopping. Al is a dopant used to obtain n-type ZnO with high conductivity, crystal quality, and optical properties. Adding Al in ZnO can reduce the energy gap from 3.37 eV to 3.28 eV. This is essential information for synthesizing ZnO as a photocatalyst agent [16].

Modifying ZnO by adding Al doping has not significantly changed optical properties. The high doping concentration of up to 5% wt did not decrease the energy gap significantly [13, 15, 19–22]. This happens because the Oxygen Vacancy that occurs is still not optimal. Therefore, codoping methods are necessary. The candidates for the second element are transition metals such as (V, Fe, Co, Ni, Mn, etc) [9, 18, 23]. According to some research, Mn is one of the transition metals that can increase oxygen vacancy and absorb photon energy from the UV and visible ranges. However, dopping Mn with low concentrations <3% wt can reduce the energy gap value. Mn with concentrations >3% wt will increase the energy gap value with the presence of the second Mn phase [24–26].

Several methods for synthesizing ZnO with dopping include Coprecipitation, Sol-Gel, Hydrothermal, Chemical Vapor Deposition, Microemulsion Technique, Laser ablation, and Ball milling [27]. Each synthesis method has advantages and disadvantages. The physical technique can give maximum results, but the equipment setup is expensive; the chemical technique is more superficial and not so costly but has problems with reproducibility [28–30]. In this study, the synthesis technique used is co-precipitation, which is a bottom-up technique with a relatively simple and accessible tool setup. Codoping Al and Mn will synthesize ZnO material; Al concentration is fixed at 5% wt and Mn at 0% to 4% wt, respectively.

EXPERIMENTAL PROCEDURE

Material Synthesis

Zinc acetate (99.9%, Merck), Aluminum Chloride (99.9% Merck), Manganese Acetate (99.9% Merck), NaOH (97% Merck). All materials were prepared based on the concentration ratio of $Zn_{0.95-x}Al_{0.05}Mn_x$ with x = 0 to 0.04. The single Al-doped sample is referred to as 0% Mn, and the codoped sample is referred to as 1% Mn to 4% Mn. Each sample with a concentration of 1M was dissolved in 200 mL of deionized water and stirred using a magnetic stirrer at room temperature for 30 minutes. After mixing, the samples were allowed to stand for 30 minutes. After that, the sample solution was stirred again using a magnetic stirrer at a constant speed while the titration process was carried out using 1M NaOH solution. This titration process is carried out under room temperature conditions and continues to be carried out until it reaches a solution condition with a pH of 10. The titration process while stirring lasts for 90 minutes. After the solution has reached pH 10, the titration and stirring process is stopped. The beaker glass was closed using aluminum foil, and the sample was deposited overnight in room conditions. The precipitate was filtered using Whatman paper size 42 to separate the precipitate and liquid. This process was carried out by washing the sample using DI water and ethanol in a ratio of 3:1. After that, the sample was moved to the crucible and dried using an oven at 90 °C for 12 hours. This process aims to remove water and ethanol present in the sample. A temperature of 90 °C was chosen so that Al and Mn ions would not diffuse before calcination. After the samples were dried, they were pulverized using a mortar and calcined using a high furnace at 800 °C for 3 hours.

Characterization Procedure

The crystal structure of ZnO and its phase change were identified using X-ray diffraction (XRD) using a CuKα source (1.541862 Å). Crystal size was calculated using the Scherer equation

$$d = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

d is crystallite size, Lambda (λ) is the X-ray wavelength, Betha (β) is the FWHM in radians, Theta (θ) is the Bragg Angle and K is the Scherer constant 0.9.

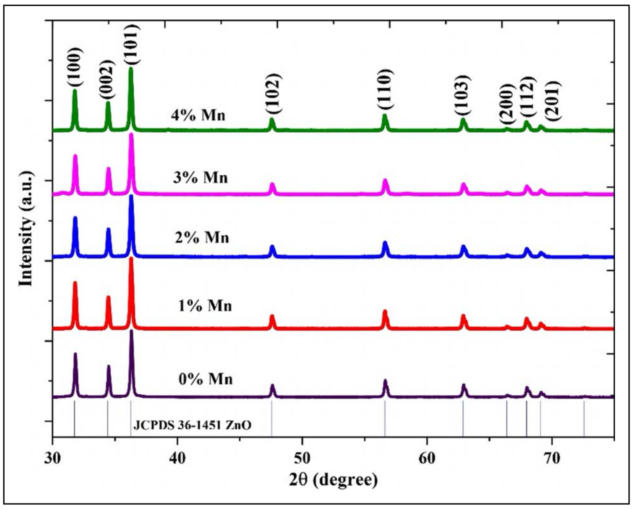

Figure 1. XRD spectra.

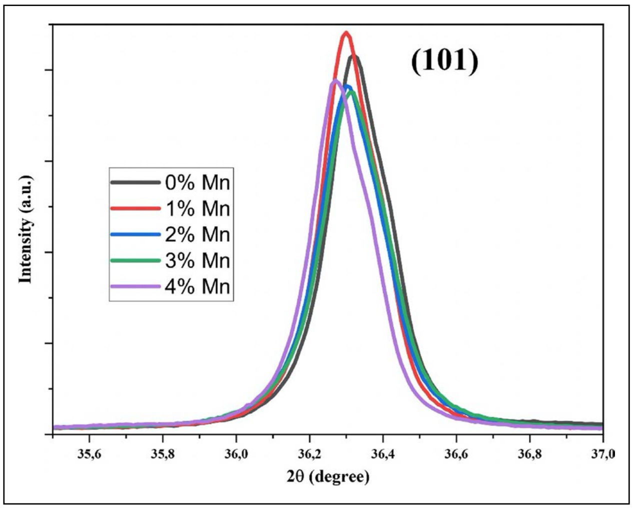

Figure 2. 101 peak shifting.

Table 1. The lattice parameter of pure ZnO and codopping ZnO

Mn concentration	2 Theta (degree) 101	Crystalline size D (nm)	d_{hkl}	Lattice parameter (Å)	
				a=b	c
Pure ZnO ref [31]	36.450	46.200	2.464	3.260	5.219
0%	36.330	39.767	2.471	2.853	5.198
1%	36.311	41.549	2.472	2.855	5.202
2%	36.313	37.736	2.472	2.854	5.201
3%	36.321	36.980	2.471	2.853	5.199
4%	36.285	40.955	2.473	2.856	5.205

Optical properties were observed using Ocean Optic reflectance spectroscopy with a wavelength range of 200–1110 nm radiation. Reflectance testing of the material was carried out to calculate the energy gap value of the material doped using Al and Mn. The optical band gap for codoping Al and Mn ZnO was measured using the following equation

$$(F(R)h\upsilon)^2=A(h\upsilon-E_g) \quad (2)$$

F(R) is an absorption value, A is a constant, hυ is the photon energy, and E_g is the energy gap of the material. The energy gap can be calculated by plotting a graph of $(F(R)h\upsilon)^2$ versus hυ. The extrapolation point of the linear part that meets the abscissa point will be given as the energy gap value of a material.

RESULT AND DISCUSSION

Structural Properties

Figure 1 shows the spectra of ZnO codoping Al and Mn with different concentrations (0, 1, 2, 3, 4 %wt). All XRD results show the hexagonal wurtzite phase form as in Pure ZnO. This is confirmed by overlaying the spectra on JCPDS data No. 36-1451, which matches the space group P_{63}mc. The spectra show that the structure of ZnO remains unchanged in single dopping of Al and codoping of Al, Mn, both at low to highest percentages, and the observed phase remains a Wurtzite structure. Figure 1, which shows the XRD pattern, shows no additional peaks. This means that the incorporation of Al^{3+} and Mn^{2+} ions substitute into interstitial sites or replace the presence of Zn^{2+} ions in the lattice without changing the wurtzite ZnO structure. In pure ZnO, Zn^{2+} ions have an ion radius of 0.74Å, smaller than Mn^{2+} ions of 0.80 Å, and larger than Al^{2+} ions of 0.53Å.

From the XRD pattern in Figure 1, grating 101 has the highest intensity of all gratings in all samples. Peak 101 is enlarged to see changes in the pattern of each sample. Figure 2 is a magnification of peak 101. There is a 1% to 4% peak shift pattern rather than 0% samples. This shift occurs because Mn^{2+} ions, which have a larger ion radius, replace Zn^{2+} ions in the crystal lattice. The presence of Al^{3+} ions also determines the peak height. The 1% Mn peak shows the highest position, which indicates that Al^{3+} ions are inserted more in place of Zn^{2+} than Mn^{2+}. This event occurs because the percentage of dopping in the sample is indeed more excellent Al with a ratio of Al % to Mn of 5%: 1%. However, as the percentage of Zn decreases and the rate of Mn increases, the peak also decreases until the Mn 4% condition changes to a non-linear pattern. This is indicated due to changes in the lattice parameters.

The lattice parameter values calculated using the equation written in Ravi Kant's [30] part of the data are presented in Table 1. The lattice value c looks smaller than the pure

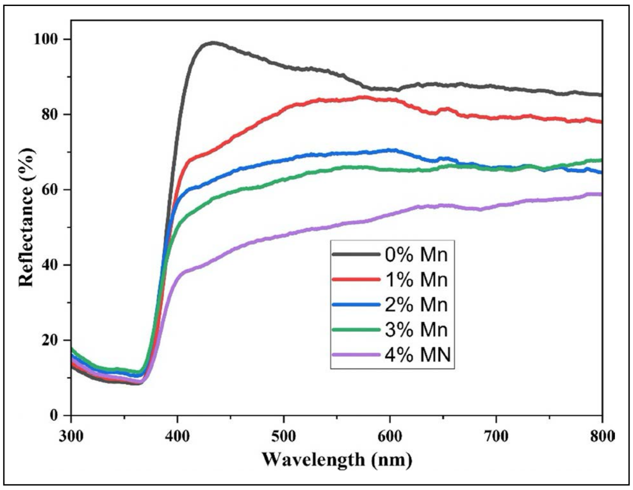

Figure 3. Reflectance graphic.

ZnO standard of 5.219 Å. This indicates the presence of oxygen vacancies in the material dropped by Al^{3+} and Mn^{2+} ions. The lattice parameter value does not show a value that continues to rise with the increase in Mn doping, but the lattice parameter value changes along with the doping ratio. For ZnO with a single Al dopping or Mn 0% sample, lattice parameters a and c values are the smallest compared to the other four samples. This may be due to the small dopant radius of Al^{3+} ions that replace Zn^{2+}. This also has an impact on the small lattice parameter values. However, when the percentage of Mn^{2+} dopping increases to the highest ratio of 4% Mn. The lattice parameter value reaches its highest value compared to the other four samples. This is probably because Mn^{2+} ions dominate in the replacement of Zn^{2+} ions. The lattice parameter value becomes larger since Mn^{2+} ions are more significant than Zn^{2+}. The size of the lattice parameter is substantial to discuss because it relates to the oxygen vacancy in the sample; the smaller the size of the lattice parameter, the more likely the presence of oxygen vacancy, which is helpful in the photodegradation process. ZnO (Al+Mn) with 0% Mn percentage shows the smallest lattice parameter. It indicates that this sample will produce more oxygen vacancy than others.

Optical Properties

Figure 3 represents the reflectance spectra of the Al and Mn codoping ZnO samples in the wavelength range of 300 to 800 nm. Uv-Vis spectroscopy is used to study the reflectance pattern of solid materials with a certain thickness. This helps scientists determine the energy gap value of the modified material, especially the effect of co-dopping ZnO (Al+Mn). Figure 4 shows the energy gap value of each of the characterized samples. The linear dependence between the value of $(F(R)h\nu)^2$ versus hν indicates that Al and Mn codoped ZnO is a semiconductor with a direct band gap. The direct band gap is calculated using the Kulbecka-Munk method in Equation 2.

The calculated band gap change values and comparison with the reference band gap are shown directly in Figure 4a. All band gap values of materials doped using Al and Mn are lower than that of pure ZnO. This decrease in band gap value, as shown in Figure 4b, is likely due to the incorporation of Al and Mn ions in the Zn lattice, which creates a new recombination pattern. This can be confirmed from the discussion of changes in the crystal structure of XRD results. As described by Gaurav Saxena [31], the decrease in energy gap value, along with the addition of Al and Mn doping, can be illustrated as a form of p-d spin exchange interaction between localized d electrons resulting from the substitution of Al^{3+} and Mn^{2+} ions. The sample with the largest percentage of Mn produces the most significant decrease in the energy gap. This is due to the solid p-d assimilation between O and Mn. So, adding Al and Mn co-dopping will reduce the energy gap value; this is in line with the initial purpose of the experiment, which is to reduce the energy gap of the material as a candidate for photocatalyst and pollutant removal applications.

Photodegradation Mechanism and its Relationship with the Energy Gap of the Material

The mechanism of photodegradation can be seen visually in Figure 5. What is modified is the value of Eg. The smaller the energy gap value, the easier for electrons to excite from VB (Valency Band) to CB (Conduction Band). The

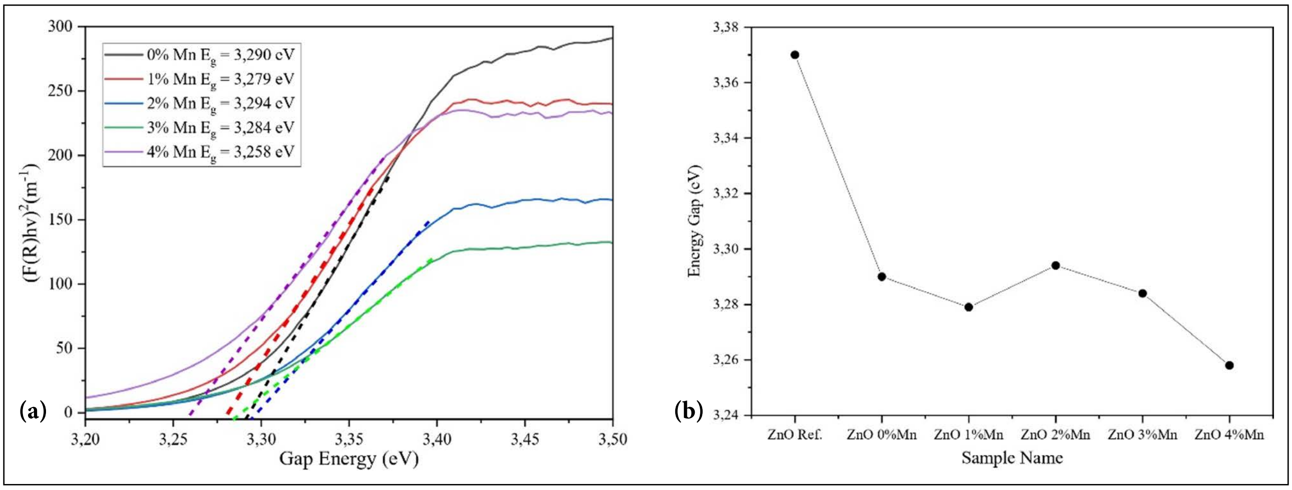

Figure 4. Band gap energy **(a)** Kubelcka Munk measurement **(b)** decreased energy gap value.

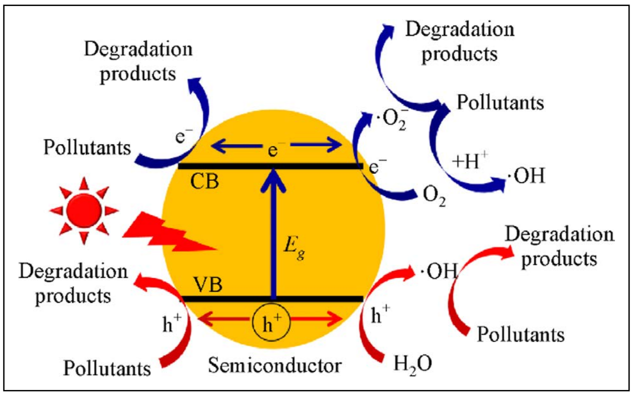

Figure 5. Photodegradation mechanism [33].

Table 2. Reference data ZnO dopping as a dye photodegradation

No	Doppant %wt	Gap energy (eV)	Dye	Ref
1	Cr^{3+} 9%	3,27	MG	A Mahesha [15]
2	Co^{2+} 2%	3,06	MG	Al-Namshah [32]
3	Fe^{2+} Pure	2,97	MB	Sabrina [28]
4	Cu^{2+} 3%	3,19	MB IC	KV Karthik [33]
5	Cu^{2+} 5%	3,23	RhB	KV Karthik [33]
6	Pure Zn^{2+} Nps	3,30	CR	B C Nwaiwu [34]

MG: Methylene green; MB: Methylene blue; IC: Indigo carmine; RhB: Rhodamine B; CR: Congo red.

smaller the energy gap, the narrower the gap between the ribbons. The narrower the band gap, the easier for electrons to excite. If electrons are easily excited by small energy, the oxygen vacancies will get bigger. This will affect the formation of •O2- (Oxygen Free Radicals), determining the photodegradation rate.

Various researchers have examined the photodegradation of textile dye effluents using ZnO materials. The photodegradation mechanism is that ZnO powder modified using codoping is dissolved in textile dye waste. Then, the mixture is irradiated using light in the UV-Vis range. However, UV irradiation is recommended for UV materials because it has a maximum energy value of 3–4 eV to reach the ZnO energy gap. This increases the possibility of expanding the photodegradation ability of the five modified ZnO (Al+Mn) samples with the highest Mn concentration of 4% Mn and the smallest gap energy value of 3.258 eV. Using a 4% Mn doping sample and comparing it with related research shown in Table 2, this modified sample can be a candidate for degrading Methylene Green textile dyes, as done by A. Mahesha [15] using ZnO doped with Cr^{3+} ions. This modification decreased the energy gap to 3.27 eV. Sample ZnO (Al+Mn) with 0% Mn, which has the most significant gap energy value (3.29 eV), also needs to be considered for use as a photodegradation agent. This is based on the high possibility of vacant oxygen due to the single doping of Al. The textile dye that this sample can degrade is Congo Red. According to Table 2, Congo Red requires a degradation agent with an energy gap of 3.3 eV, and this sample is suitable for degrading Congo Red.

CONCLUSION

ZnO material with fixed Al doping and Mn variation has been successfully made using a simple coprecipitation method. Various characterizations have ensured this newly modified material is suitable as a textile dye degradation agent candidate. The parameters used as a benchmark are structural and energy gap changes. Crystal structure observation was done using X-ray diffraction. From the reported discussion, it can be concluded that the single doping of ZnO with Al and codoping of ZnO with Al and Mn did not change the main crystal structure, which is still observed as Hexagonal Wurtzite. In diffraction peak 101, it is observed that the higher the percentage of dopping, the more the peak shifts towards the slight diffraction angle. This indicates that the presence of oxygen vacancies is more significant. This structural pattern is confirmed by reflectance characterization, which calculates the energy gap value. The higher the doping of Mn, the smaller the energy gap. However, this energy gap change does not occur linearly because an atomic insertion behavior has not been fully revealed. Modification of ZnO (Al+Mn) with a 4% Mn percentage produces the smallest energy gap of 3.258 eV and the highest energy gap reached by ZnO (Al+Mn) with a 4% Mn which is 3.290 eV. The type of textile dye that can be degraded with this modification is Methylene Green for (Al+Mn) with 4% Mn and Congo Red for (Al+Mn) with 0% Mn.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Phytoremediation of Cr(VI)-rich wastewater using water hyacinth, water lettuce and duckweed

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ABSTRACT

Chromium(VI) contamination is carcinogenic and largely anthropogenic, stemming from specific industries. With Bangladesh experiencing rapid industrialization, the increasing number of industries necessitates an economic and sustainable secondary treatment process to maintain acceptable chromium levels. Phytoremediation, an environmentally friendly biochemical technique, has been extensively researched, particularly in the context of constructed wetlands. However, due to land scarcity and legal issues a constructed wetland is not the most viable option. In this study, three native aquatic plants—Eichhornia crassipes (Water Hyacinth), Pistia stratiotes (Water Lettuce), and Lemna minor (Duckweed)—were chosen to evaluate their effectiveness in removing chromium from wastewater. These plants underwent testing with five different chromium concentrations (1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L, 5 mg/L) and two pH values (6 and 8) using natural ditch water as the feed solution. All the experiments were performed for 7 days in duplicate, along with a control experiment of chromium without plants. The study was conducted at Shahjalal University of Science and Technology campus, Bangladesh, from May 25 to June 1, 2023. Atomic Absorption Spectrometer was employed to measure Cr(VI) concentration, revealing average chromium removal rates of 29.4%, 81.1%, and 81.5% for Eichhornia crassipes, Pistia stratiotes, and Lemna minor, respectively, after seven days. Notably, on day three, Lemna minor exhibited the highest average removal efficiency at 84.7%.

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INTRODUCTION

In this era of industrialization, the disposal of effluents enriched with heavy metals into water bodies has become an alarming issue [1]. Toxic heavy metals pose a threat due to their potential entry into the food chain [2]. Therefore, the development of an efficient process to remove heavy metals from wastewater during disposal is gaining significant importance within scientific communities [3]. Chromium, found as Chromite ($FeCr_2O_4$), ranks as the 21st most abundant heavy metal in the Earth's crust [4]. It exists in both trivalent and hexavalent forms (i.e., Cr(III) and Cr(VI)) in aquatic systems [5]. Cr(VI) is particularly concerning, being five hundred times more toxic than Cr(III) [5]. Moreover, among the various effluents from different industrial operations, Cr(VI) is the 16th most toxic and carcinogenic substance [2]. Cr(VI) significantly harms human health, causing issues such as lung cancer, kidney and liver damage, gastric problems, and skin irritation [4]. The maximum allowable concentration for Cr(VI) discharge into inland surface water is 0.1 mg/l, and for drinking water, it is 0.05 mg/l [6]. Various industrial activities, including leather

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tanning, textile dyeing, electroplating, paint production, cement manufacturing, nuclear power plants, steel industries, cooling water towers, refractory materials production, metallurgy and mining [6, 7]. If there are high quantities of Cr in the ambient water, the tissues or the organs of the aquatic organisms and especially fishes can be affected [8, 9]. Therefore, treating wastewater to remove Cr(VI) before disposal into the environment is imperative.

Several methods, such as ion exchange, flotation, activated carbon, reverse osmosis, coagulation-flocculation, membrane technologies, chemical precipitation, and adsorption, are used for Cr(VI) removal from wastewater [4]. Often, these physicochemical processes involve substantial expenses and generate a considerable amount of toxic chemical sludge [10]. Thus, for most developing countries, alternative processes are necessary that align with their financial and technological capacities.

Phytoremediation, a novel technology for dealing with contaminated sites, can be cost-effective and offers aesthetic benefits and long-term applicability. This technology relies on the effective use of plant species to remove, sequester, or immobilize impurities from a growth matrix in soil, water, and sediments through organic processes [11]. Aquatic macrophytes are highly valued in the phytoremediation of water pollutants because of their rapid growth, substantial biomass, high tolerance, and exceptional accumulation capacity [12]. Research has been conducted using Eichhornia crassipes, Pistia stratiotes, and Lemna minor separately as phytoremediation techniques to mitigate chromium contamination in aqueous or wastewater. For instance, [13–15] used Eichhornia crassipes's (water hyacinth) root biomass-derived activated carbon, root powder, and biochar, respectively, for removing Cr(VI) from aqueous solutions. [13, 14] found the maximum adsorption capacity of 36.34 mg/g and 33.98 mg/g, respectively while [15] found the maximum removal efficiency of Cr(VI) as 97.34% [16, 17] used Eichhornia crassipes for removing chromium without considering the effect of pH and the maximum sorption was found as 108 mg/kg and maximum removal efficiency as 84%, respectively. Pistia stratiotes has also been used for remediation and detoxification of heavy metals in various studies [18–21]. The maximum removal efficiency of Cr(VI) was found by [18] as 58.8% while [18, 21] did not study Chromium. However, the effect of pH was not considered in these Pistia stratiotes-related studies. A few researchers have also studied another important floating plant, Lemna minor [22–24], to evaluate Cr(VI) removal efficiency from aqueous solutions. The maximum removal efficiency of Cr(VI) was found by [22–24] to be 49.79%, 64%, and 77.26%, respectively. However, no study in the literature compares these three plants in removing Cr(VI) from aqueous solutions considering both acidic and alkaline conditions. In this study, the Cr(VI) removal efficiency of three locally available aquatic plants, Pistia stratiotes (Water Lettuce), Lemna minor (Duckweed), and Eichhornia crassipes (Water Hyacinth), has been investigated considering acidic and alkaline pH conditions. Natural ditch water, from where the plants were collected, was used for water media preparation.

MATERIALS AND METHODS

Plants and Water Sample Collection

Eichhornia crassipes, Pistia stratiotes, and Lemna minor are abundant in Bangladesh, and are found worldwide. The plants for this study were gently collected using a net from the water surface of a ditch in the Shahjalal University of Science and Technology campus area (24° 55' 6.61"N and 91° 49' 53.88"E) while in fresh condition and were immediately transported to the laboratory within 10 minutes. Subsequently, the plants underwent a thorough rinse in tap water to eliminate unwanted particles and insect larvae from their roots and leaves [25]. Following this, the plants were air-dried for 24 hours to remove surface water from their bodies [26]. For each plant, 50 g of air-dried samples were considered for testing. Additionally, water samples were collected from the same ditch to prepare the water media.

Preparation of Synthetic Sample of Cr

A 1000 mg/l Cr(VI) stock solution was prepared using analytical-grade $K_2Cr_2O_7$ dissolved in distilled water. This solution was stored and utilized to create Cr(VI) solutions of concentrations at 1 mg/l, 2 mg/l, 3 mg/l, 4 mg/l, and 5 mg/l in natural ditch water for laboratory-scale experiments.

Water Media Preparation

Before initiating the experiment, various parameters, including dissolved oxygen (DO), conductivity, total dissolved solids (TDS), turbidity, pH, CO_2, and chemical oxygen demand (COD) of the ditch water sample, were tested. Plastic bowls with a depth and diameter of 13.5 cm and 12.7 cm, respectively, and a maximum capacity of 1.77 liters were prepared for Eichhornia crassipes and Pistia stratiotes. However, for Lemna minor, the plastic bowls were 6.3 cm in depth and 19.3 cm in diameter, with a maximum capacity of 1.86 liters. The rationale for the two different bowl sizes was that the main method of metal uptake for the plants is through the roots, and Lemna minor's roots were considerably shorter compared to the other two plants. Each experiment required 36 plastic bowls (3 plants × 5 concentrations + 3 controls) × 2 (duplicate).

The aquatic plants were individually exposed to solutions of Cr(VI) at different initial concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 mg/L, respectively, for two different pH levels with chromium control. In a controlled set, no plants were present. Following the guidelines of APHA [27], chromium was analyzed using an atomic absorption spectrophotometer. In all experiments except for the controlled set, 50 gm plant samples (air dry weight) were placed in a 1-liter water sample with a specific initial Cr(VI) concentration under respective pH conditions (Fig. 1). All experiments were conducted in duplicate. The sample bowls were appropriately marked and kept in moderate sunlight through glass windows during the daytime. The pH of the water media was adjusted to a value of 6.0 after adding the plants using phosphoric acid. Similarly, the pH of the water media was adjusted to a value of 8.0 using sodium hydroxide. Daily water loss

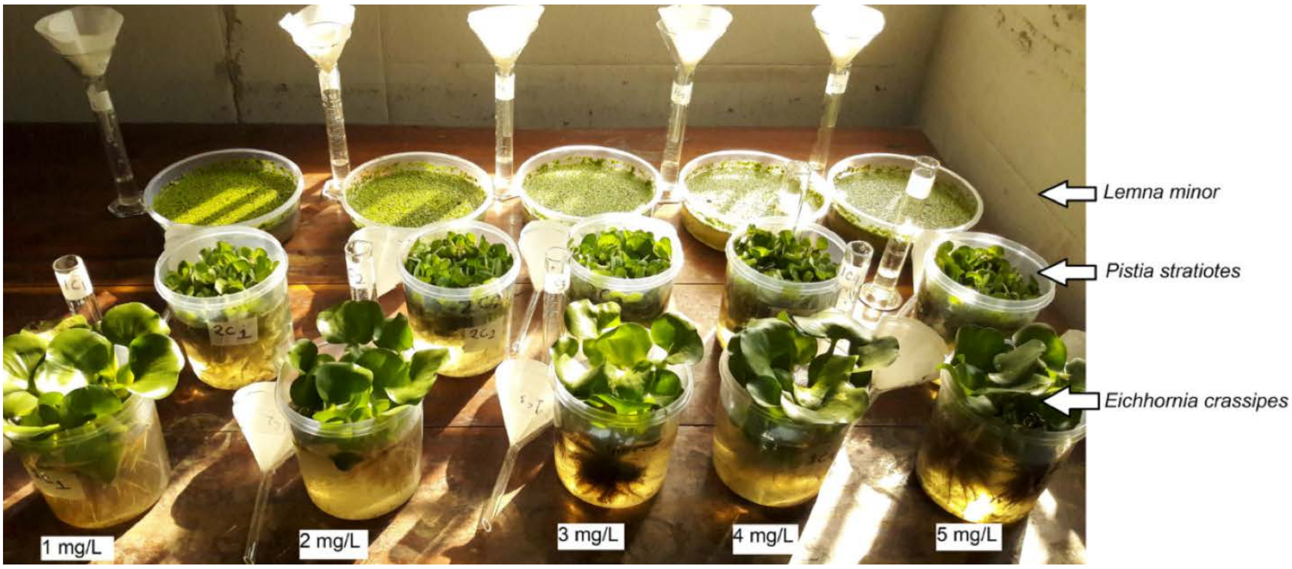

Figure 1. Water media preparation for the three plants with five different initial Cr(VI) concentrations.

due to evaporation was compensated by adding the same ditch water to the mark in the experimental tank. The natural ditch water used was found to be without any detectable chromium concentration.

Data Collection Protocol

The AAS was calibrated using a Cr(VI) solution with three different concentrations: 1.25 mg/L, 2.5 mg/L, and 5 mg/L. The entire experimental setup was completed at 10 am on the first day, and the initial data on Cr(VI) concentration in the water in each bowl was recorded at 11 am. Subsequently, hourly data were collected from the respective bowls with specific pH and Cr(VI) concentrations throughout the first day until 10 pm. Following this pattern, data were recorded at 10 am and 10 pm from the second day, resulting in 12 hourly data points, and this continued until the third day. After three days, data collection shifted to once daily at 10 am, generating 24 hourly data points, and this continued until the seventh day. Most of the literature [17, 22] took daily measurements. However, in this research, we implemented a more frequent measurement protocol because the rate of chromium adsorption is likely to be higher during the initial period.

Cr(VI) in Plants

At the conclusion of the seven-day experiment, the test plants were harvested, and tap water and distilled water were employed for washing the harvested plants twice. To eliminate any residual moisture, all plants were dried in an oven at 80°C. Subsequently, the oven-dried samples were ground to a powder and stored for wet digestion to measure Cr(VI). For the metal concentration analysis, duplicate portions of the ground plant material (2 g) were utilized. The sample was digested using HNO_3:$HClO_4$ in a 2:1 ratio (v/v) and then diluted to 100 ml with distilled water. The digested plant samples were analyzed for Cr(VI) using atomic absorption spectrophotometry (AAS, Varian).

The Bioconcentration Factor (BCF) is the ratio of the concentration of the chemical (chromium) in the plant tissues at harvest to the concentration of that element in the external environment [28]. BCF is a valuable parameter for evaluating the potential of a plant in accumulating a metal, with a higher value indicating a better bioaccumulation capacity of that plant. BCF for all three plants was calculated as follows:

$$BCF=P/E$$

Where, P is the trace element concentration in plant tissues (mg/kg oven dry weight) and E is the initial trace element concentration in the feed solution (mg/L).

Statistical Analysis

All the experiments were duplicated, and the values have been expressed as the average. The Pearson correlation test was performed between the chromium concentration in the water on the final day and the chromium remaining in the plant to assess the consistency of these two datasets. The test was conducted at significance levels of 0.01 and 0.05.

RESULTS AND DISCUSSION

The analysis primarily focuses on two aspects. The first is assessing the Cr(VI) removal efficiency of the three plant species concerning the initial concentration in the feed solution, while the other is examining the influence of pH (at two levels: 6 and 8) on the removal efficiency. Additionally, the mass of Cr(VI) accumulated in the plants on the seventh day for various concentrations and pH values has also been investigated.

Basic Water Quality Parameters

The water sample was collected from a natural ditch, the same source from which the plants were gathered. Subsequently, pH adjustment was performed by adding NaOH or H_3PO_4. Some basic water quality parameters of the water sample are presented in Table 1.

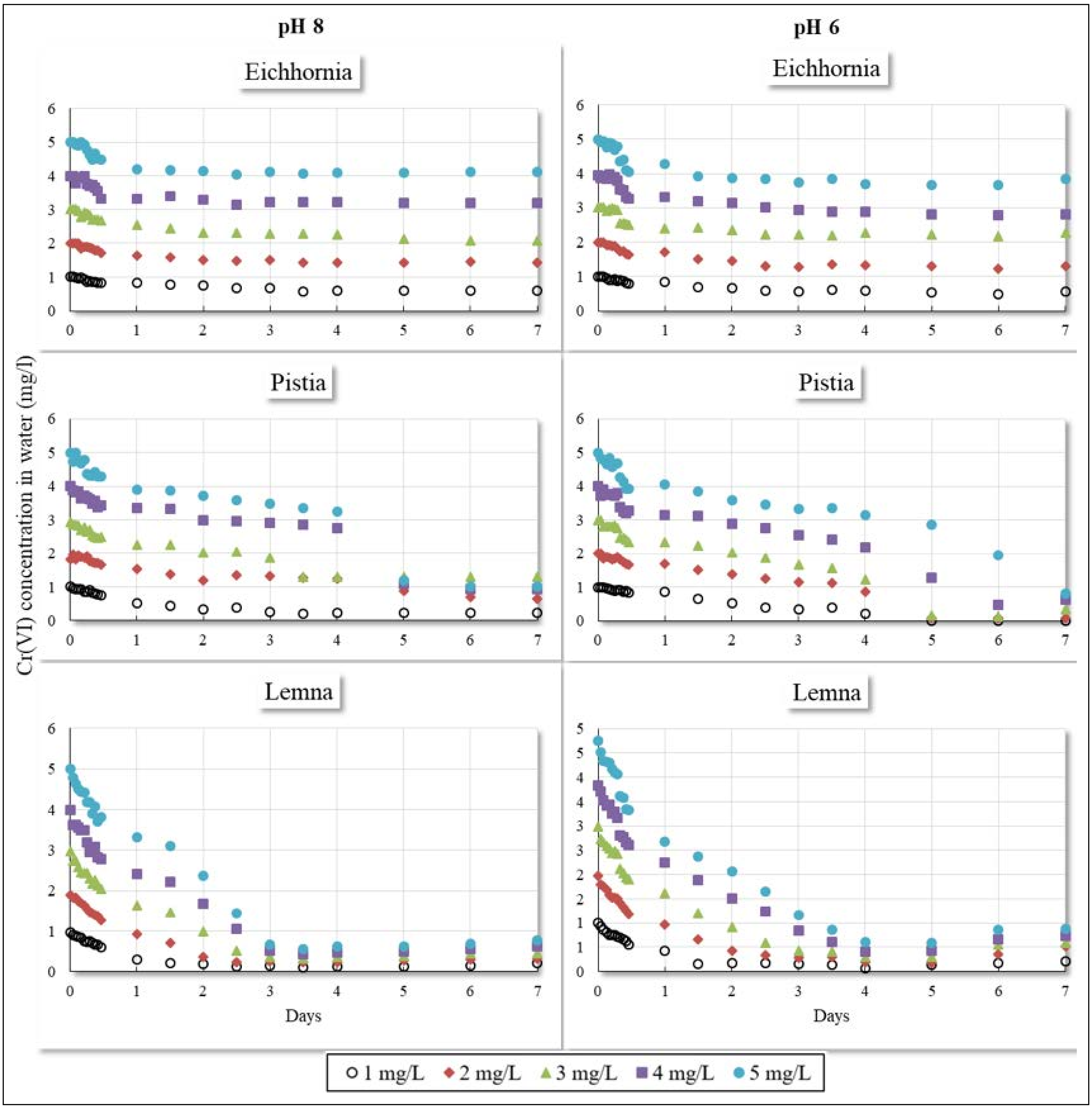

Figure 2. Remaining concentration of Cr(VI) in feed solution over time for three plant species at pH 8 and 6.

Table 1. Basic water quality parameters of the ditch sample

Parameter	Ditch sample
pH	6.8
Temperature, °C	20.6
Conductivity, µS/cm	350
DO, mg/L	6.3
Turbidity, NTU	28.9
TDS, mg/L	308
CO_2, mg/L	30
COD, mg/L	92.9
Cr(VI)	0

Effects of Initial Cr(VI) Concentration on Removal Efficiency

Synthetic Cr(VI) solutions with five different concentrations (1-5 mg/L) were prepared, and the removal rates were observed for three different plant species over seven days. Figure 2 displays the remaining average concentration in the feed solution over time. It is evident that the three plant species exhibited distinct responses to chromium exposure. Eichhornia crassipes showed very limited removal after the first day, with the removal efficiency being the least among the three species. Pistia stratiotes displayed some peculiar behaviors. While there was a gradual reduction of chromium at lower concentrations throughout the entire timespan, at higher concentrations (4 mg/L and 5 mg/L), it rapidly started to uptake chromium after 4 days. Additionally,

Table 2. Comparison of Cr(VI) removal efficiency (%) of Eichhornia crassipes, Pistia stratiotes and Lemna minor for pH 6 and pH 8 considering all five initial concentrations after 3 days and 7 days

	pH 6						pH 8					
	3 days			7 days			3 days			7 days		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Eichhornia	25.1–42.7	31.2	7.7	23.2–43.1	31.1	8.2	17.4–31.8	23.5	5.6	17.7–41	27.6	9.3
Pista	33.3–66.7	44.5	13.1	84.0–99.6	90.5	6.9	30.4–74	40.6	19.1	56.8–79.9	71.6	9.4
Lemna	76.7–85.8	82.2	4.2	74.3–82.3	80.0	3.2	86.1–88.3	87.2	0.8	79.8–84.7	83.6	2.1

SD: Standard deviation.

Figure 3. Chromium toxicity on pistia stratiotes after day four.

it was observed that these plants suffered from chromium toxicity and began to degrade after 4 days, as illustrated in Figure 3. Similar plant degradation was noted by [29], where chromium toxicity was observed at concentrations higher than 2 mg/L.

On the other hand, Lemna minor exhibited a consistent and smooth removal rate for all initial Cr(VI) concentrations. The comparison of the removal rates of the three plant species with different initial Cr(VI) concentrations is illustrated in Figure 4. Lemna minor demonstrated the highest removal rate for all initial concentrations, followed by Pistia stratiotes and Eichhornia crassipes. Moreover, for Lemna minor, the majority of Cr(VI) uptake was completed within three days for all initial Cr(VI) concentrations.

Effects of pH on Removal Efficiency

The experiment was conducted at two different pH levels: one acidic (pH 6.0) and the other alkaline (pH 8.0), to investigate whether pH influences the removal efficiency. The choice of these pH values is based on the common range of wastewater acidity. Some noteworthy findings emerged from this study. Eichhornia crassipes and Pistia stratiotes exhibited slightly better performance under acidic conditions, while Lemna minor demonstrated almost independence from pH, performing slightly better in alkaline conditions. Additionally, it was observed that the removal rate for both Eichhornia crassipes and Pistia stratiotes decreased with an increase in initial concentration, whereas for Lemna minor, the removal rate remained independent of the initial concentration. Table 2 presents the percentage of chromium removal for different initial concentrations in the feed solution for the three plants after 7 and 3 days. The seven-day average removal efficiency for chromium, considering both pH levels, was 29.4%, 81.1%, and 81.5% for Eichhornia crassipes, Pistia stratiotes, and Lemna minor, respectively. Although Pistia and Lemna exhibited similar average removal efficiency, Pistia stratiotes displayed much higher variability. Notably, considering both pH levels, Lemna minor achieved the highest average removal efficiency (84.7%) on day three. The maximum removal efficiency of Cr(VI) was found by [22] and [24] as 49.79% (on

Table 3. Bioconcentration factor (BCF) for chromium removal by three aquatic plants in different feed concentrations for pH 8 and 6

Cr(VI) Concentration in feed solution (mg/l)	BCF					
	Eichhornia crassipes		Pistia stratiotes		Lemna minor	
	pH 8	pH 6	pH 8	pH 6	pH 8	pH 6
1	238.2	180.9	258.4	407.5	290.0	383.9
2	165.7	141.2	268.0	390.1	333.0	347.7
3	124.7	105.2	225.2	331.9	304.4	373.6
4	114.7	105.3	307.1	329.01	248.6	359.9
5	92.8	89.7	284.5	313.6	297.2	331.7
Average	147.2	124.5	268.6	354.4	294.6	359.4

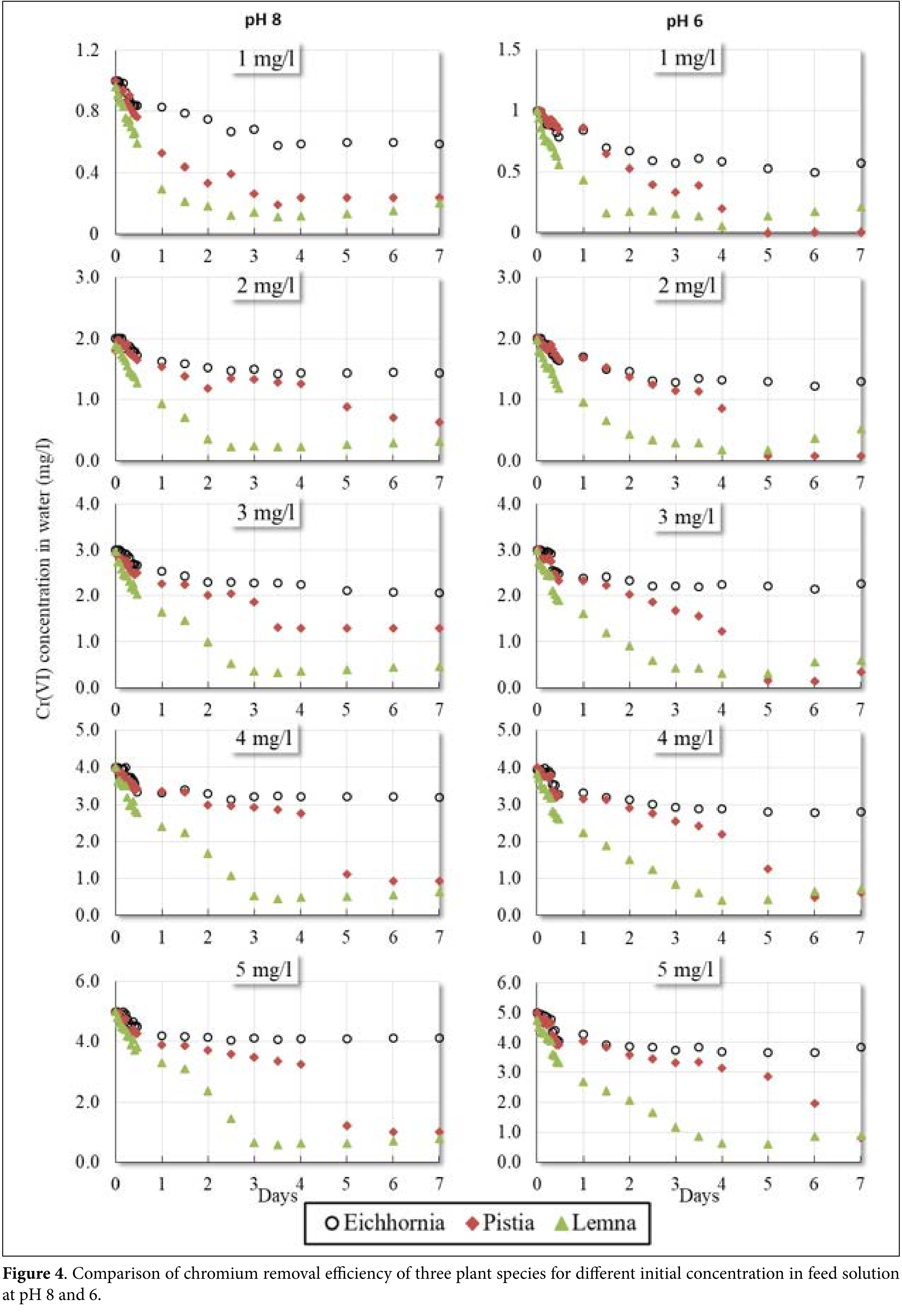

Figure 4. Comparison of chromium removal efficiency of three plant species for different initial concentration in feed solution at pH 8 and 6.

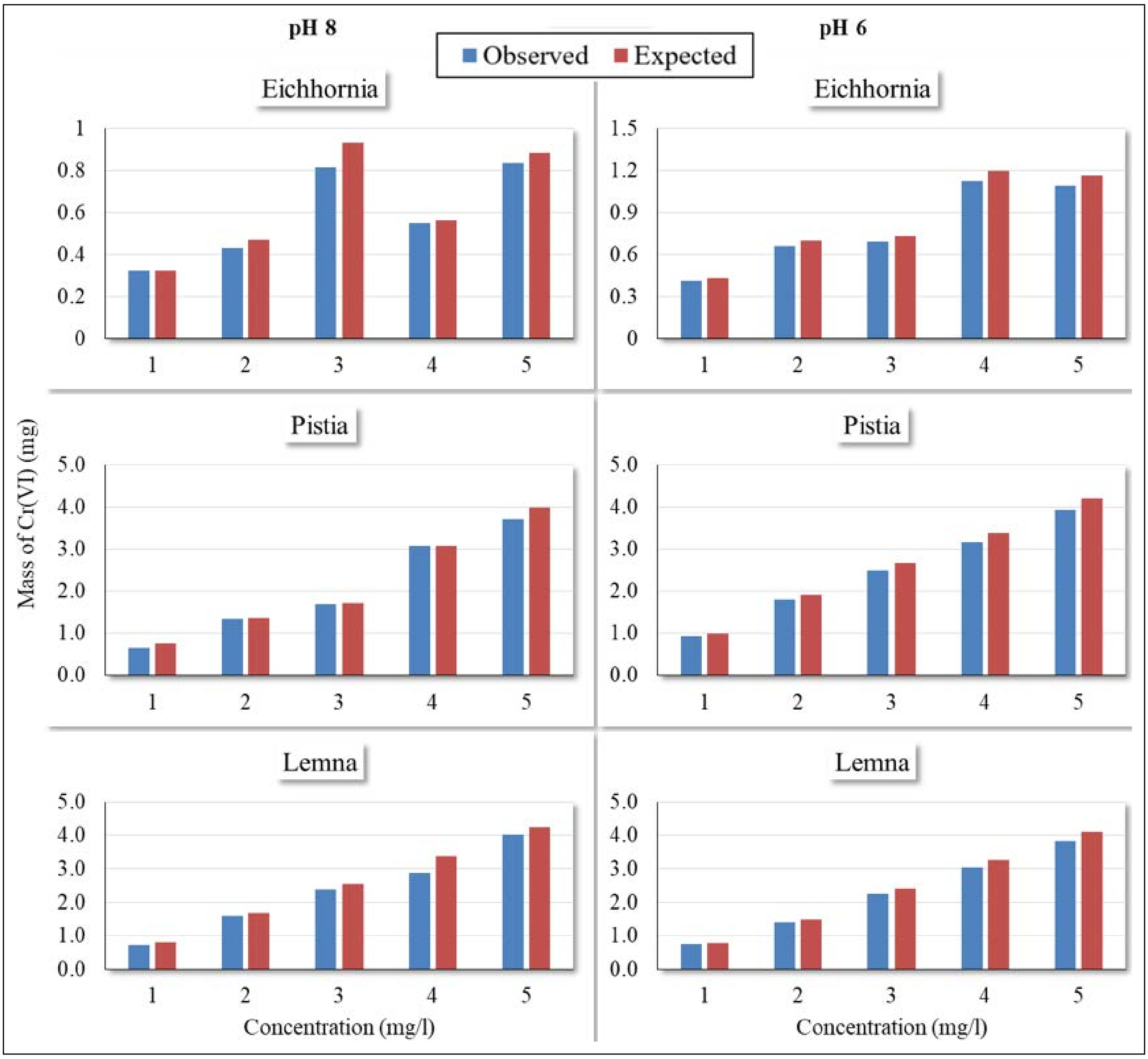

Figure 5. Comparison of expected mass and the actual mass observed in three plant species at the end of the experiment for five different initial concentrations of Cr(VI) and for two pH values.

Table 4. Pearson correlation coefficients of concentration of Cr(VI) in water vs mass of Cr(VI) in plant

	Cr(VI) in plant					
	Echhornia		Pistia		Lemna	
	pH 8	pH 6	pH 8	pH 6	pH 8	pH 6
Cr(VI) in feed solution	0.71ns	0.91*	0.59ns	0.98**	0.99**	0.97**

Not significant (ns) p>=0.05; * p<0.05; ** p<0.01.

22th day) and 77.26% (on 12th day), respectively. The reason for the lower removal efficiency in [22] could be due to the depth of the bowl used. While in this experiment, the bowl used for Lemna minor was 6.3 cm deep, [22] used a bowl that was 100 cm deep. Since Lemna minor's roots are considerably shorter compared to the other two plants, the greater bowl depth in [22] means there was less chance for chromium to come into contact with the roots.

Chromium Uptake within Plants

The BCFs of the three plant species are presented in Table 3 based on different initial concentrations of Cr(VI) in the feed solution and two pH values. The highest BCF value was observed for Lemna minor, followed by Pistia stratiotes and Eichhornia crassipes for both pH levels. For pH values 8 and 6, the average BCF values were (147.2, 124.5), (268.6, 354.4), and (294.6, 359.4) for Eichhornia crassipes, Pistia stratiotes, and Lemna minor, respectively [28] reported that the BCF of chromium for Lemna minor ranged from 280 to 660, while [24] reported the average BCF for Lemna minor as 645.

Consistency between the chromium concentration in the feed water sample on the final day and the chromium inside the plants was also assessed. The expected masses of chromium inside the plants were determined by subtracting the remaining water concentrations on the final day from the respective initial concentrations. The decrease in chromium primarily occurred due to bioaccumulation by plants, although a small portion of chromium could be diminished due to chemical precipitation or adsorption on the vessel wall. From the control experiment, it was observed that the loss of Cr(VI) in water ranged from 1.2 to 7.1%. This loss could be attributed to precipitation, adsorption of clay particles and organic matter, and precipitation with secondary minerals [17].

The actual chromium masses inside the plants were determined by acid digestion at the end of the experiment. Figure 5 illustrates the expected mass of chromium in plants and the corresponding actual mass found in the plants for two pH values. It is interesting to observe a regularity in every case for both pH values. Moreover, a strong correlation between the two datasets (chromium concentration in the water on the final day and chromium left in the plant) was obtained for Lemna minor in both pH values, and the test was significant ($p<0.01$) (Table 4).

From the above discussions, it is clear that Lemna minor has demonstrated the best performance among the three plant species for treating chromium-rich wastewater, considering fast removal rate, BCF, and chromium toxicity. This plant holds great potential for treating chromium-rich wastewater, especially in a batch form of a biological treatment facility.

CONCLUSION

This study investigated the chromium removal potential of three indigenous floating plant species: Eichhornia crassipes, Pistia stratiotes, and Lemna minor. They were tested for five different initial concentrations of Cr(VI) in the feed solution (1-5 mg/l) and two different pH values (6 and 8). The results indicate that Lemna minor exhibits a rapid chromium uptake capacity, removing 84.7% of chromium from wastewater in just three days, irrespective of the initial chromium concentration in the feed solution or pH value, and without causing any toxicity issues. This versatile nature positions Lemna minor as the most promising plant among the three for chromium removal from industrial wastewater, especially in batch-based biological treatment facilities. Pistia stratiotes also demonstrated good removal efficiency, particularly after four days under acidic conditions, along with favorable BCF values. However, Pistia stratiotes showed intolerance to chromium toxicity, making it less suitable for treating chromium-rich wastewater. In contrast, Eichhornia crassipes exhibited very low chromium removal efficiency.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

A comparative study of microplastic detection in *Nemipterus japonicus*, *Rastrelliger kanagurta*, *Arius* sp. and *Scylla olivacea* from Chennai Coastal Region, India using ATR-FTIR spectroscopy

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ABSTRACT

Microplastics (<5 mm) are omnipresent pollutants produced directly or generated because of larger plastic particle breakdown. The challenge of microplastic pollution is an emerging global concern, with India being no exception. This study investigated the prevalence and characteristics of microplastics in four commercially important aquatic species from two distinct ecosystems in Tamil Nadu, India viz., the Ennore Creek (brackish water) and the Kasimedu landing center (marine). The species examined were catfish (*Arius* sp.), mud crab (*Scylla olivacea*), Japanese threadfin bream (*Nemipterus japonicus*) and Indian mackerel (*Rastrelliger kanagurta*). Microplastics were detected in 78.57% of the 70 samples analyzed, with *Nemipterus japonicus* and *Arius* sp. showing the highest average ingestion of 5±3 and 4±2.5 microplastic items per individual respectively. A distinct organ-specific trend was observed, with gills harboring slightly more microplastics (0.35 items/gills) compared to guts (0.21 items/gut). Fibers and fragments were the predominant microplastic shapes, while off-white (translucent), white, blue and black were the most common colors detected. ATR-FTIR analysis identified low-density polyethylene (LDPE) and polyamide (nylon) as the primary polymer types. The research underscores considerable interspecies and species-specific variations in microplastic accumulation and dispersion, underscoring the necessity for precise, species-specific evaluations to comprehend the potential ecological and anthropogenic health ramifications of this escalating environmental issue. Recommendations include establishing comprehensive monitoring programs, implementing source reduction strategies, enhancing habitat conservation, and fostering collaborative research to address microplastic pollution in the studied ecosystems.

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INTRODUCTION

The environmental issue that is currently creating waves, is plastic pollution. According to Lampitt et al. [1] around 400 million tons of plastic waste is being generated every year. The first contamination caused by microplastics in water bodies, was recorded by Carpenter and Smith et al. [2] during the year 1972, detected microplastics on the Sargasso Sea surface. The plastic production increased its peak during the 1940's and it became the fastest growing industry worldwide. All developing countries contributed to the major production of plastics. During the year 2013, Asia alone contributed (45.6%) that is quarter of the world plastic production. This was followed by Europe which contributed 22.9% of plastic produce, North America with 19.4%, middle East and Africa, 7.3% and finally Central and South America with 4.8%. Packaging was the major factor for the rise of plastic manufacturing. Consumer and household products (like appliances, toys, plastic cutlery, and furniture) also act as sources for the production. During the year 2012, approximately 10 –12 million tons of plastic was found, dumped in the ocean. The Indian Ocean had about 60000 tons of plastic accumulated during the year 2014 and the Pacific Ocean had about 100000 tons of plastic in the sea, which was alarming [3–7]. According to Geyer [8], 6300 metric tons of plastic waste was generated during the year 2016. 79% of waste was being dumped in the landfills without proper disposal. Borelle et al. [9] estimated that about 19 to 23 metric tons of plastic waste was generated worldwide during 2017. One of the notable events that occurred in plastic production worldwide was during the year 2017–2018 when China imposed a plastic waste import ban, which was reported by Wen et al. [10]. This resulted in a sharp decrease in the plastic production worldwide. The usage of single use plastics (SUP) trended during the year 2019, again contributing to 50% of plastic produce worldwide. According to Chen et al. [11], 360 million metric tons of SUP's were mass produced, globally. Due to the prevalence of the COVID-19 pandemic, use of SUP's such as gloves (2.5 million per day), masks (4.6 million per day) and disposable gowns (20 million per day) peaked during the year 2020 in India. This statistical data was provided by Shams et al. [12]. According to Walker et al. [13], 8300 million tons of plastic was produced during the year 2022 to 2023, out of which 6300 million tons of plastic was not disposed properly. By the year 2050, the plastic production would be doubled to billions of metric tons per year.

Plastic waste is broadly categorized into four classes based on size: macroplastics (>25 mm), mesoplastics (5–25 mm), microplastics (<5 mm) and nanoplastics (<100 nm) [14–17]. Microplastics are further distinguished as primary or secondary based on their origin [18, 19]. Primary microplastics are miniscule particles intentionally manufactured for microscopic applications, commonly found in personal care products and synthetic textiles [20]. Secondary microplastics, conversely, originate from the fragmentation of larger plastic debris due to environmental factors [21]. These microplastics (MPs) can be of different shapes like microbeads, fibers, fragments, film foam pellets and filaments [22, 23]. They are omnipresent leading to contamination of diverse global ecosystems from the deep ocean trenches to land-based waterways and adjacent sediments [24–27]. Studies have also reported the presence of microplastics inside the aquatic organisms such as fishes [28, 29] and other invertebrates such as in bivalves - green mussel [30], edible oysters [31], great clam [30], crustaceans - white shrimps [32], mud crabs [33], cephalopods - squid [34] and even in zooplankton [35]. Ingestion of these microplastics (MP) can lead to significant health risks, causing gut blockages, oxidative stress, impaired growth, genotoxicity behavioral alterations and reproductive issues [36–38]. Moreover, microplastics act as a carrier, accumulating persistent organic pollutants, hydrophobic chemicals and heavy metals, amplifying the toxicity threats to ingesting organisms [39–41].

Plastic Overshoot Day Report for 2023 by EA-Environmental Action indicates that India is estimated to have released around 330,000 tons of microplastic and 44,000 tons of chemical pollutants into its waterways by the end of the year [42]. This poses a significant threat to the health of aquatic ecosystems and potentially to human health as well. The complete measurement of microplastic contamination and its resulting effects in India have not yet been entirely determined. Hence, regular monitoring of microplastic contamination is crucial.

This study investigates microplastic ingestion by two commonly consumed brackish water organisms, catfish (*Arius* sp.) and mud crab (*Scylla olivacea*) sourced from the Ennore creek and the two commercial important fishes Japanese threadfin bream (*Nemipterus japonicus*) and Indian Mackerel (*Rastrelliger kanagurta*) sourced from Kasimedu landing center of Tamil Nadu. The proximity of the study area to plastic industries, fishing activities, industrial discharges and domestic/urban waste inputs provides context for the potential sources of microplastics in that environment. Investigating microplastic ingestion in these specific locations can help identify hotspots and contribute to the understanding of regional microplastic pollution patterns. The species that were chosen to investigate microplastic ingestion in two commonly consumed brackish water organisms, catfish (*Arius* sp.) and mud crab (*Scylla olivacea*) from Ennore. This is relevant as these species are important for the local food supply and economy and understanding their microplastic exposure is valuable. Additionally, the two commercially important marine fish species, Japanese threadfin bream (*Nemipterus japonicus*) and Indian mackerel (*Rastrelliger kanagurta*), are appropriate for understanding microplastic contamination in seafood. Examining a range of species from different trophic levels and habitats (brackish and marine) provides a more comprehensive understanding of microplastic pollution in the local aquatic ecosystem. Hence this study aims to explore and compare the abundance of microplastics in these distinct ecosystems, shedding light on potential variations in microplastic contamination based on habitat and species characteristics.

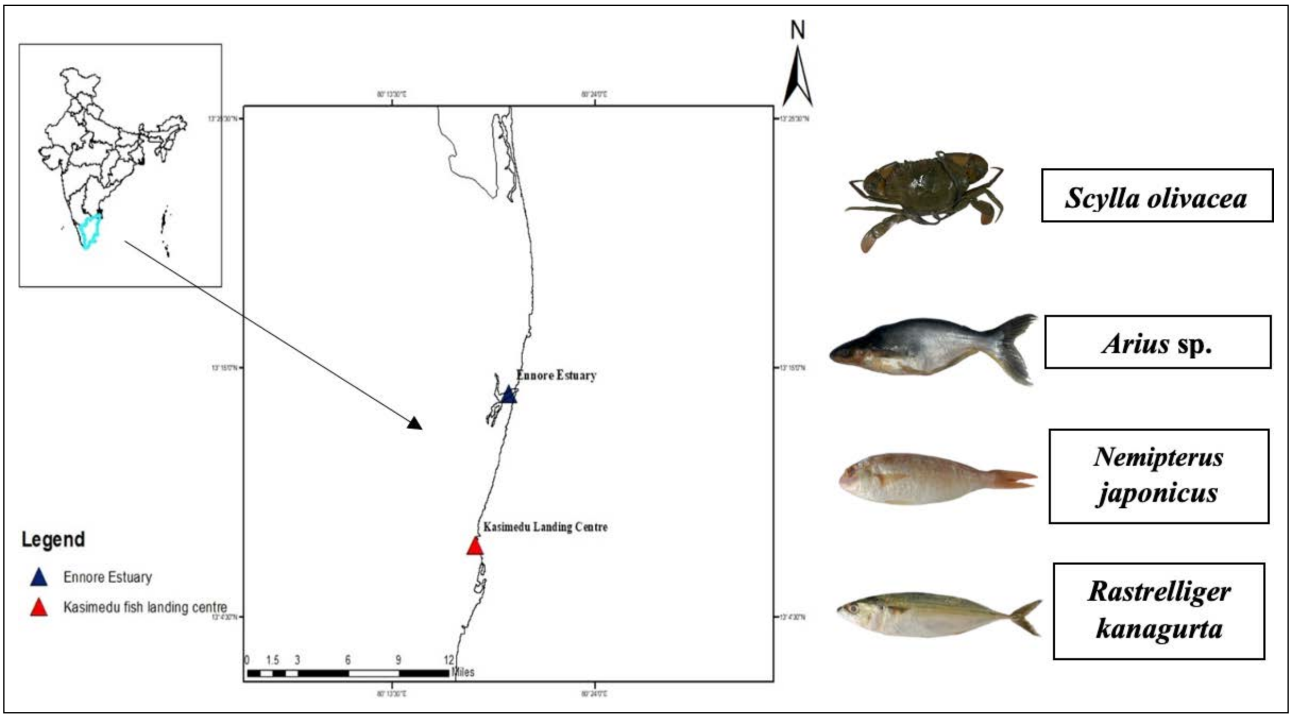

Figure 1. Indicates the sampling sites: Ennore Creek (13° 15′ 26.28″ N, 80° 20′ 16.08″ E) and Kasimedu landing centre (13° 07′ 42″ N, 80° 17′ 38″ E).

Figure 2. Ennore creek.

Figure 3. Kasimedu fish landing centre.

MATERIALS AND METHOD

Study Area

The present study focuses on the geographical coordinates of Ennore Creek (13° 15′ 26.28″ N, 80° 20′ 16.08″ E) and Kasimedu landing centre (13° 07′ 42″ N, 80° 17′ 38″ E) (Fig. 1). Ennore creek, located in Ennore, Chennai, along the Coromandel Coast of the Bay of Bengal, is identified as a backwater with distinct features such as lagoons, marshes, and submerged areas during high tide. This water body serves as a tidal arm connecting to the Bay of Bengal through its outlet at the creek. Shanthi and Gajendran [43] worked on water pollution at the Ennore creek stated that the major industrial installations that produce fertilizers, agrochemicals and petroleum were situated closer to the Ennore belt, making the estuary vulnerable and prone to contamination. Kasimedu, considered as one of the largest fish landing centre of the Chennai coast. It comprises of about 457 trawlers, engaging in fishing activities daily. The fishermen engage in both deep-sea trawling as well as inshore fishing, there by Kasimedu serves as a major hub for export of marine products from India [44]. Stretched along the shoreline for approximately 2 km, North of Chennai Port, Kasimedu plays a pivotal role in supporting the local fishing community.

Ennore Creek has been designated as the first sampling site (Fig. 2) for this microplastic study, focusing on two species: Catfish (*Arius* sp.) and mud crab (*Scylla olivacea*). In contrast, Kasimedu landing centre is identified as the second sampling site (Fig. 3), where the species under investigation are the Japanese threadfin bream and Indian mackerel. The rationale behind selecting these specific locations lies in the diverse ecosystems they represent. Ennore Creek, being a brackish water environment, serves as a habitat for organisms like Catfish and mud crab, which are not only indigenous to the region but also widely consumed by the local population. On the other hand, Kasimedu features marine habitat conditions, and the species chosen, Japanese threadfin bream and Indian mackerel, are commercially significant and readily available in the area.

Collection, Processing, and Quantification of Microplastics

Wild caught, fresh specimens were directly collected from the fishermen at the study areas mentioned above. The collected samples were placed in the icebox, to avoid any sort of damage or contamination. Then they were transferred to the laboratory, for the next step. Each specimen underwent individual measurements for length and weight, and photographs were taken. The gastro-intestinal (GI) tracts and gills of fishes, as well as the hepatopancreas and gills of crabs were isolated, weighed and stored separately in a sterile aluminum foil foam bag at -20°C.

After storage, systematic thawing done by placing the samples in a sealed metal container. Temperatures were monitored hourly using probe thermometer until the samples came to a room temperature. For fishes, the tracts and gills were homogenized separately, while for crabs, both hepatopancreas and gills were homogenized together using an autoclaved mortar and pestle. Alkaline digestion, involving approximately three times the weight/volume of 10% aqueous KOH (potassium hydroxide), was applied to the homogenized organic material, maintaining the solution at 60°C for 72 hours [45–47]. The resulting material underwent filtration through two sets of filters with mesh sizes of 1 mm and 125 µm (Whatman No. 1) using distilled water. They were inspected for the presence of microplastics under a Unilab binocular research microscope and suspected particles were isolated for further analysis.

Precaution and Safety Measures

To minimize microplastic contamination throughout the process, precaution measures were implemented as mentioned by Kumar et al. [46]. The dissection area was maintained in a clean environment to minimize airborne microplastics with a dedicated lab. All the instruments that were used during the process were properly sterilized. A dedicated, stainless-steel dissection kit was used to avoid potential microplastic shedding from plastic tools. Dissections were performed using double-distilled water to minimize any trace contaminants that might interfere with microplastic analysis. To minimize plastic usage, non-plastic containers and tools were used whenever possible and to avoid potential contamination from microplastic leaching. Rigorous cleaning was done. All the equipment used during the entire process, including containers and instruments, was thoroughly cleaned with filtered water followed by laboratory-grade ethanol to remove any residual tissue and potential microplastic contaminants.

Characterization and Identification of Microplastics

Microplastic identification initiates with a thorough visual inspection, enabling the initial recognition of particles through assessments of size, shape and color. This qualitative evaluation acts as an initial screening technique, facilitating the differentiation of potential microplastics from organic substances. After the primary confirmation test, the isolated microplastic particles underwent imaging procedures and their respective diameters were measured. Then the isolated suspected plastic particles underwent FTIR - ATR (Fourier Transform Infrared Spectroscopy - Attenuated Total Reflectance) spectrophotometer analysis.

FTIR Analysis

Obtained plastic samples from the different species were placed in the ATR window. For each sample, multiple ATR-FTIR measurements were taken at different points to ensure to capture data from as many particles as possible, including smaller ones.

ATR-FTIR spectra of samples were recorded at 4000–500 cm^{-1}. FTIR spectra were obtained using the Perkin Elmer spectrum ATR-FTIR spectrometer available at the Sophisticated Analytical Instrumentation Facility at St. Peter's Institute of Higher Education and Research, Chennai. The instrument was under continuous dry air purge to eliminate atmospheric water vapor. Interferograms were averaged for 32 scans at 4.0 cm^{-1} resolution. Perkin Elmer Spectrum software was used for the frequency measurements. The collected spectra were further analyzed by Origin 8.0 software. Microplastics are characterized by comparing the FTIR results of each functional group of spectra with standard values available from the literature.

Statistical Analyses

Statistical analyses were performed to evaluate the distribution of microplastics among species and to assess relationships between various factors. All statistical tests were conducted using IBM SPSS Statistics 27. Descriptive statistics (mean±standard deviation) were calculated for the length and weight measurements of each species. One-way Analysis of Variance (ANOVA) was used to test for significant differences in the number of microplastics found among the four species studied, with a significance level set at $p < 0.05$. To examine the relationship between microplastic abundance in gills and guts, Pearson correlation analysis was performed. The Pearson correlation coefficient (r) was calculated to determine the strength and direction of the linear relationship between these two variables. All graphs and figures were created using Microsoft Excel.

RESULTS

Abundance of Microplastics in Fish and Crab Organs

In this study 70 samples from four commercially important species (Japanese threadfin bream, Indian Mackerel, Catfish and Mud Crab) were investigated. The Japanese threadfin bream had an average length of 15.7±17.7 cm

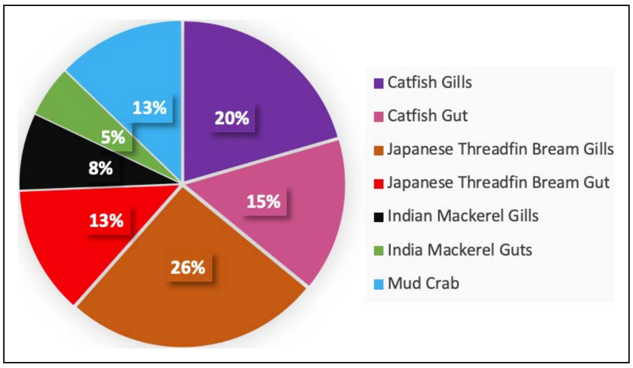

Figure 4. Overall distribution of microplastics among four species.

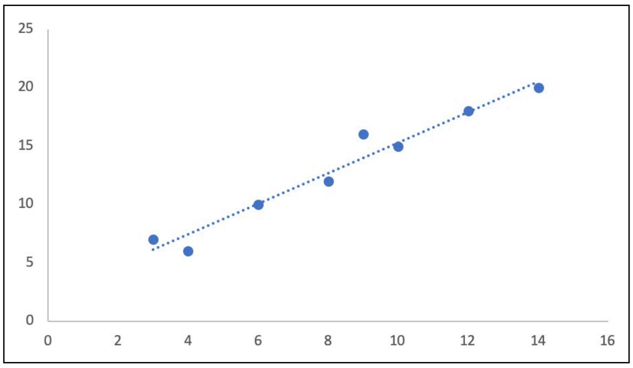

Figure 5. Correlation of microplastic abundance between gills and guts where x- axis depicts the microplastic abundance in the guts and the y-axis depicts the microplastic abundance in the gills.

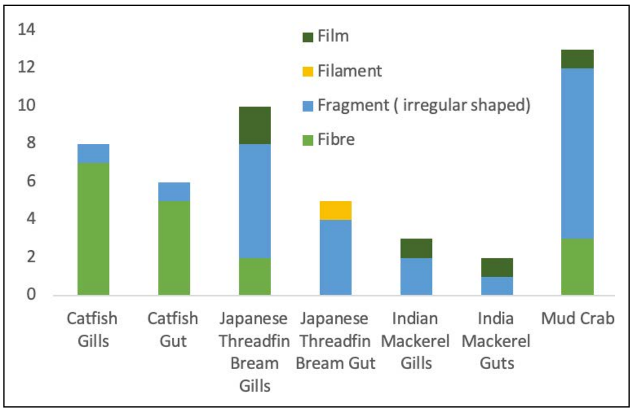

Figure 6. Different shapes of microplastics and their distribution among four species.

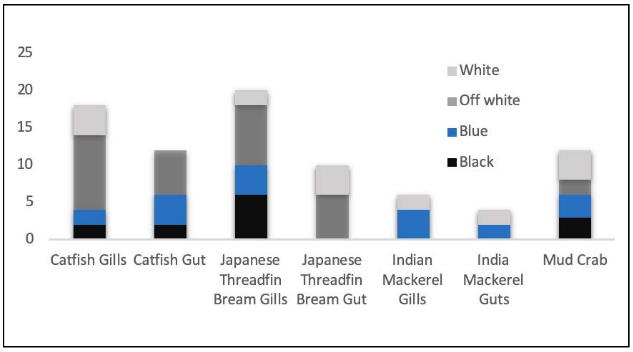

Figure 7. Different colors of microplastics and their distribution among four species.

and a gut weight ranging from 4 to 9 g. Indian Mackerel exhibited an average length of 19±21 cm with a gut weight ranging from 5 to 10 g. Catfish displayed an average length of 17±20.5 cm and a gut weight ranging from 4 to 10 g. The mud crab showed a carapace width of 10±13 cm and a hepatopancreas weight ranging from 13 to 16 g. Microplastics were detected in 55 (78.57%) samples, highlighting their widespread occurrence in these species. There were species-specific variations in distribution of microplastics as *Nemipterus japonicus* and *Arius* sp. had the highest average of 5±3 microplastic items/individual and of 4±2.5 microplastic items/individual respectively. While *Rastrelliger kanagurta* and *Scylla olivacea* showed lower averages of 2±1 microplastic items/individual each. A distinct organ-specific trends were noticed, with gills harboring slightly more microplastics (0.35 items/gills) than guts (0.21 items/gut). Statistical analysis using one-way ANOVA (Analysis of Variance) indicated a significant difference ($p<0.05$) in the number of microplastics found among the four species studied (Fig. 4).

Pearson correlation analysis of the relationship between microplastic abundance in the gills and microplastic abundance in the guts of the studied species reveals a very strong positive correlation. A Pearson correlation coefficient (r) of 0.978 was calculated, indicating a highly linear relationship between these two variables. These results demonstrate that as the microplastic levels increase in the gills, they tend to increase correspondingly in the guts and vice versa, suggesting a strong link between the accumulation of microplastics in these two organs within the studied population (Fig. 5).

Characteristics of Microplastics in Fishes and Crab

The morphological characteristics of microplastics in four different species were studied. Fibers and fragments were the predominant microplastic shapes observed in all four organisms, with thin filaments and film following. Catfish and Japanese threadfin bream displayed a notable dominance of fibers and fragments. The highest deposition occurred in gills, with catfish gills having the highest fiber concentration and Japanese threadfin bream gills and mud crab's hepatopancreas containing the highest fragment concentration (Fig. 6). Notably, microplastics in guts were generally larger than those in gills and the average size across all species ranged from 700 µm to 1 mm.

Microplastics were detected in four colors: black, blue, white and off-white (translucent). The most common color was off-white (translucent) followed by white, blue and black. White microplastics were the most dominant colour present in the mud crab's hepatopancreas. Translucent microplastics were notably concentrated in the gills of catfish and Japanese threadfin bream. In the gut of catfish, the prevailing color was blue, while black color was observed in higher proportions only in Japanese threadfin bream gills (Fig. 7).

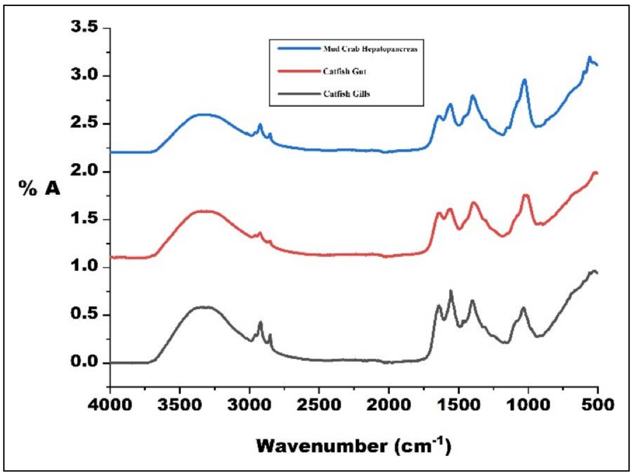

Figure 8. FT-IR spectra of catfish gill, catfish gut and mud crab hepatopancreas (Recorded in the region 4000–500 cm^{-1}).

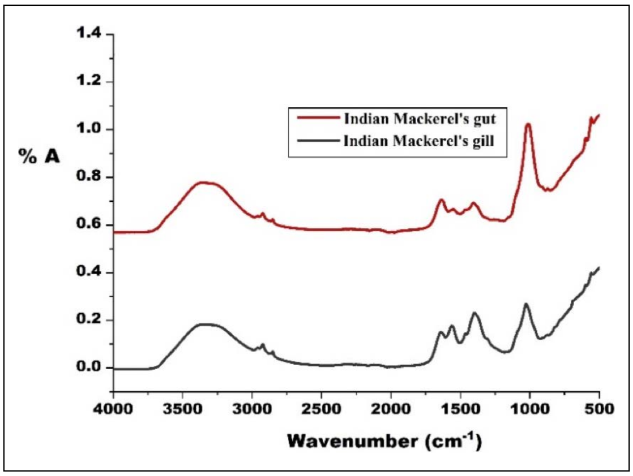

Figure 9. FT-IR spectra of Indian Mackerel gill and gut (Recorded in the region 4000–500 cm^{-1}).

FTIR Frequency Assignment of Microplastics Extracted From Different Species

Figures 8–10 shows average FTIR spectra of extracted microplastics from the gill and gut of the respective species. The spectra were recorded in the region 4000–500 cm^{-1}. Table 1 shows the tentative frequency assignment of the microplastics obtained from gill, gut of Indian mackerel, Japanese threadfin bream, catfish and crab hepatopancreas respectively. As observed from the figure and table a very weak peak ~2915 cm^{-1} corresponds to asymmetric C-H stretching occurs for the samples studied. A weak intensity 2920–2840 cm^{-1} observed corresponds to asymmetric C-H stretching of low-density polyethylene (PE). The gill and gut of the catfish have a strong and medium peak ~2915 cm^{-1} observed and for the rest of the samples, weak peaks were observed. Symmetric C-H stretching corresponds to ~2850 cm^{-1} occurs for the sample except a strong band occurs for the gill of the catfish as seen in the Table 1 and Figure 6. C=O stretching of weak to very weak appears ~ 1653 cm^{-1} and NH bend and C-N stretching frequency assigned to ~1532 cm^{-1} as observed in the samples. NH bend and C-N stretching of low-density polyethylene occurs in the range of 1530–1560 cm^{-1}. A medium to weak peak of ~ 1462 cm^{-1} occurs at the most of samples corresponding to CH_2 bending. CH_3 bending of PE occurs at 1390–1400 cm^{-1}. Our study supports the other findings showing these peaks observed are characterized as polyamide (nylon) [48–51].

A strong band of ~1015 cm^{-1} corresponds to C-O stretching polyethylene occurs at the gut of Japanese threadfin bream and weak peaks were observed in the gut of catfish were observed (Fig. 8, 10). The peaks occur in the region of 1124–1060 cm^{-1} related to photo-aging polyethylene. C-O stretch polyethylene occurs in the region 1010–1080 cm^{-1} which are the characteristics of microplastics observed in the study. The peaks ~780 cm^{-1} and ~690–710 cm^{-1} corresponds to CH_3 and CH_2 rocking respectively. This band characteristics the low-density polyethylene (LDPE) which matches with the LDPE other researchers [49–52].

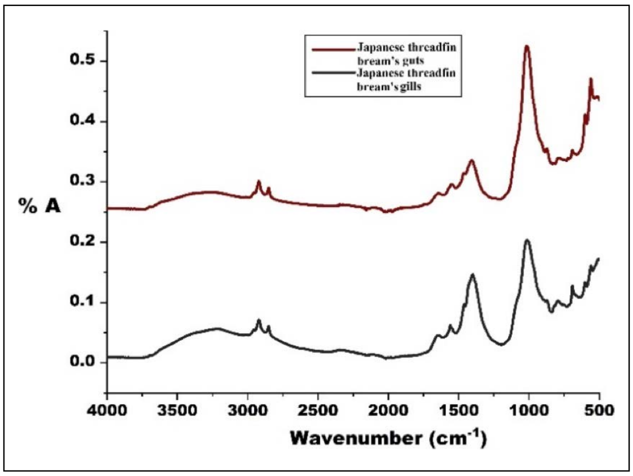

Figure 10. FT-IR spectra of Japanese threadfin bream gills and guts (Recorded in the region 4000–500 cm^{-1})

Polymer Identification

The ATR FTIR analysis identified two microplastic types: Low-density polyethylene (LDPE) and polyamide (nylon). LDPE consistently appeared in all samples where its highest concentration was seen in the gills of Japanese threadfin bream compared to its guts. In contrast, Indian mackerel displayed similar LDPE values in both gut and gill samples, indicating negligible changes in spectral intensity. The observed poor quality of plastics in the mackerel's gut may be linked to effective absorption during digestion. Japanese threadfin bream exhibited the highest LDPE absorption, implying the inefficiency of crab hepatopancreas and gills in LDPE absorption, accompanied by poor plastic quality.

This study advances our comprehension of species-specific digestion and absorption mechanisms in the presence of microplastics, emphasizing the variability among different species. Furthermore, minimal absorption bands characteristic of polyamide (nylon) was discerned in catfish gills and guts, with a significantly higher peak intensities in gills, suggesting preferential accumulation and higher abundance in this tissue. These findings underscore potential

Table 1. FT-IR spectral peaks on gill, gut of Indian Mackerel, Japanese threadfin bream, cat fish and crab hepatopancreas

Frequency assignment	Functional group	Gill of mackerel	Gill of Japanese threadfin bream	Gut of mackerel	Gut of Japanese threadfin bream	Gill of catfish	Gut of catfish	Crab Hepatopancreas
2908	Asymmetric C-H stretching	2915 (vw)	2917 (vw)	–	2925 (vw)	2916 (s)	2920 (m)	2925 (w)
2845	Symmetric C-H stretching	2850 (vw)	2850 (vw)	2856 (vw)	2868 (vw)	2858 (s)	2846 (w)	2842 (w)
	C=O stretching	1653 (vw)	1639 (vw)		1647 (vw)	1645 (vw)	1642 (w)	
						1753 (s)	1749 (m)	1642 (w)
	NH bend and C-N stretching	1532 (vw)	1556 (vw)	–	1537 (vw)	1545 (s)	1557 (m)	1554 (m)
	CH_3 bending					1455 (w)	1454 (w)	
	CH_3 bending						1405 (w)	
1463	CH_3 bending	1408 (w)	1406 (s)	–	1416 (m)	1379 (vw)	1378 (vw)	1394 (s)
	Related to photo-aging polyethylene (1124–1060 cm^{-1})	1092 (s)				1158 (vw)	1154 (vw)	
	C-O stretching polyethylene				1015 (S)		1092 (w)	
	C-O stretching			1083 (vw)		1042 (vw)	1045 (s)	
	C-O stretch polyethylene		1012 (S)			1022 (m)	1027 (s)	1029 (s)
	C-O stretch		1006 (s)	1081 (s)				
	CH_3 rocking,		794 (w)	787 (m)	784 (m)			
717	CH_2 rocking		693 (m)	693 (vw)	698 (w)	715 (vw)	715 (vw)	

S: Strong; M: Medium; w: Weak: Vw: Very weak.

variations in defense mechanisms and biological functions across species in response to microplastics, providing valuable insights for further research in this field.

Table 1 shows tentative frequency assignment of the four species. A weak intensity 2920–2840 cm^{-1} observed corresponds to asymmetric C-H stretching of low-density polyethylene (PE). The very weak intensity of C=O stretching occurs in the range of 1630–1640 cm^{-1}. NH bend and C-N stretching of low-density polyethylene occurs in the range of 1530–1560 cm^{-1}. CH_3 bending of PE occurs at 1390–1400 cm^{-1}. The peak occurs at 1120–1060 cm^{-1} related to photo-aging polyethylene. The strong to peaks occurs at 1000–1030 cm^{-1} C-O stretching polyethylene. A week peaks 680–780 cm^{-1} CH_3/CH_2 rocking polyethylene (Fig. 8–10).

DISCUSSION

Microplastics pollution is one of the major global phenomena of the current decade. Several studies have been carried out all over the world to detect the presence of microplastics and analyzing them and the impacts they cause on living organisms. They were found accumulated in the gills, gastrointestinal tract and organs of various biota. It consists of plankton with accumulation of 164 particles/m^3 [53], corals consist of 50 μg plastic cm^{-1} h^{-1} [54], marine fishes had 112 pieces of microplastics on an average [55], mangrove fishes were found to have 0.79 to 1.00 particles [56]. So, understanding the microplastics abundance is essential.

Abundance of Microplastics in Fish and Crab Organs

This study highlights the concerning prevalence of microplastics in commercially important aquatic species with detection in 78.57% of samples across four species. This widespread occurrence demands closer inspection, especially considering the observed species-specific variations and organ-specific distribution. These findings raise critical questions about the potential ecological and human health implications of microplastic pollution. The study identified *Nemipterus japonicus* (Japanese threadfin bream) harboring 5±3 microplastic items/individual and *Arius* sp. (catfish) containing 4±2.5 microplastic items/individual, showing that they have the highest microplastic accumulation rate comparatively. This may likely due to their benthic feeding habit [57] near microplastic-laden sediments. *Rastrelliger kanagurta* (Indian mackerel) and *Scylla olivacea* (mud crab) showed lower microplastic averages of 2±1 microplastic items/individual each, potentially due to their pelagic or intertidal habitats. This trend of higher abundance of microplastics were also seen in similar recent studies such as in Japanese threadfin bream (*Nemipterus japonicus*) had 28.33±8.11 particles/individual out of 9 samples, Indian Mackerel (*Rastrelliger kanagurta*) had 20.89±8.79 particles/individual out of 9 samples [58], Catfish (*Arius* sp.) showed 1.77±0.25 particles/individual out of 35 samples [59] and several other crab species also showed the presence of microplastics, emphasizing the organisms nature of microplastic consumption. However, further research considering factors like feeding ecology, prey preference and microplastic characteristics is needed [60]. Furthermore, the study revealed organ-specific distribution of microplastics. The higher microplastic presence in gills (0.35 items/gills) compared to guts (0.21 items/gut) suggests potential direct filtration and accumulation in gill structures. This aligns with previous studies reporting gills as primary accumulation sites [23]. Understanding the potential physiological impacts and translocation pathways within organisms is crucial to fully understand its effect [61]. The significant difference in microplastic distribution among species ($p<0.05$) underscores the critical need for species-specific assessments and targeted management strategies. Ignoring these variations could lead to underestimating risks for vulnerable populations and hindering effective mitigation efforts.

Sources of Microplastics

The sources of microplastics in Ennore creek and Kasimedu fish landing center are multifaceted, reflecting the heavily industrialized and urbanized nature of the region. Ennore creek, a polluted industrial estuary in Chennai, Tamil Nadu, encounters microplastic inputs from wastewater discharge by nearby industrial units and residential areas [47], runoff from roads and urban areas carrying plastic litter [62], atmospheric deposition of airborne microplastics [63], as well as fishing activities and lost fishing gear [64]. Kasimedu, the largest fish landing center in Chennai located along Ennore creek, faces microplastic pollution from discarded and lost fishing nets, lines, ropes and other gear, microplastics entering the food chain from the contaminated creek waters [65], improper waste disposal by fish vendors and workers [66] and urban runoff carrying plastic waste [62]. The high levels of industrialization, urbanization and fishing activities in the region are significant contributors to the microplastic contamination of these aquatic ecosystems [67], highlighting the need for effective waste management and better regulation of industrial effluents to address this growing environmental issue.

Characteristics of Microplastics in Fishes and Crab

The microplastics observed in four aquatic species, revealed intriguing patterns in their shapes, sizes and colors. The origin of different microplastic sizes in the samples were due to several factors, in ocean plastic particles deteriorate according to its power function resulting in different size range. Environmental degradation plays a vital role as the larger plastics break down into smaller pieces due to UV radiation, mechanical abrasion, and biological processes [14]. Different environmental conditions (e.g., temperature, salinity) affect the rate and extent of plastic fragmentation [68]. Several studies have classified microplastics based on its size such as Gad et al. [69], worked on microplastic extraction from two commercialized fishes, hardhead catfish (*Ariopsis felis*) and southern flounder (*Paralichthys lethostigma*) of the Gulf of Mexico. The microplastics were categorized into three different categories based on different sizes as small (20–1000 μm), medium (1000–2500 μm), and largest (2500 μm). Ranjani et al. [70], extracted microplastics from two major harbours, the Ennore and Chennai harbour. These microplastics were classified into five categories based on their size range. Ineyathendral et al. [71], collected four major commercial fishes *Sphyraena jello*, *Nemipterus japonicus*, *Leiognathus species*, *Sardinella longiceps* of the Chennai Coast. Each fish had different feeding habits which played a major role in microplastic accumulation in the gut region. A total of 607 microplastic pieces were observed within size range 0.1 mm to 5 mm.

Fibers and fragments were the two most dominant shapes found in all the four organisms; this is likely due to their abundance in the environment from larger plastic breakdown [20]. Interestingly, catfish and Japanese threadfin bream seem particularly susceptible to these shapes, potentially reflecting their feeding habits or habitat characteristics [60]. With larger microplastics (>700 μm) residing mainly in the guts, suggests potential ingestion and incomplete digestion. In contrast, gills harbor smaller ones, possibly due to direct filtration or passive adsorption [23]. This highlights the varying uptake pathways and potential impacts depending on the microplastic size. A range of color variations in microplastics were observed. Translucent microplastics seem favored by catfish and Japanese threadfin bream gills, while white microplastics dominates the mud crab's hepatopancreas. The transparent fragments and fibers could be derived from the decomposing of fishing nets/lines according to their features. These results were similar to Beibu Gulf [72] indicating that the plastics products from fishery activities played an essential role in microplastics pollution. These variations could be linked to factors like production processes, biofouling or selective accumulation mechanisms [73]. According to Marti et al. [74], the color of the plastic pieces fade over time when they are exposed to sunlight for long periods of time. Photo oxidative damage resulted in fragmentation of plastic pieces and color changes to white and yellow to brown color in over period. These factors affect both the mechanical properties as well as color of the plastics pieces. Additionally, blue dominates catfish guts, potentially reflecting specific prey preferences or environmental exposure. Blue could be sourced back to the fishing nets. The scarcity of black microplastics suggests lower environmental presence or different uptake pathways. Investigating the potential impacts of different shapes, sizes and colors on these species is crucial to assess the full scope of microplastic threats [75].

Polymer Identification

The ATR-FTIR analysis conducted identified two primary types of plastics: low-density polyethylene (LDPE) and polyamide (nylon). LDPE was consistently found in all four samples, indicating its widespread presence. The potential sources of LDPE include plastic bags and packaging, fishing gear and single-use plastics. On the other hand, nylon was also detected and its possible sources include fishing gear, textiles and clothing, wastewater, various industrial and commercial applications. The distinct LDPE concentrations in Japanese threadfin bream (gills > gut) vs. mackerel (gut ≈ gills) highlight species-specific variations in digestion process to breakdown poor - quality plastic and absorption mechanisms [76]. Higher LDPE concentration in Japanese threadfin bream gills than guts suggest inefficient absorption, potentially due to differences in gill morphology or filtration mechanisms impacting particle capture [20] and variations in digestive enzymes or gut microbiota composition affecting breakdown [73]. Similar LDPE levels in mackerel gut and gills imply efficient absorption, possibly linked to gut morphology or enzymes facilitating LDPE uptake [77]. Interestingly, crab hepatopancreas and gills exhibited minimal LDPE absorption, suggesting species-specific defense mechanisms or digestive processes. These findings highlight the need for further research into the factors influencing LDPE absorption and its potential ecological impacts.

Polyamide, commonly known as nylon had minimal absorption bands in catfish gills and guts and significantly higher intensities were observed in gills. This suggests preferential accumulation of nylon in gills due to their filtration function or specific binding mechanisms [61]. Further research is needed to understand the implications of polyamide accumulation in gills and its effects on fish health as highlighted in the study. This study insights are in line with previous research highlighting the intricate interplay between microplastics and aquatic organisms' physiological processes [61]. Future research needed in understanding the digestive and absorption mechanisms employed by different species, exploring factors like gut morphology, enzymatic activity and plastic characteristics [18].

Potential Risks to the Studied Species and Human Consumption

The widespread presence of microplastics observed in this study raises concerns about the potential health impacts on the targeted marine species and the humans who consume them. Microplastic ingestion has been shown to have physiological and ecological consequences, such as impaired growth, reduced reproductive fitness and disruption of overall organismal function, in similar marine organisms [60]. Given the high levels of microplastic accumulation found in species like *Nemipterus japonicus* and *Arius* sp., further research is needed to elucidate the specific health impacts on these species and the implications for their population dynamics and the broader ecosystem. Additionally, the presence of microplastics in the studied species poses a potential risk to human consumers, as these contaminants may bioaccumulate and transfer up the food chain. Existing literature suggests that microplastic ingestion in humans can lead to gastrointestinal, immunological and endocrine-disrupting effects [23, 77], highlighting the importance of monitoring microplastic levels in seafood and establishing safe consumption guidelines.

Limitation of the Study

The study is limited to the accumulation of MPs in specific species. Broader ecological and health impacts of MPs, particularly within the framework of the One Health approach, have not been addressed. This represents a significant research gap that needs to be explored in future studies. The MPs were separated into size classes and concentrated ATR-FTIR analysis were done only on the larger fractions (>500 μm), where the technique is most effective. The findings are based on samples collected within a specific time frame and geographic area. MP pollution can vary significantly over time and across different locations, so the results may not be generalizable to other regions or time periods. Longitudinal studies are needed to understand the chronic impacts of MP exposure.

CONCLUSION

The study investigated the presence and characteristics of microplastics in four commercially important aquatic species - Japanese threadfin bream, Indian mackerel, catfish, and mud crab from two locations in Tamil Nadu, India. Microplastics were found in 78.57% of samples, indicating their widespread presence. Significant species-specific variations in accumulation of microplastics were observed with *Nemipterus japonicus* and *Arius* sp. showing the highest levels of microplastic deposition which is likely influenced by their feeding habits. Gills exhibited slightly more microplastics than guts, implying direct filtration and accumulation. Fiber and fragment shapes were the most prevalent microplastic shapes, reflecting their environmental abundance, while the most common microplastic colors were off-white (translucent), white, blue and black. The determination of microplastic colors and their origin is a complex issue because these colors may not necessarily reflect the original color of the plastic products. The colors that were observed were not bright but merely faded due to possible several factors such as photo oxidation, weathering, additive leaching etc. that can influence the observed colors. Larger microplastics were in guts, while smaller ones were in gills, suggesting different uptake pathways. FTIR analysis identified two main polymer types – low density polyethylene (LDPE) and polyamide (nylon). Species-specific differences were observed in the absorption and accumulation patterns of these polymers. Further research is essential for understanding digestive and absorption mechanisms, potential health impacts and population dynamics. The results of this study highlight the need for targeted, species-specific assessments and management strategies to address the growing issue of microplastic pollution in the studied ecosystems. To facilitate immediate action for mitigating microplastic pollution in the studied areas, an establishment of comprehensive monitoring programs are recommended, implementing source reduction strategies, enhancing habitat conservation and restoration, developing fisheries management plans that incorporate microplastic contamination as a key consideration and fostering collaborative research to better understand the fate, transport and biological impacts of microplastics in the studied ecosystems. By implementing these targeted actions, tailored to the specific ecological and socio-economic contexts of the study regions, proactive steps can be taken to address the microplastic pollution challenge and safeguard the health of the studied marine species and the communities that depend on them.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

A bibliometric analysis of blue growth: Trends, challenges, and opportunities

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ABSTRACT

The European Union is leading the Blue Growth initiative as a strategic approach to increasing economic prosperity in Europe's seas despite today's challenges. Drawing on the EU's Green Growth initiative, Blue Growth extends sustainability principles to marine areas, solidifying commitments to the sustainable management of marine ecosystems and the promotion of technological innovations. This initiative focuses on sectors such as energy, aquaculture, tourism, and biotechnology in coastal and offshore environments. Blue Growth has increased in importance following major events such as Rio+20 and has had a significant impact on ocean and marine resource management practices. In this study, we conduct a comprehensive bibliometric analysis to trace the trajectory of global research on blue growth across science, policy, and the blue economy over the 17 years since the term's inception in 2007. We analyze blue growth using bibliometric techniques. Examining the blue growth literature, identifying key contributors, collaborations, research trends, and gaps. Our analysis covers publication outputs, institutional affiliations, author collaborations, research themes, and alignment with the Sustainable Development Goals (SDGs). Blue growth research is aligned with several Sustainable Development Goals, particularly SDG 14 (Life Below Water) and SDG 15 (Life on Land), highlighting marine conservation and land-sea ecosystem connectivity. Keyword analysis underlines the interdisciplinary nature of blue growth research, highlighting key themes such as the blue economy, aquaculture, and sustainable development. Institutional analysis identifies the University of Exeter and CNR as key contributors, while country-level analysis highlights global collaboration networks. Citation analysis reveals the intellectual structure of blue growth research, with marine biology, oceanography, sustainability science, and climate change among the prominent themes. During the 17-year period from 2007 to 2024, there was a significant increase in publication output, especially from 2013 onwards. Key countries contributing to this research include the UK, US, Germany, Italy and Spain, reflecting extensive global collaboration. The research emphasizes a strong commitment to sustainability, with a heavy emphasis on Environmental Science and Ecology. Alignment with the Sustainable Development Goals (SDGs) emphasizes a focus on marine conservation (SDG 14) and land-sea ecosystem connectivity (SDG 15). Keyword analysis reveals critical themes such as "blue economy," "aquaculture," and "sustainable development," with an emphasis on interdisciplinary approaches. Institutionally, the University of Exeter and CNR stand out among the contributors.

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INTRODUCTION

The European Union has spearheaded the Blue Growth initiative, envisioning it as a strategic tool for fostering economic prosperity within European seas amidst challenges such as climate change, dwindling natural resources, heightened environmental vulnerabilities, urbanization trends, and the burgeoning population in coastal areas [1]. Building upon the EU's 2010 Green Growth initiative, Blue Growth extends its sustainability ethos to marine domains [2,3]. This strategic framework is anchored in pledges for the sustainable stewardship of marine ecosystems and the promotion of technological innovations, which serve as catalysts for both technological and economic advancement [4]. Blue Growth focuses particularly on sectors such as energy, aquaculture, tourism, mining, and biotechnology within coastal and offshore environments [5]. The prominence of Blue Growth and its allied concepts has surged in recent years, particularly following significant events like Rio + 20, exerting a substantial influence on oceanic and marine resource management practices [6,7]. Blue growth is a term that was introduced in 2007 to describe a sustainable growth strategy that aims to harness the economic potential of oceans, seas, and coastal areas while preserving their environmental health. This concept is part of the broader sustainable development agenda and focuses on balancing economic growth with the need to protect marine ecosystems. [7]. Moreover, this holistic approach to marine resource management not only underscores the importance of conservation but also emphasizes the potential for innovation and economic growth within sustainable parameters [8,9]. By integrating environmental preservation with technological progress, Blue Growth not only addresses immediate challenges but also paves the way for a more resilient and prosperous future for coastal communities and marine ecosystems alike [10,11]. Efforts to manage marine resources are increasingly streamlined with the concept of 'blue growth', a recent addition to the discourse [12,13]. Stemming from the principles of sustainable development (SD), which have been under international scrutiny since the 1960s, blue growth seeks to balance the sustainable utilization of natural resources with economic and social objectives [14]. The European Commission (EC) introduced the Blue Growth agenda in 2012, extending the ethos of the 'Green Economy' to encompass the 'Blue World' or 'Blue Economy' [15]. This paradigm shift aims to harness sustainable growth opportunities in marine, maritime, and coastal domains. The overarching goal is to maximize benefits from the responsible development of marine ecosystems [16,17]. Under the Blue Growth agenda, economic activities are poised to impact the marine environment, particularly concerning the concept of Good Environmental Status (GES). Within the framework of European Union (EU) policies, a clean, healthy, and productive marine environment is paramount [18,19]. National governments and corporate entities alike are championing the blue growth agenda, positioning oceans as fertile ground for development, replete with opportunities to fuel economic expansion [20], [21]. The European Union, with its 'Blue Growth Strategy', identifies oceans as pivotal drivers of the European economy. Realizing their potential necessitates fostering market forces by dismantling barriers and addressing market failures that impede innovation and investment. Within the scope of bibliometric analysis, the field of blue economy, which forms the basis for global studies on Blue Growth, should be discussed. This study aims to explore the trajectory of global research concerning Blue Growth, encompassing its implications across science, policy, and the blue economy. The purpose is to trace the expansion of literature, identify key contributors, analyze collaborative efforts, and highlight research trends and gaps within this domain.

To effectively measure and analyze the progress and impact of these efforts, bibliometric analysis provides a valuable tool. Bibliometric analysis is an analytical technique that is often employed in systematic literature reviews—it involves the quantitative analysis of scholarly works [22]. Through bibliometric analysis, we can evaluate the productivity (i.e., publications) and impact (i.e., citations) of research (e.g., articles) and contributors (e.g., authors, institutions, countries/territories, funders, subject areas) in the field—this relates to “performance analysis,” [23-25] which is one of the two major components in bibliometric analysis. Nonetheless, given the complex world of scholarly research, bibliometric data is often ambiguous, in that it can be meaningless on its own, diverse due to varying formats, and expansive, often including hundreds to thousands of records. These characteristics reflect the multifaceted dynamics of research production (i.e., publication) and consumption (i.e., citation).

In this study, we examine the trajectory of global research concerning blue growth within the realms of science, policy, and the blue economy. Our analysis offers a comprehensive overview of the developments observed and the publications produced during the 17-year span following the introduction of the term "blue growth" in 2007. These objectives encompassed: a) tracing the expansion of blue growth literature across time; b) delineating the countries, institutions, publishing entities, and authors contributing to blue growth discourse; c) uncovering collaborative efforts among nations and institutions in advancing blue growth initiatives and disseminating related studies; and d) discerning prevailing research trends and identifying gaps within this domain.

MATERIALS AND METHODS

The study employs bibliometric analysis to examine the evolution of Blue Growth literature from its inception in 2007. This analytical technique involves quantitative assessment of publications and citations to elucidate productivity and impact across various dimensions: countries, institutions, authors, and collaborative networks. By synthesizing data from scholarly databases, the study aims to provide a comprehensive overview of research dynamics in the field. In May 2024, our study utilized a bibliographic search employing the Web of Science (WoS) database. WoS stands as a premier academic information resource, encompassing an extensive array of subjects worldwide, thereby furnishing scholars with comprehensive academic insights [26]. The core collection of WoS, which serves as the primary data source for this paper, comprises several key databases, namely Conference Proceedings Citation Index-Science (CPCI-S), Science Citation Index Expanded (SCI-EXPANDED), Social Sciences Citation Index (SSCI), Current Chemical Reactions (CCR-EXPANDED), and Index Chemicus (IC).

We examined publications from WoS's proprietary data spanning 2007 to 2024, utilizing "blue growth" as the search criterion. Documents featuring "blue growth" in the title, keywords, and/or abstract were included. Bibliometric analysis was carried out utilizing VOSviewer an open-source tool facilitating data visualization and both descriptive and quantitative analysis of bibliographic data. To ascertain the most prolific countries, each publication was attributed to the country of its corresponding author. A collaboration world map was generated to enhance the visualization of international cooperation among countries, distinguishing between Single Country Publications (involving authors from the same country) and Multi-Country Publications (featuring authors from multiple countries). To complement the global perspective provided by the collaboration world map, we conducted a network analysis utilizing authors' affiliations as the units of analysis. The institution collaboration network illustrates how institutions interact in blue growth research, highlighting pertinent institutions within specific research themes. The graphical representation of this network comprises several clusters, with institutions depicted as nodes (scaled according to their significance) and links denoting collaborations. Furthermore, we conducted a co-word analysis utilizing publication keywords to identify and visualize key themes within blue growth research.

RESULTS AND DISCUSSIONS

Results

Bibliometric analysis provides significant insights into the research landscape in a specific discipline, offering light on trends, patterns, and areas of attention. The wide range of article types encountered in the analysis of blue growth literature, including articles, books, book chapters, data papers, early access publications, editorial materials, letters, reviews, and proceeding papers, demonstrates the multifaceted nature of scholarly contributions to this field. Each sort of publication serves a certain purpose and contributes to the advancement of knowledge in blue growth. For example, research articles and data papers present empirical evidence and theoretical frameworks, whereas book chapters and books give detailed analyses and synthesis of current information. Editorials and letters may offer perspectives on new issues or conflicts, whereas reviews provide critical assessments of current work. Proceeding articles frequently report preliminary results or explain ongoing scientific projects. The variety of publication types reflects the interdisciplinary character of blue-growth research, with contributions from domains like marine biology, economics, policy studies, and engineering.

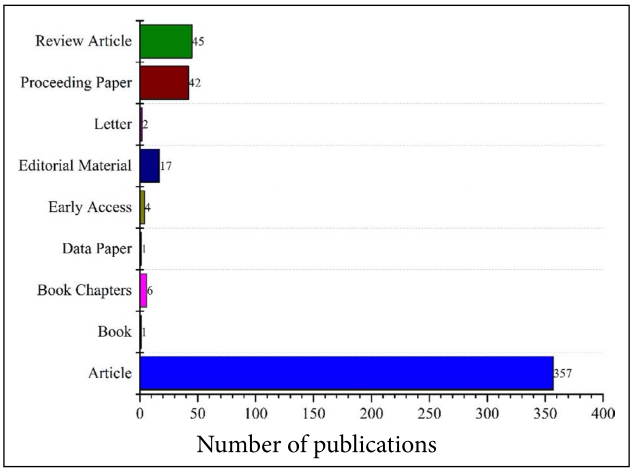

Figure 1. Research type of blue growth articles regarding WoS data.

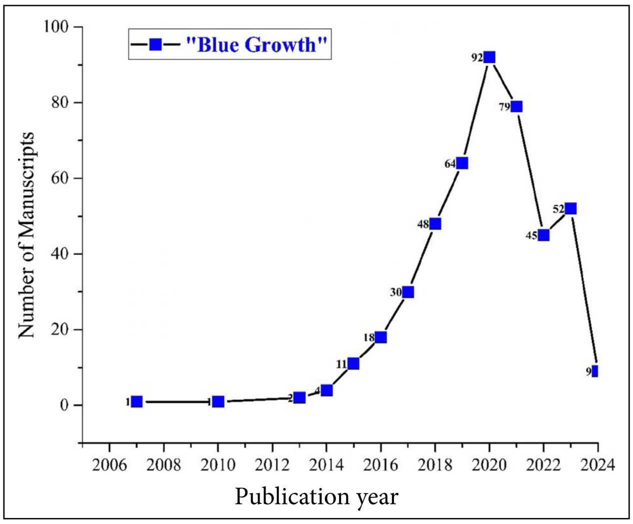

Figure 2. Number of articles published on blue growth by year according to the WoS data.

Understanding the distribution of various publication genres can assist academics and policymakers in assessing the breadth and depth of scholarly engagement with blue growth, identifying gaps in knowledge, and prioritizing areas for future research and collaboration. As shown in Figure 1, a significant 75.16 percent of research-focused articles in the field of blue growth compiled from WoS data are articles.

This statistic underscores the heavy focus on empirical research and scientific discourse within the discourse surrounding blue growth. Based on the article "The sheer breadth of contributions highlights the depth of research and scholarly engagement within academic communities in uncovering the complexities of the blue growth phenomenon.

Figure 2 shows the number of published articles on blue growth in 2007-2024. From 2007 to 2022, there was a discernible upward trajectory in the volume of published articles. The study period is delineated into three distinct phases: Phase I spanning 2007–2013; Phase II from 2013–2022; and Phase III from 2022 onwards. Initially, during Phase I, the

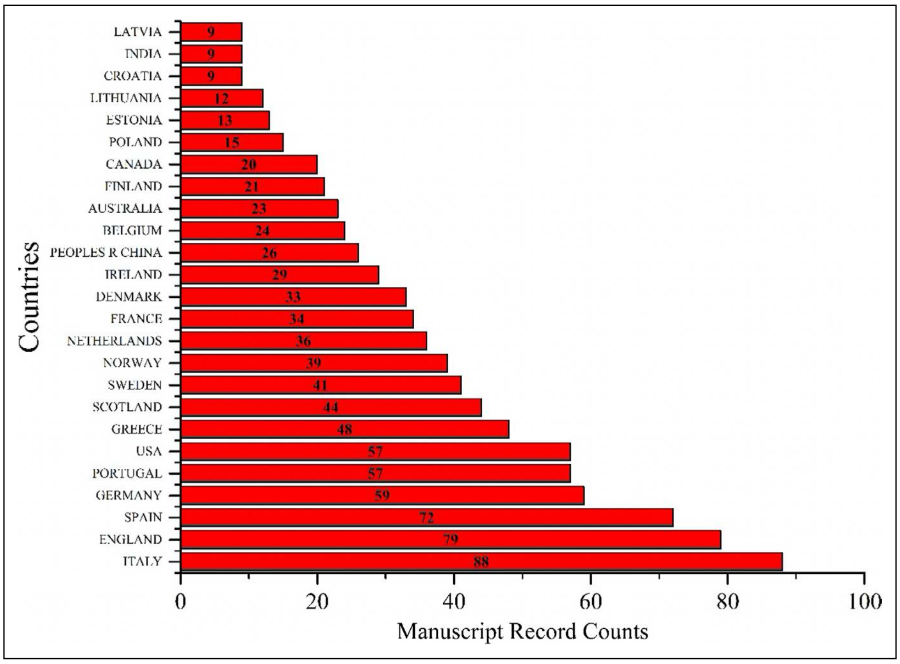

Figure 3. Countries contributed to the manuscripts of the blue growth field according to the WoS data.

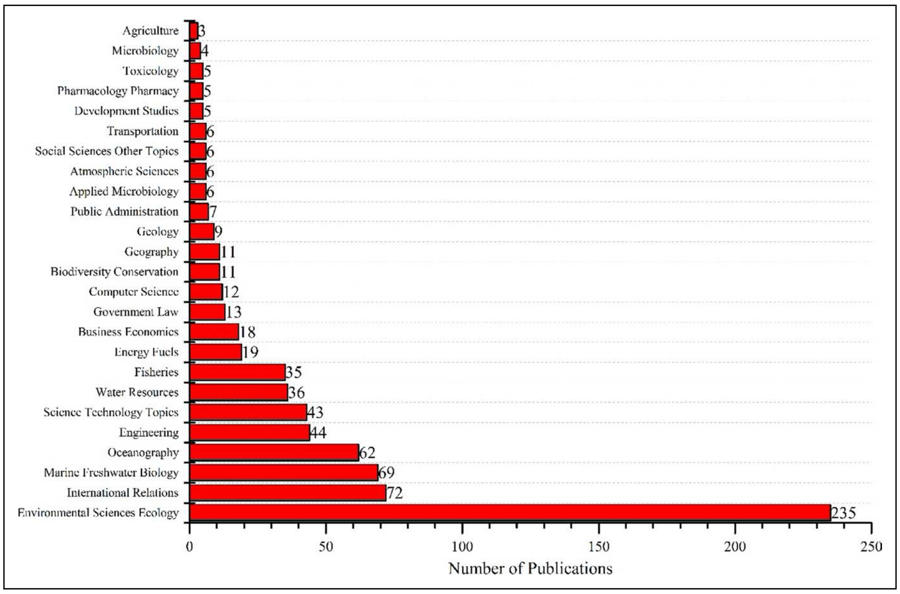

Figure 4. Research areas of blue growth articles according to the WoS data.

number of publications remained relatively stagnant from 2007 to 2013. However, from 2013 to 2022, there was a noticeable uptick in publication numbers. Subsequently, post-2022, there was a discernible decline in publication output.

Knowing which nations have contributed publications on the subject of blue growth based on WoS data provides various bibliometric benefits. For starters, it sheds light on the global distribution of research activities and identifies geographic regions with a high level of interest and investment in blue growth. This data can be used to pinpoint locations that may be underrepresented or ignored in blue growth research and development, as well as those that are at the forefront of the field. Furthermore, examining national contributions makes it possible to evaluate global alliances and collaborations, exposing trends in information sharing and cooperation among researchers worldwide. In order to promote innovation and sustainable development in the marine and maritime sectors globally, strategic decisions on funding priorities, policy development, and resource allocation can be made with more knowledge about the geographic distribution of blue growth research output. The countries that spent the most effort on bibliometric studies were Italy, England and Spain (Fig. 3). It is noteworthy that researchers in Republic of China, who have made many contributions to the scientific literature, do not show interest in this issue.

To delve deeper into the research themes within the realm of blue growth over the past 17 years, an analysis was conducted using WoS data (Fig. 4). The findings indicate that

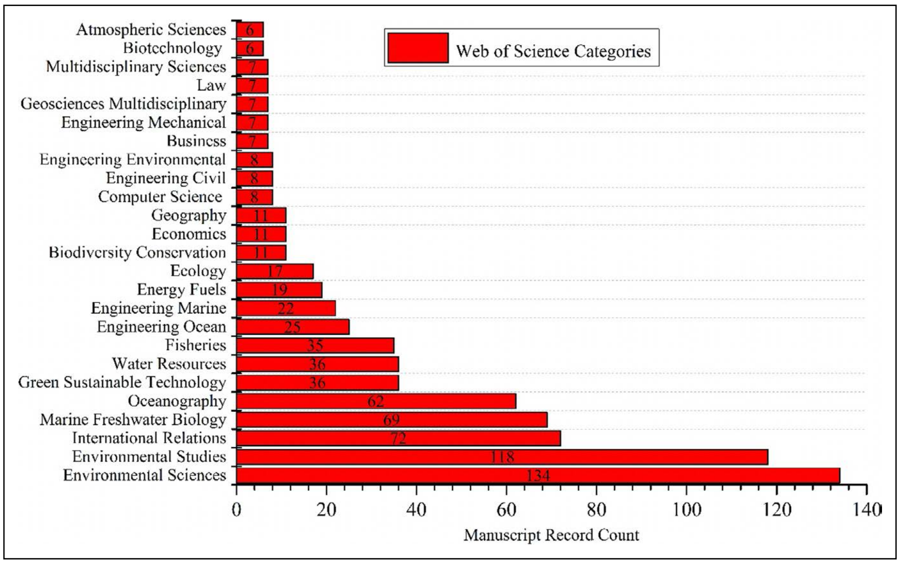

Figure 5. Categories of blue growth articles according to the WoS data.

the primary areas of research focus are Environmental Science and Ecology, followed closely by Business Economics. This suggests that environmental science has emerged as the predominant direction within this field of study, serving as its cornerstone for advancement. Consequently, disciplines related to the environment lay the groundwork for research on the sustainable progression of blue growth. Categories of blue growth articles according to the WoS data is shown in Figure 5.

The examination of Web of Science (WoS) data sheds light on how blue growth research aligns with the European Union's (EU) Sustainable Development Goals (SDGs). It is worth noting that the corpus of studied publications addresses the bulk of the SDGs, except for targets 1, 5, and 10. A major amount of the study, consisting of 289 papers, is related to SDG 14: Life Below Water, demonstrating a strong emphasis on marine conservation, sustainable fishing, and the overall health of ocean ecosystems. Furthermore, the findings show a strong emphasis on SDG 15: Life on Land, with 264 items tagged as relevant to this target. This implies an understanding of the connectivity of terrestrial and marine ecosystems, emphasizing the significance of comprehensive approaches to environmental sustainability and biodiversity conservation. Moreover, the presence of research linked to SDG 13: Climate Action (64 articles) and SDG 7: Affordable and Clean Energy (31 articles) underscores the recognition of the crucial role of renewable energy, mitigation of climate change impacts, and sustainable resource management in the context of blue growth initiatives (Table 1). Overall, the observed alignment between blue growth research and a wide range of SDGs signifies the interdisciplinary nature of efforts aimed at advancing sustainable development in coastal and marine environments. By addressing various dimensions of sustainability, from environmental conservation to socioeconomic equity, researchers and policymakers contribute to the collective endeavour of achieving a more resilient and prosperous future for both humanity and the planet.

The analysis, carried out using VOSviewer, provided insights into the keywords associated with blue growth. 1,239 keywords were examined. Among these, "blue growth" stood out with 175 occurrences (O) and a total link strength (TLS) of 846. In addition, keywords such as "blue economy" (O: 78, TLS: 381), "aquaculture" (O: 51, TLS: 274) and "sustainable development" (O: 30, TLS: 150) were identified as significant (Fig. 6). Highlighting the importance of the data mining analysis of keywords within the articles, it becomes clear that certain terms play a crucial role in understanding the discourse on blue growth. Notable keywords include "maritime spatial planning", "sustainability", "climate change", "fisheries", "ocean governance", "Baltic Sea", "ecosystem services" and "ocean economy". Such an analysis underlines the importance of delving into the intricate web of article's keywords in order to grasp the multifaceted dimensions of blue growth. This can enhance our understanding and guide future research efforts. Keyword usually indicates the main purpose of any article in depth and they can easily explain as shown in Figure 6, some keywords were found whose occupancy rates maintained their position in both. Figure 6 shows the most common author keywords and the author keyword network in articles. The most popular keywords of the authors are blue growth, blue economy and sustainable economy.

This is confirmed by the fact that the topic of innovation in the field of blue growth is a development topic. The bibliographic coupling of universities studied on blue growth subjects can be seen in Figure 7.

Institutional analysis has proven to be more insightful than author-centered analysis because of its immunity to the mere act of renaming, which often occurs without changing the underlying institutional hierarchy. In this regard, the University of Exeter stands out as the university that hosts the highest number of published academics.

Table 1. Distribution of blue growth articles regarding EU sustainable development goals

EU Sustainable Development Goals	Manuscript Record Count
2 ZERO HUNGER	1
3 GOOD HEALTH AND WELL-BEING	15
4 QUALITY EDUCATION	5
6 CLEAN WATER AND SANITATION	11
7 AFFORDABLE AND CLEAN ENERGY	31
8 DECENT WORK AND ECONOMIC GROWTH	3
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE	12
11 SUSTAINABLE CITIES AND COMMUNITIES	22
12 RESPONSIBLE CONSUMPTION AND PRODUCTION	2
13 CLIMATE ACTION	64
14 LIFE BELOW WATER	289
15 LIFE ON LAND	264
16 PEACE, JUSTICE AND STRONG INSTITUTIONS	4

Table 2. Top 25 research profiles of mostly published authors of blue growth articles

Researcher profiles	Record count
Kotta, Jonne	8
Van Den Burg, SanderW. K.	7
Galparsoro, Ibon	7
Kyvelou, Stella Sofia	6
Borja, Angel	6
Murillas-Maza, Arantza	6
Barbanti, Andrea	5
Aura, Christopher Mulanda	5
Rebours, Celine	5
Collu, Maurizio	5
Calado, Helena	5
Hicks, Christina	5
Krost, P.	4
Guerreiro, Jose	4
Kaasik, Ants	4
Depellegrin, Daniel	4
Gissi, Elena	4
Soma, Katrine	4
Johnson, Kate	4
Froehlich, Halley E.	4
Alsaleh, Mohd	4
Ierapetritis, Dimitrios	4
Muggiasca, Sara	4
Lillebø, Ana I	4
Flannery, Wesley	4

Additionally, leveraging the WOS database allows determining the number of co-authors affiliated with a particular institution, providing an estimate of the size of the research community. However, it is important to recognize inherent disparities in institution sizes, as top-tier institutions often have larger research groups than their lower-ranked counterparts. Considering these factors, it was concluded that University Exeter and CNR emerged as the most efficient institutions.

The analysis conducted using VOSviewer, based on the aforementioned results, sheds light on the scholarly contributions of various countries to the discourse on blue growth. A time frame from 2007 to 2024 was chosen to identify node types, with each year represented separately. Vosviewer was used to create a co-occurrence knowledge map showing research on sustainable development within the blue economy across countries (Fig. 8). In this map, each node corresponds to a specific country or region, with a size indicator showing the volume of articles published. Links defined by lines between nodes express cooperative relationships and proximity between countries or regions.

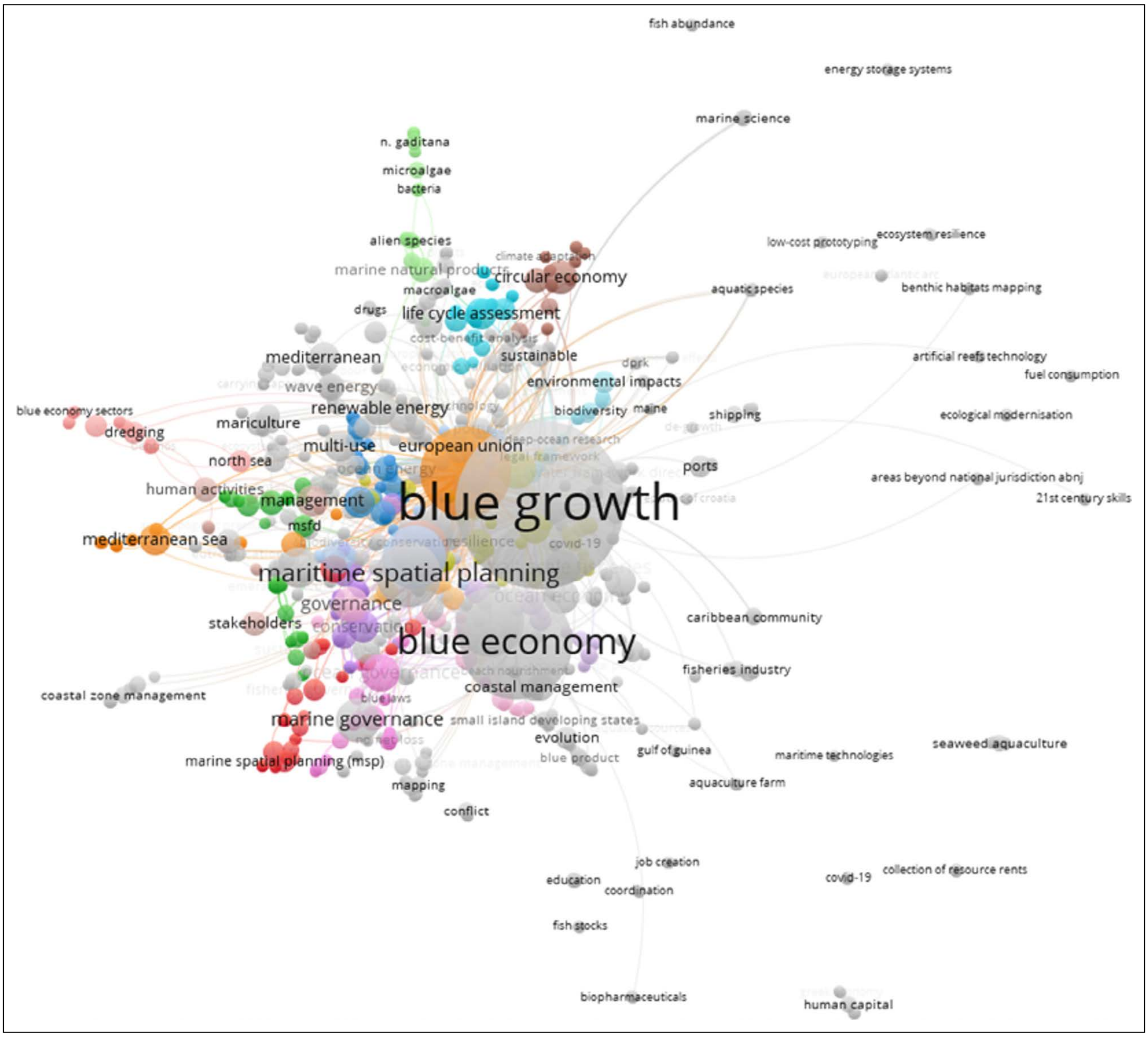

Figure 6. Keywords analysis of "blue growth" according to the Web of Science database.

Examining the frequency of publications on sustainable blue economy development from 2007 to 2024 it can be seen that the biggest contributors in terms of publication volume are the UK, the USA, and Germany. Italy emerges as a notable contributor with 86 articles, accompanied by an impressive citation count of 1844 and a total link strength (TLS) of 31707. Similarly, Spain exhibits substantial involvement, with 70 documents, 1609 citations, and a TLS of 33854. Moreover, it is evident that countries like England, Germany, Portugal, the USA, Scotland, France, Sweden, Norway, and Greece also have a significant presence in terms of the number of articles contributed to this field. This global distribution underscores the international interest and collaboration in researching and understanding blue growth, reflecting the diverse perspectives and expertise involved in advancing knowledge and solutions in this domain. Such analyses not only highlight the geographical distribution of research efforts but also provide insights into the interconnectedness and collaboration networks among researchers and institutions worldwide. This collective endeavor is crucial for addressing the challenges and opportunities posed by blue growth, fostering innovation, and promoting sustainable practices for the benefit of both marine ecosystems and human societies.

Abstract field analysis of blue growth articles based on WoS data reveals the most frequently used keywords as "blue," "ecology," "tourism," and "production." These keywords highlight the primary focal points of research on blue growth. Figure 9 provides a more detailed depiction of the frequency and relationships of these keywords.

Table 2 shows the research profiles of the authors of articles published on the topic of "blue growth". "Blue growth" is a term often used for sustainable use of marine and ocean resources and economic growth. The name and number of records of each researcher in the articles are listed. Researchers may have discussed the issue of blue growth in their articles and conducted studies in this area. Jonne Kot-

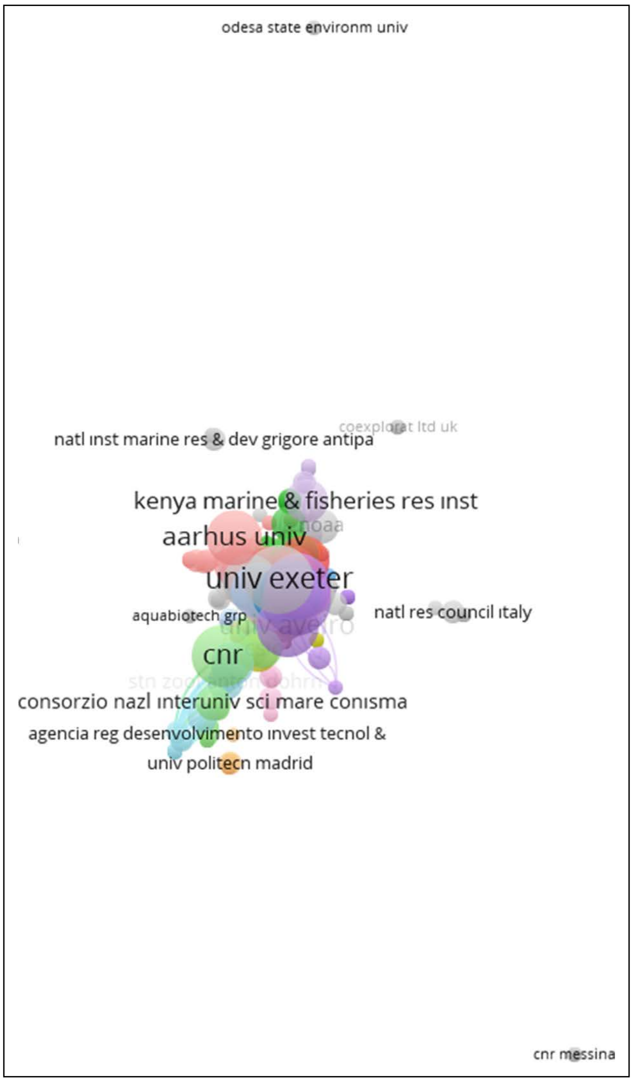

Figure 7. Bibliographic coupling of universities according to the WoS data.

Table 3. Citation topics meso records of blue growth regarding WoS data

Record count	**Citation topics meso**
3.2 Marine biology	272
8.205 Ocean dynamics	26
6.115 Sustainability science	17
6.153 Climate change	9
3.40 Forestry	8
6.27 Political science	8
3.198 Mycotoxins	7
6.223 Hospitality, leisure, sport & tourism	7
6.122 Economic theory	6
6.86 Human geography	6
8.19 Oceanography, meteorology & atmospheric sciences	6
4.84 Supply chain & logistics	5
6.3 Management	5
8.8 Geochemistry, geophysics & geology	4
3.171 Photoproductivity	3
3.60 Herbicides, pesticides & ground poisoning	3
4.169 Remote sensing	3
6.10 Economics	3
6.294 Operations research & management science	3
8.283 Archaeometry	3
2.241 Membrane science	2
3.83 Bioengineering	2
4.237 Safety & maintenance	2
4.284 Human computer interaction	2
1.163 Parasitology - general	1

ta wrote eight articles, while Sander W.K. Van Den Burg and Ibon Galparsoro are authors of seven articles each. Some researchers are represented by six, five or four articles, while others are represented by fewer articles. Table 3 shows the density and contributions of researchers working in the field of blue growth.

Citation themes offer important insights on the thematic focus and the most important study subjects in the field, especially when considered in the context of meso records of blue growth based on WoS data. Researchers can find important themes, new trends, and foundational publications that have greatly advanced our understanding of blue development by examining citation patterns. Many areas, such as marine biology, oceanography, fisheries management, aquaculture, marine biotechnology, coastal zone management, maritime transportation, marine renewable energy, and blue economy policies, may be covered by these citation topics. Researchers can map the field's intellectual structure, find interdisciplinary linkages, and uncover areas of convergence or divergence within blue-growth research by having a thorough understanding of the issues that receive the most citations. It also makes it easier to find gaps in the literature, emphasizing areas that require more research and cooperation to address urgent issues and progress the sustainable development of marine resources and ecosystems. Blue growth is a concept that includes the aim of sustainably sustaining growth in the sea and ocean and the economic, social, and growth derived from these resources. These citations reflect the diversity of research conducted in various disciplines on the resilience of blue growth. Topics such as marine biology, economics, sustainability science, climate change, and tourism are prominent areas expanded on blue growth.

Table 4 shows and it can be noted that the journals Marine Policy and Frontiers in Marine Science are prominently featured among the journals where blue growth articles are published.

Table 4 provides a breakdown of the journals in which articles on blue growth have been published and the number of records corresponding to each publication title. These jour-

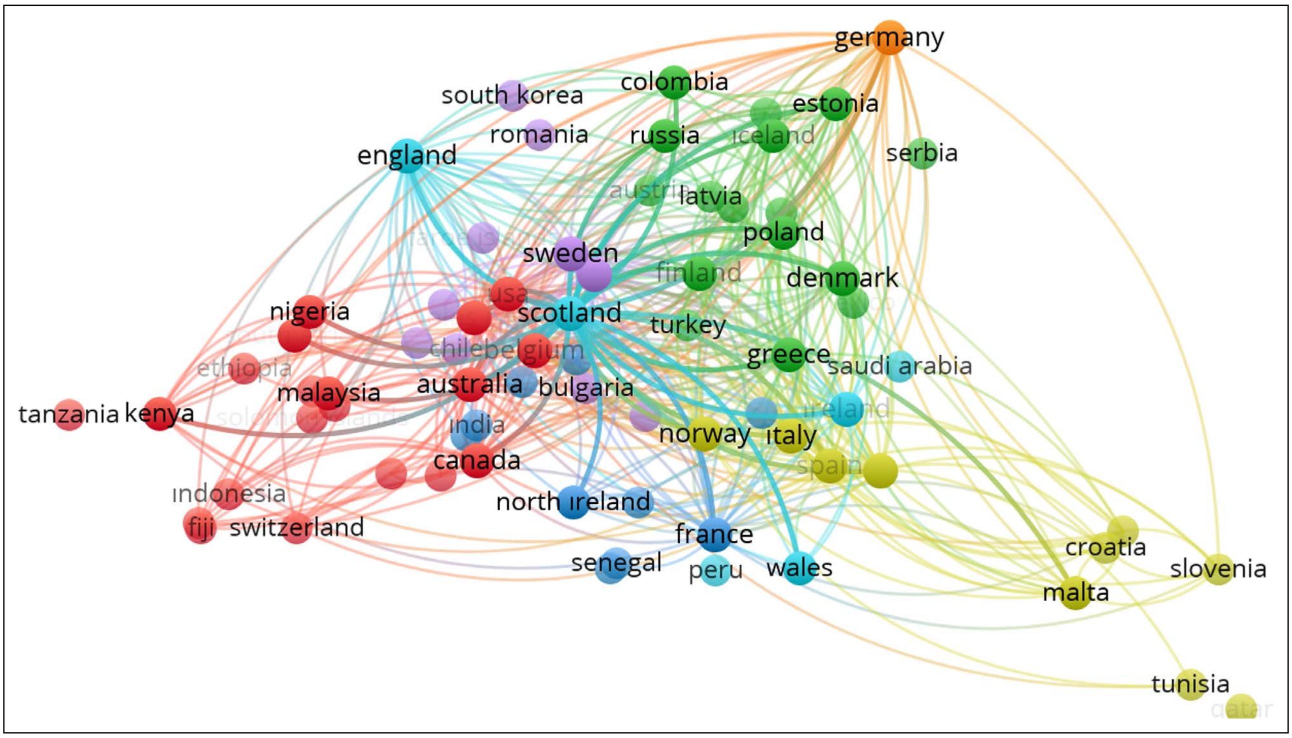

Figure 8. Countries' manuscripts and citations, and their collaboration relations on the blue growth subject.

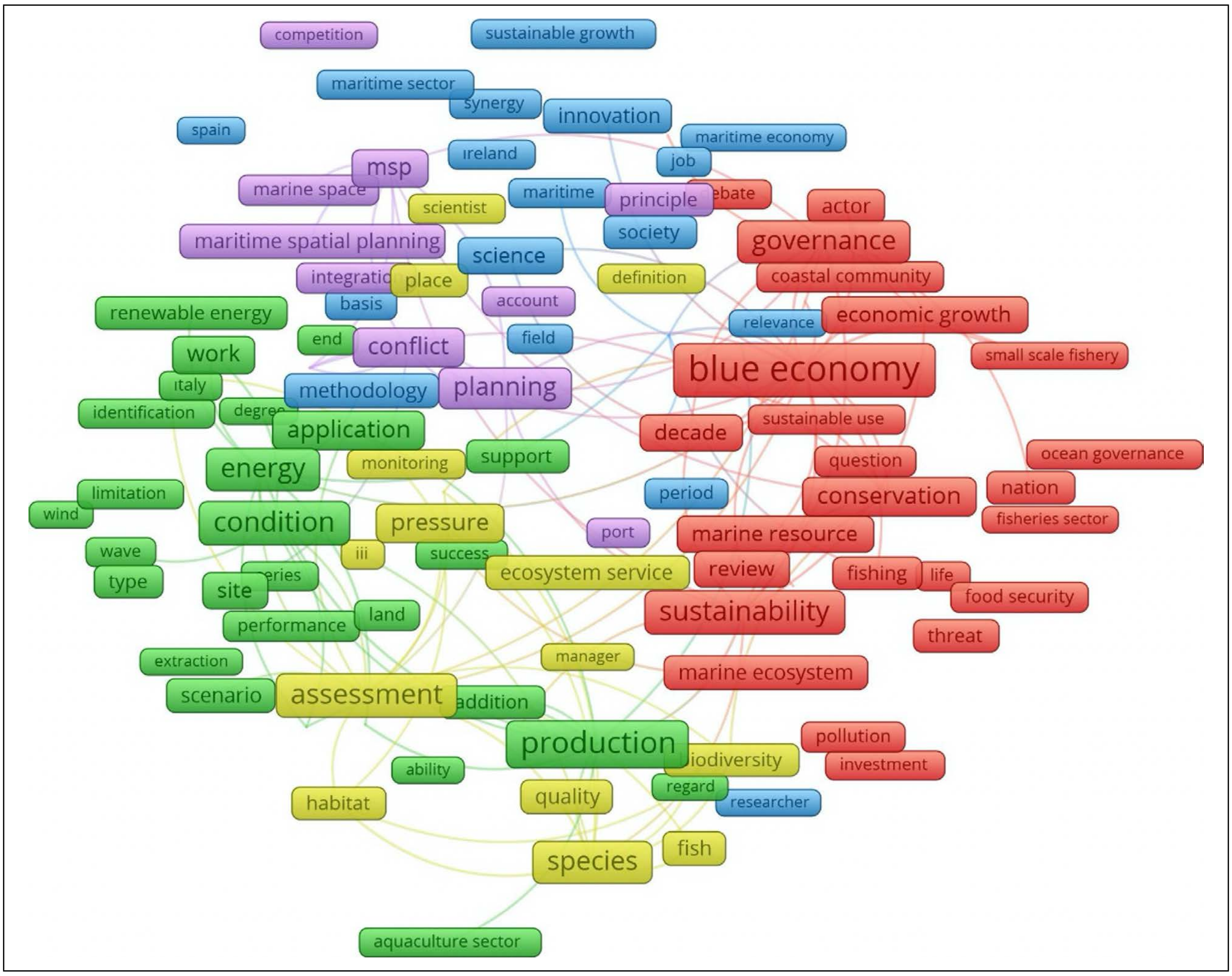

Figure 9. Abstract field analysis of blue growth articles according to the WoS data (10 occurrences).

Table 4. Journals that blue growth articles published

Publication titles	Record count
Marine Policy	68
Frontiers in Marine Science	33
Ocean Coastal Management	23
Maritime Studies	15
Sustainability	13
Science of the Total Environment	12
Sustainability Science	8
Ices Journal of Marine Science	7
Ocean Engineering	6
Water	6
Algal Research Biomass Biofuels and Bioproducts	5
Aquaculture	5
Journal of Marine Science and Engineering	5
Reviews in Aquaculture	5
Frontiers in Energy Research	4
Proceedings of the ASME International Conference on Ocean Offshore and Arctic Engineering	4
Ambio	3
Building Industries at Sea Blue Growth and the New Maritime Economy	3
Coastal Management	3
Ecosystem Services	3
Environmental Engineering and Management Journal	3
Ercim News	3
Journal of Cleaner Production	3
Journal of Coastal Conservation	3
Lecture Notes in Computer Science	3

Table 5. Funding agencies of blue growth articles

Funding agencies	Record count
European Union (EU)	90
Horizon 2020	32
H2020 Societal Challenges Programme	26
UK Research Innovation (UKRI)	21
Fundacao Para a ciencia e a Tecnologia (FCT)	19
Spanish Government	14
Natural Environment Research Council (NERC)	12
Interreg Europe	11
European Commission Joint Research Centre	10
Swedish Research Council Formas	9
Research Council of Norway	8
European Union's Horizon 2020 Research and Innovation Programme	6
Research Council of Finland	6
Australian Research Council	5
Economic Social Research Council (ESRC)	5
Marie Curie Actions	5
National Natural Science Foundation of China (NSFC)	5
Azti	4
Cgiar	4
Engineering Physical Sciences Research Council (EPSRC)	4
European Union's Horizon 2020 Research and Innovation Program	4
Vapem Project Fisheries and Aquaculture Directorate of the Basque Government	4
Xunta de Galicia	4
Australian Government	3
Cesam	3

nals cover a wide range of fields, reflecting the interdisciplinary nature of blue growth research. "Frontiers in Marine Science" emerges as a prominent platform for blue growth discourse with 33 entries. This journal can be considered a primary outlet for researchers to disseminate their findings and insights within the marine science community. Similarly, "Marine Policy" stands out with 68 contributions and reveals its importance as an important publication in shaping policies and strategies regarding blue growth initiatives.

In Table 5, it is emphasized that the funding agencies of the articles are shown, with particular importance placed on the 90 supports from the European Union.

Table 5 presents the funding agencies that have supported research articles related to blue growth, along with the corresponding record counts for each agency. These funding bodies play a crucial role in promoting and advancing research efforts aimed at understanding and promoting sustainable ocean-based economies. The European Union (EU) emerges as a significant contributor, with various programs and initiatives such as "European Union's Horizon 2020 Research and Innovation Program" and "H2020 Societal Challenges Programme" collectively accounting for a substantial portion of the records, totaling 90. This underscores the EU's commitment to fostering innovation and addressing societal challenges, including those related to blue growth, across member states. Other notable funding agencies include national research council's such as the "National Natural Science Foundation of China (NSFC)" and the "Research Council of Norway," reflecting the global interest and investment in blue growth research and development. Additionally, the "Fundação para a Ciência e a Tecnologia (FCT)" in Portugal and "Swedish Research Council Formas" in Sweden have provided significant support, with 19 and 9 records respectively, indicating the commitment of these countries to advancing blue growth initiatives. Furthermore, regional entities such as the "Xunta de Galicia" in Spain and the "Vapem Project Fisheries and Aquaculture Directorate of the Basque Government" demonstrate localized efforts to promote sustainable practices within specific maritime regions.

Table 6. Web of Science Index of articles of blue growth

Web of Science Index	Record count
Science Citation Index Expanded (SCI-EXPANDED)	266
Social Sciences Citation Index (SSCI)	189
Emerging Sources Citation Index (ESCI)	56
Conference Proceedings Citation Index – Science (CPCI-S)	33
Conference Proceedings Citation Index – Social Science & Humanities (CPCI-SSH)	11
Book Citation Index – Social Sciences & Humanities (BKCI-SSH)	4
Book Citation Index – Science (BKCI-S)	3
Arts & Humanities Citation Index (A&HCI)	1

Table 6 shows the distribution of articles on blue growth in the Web of Science database according to different indices. These indexes serve as important tools for categorizing and indexing scientific publications, allowing researchers to access and evaluate the impact of research in various fields.

"Science Citation Index Expanded (SCI-EXPANDED)" emerges as the most prominent index with a remarkable record number of 266 articles. This index is widely recognized for covering a wide range of scientific disciplines and is an important resource for researchers seeking to access high-impact scientific literature on blue growth. The "Social Sciences Citation Index (SSCI)" follows closely with 189 records.

This index is effective in providing access to scientific literature in the social sciences, including fields such as economics, sociology and environmental studies, which are integral to understanding the socio-economic dimensions of blue growth. Additionally, the "Emerging Sources Citation Index (ESCI)" showcases 56 records and highlights the growing visibility and recognition of blue growth research within the academic community. ESCI serves as a platform for indexing high-quality, peer-reviewed journals that are in the process of being evaluated for inclusion in other citation indexes. Additionally, the table includes indices such as "Conference Proceedings Citation Index – Science (CPCI-S)" and "Conference Proceedings Citation Index – Social Sciences and Humanities (CPCI-SSH)", which indicate the existence of conference proceedings on blue growth. It is included in the Web of Science database.

DISCUSSIONS

The bibliometric analysis undertaken in this study provides useful insights into the current state of blue growth research. The analysis of publication trends, citation patterns, and keyword relationships provides a thorough insight into the growing discourse surrounding this crucial field of study. The popularity of phrases such as blue growth, blue economy, and sustainable development emphasizes the interdisciplinary nature of the study in this topic, which reflects the junction of environmental, economic, and social factors. Furthermore, an examination of country-specific contributions reveals a global dispersion of research activities, with Italy, Spain, England, and Germany appearing as important participants. This international collaboration demonstrates the broad interest and joint effort required to handle the challenges and opportunities afforded by blue growth. Furthermore, the presence of major phrases such as maritime/marine spatial planning, 'sustainability,' and 'ocean governance' emphasizes the diverse nature of blue growth research, which includes policy, governance, ecological sustainability, and socioeconomic factors.

Overall, the findings of this bibliometric analysis lay the groundwork for future research endeavors, assisting scholars, policymakers, and stakeholders in identifying topics for additional investigation and intervention. By encouraging collaboration, interdisciplinary methods, and knowledge exchange, we can effectively negotiate the complexity of blue growth and strive toward a sustainable and resilient future for our oceans and coastal communities.

CONCLUSION

In the context of blue growth, bibliometric analysis offers insightful information on the field's distribution of knowledge, trends, and patterns, which advances our understanding of ocean literacy. Bibliometric analysis presented here offers a comprehensive overview of the evolving landscape of blue growth research from 2007 to 2024. The study has illuminated key trends, thematic concentrations, and international collaborations within this interdisciplinary field, underscoring its critical importance at the nexus of environmental sustainability, economic development, and social equity. The analysis of publication types revealed a diverse array of scholarly contributions, from empirical research articles to comprehensive reviews and policy-oriented editorials, reflecting the multifaceted nature of scholarly engagement in blue growth. Notably, environmental science emerged as a dominant thematic focus, aligning closely with Sustainable Development Goals (SDGs) such as Life Below Water and Life on Land, highlighting the field's commitment to addressing global challenges through integrated approaches. Geographically, the study identified significant contributions from countries like Italy, Spain, England, and Germany, indicating robust international collaboration and knowledge exchange. This global dispersion underscores the shared responsibility and collective efforts required to advance sustainable practices in marine and coastal environments. Keyword analysis further delineated critical concepts such as blue economy, sustainable development, and ocean governance, signifying the thematic breadth and depth of blue growth research. These keywords serve as pivotal indicators of research priorities and emerging trends, guiding future investigations and policy interventions aimed at promoting ocean health and resilience. Moreover, institutional analysis pinpointed leading contributors such as the University of Exeter and CNR, illustrating their pivotal roles in shaping discourse and advancing knowledge within the field. Funding agencies, notably the European Union through programs like Horizon 2020, played a crucial role in supporting research initiatives, highlighting the importance of strategic investment in blue growth research and innovation. The study's findings underscore the interdisciplinary nature of blue growth research, emphasizing the interconnectedness of ecological, economic, and social dimensions. By fostering collaboration and leveraging diverse expertise, stakeholders can effectively navigate the complexities of blue growth, paving the way for sustainable development and resilient coastal communities.This bibliometric analysis not only provides valuable insights into current research trends but also informs strategic decision-making processes aimed at achieving a more sustainable and equitable future for marine ecosystems and human societies globally. Continued interdisciplinary engagement and knowledge exchange will be essential in addressing emerging challenges and seizing opportunities in the evolving field of blue growth.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Assessing the potential of rainwater harvesting and reuse for sustainable university campus

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ABSTRACT

Water resource management, one of the paradigms for creating sustainable universities, ensures that universities manage the quantity of water used and maintain the quality. Water resource management models that begin with campus priority create input for cities at a higher scale. Water resource management encompasses a variety of sustainable practices. One of the most applicable is the reuse of rainwater. The study aims to propose site-specific solutions for reusing harvested rainwater and contribute to nature and the water cycle. In the study, the Rational Method was used to calculate the amount of rainwater. Hardscape (roads, parking lots), landscaped areas (landscaped and wooded areas) and roofing materials within the campus were determined and the amount of rainwater was calculated for each material. In a year, the total water consumption was calculated at 54,773,000 liters. The valuable volume of annual rainwater is 296,400,000. It can be seen that a volume that is approximately 5 times the amount of water required is achieved.

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INTRODUCTION

Water, one of the essential natural resources, is indispensable for human civilization and life on Earth. Recently, the increase in human population and environmental degradation in many countries worldwide, especially in developing countries, have limited people's access to clean drinking water. As landscapes are transformed for agriculture, industry and urban development, many water sources are being altered or eliminated [1]. As a result, users have gradually become aware of the interrelationships and the extent of environmental changes and ecological services. The development of environmental science and policy also brought new developments, and from the 1980s onwards, the concept of sustainable development emerged.

It is emphasized that sustainable development, which is generally recognized, must be considered in its entirety with its environmental, economic and social dimensions. For environmental sustainability and sustainable development practices to be successful, they must also be integrated into education systems. Universities can serve as models in which sustainable management practices and technologies for cities are developed and tested [2–4]. To achieve environmental sustainability in universities, studies are being conducted in the areas of environment and infrastructure, energy and climate change, waste manage-

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ment, water use, transportation, education and research. Due to the water crises that have occurred and will occur in recent years, studies on water efficiency, rainwater harvesting, recycling and reuse of wastewater have begun to gain momentum. Higher education institutions have the potential to promote sustainable and integrated water management through education, research, services and business activities [5].

At this point, the current need to address water management on campus is highlighted by the United Nations, "2005- 2014: UN Decade of Education for Sustainable Development" and "International Decade for Action "Water for Life", 2005–2015" through the development of programs. Both programs were created to draw special attention to sustainability and water issues in higher education, which are seen as necessary for ensuring environmental sustainability. By linking them to social and economic considerations, students can adopt new behaviors to protect the world's natural resources, which are important for human development and survival. For this reason, it is emphasized that the protection and restoration of the Earth's ecosystems is an important task [6, 7]. As a result, the United Nations has declared 2018 to 2028 as the international decade of action, "Water Action Decade 2018–2028". The aim is to implement and promote the sustainable development and integrated management of water resources and to implement and promote relevant programs and projects to achieve social, economic and environmental goals. The focus is on promoting cooperation at all levels to achieve internationally agreed water-related goals and targets, including those in the 2030 Agenda for Sustainable Development [8].

United Nations by 2030; by halving the amount of untreated wastewater, improving water efficiency, including rainwater harvesting, wastewater treatment, recycling and reuse technologies, integrated water resources management, reducing pollution, significantly increasing recycling and restoring safety, it emphasizes improving water quality worldwide. As a result, the study presents research findings that support the articles of "Goal 6 Clean Water and Sanitation" and "Goal 11 Sustainable Cities and Communities" of the UN Sustainable Development Goals.

Urban transitions that provide benefits for climate mitigation, adaptation, human health and well-being, ecosystem services, and reducing the vulnerability of low-income communities are promoted through inclusive long-term planning that takes an integrated approach to physical, natural, and social infrastructure. Green/natural and blue infrastructure (such as rain gardens, dry wells, bioswales, infiltration basins) support carbon uptake and storage and, either individually or in combination with grey infrastructure, can reduce energy consumption and the risk of extreme events such as heat waves, floods, heavy rains and droughts, while providing co-benefits for health, well-being and livelihoods [9].

Significance

Water problems around the world are becoming visible through digital data. It is estimated that 3.5 billion people could be affected by water scarcity by 2025, while demand will increase by up to 30% by 2050. Unsustainable management and climate change severely threaten the world's water systems. The problem of climate change is worsening, and its consequences are leading to increased floods and droughts, changes in rainfall patterns and rising sea levels [10].

In these conditions where water is becoming increasingly scarce, securing water supply to avoid water scarcity becomes the primary concern of societies. Water scarcity generally refers to the demand and availability of freshwater in physical terms. Water security is defined as ensuring sustainable access to water in sufficient quantity and acceptable quality to protect against water-related pollution and water-related disasters and to ensure the continuity of the world's ecosystems while safeguarding livelihoods, human well-being and socio-economic development [11]. In addition to physical water scarcity, water security includes access to water services, protection from poor water quality and flooding, and appropriate water governance that ensures access to safe water [12]. Implementing the Sustainable Development Goals and climate-resilient strategies is crucial for water security. However, when implementing mitigation measures, care should be taken to ensure that the water footprint is not so large that it jeopardizes the Sustainable Development Goals and adaptation outcomes [13].

When estimating drinking water consumption for the future, it is assumed that Türkiye's population will reach 100 million in 2030. It is said that the amount of usable water per person, which is 1500 m^3 today, will be about 1100 m^3 / year in 2030. The annual drinking water demand, which was 5 billion m^3 in 2000, is estimated to reach 18 billion m^3 in 2030 [14]. The provision and protection of clean water for all should not only be accepted as a problem of developing countries but as a global priority, and sustainable water management practices should be introduced [12].

Rainwater is a resource that should be easy to collect on university campuses due to the large catchment areas and large impervious surfaces. If rainwater can be utilized, it will reduce the cost of stormwater management and alleviate the pressure of water scarcity through water conservation [15]. Based on these findings, the study's main objective is to re-evaluate rainwater, which is one of the most effective methods of water utilization, with proposed solutions on site and contributing to nature and the water cycle. Studies on rainwater harvesting usually only calculate the amount harvested from roof surfaces [16–19]. This study calculated the amount of rainwater harvested from hardscape, landscape and rooftop areas.

Rainwater Management

In historical management strategies, rainwater was often treated as a problem to be mitigated, a waste product to be eliminated or controlled [20]. Factors such as industrialization, migration and technological development are leading to increasing urbanisation. From a hydrological point of view, there are two important physical changes resulting from urbanisation. The first is the increasing proportion of impermeable surfaces such as roofs, roads,

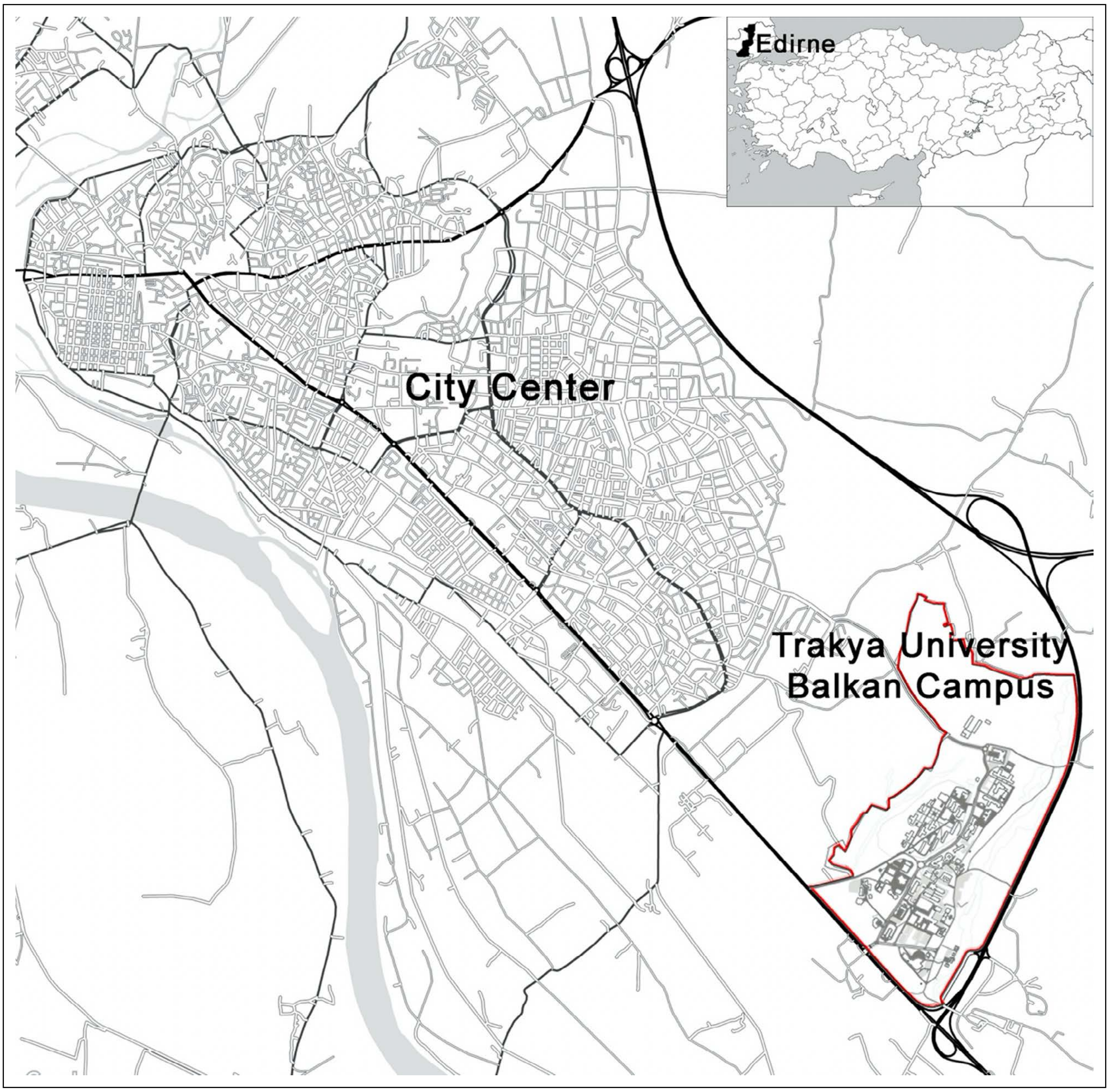

Figure 1. The study area location (Source(s): Created by authors).

parking lots and sidewalks. The second is the transformation of natural drainage systems into artificial transportation systems consisting of pipes and channels with a uniform slope [21].

The loss of vegetation cover and changes in surface properties such as roughness or permeability mean that precipitation is quickly converted into rainwater runoff. This leads to erosion, destroys habitat and deforms the natural channel [22–25]. In many cases, the volumes of rainwater after extremely intense, short periods of rain are too large for the drainage network to drain away. This leads to localised flooding and disruption to transport systems [26, 27].

Rainwater management, a distinction is made between traditional (convective) and sustainable methods [24, 28]. Traditional methods generally convey runoff from impervious surfaces to streams and rivers by the most direct and fastest route. Traditional methods refer to drainage systems consisting of devices such as downspouts, manholes, inlets, small gutters, street gutters, and curb inlets [29]. Sustainable practises follow a progressive hierarchy commonly known as the 'surface water management sequence', which consists of a series of measures to store, convey and minimise stormwater runoff and pollution [30].

MATERIALS AND METHODS

The Balkan campus of Trakya University was chosen as the study area. The campus is located at the coordinates 41°38'19.3"N and 26°36'58.1"E in the central district of the city of Edirne in Türkiye (Fig. 1). It covers an area of approximately 2,260 hectares.

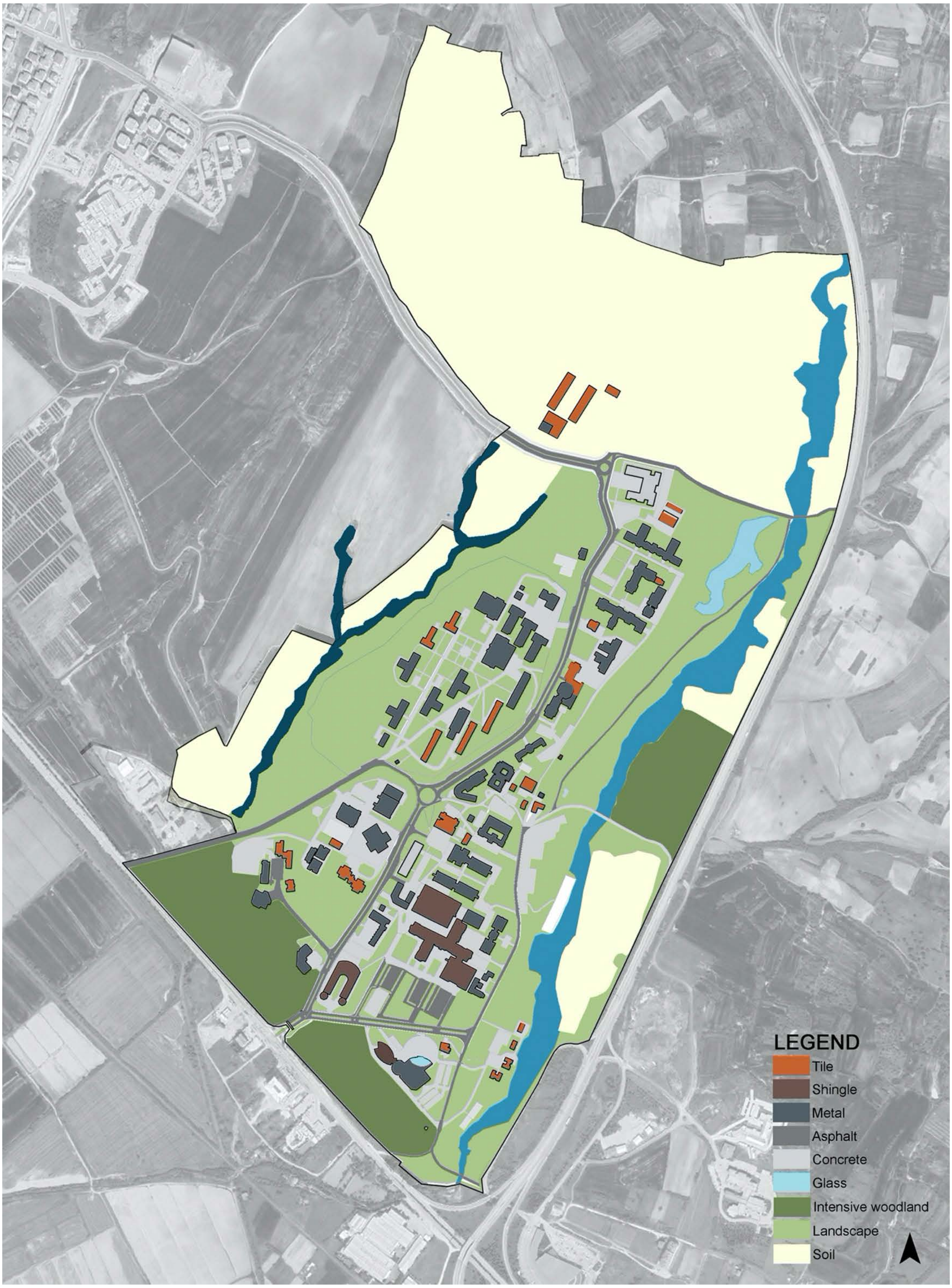

Figure 2. Material map within the campus (Source(s): Created by authors).

The campus includes buildings such as the rectorate, library, faculties, institutes, hospitals and dormitories. The campus is home to 24,000 students and 3,000 academic and administrative staff. There is also social housing on campus.

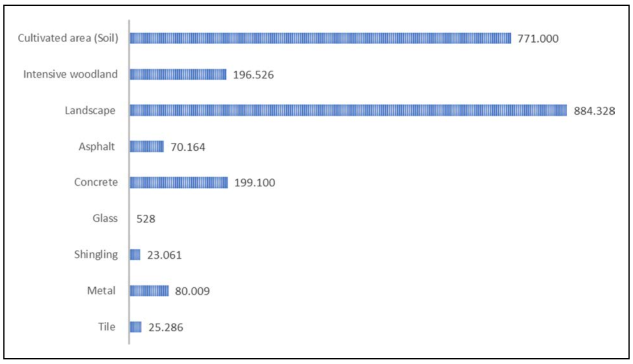

Figure 3. The collecting area in square meters (m^2).

Patients and visitors also actively use the medical school and dental hospital. There is no active water management program on campus. The municipal water supply is used within the building. Wells and the municipal water supply provide the water needed to irrigate the green areas. There are 15 wells in total, including nine active, three collapsed, and three construction wells.

The Rational Method was used to calculate the amount of rainwater on campus using equation (1) [31]. This method was developed in 1851 by Irish engineer Thomas Mulvaney and was widely used in the United States by Emil Kuichling. It was developed to predict peak rainfall runoff rates in impermeable urban areas. This method is still used today to calculate surface water runoff [20]. The Rational Method gives good results up to 1-1.5 km^2 and can be used in catchment areas up to 5 km^2 [32, 33]. Since the study area is approximately 2.3 km^2, the Rational Method was chosen.

$$V = \text{Sum}\ (R*A*RC/1000) \quad (1)$$

V: The rainwater yield in m^3 per year

R: The quantity of precipitation in liters per square millimetre (mm)

A: The collecting area in square meters (m^2)

RC: The efficiency coefficient in %

One thousand stands for the conversion factor from mm to m. Regularly maintained filter systems usually achieve a hydraulic efficiency of 0.9. Therefore, the total water volume is multiplied by the coefficient of 0.9 [34].

RESULTS AND DISCUSSION

According to the "Köppen Climate Classification", Edirne is classified as a "Csa climate with warm winters, very hot and dry summers (Mediterranean climate)". Summer temperatures are above 22°C [35]. According to measurements taken between 1930–2021, the average annual temperature in Edirne province is 13.7°C and the average annual rainfall is 604.4 mm [36].

The materials on the campus were determined by overlaying on-site observations, measurements and Google Earth maps. A digital map was created showing the area covered by each material: tile, metal, shingle, glass, concrete, asphalt, landscape, intensive woodland, and cultivated area (soil) (Fig. 2).

Table 1. The efficiency coefficient

Material	The yield coefficient	References
Tile	Worn old: 0,75	[37]
	Unworn old: 0,80	[37]
	New: 0,90	[37]
Metal	Wavy old: 0,70	[37, 38]
	Unwavy old: 0,75	[37, 38]
	Wavy new: 0,85	[37, 38]
	Unwavy new: 0,90	[37, 38]
Shingle	Worn old: 0,70	[39]
	Unworn old: 0,75	[39]
	New: 0,80	[39]
Glass	0,90	[39]
Concrete	0,60-0,80	[37]
Asphalt	0,80	[34]
Landscape	0,05-0,10	[40]
Intensive woodland	0,10	[40]
Cultivated area	Plane: Sandy-loamy: 0,30	[32]
	Clayey-silty-loamy: 0,50	[32]
	Clayey: 0,60	[32]
	Undulating: Sandy-loamy: 0,50	[32]
	Clayey-silty-loamy: 0,60	[32]
	Clayey: 0,70	[32]
	Sloping: Sandy-loamy: 0,52	[32]
	Clayey-silty-loamy: 0,72	[32]
	Clayey: 0,82	[32]

The collection areas within the campus, which are square meters in material type, are shown in Figure 3. The respective area was calculated using the material map.

All of the yield coefficients are shown in Table 1. The accepted yield coefficients are tile (0.8), metal (0.75), shingle (0.75), glass (0.9), concrete (0.7), asphalt (0.8), landscape (0.05), intensive woodland (0.1) and cultivated area (soil) (0.72).

Using Equation 1, the total amount of rainwater harvested on the Balkan Campus of Trakya University was calculated as 494,000 m^3/year (Table 2).

The useful volume of all rainwater is based on the following equation (2) [34];

$$Vn = \text{Minimum of}\ (BWa\ \text{or}\ ER) \times 0.06 \quad (2)$$

With the following meanings here:

Vn Useful volume

BWa Annual process water requirements

ER Rainwater yield in liters per year (l/a)

Table 2. Calculation for Determining the Rainwater Yield, Reuse, and Useful Volume of Rainwater Reservoirs (The authors edited it from [34])

Rainwater yield				Annual quantity of precipitation					
Collection Area A [m²]		Yield Coefficient e		A_{eff} [m²]		Precipitation Quantity h [mm/m²]		Hydrl. Filter Efficiency	
Tile	25.286	x	0,8	=	20.228	604.4		e.g. 0.9	
Metal	80.009	x	0,75	=	60.000				
Shingle	23.061	x	0,75	=	17.295				
Glass	528	x	0,9	=	475				
Concrete	199.100	x	0,7	=	139.300				
Asphalt	70.164	x	0,8	=	56.131				
Landscape	884.328	x	0,05	=	44.216				
Intensive woodland	196.526	x	0,1	=	19.652				
Cultivated area	771.000	x	0,72	=	555.120				
				∑	912.491	x	604.4	x	0.9
				Annual rainwater yield in 1				=	494.000
Process water requirements									
Drainage object		Process water requirements in m³ per day and pers.		Number of persons		Period of time in days per year		Process water requirements in m³ per year	
Toilet			0,009			Year			
		∑	0,009	x	27.000	x	1	= (1)	243
Garden watering		Garden size in m²							
		∑	884.328					= (2)	54.530
Process water requirements ∑ (1) + (2) in m³ per year =									54.773
Process water requirements ∑ (1) + (2) in lt per year =									54.773.000
Useful volume of the rainwater reservoir									
6 % of the annual process water requirements or annual rainwater yield									
Useful volume in liters =		494.000.000		[l/a] x 0,06				= 296.400.000	

As a result of this study, the rainwater harvested on the Balkan campus of Trakya University will be reused for irrigation in reservoirs and green areas. The average volume of the reservoir is calculated at 9 liters. It is estimated that an average of 243,000 liters of water is needed per year. The amount of water required to irrigate the green areas is considered the total water requirement of the plants on campus. The amount of water required to irrigate the plants annually is 54,530,000 liters. Total water expense was calculated as 54,773,000 liters.

According to equation (2), 296,400,000 liters were calculated as the valuable volume of the annual harvested rainwater volume. It can be seen that a volume that is approximately 5 times the amount of water required is achieved. Proper storage areas are required to reuse the rainwater collected across the campus effectively. A hydrological map was created to determine the location of the storage tanks. It was created by determining the flow directions of the rainwater by the area curves after determining the 5 m curves and the hydrological networks in the area using the ArcMAP program. Due to the size of the area and the different water flow directions, the campus was divided into zones. The water flow directions, the main roads and the buildings on the campus were used to determine these regions. Suggestions were made for the location of the tank in each region (Fig. 4).

After storing rainwater in tanks, various sustainable solutions can be offered in place of residual rainwater or storage. One of these is the rain garden. In this context, a suggestion for a rain garden on campus was developed (Fig. 5). It is located on Prof. Dr. Cahit Arf Boulevard. On the boulevard there is a road for vehicles, a cycle path, a pedestrian path, a green area and a passageway for pedestrians with wheelchairs. The existing road and cycle path have been retained. A green area is planned adjacent to the cycle path. The green area here is specifically designed as a rain garden. The plants used in the proposed rain garden areas are compatible with natural vegetation. Plants that have a high tolerance to factors such as frost, temperature and drought and that do not require chemicals were preferred. In addition, plants with specific water requirements were selected for the three levels of water demand - high, medium and low - in the rain gardens. Next, the pedestrian path was designed and seating was installed. To provide continuity between the walkway and the street, wrought iron grates were placed on the rain gardens to create a transition [37–40].

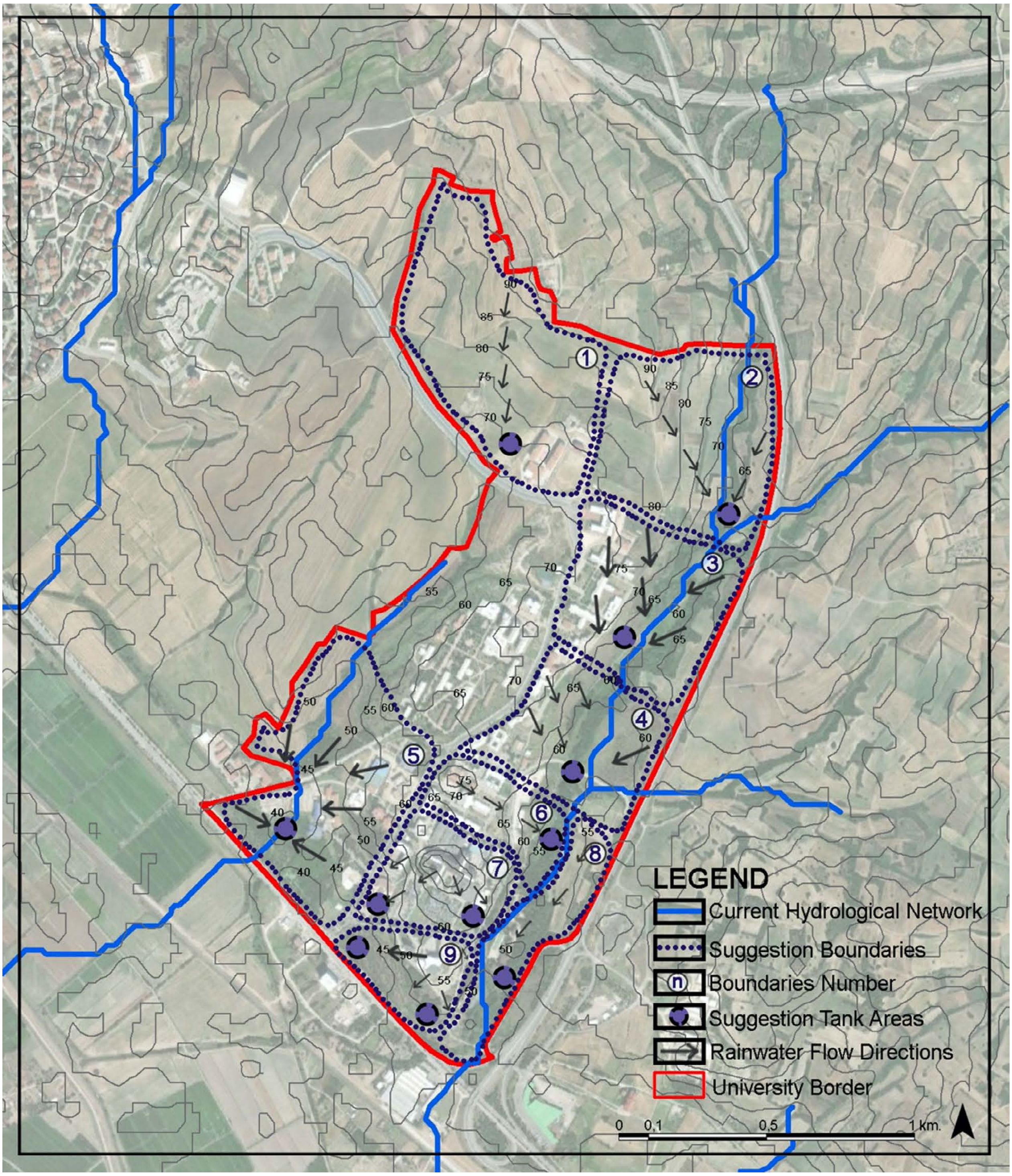

Figure 4. Suggestion tank areas (Source(s): Created by authors).

CONCLUSION

Since most of the water consumed in cities cannot be safely returned to nature, underground and surface water resources are diminishing. The benefits of the water reuse strategy include cost savings, protection of groundwater resources, reduction of natural water abstraction and long-term water supply [41–44]. Due to its species-specific properties, reclaimed water can be used to irrigate urban and residential landscapes, for industrial purposes, for the water needs of air conditioning systems and as a backup source for fire protection [45]. Rainwater makes up a significant portion of the water used to meet irrigation needs, reducing the amount of rainwater that cannot be controlled on-site [46, 47]. Irrigation of urban landscapes with recycled water has become one of the practices that can significantly contribute to the sustainability of existing urban water resources and urban green spaces [48, 49]. Depending on the

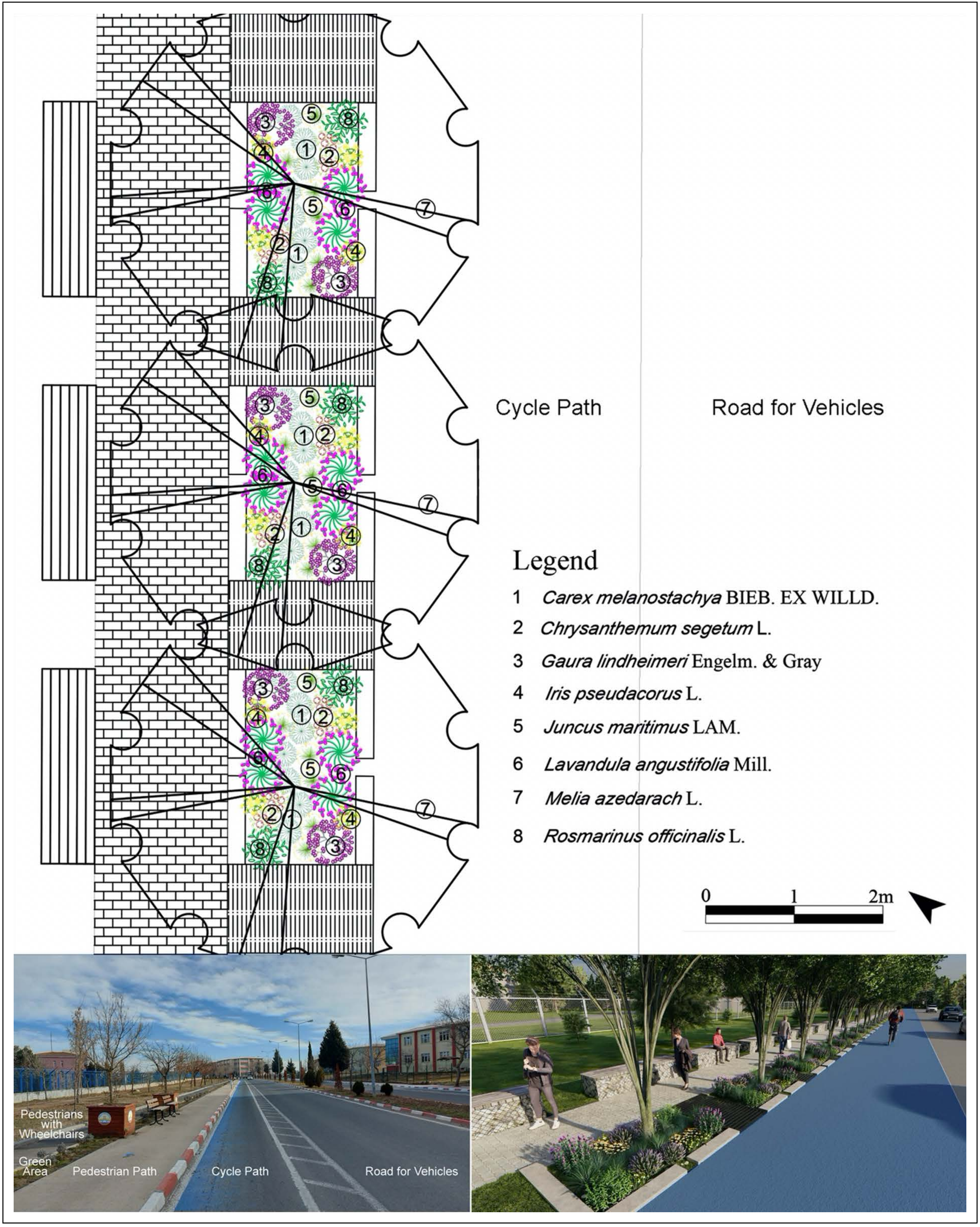

Figure 5. Suggestion for a rain garden (Source(s): Created by authors).

morphological and physiological structure of the plant, the amount of water it consumes and the amount of irrigation water that needs to be supplied to the plant will vary. Since the amount of water consumed by each plant is different, the water consumption of plants must be determined [50]. To create a healthy landscape with recycled water, several factors must be considered, including local climatic conditions, plant and soil characteristics, water quality depending on the sensitivity of plant species, and soil texture and drainage [51].

For water to be used for irrigation, policymakers need to make and implement decisions on water harvesting. In the “Regulation Amending the Planned Areas Zoning Regulation” published by T.C. Ministry of Environment, Urbanization and Climate Change in the Official Gazette No. 31538 in 2021, Article 5, Paragraph a states: “The mechanical installation projects of buildings to be built on plots larger than 2000 m^2 must include a rainwater collection system to collect rainwater to be collected from the roof surface, if necessary filtered and collected in a tank and used to flush the building's toilets. ... The part of the collected rainwater that exceeds the needs of the building's toilets can be used in the garden or other common areas by indicating it in the installation project...”. The implementation of these practices through the creation of legal infrastructures increases the contribution to the water cycle. It should be ensured that the practices started on a small scale are made widespread in public areas or in areas that can serve as an example to society, such as universities.

In this study, the Balkan campus of Trakya University was chosen as the study area because it is the size of the city and university campuses are a prototype of cities. The study evaluated the potential amount of rainwater that could be harvested on the campus. Three different results were obtained from the study. The amount of rainwater that could be captured by different materials on campus and the amount of this water that would meet the needs of the reservoir and irrigation of plants were determined. It turns out that the amount obtained is about five times the amount of water needed. It is also possible to create solutions such as rain gardens that are sustainable and functional while improving visual quality.

This study aims to show that it is possible to harvest water from roofs, but also from other hardscapes and green areas. Most studies in the literature, such as the examples of Karadeniz Technical, Ege, Sinop, Bursa Uludağ Universities, focus only on roof areas. [16-19]. This has the disadvantage that the water potential to be collected is reduced in these studies. In the application phase, the collection of roof surfaces can be started as this is the easiest surface to harvest. For areas such as roads or parking lots, a system should be set up by creating drainage channels. You should bear in mind that the costs will increase in the first phase. It should also be considered that there are applications throughout the campus, such as Istanbul Technical University Ayazağa campus [52]. Studies were conducted on the campus where permeable surfaces were created, water was harvested and channeled.

If these applications are realised, we can foresee that TL 1,230,000 will be paid for 54,773 m^3 of water consumption at a price of TL 22.5[1] per unit/m^3. The profit to be realised will represent a significant share for the public institutions. As a result of these measures, the reuse of rainwater reduces the reliance on groundwater resources and municipal water supplies. In addition, rainwater that enters rivers without being considered surface water or that causes flooding in cities is eliminated on site and effective water use is ensured.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Impact of temperature on ferric chloride performance in water coagulation

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ABSTRACT

Temperature has an essential function and becomes an important parameter in a coagulation process as it influences metal ion hydrolysis reaction rate. In order to get further explanation, a research using ferric chloride as a coagulant has been performed. The research aims to find out more about the effect of temperature on coagulation performance using turbidity, floc size, ferric, and water content parameter. The temperature 5□–45□ with an interval of 5°C has been investigated to simulate field (i.e. outside) measurements in winter, spring and autumn, and summer, respectively. The result shows coagulation performance isaffected by temperature elevation. Turbidity gets lower for temperature between 5□–40□ and gets higher for temperature 45□. Floc size becomes larger for temperature 5□–40□ and becomes smaller as temperature increase.At temperature between 5□ and 15□, the higher the temperature, the lower the ferric residue produced in coagulation water. For floc water contents, there is no virtually link between temperature and floc water contents. Temperature correlated well with turbidity value (-0.876) and floc size (0.985) but not correlated with ferric residue (0.366) and floc water content (0.179).

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INTRODUCTION

Coagulation is one of physicochemical processes that produce contaminants or particles agglomeration [1-3], where the agglomeration is essential to produce a larger size of floc. Larger and denser floc is preferred as it will settle more easily [4] and dewater more readily [5–7] which is effective to reduce turbidity and floc water contents, floc structure and its physical characteristics (size and density).

Amongst other parameters in coagulation, temperature is a key factor as it highly affects the metal ion hydrolysis reaction rate [8–10]. When the temperature increases, it will increase the reaction rate and vice versa [11]. In addition, the temperature also determines the distribution of coagulant [8] and the formation of the hydrolysis products, which, in turn, affects the coagulation and flocculation efficiency [12].

Ferric is one of common used metal coagulant amongst many synthetic coagulants [13] and has good coagulant properties [14]. Experimental research about temperature effects on the use of Fe coagulants for water and sludge treatment have been conducted [8, 10, 15–17]. Low water temperature causes poor coagulation due to inhomogeneous distribution of coagulation species as an impact of poor reaction rate. Ferric has a better performance than alum does under low temperature conditions [8]. In addition, [17] stated that low water temperature has an important effect on flocculation kinetics by decreasing the minimum solubility of $Fe(OH)_3$ in water. A higher temperature and pH play a significant role on an acceleration of the Fe (III) salt hydrolysis rate and a decrease on soluble polymeric iron species formation time [15, 16].

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On contrary, some of the findings indicated that temperature does not have an impact on coagulation efficiency [18, 19]. Moreover, another finding stated that temperature under 26 did not affect $Fe(OH)_3$ performance on sludge dewaterability as a result of sludge coagulation [10] because as temperature raises, it will inhibit the formation of iron salts due to reducing the amount of soluble oxygen.

Previous investigation mostly used low temperature in their investigation and due to contrary in previous investigation, further explanation is still needed to explain about the effect of temperature on ferric performance. This research investigates more the impact of temperature on ferric coagulant performance on important coagulation parameters such as turbidity removal, floc size, residual ferric and floc water content. This research study the effect of temperature on ferric performance simultaneously with wider range temperature. Temperature ranges from 5°C to 45°C has been used in this investigation. Temperatures of 5°C and 45°C used to simulate field (i.e. outside) measurements in winter, spring and autumn, and summer, respectively. The highest temperature may also reflect operating temperatures in laboratories located in warmer countries. All target temperatures were obtained by adjusting the temperature in the laboratory. By providing further information about the effect of temperature on ferric performance, it is hoped that the use of ferric can be more effective according to temperature setting in the coagulation process.

MATERIALS AND METHODS

Materials

Water sample was taken from The Intake of Water Treatment Plant in Siteba, Padang-West Sumatra, Indonesia. All samples were stored in plastic carboys and were kept in a refrigerator at 5°C before use. For Ferric chloride coagulant stock solution, it was prepared by adding 10 g ferric chloride powder into 1 L distilled water and stirred well to produce ferric solution.

Temperature Preparation

Wide temperature ranges from 5°C to 45°C has been used to simulate field (i.e. outside) measurements in winter, spring and autumn, and summer, respectively. All target temperatures were obtained by adjusting the temperature in the laboratory. Water temperature was set between 5°C and 45°C and was applied with an interval of 5°C using control temperature equipment to set temperature.

Coagulation Procedure

A 500 ml water sample was poured into a glass beaker followed by adding the coagulant Ferric Chloride (Sigma Aldrich Company Ltd., England, UK). Optimum coagulant dose was used. In order to reach a pH value of approximately 6.5, adjustment was with sulphuric acid (H2SO4) or sodium hydroxide (NaOH). The fluid was then mixed rapidly using a conventional jartest (Jartest JLTG VGLP, Velp Scientifica, Italy) at a variable high rate of 100 rpm for 60 seconds and then at a moderate rate of 40 rpm for 30 minutes to accommodate the agglomeration process. Floc or sediment was allowed to settle for 15 minutes.

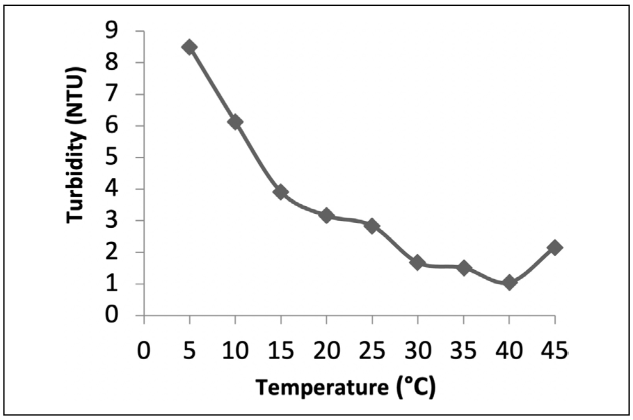

Figure 1. Correlation between temperature and turbidity using coagulant ferric chloride.

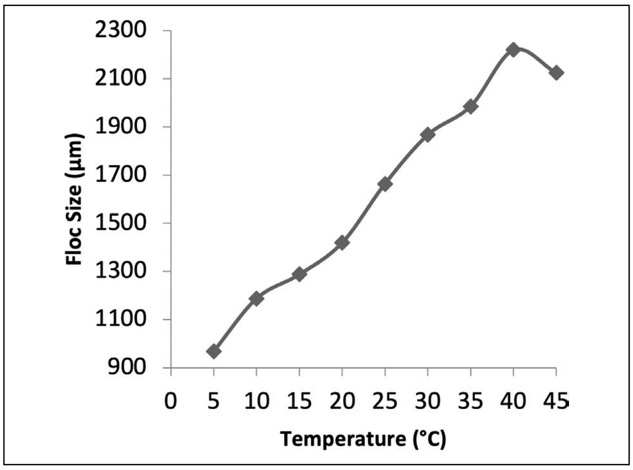

Figure 2. Correlation between temperature and floc size using coagulant ferric chloride.

Analytic Methods

Decanting process method was used to separate the supernatant and floc. This supernatant was used to measure water turbidity using Spectrophotometer UV Vis (Shimadzu, Japan) and ferric residue using Atomic Absorbance Spectrophotometer (Rayleigh WFX – 310/320, China). The settled floc in the bottom of a glass beaker was used to measure floc size using Shimadzu Optical Microscope and water floccontent using DTG (Shimadzu DTG-60, Japan).

RESULTS AND DISCUSSIONS

The Impact of Temperature on Turbidity

This research assessed the influence of different temperatures on coagulation performance by using ferric chloride as a coagulant. In the first stage, the effect of different temperatures on turbidity has been assessed. The impact of temperature between 5°C to 45°C with 5°C interval were compared each others. The result is presented in Figure 1.

Figure 1 shows the response of turbidity value to variations of temperature. The figure shows the turbidity value is getting lower as temperature increases at a temperature between 5°C and 40°C and is getting higher as temperature increases to 45°C.

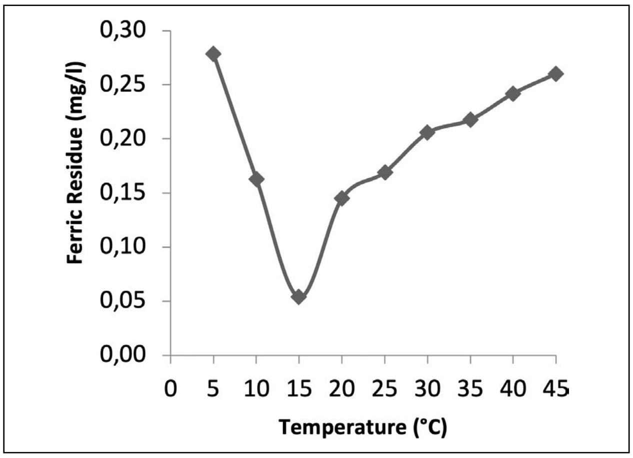

Figure 3. Correlation between temperature and ferric residue in water.

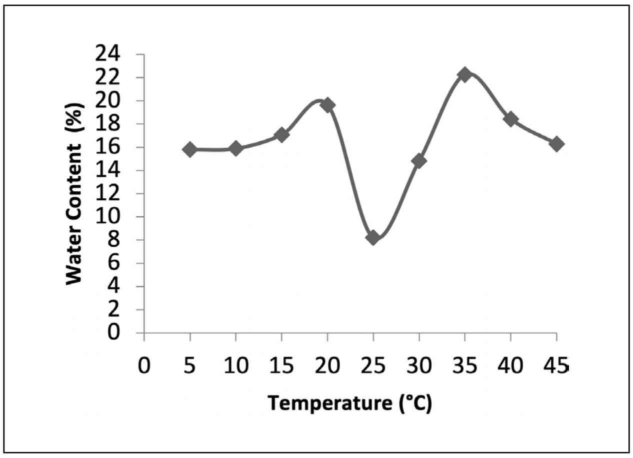

Figure 4. Correlation between temperature and floc water content using coagulant ferric chloride.

At a temperature between 5°C to 40°C, the result shows the higher temperature, the higher ferric ability to remove turbidity in water. Turbidity value at a temperature of 45°C gets higher than that at a temperature of 40°C which indicates a temperature of 40°C as the optimum temperature on turbidity removal using coagulant ferric chloride. Turbidity value in the water gets higher after the optimum temperature has exceeded. The addition of coagulant must be in accordance with the needs in forming flocs, because the concentration of coagulant greatly affects the collision of particles [1]. Flocs will be difficult to form if the addition of coagulant concentration is lacking, likewise the addition of too much coagulant can cause turbidity to occur again and the flocs are not formed properly

Figure 1 indicates that temperature plays an important role in turbidity removal. This result is similar to [8] results where temperature highly affected coagulation efficiency; different temperature delivers different impact. [15, 16] and [20] stated that increasing temperature can accelerate the Fe (III) salt hydrolysis rate and decrease soluble polymeric iron species formation time. Enough Fe (III) salt in solution will produce enough contact between salt and colloid then adsorb the colloid particles onto its surface and destabilize the otherwise stable colloid charge [21, 22] so that the turbidity will be removed efficiently.

Impact of Temperature on Floc Size

Coagulation efficiency and turbidity removal are correlated with floc size. Floc size investigation also has been examined to investigate the temperature's effect on floc formation. Using ferric chloride as a coagulant, a temperature between 5°C and 45°C was set to analyze the correlation between temperature and floc size (Fig. 2).

At a temperature between 5°C and 40°C, as the temperature increases, floc size gets larger but when temperature rises to 45□, floc size getting smaller. For temperature lower than 40□, the higher temperature, the larger floc size produced by ferric chloride in coagulation process. It is likely that the temperature's increase from 5□ to 40□ supports the agglomeration of colloid to perform larger ferric chloride floc size. This result related to [18] investigation, it is due to at the lower temperature, the floc will less compact compare to floc produced by higher temperature. Furthermore, coagulation mechanisms strongly influence floc size [12, 23]. As one of the factors that determines coagulation mechanisms, [8, 12] stated that temperature influences the distribution of the coagulant, hydrodynamic process and the formation of the hydrolysis products, which affect both coagulation and flocculation efficiency to form floc.

Impact of Temperature on Ferric Residue in Water

Coagulant residue in the water after process determines the coagulation performance [1]. To investigate furthermore the impact of temperature on ferric performance as a coagulant, this research has examined the investigation to observe the effect of temperature variations on ferric residue in water after coagulation process (Fig. 3).

Figure 3 shows that at a temperature between 5°C and 15 °C, the higher the temperature, the lower the ferric residue produced in coagulation water. On contrary, at a temperature between 15°C and 45°C, the higher the temperature, the higher the residual ferric produced in coagulation water. For temperatures under 15°C, the mechanisms can be explained by the result of [15] and [16] which stated that increasing the temperature and pH can accelerate the Fe (III) salt hydrolysis rate and decreases soluble polymeric iron species formation time. In contrary, for temperature above 15°C, the increasing temperature increase ferric oxidation rate and cause higher ferric concentration in water [24].

Impact of Temperature on Floc Water Content

Floc water content has a correlation with coagulation performance, the lower water content in floc will have the better coagulation process [25] confirmed sufficient coagulation condition is needed to enable a floc formation to separate and dehydrate easily. The observation of floc water content and its correlation with temperature has been performed using DTG apparatus and temperature between 5°C and 45°C. Figure 4 shows temperature variations affect on floc water contents.

Table 1. Correlation between temperature with turbidity, floc size, residual ferric and floc water contents

Variables	R
Turbidity	-0.876
Floc size	0.985
Ferric residue	0.366
Water content	0.179

Figure 4 inform that there is no correlation between temperature and floc water content using ferric chloride coagulant. Floc water contents increases as temperature decreases at temperature between 5°C and 20°C. As temperature increases to 25°C, the floc water content is getting lower. Temperature of 25°C is the best in this investigation as it produces the lowest floc water contents. Floc water contents get higher when temperature increases between 30°C and 35°C, then get lower at temperature between 40°C and 45°C.

Floc water contents is depended on the ability of floc to release the water (water dewaterability). The easier the floc to release the water, the lower the amount of water in floc and vice versa. The harder the floc to release the water, will be the higher the water contents in floc. As one of the important factor in coagulation process, the effect of temperature on sludge dewaterability have been investigated inconsistent on sludge dewaterability [10]. Floc physichochemical properties such as desorptivity, particle size composition and chemical constituent which is associated with flocculation efficiency, moderated the effect of temperature [25].

Correlation between Temperature with Turbidity, Floc Size, Residual Ferric and Floc Water Contents

Table 1 shows the correlation (r) between temperatures with coagulation variables in this study. The result shows that temperature has the strongest correlation with floc size (0.985), followed by turbidity (-0.876), ferric residue (0.366) and floc water contents (0.179).

From the correlation values of each variable, it is known that floc size is related to turbidity removal, where floc size determines the removal of water turbidity. The bigger of the floc size, the higher of turbidity removal. This is similar to the statement of [4] where the larger floc size reduces the turbidity better, because of its ability to settle easier, than the smaller floc size does.

Residual ferric does not correlated well with increasing temperature. This is due to temperature raise will reduced the amount of soluble oxygen and inhibits formation of iron salt [26]. As well as residual ferric, floc water contents does not correlated either with variation of temperature. This result confirms a statement from previous investigation where temperature does not have any impact on sludge dewaterability of coagulation floc using coagulant ferric [10] because temperature raises will eliminate the ability of coagulant ferric on sludge and floc formation due to the limit in formation of iron salt in responding temperature increases.

CONCLUSION

Temperature is one of the most important elements in coagulation process. To investigate the effect of temperature on Ferric Chloride performance, four parameters used in the investigation; turbidity value, floc size, residual ferric and floc water contents. Different temperatures result in different values on the four parameters. Turbidity value and floc size correlate well with temperature but not ferric residue and floc water contents. Among those four parameters, floc size has the strongest correlation with temperature which means the temperature variations influence the floc size more than turbidity value, residual ferric and floc water contents.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Sustainable airline company selection using SWARA Weighted VIKOR and COPRAS methods

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ABSTRACT

Global climate crisis necessitates all countries to swiftly and agilely conduct their economic activities in accordance with green sensitivity and sustainability principles. The aviation sector, one of the industries most affected by socio-economic and socio-cultural changes worldwide, cannot avoid this trend. Consequently, significant studies exist in the literature on the effects of the global climate crisis and sustainability efforts in the aviation sector. This study aims to measure the approaches of the world's leading international air cargo companies to the 2030 and 2050 European Green Deal targets. Among the criteria weighted using the SWARA method are 'carbon dioxide emissions,' 'energy consumption,' 'employment,' and 'water consumption.' The results indicate that the most critical criterion for airline sustainability is reducing CO_2 emissions, followed by reducing energy consumption. Water consumption reduction ranks third, and employment ranks last in terms of importance. The study examines air cargo companies ranked in the top 10 globally by revenue and ranks them using the VIKOR and COPRAS methods. According to data from 2021, Korean Air, Turkish Airlines, and Cathay Pacific emerge as the top performers in sustainability among air cargo companies, while Cargolux and UPS lag behind others in their sustainability efforts when evaluated using VIKOR and COPRAS methods.

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INTRODUCTION

In recent years, sustainability has become a widely discussed and examined topic both for individuals and businesses. Sustainability in supply chain management involves managing materials, information, and capital across the chain and fostering collaboration among businesses within the chain. It also aims to set goals for and achieve sustainable development in three dimensions defined by stakeholders and customer expectations [1].

The concept of sustainability fundamentally includes preserving today's conditions and ensuring equal opportunities for all individuals in society to meet their rights and needs, as well as providing equal conditions for future generations [2]. According to the definition by the World Commission on Environment and Development, sustainability means meeting the needs of current generations without compromising the ability of future generations to meet their own needs [3]. Sustainability comprises three components: society, environment, and economy [4]. For

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social sustainability, governments need to implement equitable policies in education, health, security, transportation, etc. Issues such as air quality, waste management, noise, biodiversity conservation, and water resource conservation are examined to ensure environmental sustainability. Economic sustainability, on the other hand, requires studies supporting issues such as employment, economic growth, productivity, and efficiency. Enhancing environmental sustainability and raising awareness among all stakeholders are crucial for businesses operating in logistics, particularly in minimizing environmental damage in transportation. To achieve sustainability in aviation transportation, measures such as using Sustainable Aviation Fuels (SAF) derived from renewable or recyclable waste as alternatives to fossil fuels are taken to reduce carbon emissions, energy consumption, and water use. Without the participation of airports in the process, achieving sustainability in aviation is not possible, hence airports are recognized as 'green airports' aiming to reduce environmental pollution arising from their operations by fulfilling international criteria. Aviation transportation is particularly susceptible to both local and global fluctuations, leading airlines to adjust flight frequencies and schedules accordingly. Consequently, shifts in airlines' employment policies often culminate in workforce reductions.

Every decision leading to employment shortages globally creates serious problems. Problems arising in a strategic field such as aviation can pose greater risks for countries. Due to the significant impact of external environmental factors on aviation transportation levels, sustainability efforts have become mandatory for airline companies. This phenomenon can create negative impacts not only on job loss issues but also on many stakeholders in the aviation transportation sector. Sustainability efforts not only evaluate whether airline companies can survive from a management perspective but also assess them from perspectives of environmental protection, combating climate change, and green management.

In this study, the increasingly important concept of sustainability has been evaluated from the perspective of the strategic sector of aviation transportation. Prominent global airline cargo companies have been ranked in terms of sustainability using SWARA-weighted VIKOR and COPRAS analyses. Through these analyses, the top 10 airline cargo transportation companies worldwide have been subjected to performance evaluation within the context of the European Green Deal objectives. Thus, the sustainability levels of globally renowned airline companies and areas requiring sustainability improvements have been identified. In this context, the necessary criteria for sustainable and green airlines have been determined through a literature review. These criteria include carbon dioxide emissions, water consumption, employment, and energy consumption. The importance levels of these criteria were determined based on the opinions of 4 experts. Following the determination of criterion weights (importance levels), 10 airline companies were evaluated using VIKOR and COPRAS methods. The results can provide information to the sector and policymakers about the status of aviation transportation. The findings demonstrate how airline companies perform in critical areas such as carbon emissions, water consumption, employment policies, and energy use. This assessment serves as an important starting point for identifying improvement areas in the sector and encouraging sustainability efforts.

Furthermore, future studies should conduct more comprehensive assessments from a sustainability management perspective to examine how aviation transportation can contribute to achieving long-term sustainability goals. Research in this direction can play a critical role in strengthening the sustainability strategies of airline companies and aligning with global environmental targets.

LITERATURE RESEARCH ON SUSTAINABILITY, GREEN LOGISTICS AND AIRLINE COMPANY SELECTION

Researchers have been working on green activities and sustainability for many years. Table 1 presents the literature review conducted between 2015–2024 and current studies on sustainability, green logistics, and airline company selection. Among these studies, especially the studies in which analyses were made using multi-criteria decision methods were discussed.

When examining Table 1, numerous studies focusing on green logistics, sustainability in transportation, and sustainable firm selection using multi-criteria decision-making methods are observed in the literature. Additionally, studies evaluating global airline companies from a sustainability perspective are also documented. However, no study applying the SWARA-VIKOR-COPRAS model has been encountered. This highlights the contribution of the current study in filling this gap in the literature. The insights generated by this model's results can offer notable predictions when compared with findings from different models.

MATERIALS AND METHODS

In this study on Sustainable Airline Selection, the top 10 global air cargo companies were selected as the sample, aiming to identify the sustainable companies among them. The WATS+ 2021 report was used as a source for selecting the companies in question. Initially, a literature review was conducted to determine the criteria for a sustainable airline company. Aracı and Yüksel [20] calculated the sustainable added value in their study, aiming to consider all the social and environmental resources that a business uses and affects. Due to the scarcity of data published by companies in their sustainability reports, the CO_2 (greenhouse gas) emissions, energy use, water use, and the number of employees of the companies included in the sample were taken as sources, and calculations were made based on these criteria. In this study, the criteria required for the analysis are discussed through the sources used by Aracı and Yüksel [20] in their research. After defining the research problem, a method search was conducted to solve this problem, and it was determined that the SWARA-weighted VIKOR and COPRAS methods, which are multi-criteria decision-making methods, were appropriate.

Table 1. Studies on sustainability, green logistics, airline company selection (2015–2024)

Author	Year	Title of the study	Subject of study	Analysis methods used
Sijin Wu, Marios Dominikos Kremantzi, Umair Tanveer, Shamaila Ishaq, Xianghan O'Dea, Hua Jin [5]	2024	Performance evaluation of the global airline industry under the impact of the COVID-19 pandemic: A dynamic network data envelopment analysis approach	The impact of the COVID-19 pandemic on the airline industry and analysis of the efficiency performance of international airline companies during this period	Dynamic DEA model
Gökhan Tanrıverdi, Rico Merkert, Çağlar Karamaşa, Veysi Asker [6]	2023	Using multi-criteria performance measurement models to evaluate the financial, operational and environmental sustainability of airlines	Examining the impact of the COVID-19 crisis on airline sustainability performance.	MEREC–CoCoSo/ Borda
Sukran Seker [7]	2024	Evaluation of agile attributes for low-cost carriers to achieve sustainable development using an integrated MCDM approach	Evaluating agile attributes for managing the operations of low-cost carriers (LCCs) in Türkiye	SWARA and MABAC
Thanh-Tuan Dang, Ngoc-Ai-Thy Nguyen, Van Thanh-Tien Nguyen and Le-Thanh-Hieu Dang [8]	2022	A Two-Stage Multi-Criteria Supplier Selection Model for Sustainable Automotive Supply Chain under Uncertainty	Selecting and evaluating a potential supplier based on their ability to adapt sustainably to the COVID-19 pandemic	SF-AHP, G-COPRAS
Kumari and Mishra [9]	2020	Multi-Criteria COPRAS Method Based On Parametric Measures For Intuitionistic Fuzzy Sets: Application Of Green Supplier Selection	Green supplier selection problem.	COPRAS
Kaya and Erginel [10]	2020	Futuristic Airport: A Sustainable Airport Design By Integrating Hesitant Fuzzy SWARA And Hesitant Fuzzy Sustainable Quality Function Deployment	Designing sustainable airports with environmental sensitivity.	Hesitant Fuzzy SWARA
Kutlu and Erçoşkun [11]	2021	Evaluation Of Logistic Firms In Türkiye On Green Logistics Applications	Green logistics practices of 17 companies	Comparison matrix
Semercioğlu and Özkoç [12]	2019	Social Choice Theory Supported By Analytical Hierarchy Process: Aircraft Charter Selection Process	Determining the criteria for which airline the three aircraft flying in medium and short distances should work in	AHP
Osintsev [13]	2021	Multi-Criteria Decision Making Methods In Green Logistics	Selection of green logistics methods and technologies	Fuzzy AHP, SAW, TOPSIS, PROMETHEE, COPRAS, ARAS, WASPAS, MAIRCA,

Table 1 (cont). Studies on sustainability, green logistics, airline company selection (2015–2024)

Author	Year	Title of the study	Subject of study	Analysis methods used
				EDAS, MABAC, CODAS
Alkhatib and Migdadi [14]	2021	A Novel Technique For Evaluating And Ranking Green Airlines: Benchmarking-Base Comparison	Evaluating and ranking 20 green airways	DEMATEL, AHP, TOPSIS
Kuo et al. [15]	2015	Developing a Green Supplier Selection Model by Using the DANP with VIKOR	The evaluation of green suppliers in electronics companies according to seventeen criteria related to environmental and management systems under the Electronic Industry Citizenship Coalition's (EICC) Code of Conduct.	DEMATEL, ANP, VIKOR
Alharasees and Kale [16]	2023	Applying AHP for supplier selection in aviation: a multi-criteria decision-making approach	Examining the development of complex air transport systems in the aviation industry that can rapidly adapt to increasing demand while balancing reliability and performance, emphasizing the importance of quality measurements and assessing air transport supply-side quality across four groups of aviation professionals.	AHP
Kılkış and Kılkış [17]	2017	Benchmarking aircraft metabolism based on a Sustainable Airline Index	Comparing the aircraft metabolism of 16 airline companies and identify aspects related to sustainable aviation.	EFA
Durak and Yılmaz [18]	2016	Airline Selection Criteria At Air Cargo Transportation Industry	Determining the criteria influencing the selection of transportation services for air cargo transportation.	AHP
Elhmoud and Kutty [19]q	2021	Sustainability Assessment in Aviation Industry: A Mini-Review on the Tools, Models and Methods of Assessment	A small-scale literature review on various tools and methods used for sustainability assessment in the aviation industry.	AI, NN, DSS

Multi-Criteria Decision Making (MCDM) is a scientific field that provides tools, models, and methodologies to effectively address decision problems. MCDM supports the decision-making process by enabling the analyst to compare and evaluate different actions/alternatives based on specific criteria, allowing the decision-maker to reach an efficient solution according to their preferences [21]. Among the multi-criteria decision-making methods, the VIKOR method defines a compromise ranking list, a compromise solution, and the decision-making stability intervals based on the weights provided by experts. It allows ranking and selection among alternatives in problems with conflicting criteria. The method ensures maximum group utility and minimum individual regret values and provides various ranking indices based on the closeness to the ideal solution. Therefore, the use of the VIKOR method was deemed appropriate for this study [22]. The COPRAS method, introduced into the literature by Zavadskas and colleagues in 1994, is a method whose reliability and accuracy have been acknowledged by many scholars. Today, it is used to solve a

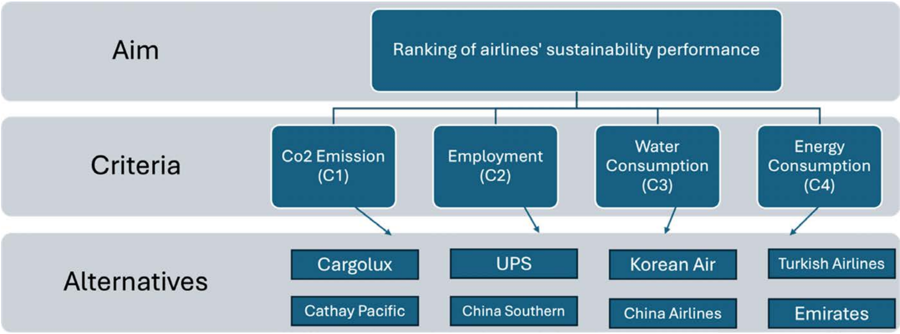

Figure 1. Model of the study.

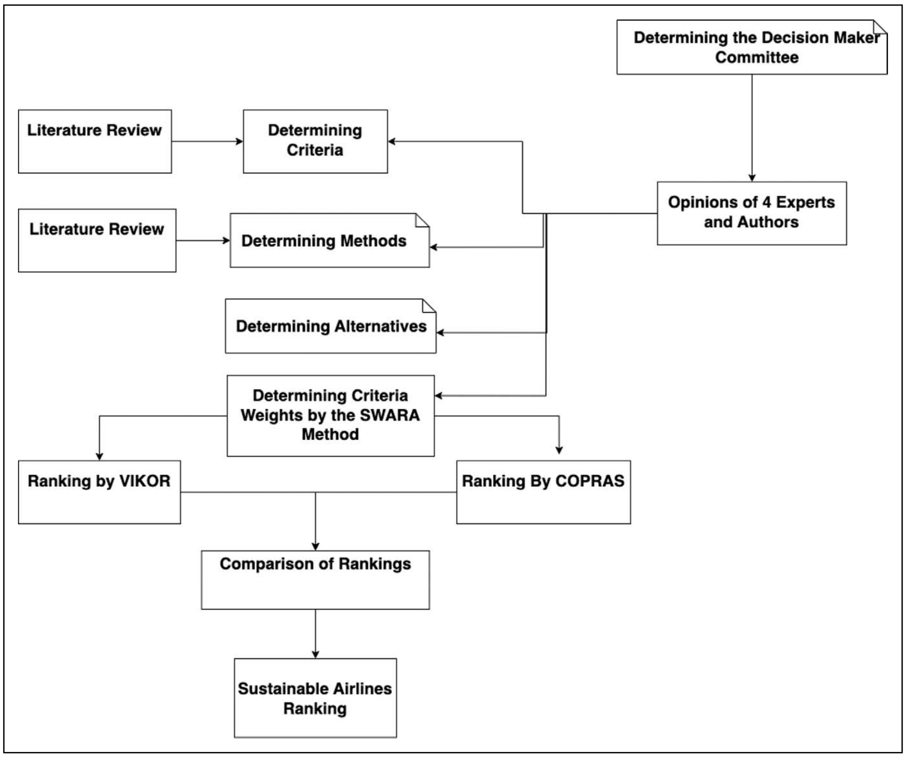

Figure 2. Flowchart depicting the decision-making process.

wide range of problems in various fields of engineering and management. One of the advantages of the method is the relatively short calculation stages and duration. To ensure the reliability of the research results, an additional method was required after the VIKOR method, and thus the COPRAS method was applied [23].

The criteria and alternative hierarchy discussed in the study are given in Figure 1.

The detailed flowchart of the research is depicted in Figure 2.

The methods used in the research, along with their mathematical steps, are explained in the below section.

SWARA Method (Step-Wise Weight Assessment Ratio Analysis)

Step-Wise Weight Assessment Ratio Analysis is one of the frequently preferred criteria weighthing methods in solving MCDM problems. The SWARA method developed by Kersuliene, Zavadskas and Turksis [24] is an export-oriented method. Due to the fact that it requires subjective evaluations, decision-makers can determine their priorities within the framework of current conditions and thus play a more active role compared to other methods [25]. The method steps are as follows:

Step 1: The experts rank the criteria in order of importance, with the most important criterion first.

Step 2: Starting from the second criterion, i–1. criterion and i. criteria are compared and the relative importance value is calculated for the other criteria except the first criterion. It is found how important i–1. criteria are compared to i. criteria. When calculating this value, it uses a multiple of 0.05 and is expressed as s_i.

Step 3: Using Eq (1), the coefficient of (k_i) is calculated.

$$k_i = \begin{cases} 1 & i=1 \\ s_i + 1 & i>1 \end{cases} \quad (1)$$

Step 4: Using Eq (2), the corrected weight value (q_i) is calculated.

$$q_i = \begin{cases} 1 & i=1 \\ \frac{q_{i-1}}{k_i} & i>1 \end{cases} \quad (2)$$

Step 5: Using Eq (3), the criterion weight (w_i) is obtained.

$$w_i = \frac{q_i}{\sum_{i=1}^{n} q_i} \quad (3)$$

Step 6: If more than one decision maker is used in the solution of the problem, the final criterion weights are reached by taking the geometric mean of all w_i values.

VIKOR Method (Vise Kriterijumska Optimizacija I Kompromisno Resenje)

VIKOR (Vise Kriterijumska Optimizacija I Kompromisno Resenje), translated into English as "Multi-Criteria Optimization and Compromise Solution", is a method used to rank multiple alternatives in multi-criteria decision making problems. It helps to determine the solution that can be closest to the ideal solution point by evaluating the alternatives on the basis of each criterion. The VIKOR method, which was first introduced by Opricović and Tzeng [26] is often preferred for selection and ranking in situations where there are conflicting criteria. The method steps are as follows:

Step 1: With the help of Eq (4) and Eq (5), the best (f_i^*) and worst (f_i^-) values are determined based on criteria. While determining these values, it is taken into account whether the criterion is benefit or cost criterion.

$$f_i^* = \underset{j}{max} f_{ij} \quad (4)$$

$$f_i^- = \underset{j}{min} f_{ij} \quad (5)$$

Step 2: Using Eq (6) and Eq (7), alternative-based S_j and R_j values are determined. Here w_i are predetermined criteria weights.

$$S_j = \sum_{i=1}^{n} \frac{w_i(f_i^* - f_{ij})}{(f_i^* - f_i^-)} \quad (6)$$

$$R_j = max\left[\sum_{i=1}^{n} \frac{w_i(f_i^* - f_{ij})}{(f_i^* - f_i^-)}\right] \quad (7)$$

Step 3: Using Eq (8), Q_j values are calculated for each alternative.

$$Q_j = \frac{v(S_j - S^*)}{(S^- - S^*)} + (1-v)\frac{(R_j - R^*)}{(R^- - R^*)} \quad (8)$$

In this section;

$$S^* = \underset{j}{min} S_j \quad (9)$$

$$S^- = \underset{j}{max} S_j \quad (10)$$

$$R^* = \underset{j}{min} R_j \quad (11)$$

$$R^- = \underset{j}{max} R_j \quad (12)$$

calculated using the formulas. $\underset{j}{min} S_j$ refers to choosing the largest group benefit, and $\underset{j}{min} R_j$ refers to choosing the smallest among the biggest personal regrets. The value v indicates the importance level for the strategy that provides the maximum group benefit, while the value (1–v) expresses the importance level of the minimum regret of the opponents. It is usually used as v=0.5.

Step 4: The calculated S_j, R_j and Q_j values are sorted. The alternative with the smallest Q_j value is defined as the best alternative among the options. Two conditions must be met for the result obtained to be valid. These conditions are as follows;

Condition 1: This is the condition that involves proving that there is a significant difference between the best and the closest option. The mathematical representation of the relevant condition is given in Eq (13).

$$Q(P_2) - Q(P^1) \geq D(Q) \quad (13)$$

Here P_1 is the 1st best alternative with the least Q value. $D(Q)$ is calculated with the formula in Eq (14);

$$D(Q) = \frac{1}{(j-1)} \quad (14)$$

If the number of alternatives (j) is less than 4, $D(Q)$=0.25 is taken.

Condition 2: For the obtained compromise solution to prove stable, the alternative P_1 with the best Q value must have the best score in at least one of the S and R values.

If one of the two specified conditions is not met, the compromise solution set is suggested as follows:

If Condition 2 cannot be met, the condition in Eq (14) is sought by considering alternatives P_1 and P_2,

If Condition 1 cannot be met, $P_1, P_2, \dots, P_M$ alternatives are going to be considered.

$$Q(P_M) - Q(P_1) \geq D(Q) \quad (15)$$

Within the compromise solution set, sorting is done according to the Q values. The best alternative is one with the minimum Q value.

COPRAS Method (Complex Proportional Assessment)

The performance evaluations of M alternatives according to n criteria are assumed to be represented by a decision matrix $X=[x_{ij}]_{mxn}$, where x_{ij} represents the rating of the *i–th* alternative on the *j–th* criterion.

The Eq (16) representing the decision matrix X formed with performance values x_{ij} is expressed as follows [24]:

$$X = [x_{ij}]_{mxn} = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1n} \\ x_{12} & x_{22} & \cdots & x_{2n} \\ \vdots & \ddots & \ddots & \vdots \\ x_{m1} & x_{m2} & \cdots & x_{mn} \end{bmatrix} \; i = 1,2,3,\dots,m \text{ and } j = 1,2,3,\dots,n. \quad (16)$$

Step 1: Normalization and the creation of the normalized decision matrix: In the COPRAS method, the performance values x_{ij} constituting the X decision matrix obtained through regularization are transformed into normalized performance values $\bar{x}_{ij}$ using;

$$\bar{x}_{ij} = \frac{x_{ij}}{\sum_{i=1}^{m} x_{ij}} \quad (17)$$

thus the normalized decision matrix $\overline{X}$ is represented by;

$$\bar{X} = [\bar{x}_{ij}]_{mxn} = \begin{bmatrix} \bar{x}_{11} & \bar{x}_{12} & \cdots & \bar{x}_{1n} \\ \bar{x}_{12} & \bar{x}_{22} & \cdots & \bar{x}_{2n} \\ \vdots & \ddots & \ddots & \vdots \\ \bar{x}_{m1} & \bar{x}_{m2} & \cdots & \bar{x}_{mn} \end{bmatrix} \; i = 1,2,3,\dots,m \text{ and } j = 1,2,3,\dots,n. \quad (18)$$

Table 2. Calculations of criterion (CR) importance values of decision maker 1

CR	Importance level	s_i	k_i	q_i	w_i
C1	1		1	1	0.4
C3	2	0.6	1.6	0.6	0.2
C4	3	0.5	1.5	0.4	0.1
C2	4	0.3	1.3	0.3	0.1

Table 3. Calculations of criterion (CR) importance values of decision maker 2

CR	Importance level	s_i	k_i	q_i	w_i
C4	1		1	1	0.3
C1	2	0.3	1.3	0.7	0.3
C3	3	0.5	1.5	0.5	0.2
C2	4	0.9	1.9	0.2	0.1

Step 2: Weighting and the creation of the weighted normalized decision matrix: The normalized performance values $\bar{x}_{ij}$ constituting the $\bar{X}$ normalized decision matrix are transformed into weighted normalized performance values $\hat{x}_{ij}$ using,

$$\hat{x}_{ij} = \bar{x}_{ij}.w_j \tag{19}$$

As a result, the weighted normalized decision matrix $\hat{X}$ is represented by

$$\hat{X} = [\hat{x}_{ij}]_{mxn} = \begin{bmatrix} \hat{x}_{11} & \hat{x}_{12} & \cdots & \hat{x}_{1n} \\ \hat{x}_{12} & \hat{x}_{22} & \cdots & \hat{x}_{2n} \\ \vdots & \ddots & \ddots & \vdots \\ \hat{x}_{m1} & \hat{x}_{m2} & \cdots & \hat{x}_{mn} \end{bmatrix} \; i = 1,2,3,\ldots,m \text{ and } j = 1,2,3,\ldots,n. \tag{20}$$

Step 3: Calculation of total weighted normalized values based on benefit and cost criteria: Criterion-based total weighted normalized values, considering the benefit or cost nature of the criterion, are calculated using;

$$S_{+i} = \sum_{j=1}^{k} \hat{x}_{+ij} \; i = 1,2,3,\ldots,m \text{ and } j = 1,2,3,\ldots,n \tag{21}$$

$$S_{-i} = \sum_{j=k+1}^{n} \hat{x}_{-ij} \; i = 1,2,3,\ldots,m \text{ and } j = k+1,k+2,k+3,\ldots,n \tag{22}$$

where S_{+i} represents the sum of benefit criteria and S_{-i} represents the sum of cost criteria. The weighted normalized performance values $\hat{x}_{+ij}$ and $\hat{x}_{-ij}$ appearing in the equations respectively indicate performance values with benefit and cost criteria.

Step 4: Calculation of relative importance values:

The value Q_i to indicate the relative importance value of the *i–th* alternative will be determined using,

$$Q_i = S_{+i} + \frac{S_{-min} \cdot \sum_{i=1}^{m} S_{-i}}{S_{-i} \cdot \sum_{i=1}^{m} \left(\frac{S_{-min}}{S_{-i}} \right)} \; i = 1,2,3,\ldots,m \tag{23}$$

calculated using the parameters S_{+i} and S_{-i}. The parameter S_{-min} in the equation represents the minimum value among the S_{-i}) values.

Step 5: Calculation of performance index values:

The value P_i, representing the performance index value of the *i–th* alternative, is calculated using,

Table 4. Calculations of criterion (CR) importance values of decision maker 3

CR	Importance level	s_i	k_i	q_i	w_i
C2	1		1	1	0.4
C1	2	0.8	1.8	0.5	0.2
C3	3	0.7	1.7	0,3	0.1
C4	4	0.9	1.9	0.1	0.08

Table 5. Calculations of criterion (CR) importance values of decision maker 4

CR	Importance level	s_i	k_i	q_i	w_i
C1	1		1	1	0.4
C4	2	0.9	1.9	0.5	0.2
C3	3	0.5	1.5	0.3	0.1
C2	4	0.1	1.1	0.3	0.14

Table 6. Criterion (CR) weights obtained from the SWARA method

CR	DM-1	DM-2	DM-3	DM-4	Final w_i	Norm.final w_i	Rank
C1	0.42	0.30	0.27	0.45	0.35	0.38	1
C2	0.13	0.10	0.48	0.14	0.17	0.19	4
C3	0.26	0.20	0.15	0.15	0.19	0.20	3
C4	0.17	0.39	0.08	0.23	0.19	0.21	2
Total	0.19	1					

$$P_i = \left[\frac{Q_i}{Q_{max}} \right].100\% \; i = 1,2,3,\ldots,m. \tag{24}$$

Step 6: Evaluation of alternatives:

After completing all calculation steps, the obtained P_i values are sorted in descending order to obtain the preference ranking of alternatives.

FINDINGS

In this section, the analysis results have been interpreted in detail.

Determination of Criteria Weights

2 academicians and 2 private sector employees were included in the research for the expert opinions required for the application. Decision makers were asked to rank the criteria according to their importance and give their s_i values. As a result of the s_i values obtained, k_i q_i and w_i values were calculated for each decision maker by using Eqs (1–3). The criteria weights calculated on the basis of the decision maker are given in Table 2, Table 3, Table 4 and Table 5.

Since there is more than one decision maker, after the criterion weights (w_i) were determined on the basis of the decision maker, the final criterion weights were reached

Table 7. Data on alternatives

Criteria/alternatives	Co_2 emission (tonne) (C1)	Employment (C2)	Water consumption (m^3) (C3)	Energy consumption (GJ) (C4)
Cargolux [27]	158,191	83	313	2,841
UPS [28]	119,827	1,855	20,000	887,356
Korean Air [29]	58,149	122	3,574	7,966
Turkish Airlines [30]	44,842	75	690	506,289
China Airlines [31]	68,548	127	1,571	1,014,468
Emirates [32]	71,773	140	9,665	994,062
Cathay Pacific [33]	25,520	93	44,958	358,601
China Southern [34]	21,918	112	519,566	299,898
W_j	0.39	0.2	0.2	0.21

Table 8. Best and worst values of criteria (CR)

CR	C1	C2	C3	C4
f_i^*	21,918	1,855	313	2.841
f_i^-	158,191	75	519,566	1,014,468

by taking the geometric mean of all w_i values. The criterion weight values to be used in VIKOR and COPRAS were obtained by performing normalization on the final weights obtained by the SWARA method. Information on criterion weights is given in Table 6.

According to the results of the SWARA analysis, the most crucial criterion for airlines to achieve sustainability is reducing CO_2 emissions, followed by reducing energy consumption in second place and reducing water consumption in third. Employment ranks as the fourth criterion. These findings highlight the importance of reducing CO_2 emissions. (Fig. 3).

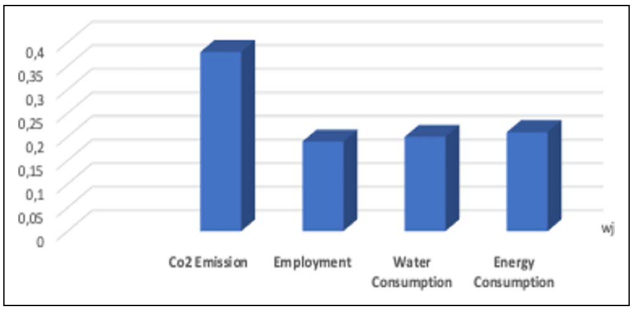

Figure 3. Ranking criteria by their level of importance.

Evaluation of Alternatives

The research utilized data sourced from the 2021 sustainability reports of airline companies. Due to incomplete data availability at the time, FedEx and Qatar Airways, both ranked in the global top 10, were excluded from consideration. Company metrics were normalized based on fleet size to ensure accurate comparative analysis. For instance, Cargolux, with 30 fleets, was adjusted relative to Turkish Airlines, which operates 370 fleets. These normalized values were tabulated to ensure equitable assessment across criteria, as detailed in Table 7.

With the help of Eqs (4–5), criteria-based best (f_i^*) and worst (f_i^-) values were determined and given in Table 8.

The weighted decision matrix is given in Table 9.

Alternative-based S_j and R_j values were determined using Eqs (6–7). Then, using Eq (8), Q_j values were calculated for each alternative. In Eq (8) the "v" value is taken as 0.5. The S_j, R_j and Q_j values of the alternatives are given in Table 10.

Table 9. Weighted decision matrix

Criteria/alternatives	Co_2 emission (tonne) (C1)	Employment (C2)	Water consumption (m^3) (C3)	Energy consumption (GJ) (C4)
Cargolux [27]	0.390	0.001	0.000	0.000
UPS [28]	0.280	0.210	0.008	0.175
Korean Air [29]	0.104	0.006	0.001	0.001
Turkish Airlines [30]	0.066	0.000	0.000	0.100
China Airlines [31]	0.133	0.006	0.000	0.200
Emirates [32]	0.143	0.008	0.004	0.196
Cathay Pacific [33]	0.010	0.002	0.017	0.070
China Southern [34]	0.000	0.004	0.200	0.059

Table 10. S_j and R_j values of alternatives

Alternatives	S_j	R_j
Cargolux [27]	0.391	0.390
UPS [28]	0.671	0.280
Korean Air [29]	0.111	0.104
Turkish Airlines [30]	0.170	0.105
China Airlines [31]	0.350	0.210
Emirates [32]	0.359	0.206
Cathay Pacific [33]	0.103	0.074
China Southern [34]	0.266	0.200
Min	0.103	0.074
Max	0.671	0.390

The Q_j values of alternatives are given in Table 11. The value of DQ = 0.143 was calculated.

By obtaining the Q(a") - Q (a') ≥ DQ values, the values in Table 12 were found.

Obtained Q_j values are ordered from smallest to largest and the alternative with the smallest value is selected as the best alternative. Condition 1 and Condition 2 were examined in order to ensure the validity of the obtained ranking.

Condition 1: $Q(P_2)–Q(P_1)≥D(Q)$

$Q(P_2)$-$Q(P_1)$= 0.05 – 0 = 0.05

$D(Q)$=1\((j–1)) = 1 / (8 – 1) = 0.143

0.05 ≤ 0.143

Condition 2: The P_1 alternative with the best Q value must have achieved the best score in at least one of the *S* and *R* values.

min_S=0.1

$S_{Cathay\ Pacific}$=0.1

As a result of the examination, it was seen that while Condition 2 was met, Condition 1 was not. For this reason, the condition in Eq (13) is discussed. When Table 13 is examined, it is seen that this condition is met in the 4th alternative.

Accordingly, Alternative 1, Alternative 2 and Alternative 3 were determined as compromise solutions. The final ranking of the alternatives is given in Table 14.

Using the same data, COPRAS analysis has been conducted. Data has been normalized using Eq (17). In Table 15, the first step of the COPRAS method has been applied and is shown as the normalized decision matrix.

Using the criteria weights obtained through the SWARA method, calculations were performed with Eq (18) to create the weighted normalized decision matrix. Table 16 presents the weighted normalized decision matrix which is the next step in the COPRAS method.

The results have been obtained using Eqs (21-24), and are shown in Table 17.

According to COPRAS results, sustainability rankings among alternatives show significant differences. China Southern ranks first with a Q_i value of 0,350 and a P_i value of 100. Cathay Pacific follows closely in second place with Q_i of 0,176 and P_i of 50,134. Korean Air secures the third position with Q_i of 0,141 and P_i of 40,182. Turkish Airlines and Emirates occupy the fourth and fifth positions respectively, with lower Q_i and P_i values. UPS, China Airlines, and Cargolux rank lower, indicating comparatively lower sustainability performance based on their Q_i and P_i values. These findings provide important insights into how sustainability efforts vary among different companies in the air cargo transportation sector and highlight areas for improvement.

Table 18 allows for the comparison of the ranking results given by both methods.

According to the findings of the COPRAS method, China Southern Airlines holds the 1st position, whereas in the VIKOR results, it occupies the 4th position. Cathay Pacific is ranked 2nd by COPRAS, whereas it claims the top spot according to VIKOR. Korean Air secures the 3rd position in COPRAS and also ranks 1st in VIKOR. Turkish Airlines ranks 4th in COPRAS and 1st in VIKOR. Following these, China Airlines holds the 5th position in one method and the 6th in the other, while Emirates similarly ranks 6th in one and 5th in the other. The rankings of the remaining companies remain consistent across both methods (Fig. 4).

Table 11. Q_j values of alternatives

Alternatives	Q_j=0	Q_j=0.25	Q_j=0.5	Q_j=0.75	Q_j=1
Cargolux [27]	1.000	0.877	0.753	0.630	0.506
UPS [28]	0.653	0.740	0.826	0.913	1.000
Korean Air [29]	0.094	0.074	0.054	0.034	0.014
Turkish Airlines [30]	0.097	0.102	0.107	0.113	0.118
China Airlines [31]	0.431	0.431	0.432	0.433	0.434
Emirates [32]	0.417	0.426	0.434	0.442	0.451
Cathay Pacific [33]	0.000	0.000	0.000	0.000	0.000
China Southern [34]	0.399	0.371	0.342	0.314	0.286

Table 12. Ranking of alternatives

Alternatives	Q_j=0.5	Rankings
Cargolux [27]	0.753	7
UPS [28]	0.826	8
Korean Air [29]	0.054	2
Turkish Airlines [30]	0.107	3
China Airlines [31]	0.432	5
Emirates [32]	0.434	6
Cathay Pacific [33]	0.000	1
China Southern [34]	0.342	4

Table 13. Finding the set of compromise solutions

$Q(P_M) - Q(P_1)$	≥D(Q)	$Q(P_M) - Q(P_1)$
0.05	≤DQ	P2-P1
0.1	≤DQ	P3-P1
0.35	≥DQ	P4-P1
0.43	≥DQ	P5-P1
0.44	≥DQ	P6-P1
0.75	≥DQ	P7-P1
0.82	≥DQ	P8-P1

Table 14. Final ranking of alternatives

Alternatives	Ranking
Cargolux [27]	1
UPS [28]	1
Korean Air [29]	1
Turkish Airlines [30]	4
China Airlines [31]	5
Emirates [32]	6
Cathay Pacific [33]	7
China Southern [34]	8

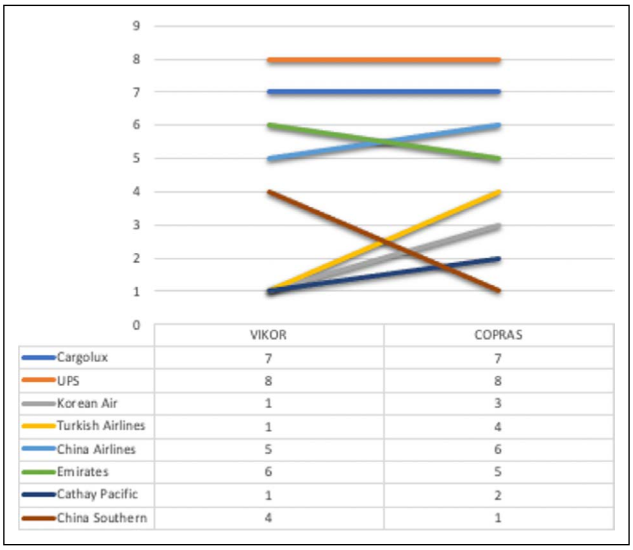

Figure 4. Comparing the results of two methods.

Table 15. Normalized decision matrix table

Alternatives	C1	C2	C3	C4
Cargolux [27]	0.278	0.032	0.001	0.001
UPS [28]	0.211	0.712	0.033	0.218
Korean Air [29]	0.102	0.047	0.006	0.002
Turkish Airlines [30]	0.079	0.029	0.001	0.124
China Airlines [31]	0.121	0.049	0.003	0.249
Emirates [32]	0.126	0.054	0.016	0.244
Cathay Pacific [33]	0.045	0.036	0.075	0.088
China Southern [34]	0.039	0.043	0.865	0.074

Table 16. Weighted normalized decision matrix

	Min	Min	Max	Min
	0.39	0.20	0.20	0.21
Alternatives	**C1**	**C2**	**C3**	**C4**
Cargolux [27]	0,108	0,006	0,000	0,000
UPS [28]	0,082	0,142	0,007	0,046
Korean Air [29]	0,040	0,009	0,001	0,000
Turkish Airlines [30]	0,031	0,006	0,000	0,026
China Airlines [31]	0,047	0,010	0,001	0,052
Emirates [32]	0,049	0,011	0,003	0,051
Cathay Pacific [33]	0,017	0,007	0,015	0,018
China Southern [34]	0,015	0,009	0,173	0,015

Table 17. Relative importance and index values

Alternatives	S_{+i}	S_{-i}	Q_i	P_i	Ranking
Cargolux [27]	0,000	0,115	0,060	17,231	7
UPS [28]	0,007	0,270	0,032	9,221	8
Korean Air [29]	0,001	0,050	0,141	40,182	3
Turkish Airlines [30]	0,000	0,063	0,111	31,653	4
China Airlines [31]	0,001	0,109	0,064	18,283	6
Emirates [32]	0,003	0,111	0,066	18,701	5
Cathay Pacific [33]	0,015	0,043	0,176	50,134	2
China Southern [34]	0,173	0,039	0,350	100,000	1

Table 18. Comparison of rankings for both methods

Alternatives	VIKOR	COPRAS
Cargolux [27]	7	7
UPS [28]	8	8
Korean Air [29]	1	3
Turkish Airlines [30]	1	4
China Airlines [31]	5	6
Emirates [32]	6	5
Cathay Pacific [33]	1	2
China Southern [34]	4	1

CONCLUSION

All commercial activities carried out on a global scale primarily shape themselves through short-term effects. Although its effects are on the way of fading, the COVID-19 pandemic and the Russia-Ukraine War, are the most recent examples. On the other hand, the fact that all companies that will struggle to survive in global competition will be preferred for the medium and long term will be largely decisive if they have maximized their sustainability with green activities.

In light of this reality, the study aimed to choose a sustainable company among the top 10 airline cargo companies according to the CTK (Cargo Ton-Km) published in the WATS+ (World Air Transport Statistics) report [35]. The data used in the analysis of the research were obtained from the companies' 2021 sustainability reports. Since all of the 2022 sustainability reports have not been published yet, it has been decided to use the data for 2021. For this reason, two companies that did not have a sustainability report were excluded from the study. Based on the SWARA analysis findings, the top priority for airlines in achieving sustainability is the reduction of CO_2 emissions, followed by decreasing energy consumption in second place and minimizing water consumption in third. Employment is ranked fourth among the criteria. These results underscore the critical importance of CO_2 emission reduction efforts for airlines. The findings of the VIKOR method indicate a compromise cluster for selecting the most sustainable company among 8 alternatives (airline companies). In this cluster, 3 airline companies—Cathay Pacific, Korean Airlines, and Turkish Airlines—were identified as a compromise solution. According to the results of the COPRAS method, China Southern, Cathay Pacific, and Korean Air were found to be at the forefront. In both results, UPS company ranked the lowest. These findings aimed to provide information about the sustainability efforts of companies in 2021 if the top 10 airline companies in the world ranking prepared by IATA were to be re-ranked in terms of sustainability.

The Turkish aviation sector also does not show a different structure from the general aviation trends in the world. The negative developments experienced in our country, mainly due to the economic and then the epidemic, have adversely affected the air transport sector. In this process, it was observed that some airline companies ended their activities, while some airline companies had to go to operational restrictions. The actors that make up the Turkish aviation sector, as well as the aviation actors of other countries, have gained more attention in terms of sustainability criteria, especially in their international activities. The ranking of Turkish Airlines in our research also clearly reveals that this issue should be addressed.

The results of this study will demonstrate the sustainability efforts of global airlines based on 2021 data. Future research could be updated to enable time series analysis, allowing for a more comprehensive understanding of sustainability trends over the years. By comparing future studies with the 2021 data, it will be possible to assess the progress or regression of the companies in terms of their sustainability initiatives.

LIMITATIONS AND FURTHER RESEARCH

The study has several limitations. One of the limitations of this research is the difficulty in accessing data. The availability of sufficient data on sustainability index criteria such as noise pollution, waste management, social responsibility projects, natural resource use, employee rights and occupational safety, diversity and inclusion, education, and development depends on their inclusion in sustainability reports. Increasing the number of these criteria could broaden the scope of the research. In future studies, it may be suggested to create a multi-criteria decision-making model using fuzzy logic. For instance, criteria with data that are not precisely measurable or that rely on subjective assessments, such as noise pollution, social responsibility projects, or diversity and inclusion, can be more effectively analyzed using fuzzy logic. This approach can enable decision-making processes to be conducted more comprehensively and accurately, allowing for more precise ranking and evaluation of sustainability performances.

The SWARA method was used for weighting criteria in the study. SWARA method, being a subjective approach, relies on the personal experience and knowledge of experts. In future studies, it can be combined with an objective weighting method to recalculate with new weights. Data beyond what is disclosed in sustainability reports could not be accessed. With obtaining more data, the study can be expanded by considering different criteria. The criteria were weighted using the SWARA method, and a model was subsequently constructed using the VIKOR method to rank the companies accordingly. However, to ensure reliability, an additional method, the COPRAS method, was employed. This step was taken to facilitate sensitivity analysis and establish a more robust foundation for decision-making. Through sensitivity analysis, the aim was to compare the outcomes derived from different methodologies, thereby providing decision-makers with more precise insights.

In future scientific studies, it would be appropriate to evaluate the Turkish aviation industry on a firm basis within the framework of sustainability. Thus, the current situation of our country's aviation industry in terms of sustainability will be determined. It would be beneficial to carry out similar studies for different types of transportation both in the world and in our country. In addition, ranking the highways and seaports in terms of sustainability will be another research topic.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Geochemical characteristics and paleo weathering in sediments of Noyyal River Basin, Tamilnadu–India

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ABSTRACT

A geochemical study of surface sediment samples distributed in the Noyyal River basin in western Tamil Nadu was conducted for major oxides, parent rock source, and the extent of weathering. The Al_2O_3/TiO_2 ratio of the samples ranged from (4.5–18) during monsoon and (3.94–32.14) during summer and fell in the category of mafic and intermediate igneous rocks during both seasons. The samples exhibited PIA with an average value of 64.80 during monsoon and 66.36 during summer. CIA values of the samples averaged 61.48 during monsoon and 62.35 during summer. The CIA vs. PIA, CIA vs. K/Na, and CIA vs. Al/Na for the studied samples for both seasons show low to intermediate silicate weathering in almost all locations. ICV values of samples averaged 5.1 during monsoon and 5.8 during summer suggesting that rock-forming minerals like plagioclase and alkali-feldspar are more prevalent and fewer clay minerals are present. The A-CN-K plot shows the weathering tendency towards muscovite and illite, and the A-C-N plot shows the parent rocks' plagioclases are low to intermediately weathered and the sediments gradually reduce albite and are enriched in weathering of anorthite parent material. The A-CNK-FM shows all the sediment samples lying below the feldspar region, indicating garnet and biotite presence.

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INTRODUCTION

Rivers carry and deposit sediments from various sources, including geological formations that weather under various climatic and physiographic conditions [1]. The geochemistry of sediments relates to studying the chemical content, distribution, and processes that impact sediments. Numerous variables, such as the composition of the provenance, the temperature, the duration and energy of sediment movement, and the redox conditions in the depositional environment, have a significant impact on the geochemical composition of sediments [2]. Several factors, including the lithology of the watershed region, the temperature, the terrain, the flora, and the land use of the watershed region, all enhance the geochemistry of river sediments [3]. The sediment composition is also affected by the meteorological conditions that lead to weathering and erosion [4]. The physical and chemical weathering of the parent rocks influences river-borne sediments' texture, mineralogy, and geochemistry. Clay minerals like kaolinite and smectite are produced by varying degrees of chemical weathering, while sediments dominated by gibbsite and kaolinite are produced by strong chemical weathering. Sediments with illite and chlorite predominate result from physical weathering [1].

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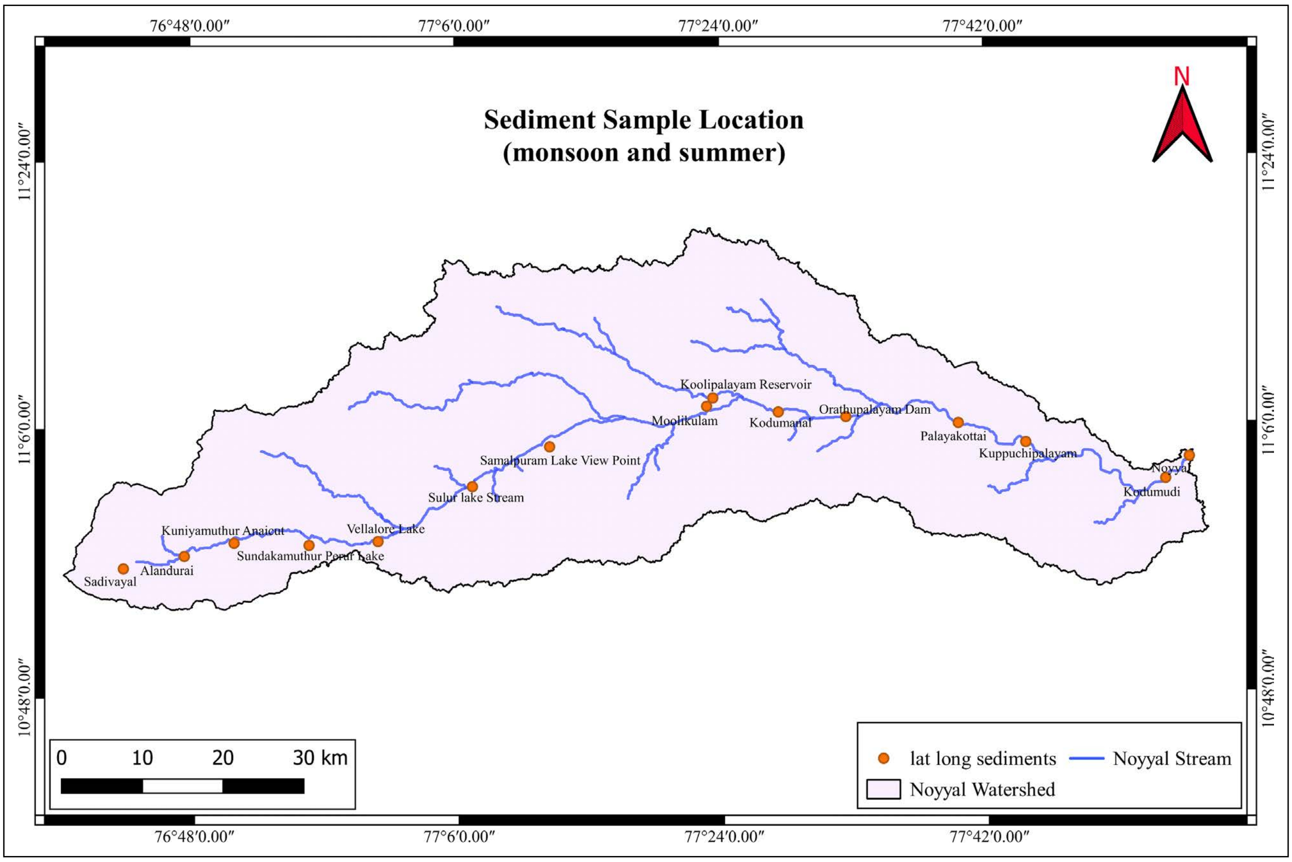

Figure 1. Study area and Sediment sample location (monsoon and summer).

Precipitation and co-precipitation, adsorption on Fe, Mn oxides, Al-hydroxides (gibbsite), kaolinite, organic matter surfaces, and human activities are other factors that impact trace elements [5]. Strong chemical weathering attaches cations like Cs, Ba, and Rb to the weathering profile and by adsorption onto clays, selectively removes cations like Ca, Na, and Sr from the weathering profile [6]. Clays and heavy minerals have higher concentrations of trace elements than silts and sands [7]. Elements usually appear in sediments as phosphates, hydroxides, carbonates, silicates, sulfides, sulfates, coupled ions, organometallic compounds, and oxides [8]. Applying chemical weathering indices reflects the strength of chemical weathering processes and quantifies the extent of soil and river sediment depletion in mobile vs immobile components as a result of weathering [9]. Chemical weathering indices, also known as indicators of modification, are often used to describe weathering profiles. Chemical weathering indices condense a sample's overall main element oxide chemistry into a single value.

Noyyal River in the southwest region of Tamil Nadu originates from the Velliangiri mountain ranges and is a major tributary of the Cauvery River. It flows through several villages in the districts of Karur, Tirupur, Erode, and Coimbatore before joining the Cauvery River near Noyyal in the Karur district (Fig. 1) [10]. The 180 km long river basin has a total area of 3,500 sq. km. The watershed has an agricultural area of 1,800 sq. km, and its populations in urban and rural areas are 1000 and 120 people per sq. km [10]. Rainfall in the basin varies greatly throughout the year; during the southwest monsoon, it receives over 3000 mm of intense rain, while during the northeast monsoon, it receives 600 mm. Pre-monsoon precipitation averages between 100 and 300 mm in April and May [10]. The geological formations of the Noyyal River basin include a wide range, from the ancient Archean crystalline rocks to the more recent alluvium deposits. Colluvial formations are seen on the western edge of the Coimbatore district [11]. The Noyyal basin has various soil types, ranging from shallow red non-calcareous soils to deep grey calcareous soils [12]. Basic and ultra-mafic rocks, garnet-sillimanite graphite gneiss, granite, charnockite, fissile hornblende biotite gneiss, and hornblende biotite gneiss cover the Noyyal River basin [13]. In the basin, there is a lack of knowledge on the features of the sediments, the weathering, and the origin of the surface sediments. Hence this study will aid in understanding the sediment geochemistry of the basin. Therefore the objective of the study is to provide an interpretation of the principal oxides geochemistry, the degree of weathering, and the provenance of the surface sediments in the basin of the Noyyal River.

MATERIALS AND METHODOLOGY

Sampling and Analysis

When selecting the sample areas, consideration was given to the industrial activity and land use along the river. These sample locations were chosen according to the area type (urban/ rural). A total of 20 sediment samples, 10 during monsoon (November 2021) (Fig. 1) and 10 during summer (May

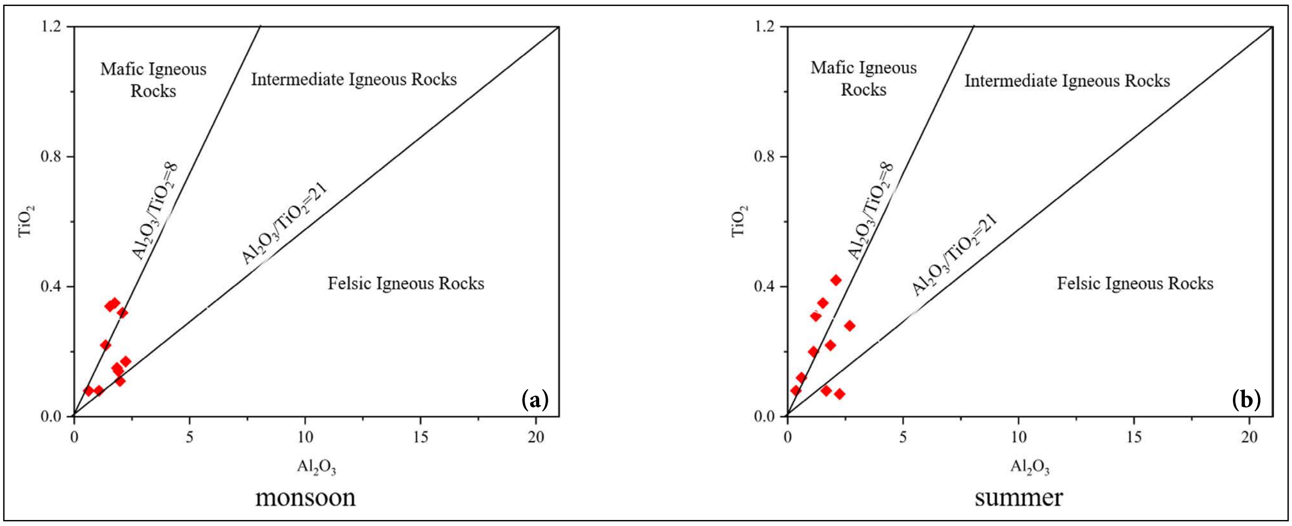

Figure 2. Al_2O_3 (wt%) and TiO_2 (wt%) ratio of the study area **(a)** monsoon and **(b)** summer.

Table 1. Major elements of monsoon samples (ppm)

Name	Ti	Al	Fe	Mg	Mn	Ca	Na	K
Sadivayal	2090.23	9238.89	32452.01	9229.28	206.78	4801.93	159.82	3478.10
Alandurai	1288.92	7203.48	33596.01	5101.04	278.73	2424.60	8.54	1899.73
Sulur Stream	998.13	11823.19	46170.78	13197.64	498.46	5625.00	239.82	2937.21
Samalpuram Lake	2040.71	8183.77	39949.88	27585.79	258.01	4283.85	171.44	3223.42
Moolikulam	679.53	10495.65	38703.93	7818.81	357.30	4111.15	105.73	2102.67
Kodumanal	1918.44	11072.31	48298.01	13955.53	332.33	5625.00	959.11	4170.25
Kuppuchipalayam	810.11	10137.44	29443.03	11790.01	355.02	4673.33	1193.04	2251.38
Orathupalayam Dam	457.23	5688.40	21047.97	9120.58	556.95	5921.00	265.59	1171.18
Kodumudi	905.44	9765.59	34298.31	10108.69	462.70	5406.44	203.82	1686.72
Noyyal	486.53	3278.83	19924.56	4883.14	127.12	4321.00	157.96	668.46

2022) (Fig. 1), were collected using a shovel from the Noyyal River basin. At each sampling location, ~1kg of sediment samples were obtained from a depth of 5cm by removing the top layer with the shovel and stored in zip-lock bags at 4°C in the laboratory until further analysis. For analysis, 0.5g of sediment sample was digested in a mixture of concentrated HNO3 and HCl (5:2, v:v) using a Microwave-assisted extraction/digestion for soil/sediment (CEM MARS 6) reaction system. The major elements were analyzed using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Make: Thermo Fisher Scientific, USA) (Model: iCAP 7400 Duo). Analysis was repeated thrice with an average error percentage of less than 1% was considered.

Determination of Weathering Intensity

The assessment of weathering intensity in sediments often relies on widely employed weathering indices, including the Plagioclase Index of Alteration (PIA), Chemical Index of Alteration (CIA), and Index of Compositional Variation (ICV). These indices play a pivotal role in characterizing the extent of weathering and are particularly essential in determining the nature of lithological changes in sediments [14].

The extent of weathering in the source rock is often measured using PIA values [15]. The PIA can be computed using Eq.1 [14, 15].

$$PIA = \frac{Al_2O_3 - K_2O}{Al_2O_3 + CaO^* + Na_2O - K_2O} x100 \quad (1)$$

Plagioclase and K-feldspars' gradual alteration to clay minerals may be quantified using the CIA [16]. The CIA can be computed using Eq.2 [14, 16].

$$CIA = \frac{Al_2O_3}{Al_2O_3 + CaO^* + K_2O + Na_2O} x100 \quad (2)$$

ICV suggested by Cox et al. [17], can be used to calculate the chemical composition of the sample's non-quartz components using Eq.3 [18].

$$ICV = \frac{Fe_2O_3 + K_2O + Na_2O + CaO^* + MgO + MnO + TiO_2}{Al_2O_3} \quad (3)$$

RESULTS AND DISCUSSION

Major Oxides Geochemistry

This study analyzed major elements (Ti, Al, Fe, Mg, Mn, Ca, Na, and K) and represented them as ppm in Tables 1, 2. The significant oxides in the sediment sample compositions

Table 2. Major elements of summer samples (ppm)

Name	Ti	Al	Fe	Mg	Mn	Ca	Na	K
Sadivayal	1197.17	5906.08	23663.62	4247.41	236.59	2836.67	137.78	1585.32
Alandurai	389.86	11889.21	38471.38	5553.56	374.67	3844.00	199.55	1799.57
Kuniyamuthur Anaicut	1313.33	9775.39	34532.62	5992.21	312.79	2741.37	309.35	2112.96
Perur Lake	470.95	1924.38	20929.23	3225.83	163.69	4481.13	290.88	717.42
Vellalore Lake	1870.82	6434.34	32626.02	10988.59	253.77	5632.00	266.81	2857.75
Sulur Stream	2101.67	8070.52	40666.00	16384.57	165.19	5982.00	432.03	2482.11
Samalpuram Lake	2530.42	11062.16	33329.15	6932.39	427.12	1443.96	51.07	4319.05
Moolikulam	499.68	8845.35	37068.61	6301.31	106.99	2208.90	146.48	1937.76
Koolipalayam Reservoir	1668.48	14214.82	44366.55	16159.83	311.43	5485.00	367.89	3661.48
Palayakottai	704.19	3180.26	29336.92	6445.71	255.33	2358.00	411.91	924.01

Table 3. Major oxide (wt%) and weathering indices of monsoon samples

Location	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	CIA	PIA	ICV
Sadivayal	0.35	1.75	4.64	1.53	0.03	0.67	0.02	0.42	61.08	65.67	4.39
Alandurai	0.22	1.36	4.80	0.85	0.04	0.34	0.00	0.23	70.51	76.89	4.75
Sulur Stream	0.17	2.23	6.60	2.19	0.06	0.79	0.03	0.35	65.57	69.65	4.56
Samalpuram Lake	0.34	1.55	5.71	4.57	0.03	0.60	0.02	0.39	60.47	65.04	7.55
Moolikulam	0.11	1.98	5.53	1.30	0.05	0.58	0.01	0.25	70.18	74.58	3.95
Kodumanal	0.32	2.09	6.91	2.31	0.04	0.79	0.13	0.50	59.59	63.44	5.26
Kuppuchipalayam	0.14	1.92	4.21	1.96	0.05	0.65	0.16	0.27	63.82	66.87	3.88
Orathupalayam Dam	0.08	1.07	3.01	1.51	0.07	0.83	0.04	0.14	51.67	51.93	5.28
Kodumudi	0.15	1.85	4.90	1.68	0.06	0.76	0.03	0.20	65.15	67.69	4.22
Noyyal	0.08	0.62	2.85	0.81	0.02	0.60	0.02	0.08	46.72	46.27	7.20

Table 4. Major oxide (wt%) and weathering indices of summer samples

Location	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	CIA	PIA	ICV
Sadivayal	0.20	1.12	3.38	0.70	0.03	0.40	0.02	0.19	64.79	69.00	4.41
Alandurai	0.07	2.25	5.50	0.92	0.05	0.54	0.03	0.22	74.19	78.23	3.26
Kuniyamuthur Anaicut	0.22	1.85	4.94	0.99	0.04	0.38	0.04	0.25	73.10	78.92	3.72
Perur Lake	0.08	0.36	2.99	0.53	0.02	0.63	0.04	0.09	32.57	29.38	12.04
Vellalore Lake	0.31	1.22	4.66	1.82	0.03	0.79	0.04	0.34	51.00	51.40	6.58
Sulur Stream	0.35	1.52	5.81	2.72	0.02	0.84	0.06	0.30	56.08	57.79	6.62
Samalpuram Lake	0.42	2.09	4.77	1.15	0.06	0.20	0.01	0.52	74.14	88.26	3.41
Moolikulam	0.08	1.67	5.30	1.04	0.01	0.31	0.02	0.23	74.83	81.39	4.19
Koolipalayam Reservoir	0.28	2.69	6.34	2.68	0.04	0.77	0.05	0.44	68.10	73.32	3.95
Palayakottai	0.12	0.60	4.19	1.07	0.03	0.33	0.06	0.11	54.74	55.95	9.84

are listed in Tables 3, 4. The calculated concentration is given as wt%. The major oxides (%) during monsoon consists of TiO_2 (0.08–0.35), Al_2O_3 (0.62–2.23), Fe_2O_3 (2.85–6.91), MgO (0.81–4.57), MnO (0.02–0.07), CaO (0.34–0.83), Na_2O (0.001–0.16), K_2O (0.08–0.50), and during summer TiO_2 (0.07–0.42), Al_2O_3 (0.36–2.69), Fe_2O_3 (2.99–6.34), MgO (0.53–2.72), MnO (0.01–0.06), CaO (0.20–0.84), Na_2O (0.01–0.06), and K_2O (0.09–0.52). Due to chemical weathering that occurred during the transit of clastic material, Ca^{2+}, Na^+, and K^+ ions were lost, as shown by the low amounts of CaO, Na_2O, and K_2O in the samples.

The K_2O/Al_2O_3 ratio is a useful indicator for determining the amount of clay and feldspar in the siliciclastic sample [19]. The K_2O/Al_2O_3 ratio ranges from 0.16 to 0.31 for clay minerals and from 0.3 to 0.9 for feldspar [17]. In the present study, the siliciclastic sediments have a higher value of K_2O/Al_2O_3 which rang-

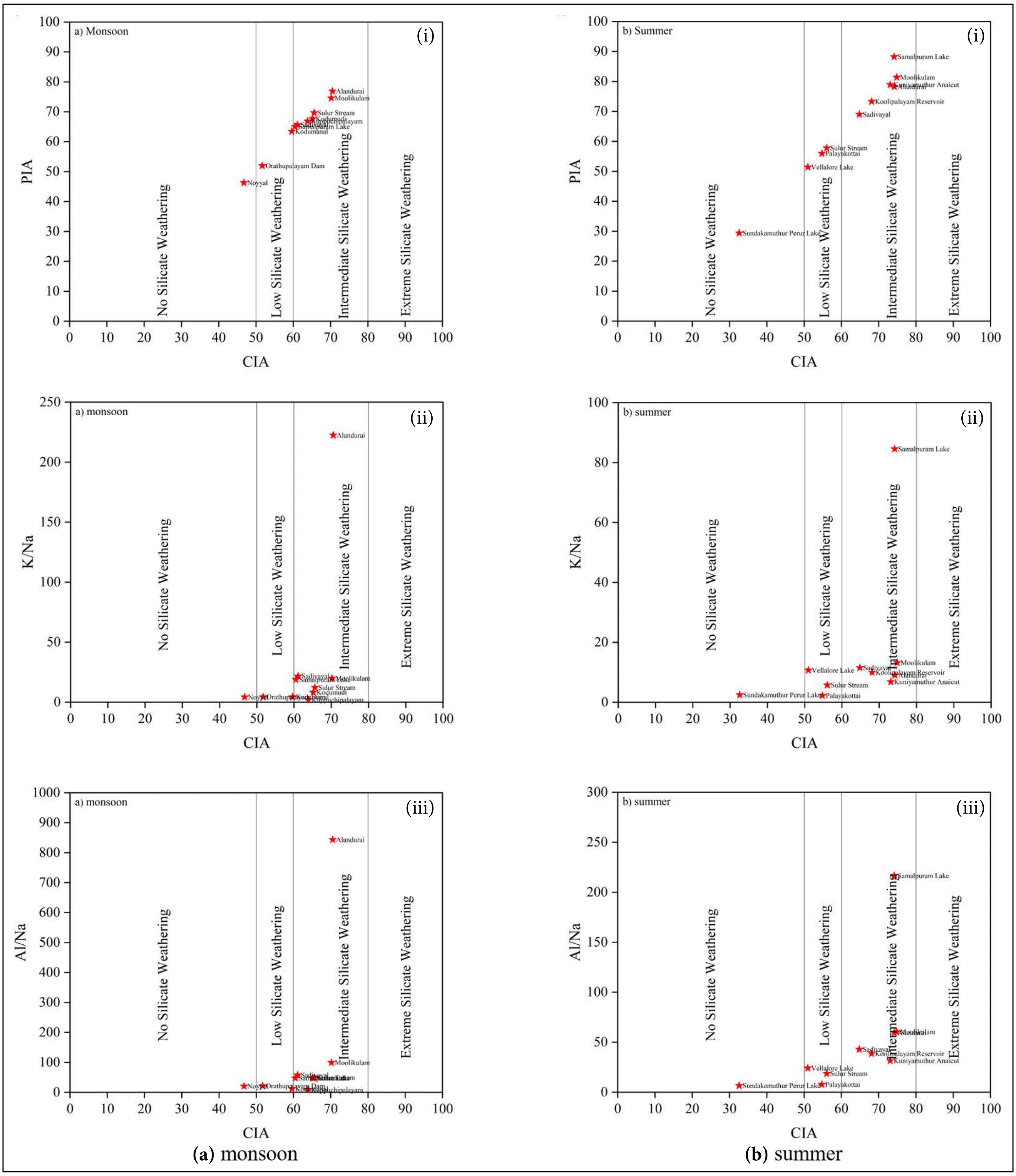

Figure 3. (i) The plot of the CIA against PIA **(a)** monsoon and **(b)** summer; (ii) The binary plot of CIA against K/Na **(a)** monsoon and **(b)** summer; (iii) The binary plot of CIA against Al/Na **(a)** monsoon and **(b)** summer.

es between 0.11–0.24 during monsoon and 0.10–0.28 during summer suggesting that most of the sediments contain more clay minerals that range from 0.16 to 0.31 due to consequences of intense weathering in a warm and humid climate [19].

Parent Rock Type

A stable composition allows for the preservation of both Al and Ti throughout the weathering process of the parent rock. As a result, the ratios of Al_2O_3/TiO_2 are typically constant with the parent rocks [20]. Al_2O_3/TiO_2 >21 denotes felsic rocks, Al_2O_3/TiO_2 in the range of 8–21 shows intermediate igneous rocks, and Al_2O_3/TiO_2 <8 suggests mafic rocks, according to the threshold established by the ratios of Al_2O_3/TiO_2 [21]. The Al_2O_3/TiO_2 ratio of the sample locations ranged from (4.5–18) during monsoon with an average of 10.06 and (3.94–32.14) during summer with

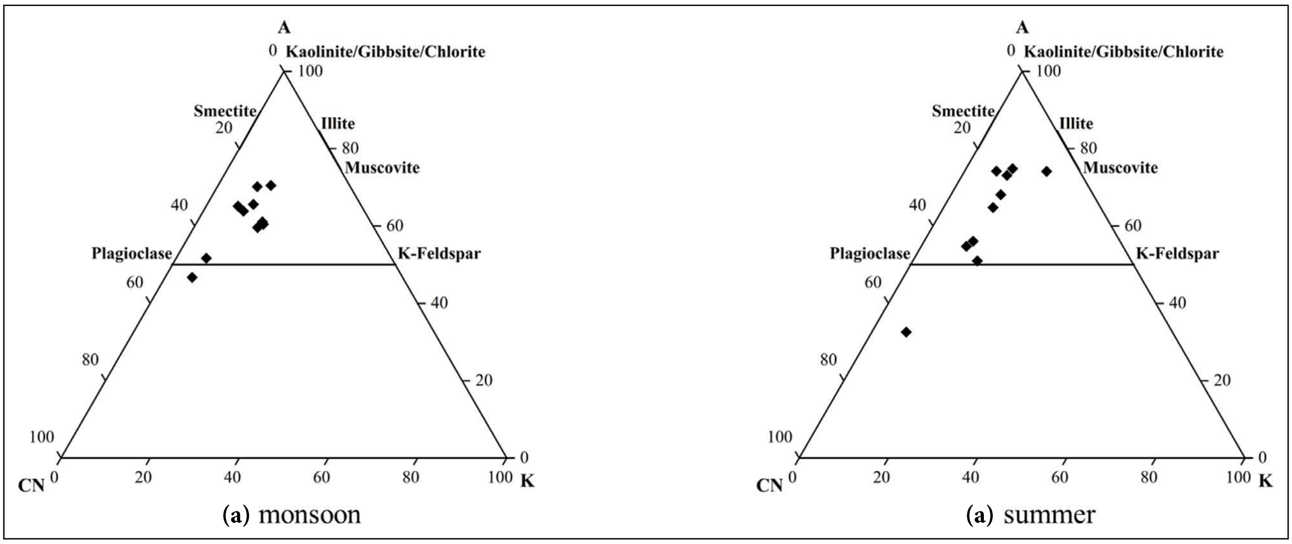

Figure 4. A-CN-K ternary diagram of the study area **(a)** monsoon and **(b)** summer.

an average of 9.94. Most of the samples were mafic and intermediate igneous rocks during both seasons (Fig. 2). Intermediate igneous rocks are formed when magma with moderate silica cools and solidifies. This magma is formed by a variety of processes occurring inside the Earth, including partial melting, fractional crystallization, and the mixing of different magmas [22]. Mafic rocks are the result of the process of magma cooling and solidifying, which occurs when the magma contains a significant amount of magnesium and iron. Mafic magma could form through two primary mechanisms; Partial melting and fractional crystallization [23].

Paleo Weathering

The highest PIA value (100) denotes entirely altered materials like kaolinite and gibbsite and unweathered plagioclase is indicated when 50% of the maximum PIA value is reached [14]. The samples exhibit the range of PIA values from 46.27–76.89 with an average value of 64.80 during monsoon and 29.38–88.26 with an average value of 66.36 during summer, illustrating the weathering characteristics of the parent rocks. Sediment CIA values are a vital measure of the degree of weathering in the provenance. CIA of fresh feldspar and unweathered igneous rocks typically fall within the range of 40 to 50, and residual rocks that have been significantly affected by weathering have values that are more proximate to 100 [16]. CIA values of the samples ranged from 46.72–70.51 with an average value of 61.48 during monsoon and 32.57–74.83 with an average value of 62.35 during summer is seen as a representation of low to intermediate degree of weathering (Fig. 3i). PIA and CIA assess the contrast between weathering occurring in the origin and distant transportation. Despite experiencing some degree of weathering at the origin, the sediments may not have traveled a significant distance before being deposited [24]. The CIA vs. K/Na (Fig. 3ii) and CIA vs. Al/Na (Fig. 3iii) for the studied samples for both seasons show low to intermediate silicate weathering in almost all locations.

ICV values below 1 signify a higher proportion of clay minerals. Conversely, values exceeding 1 show the existence of minerals found in rocks, such as plagioclase, alkali-feldspar, and pyroxenes [17]. ICV values of samples ranged from 4.39–7.55 with an average value of 5.10 during monsoon and 3.26–12.04 with an average value of 5.80 during summer (Table 2a, b). The average ICV score suggests that rock-forming minerals like plagioclase and alkali-feldspar are more prevalent and fewer clay minerals are present. This is due to the geology of the region which is dominated by ultramafic rocks and also gneiss and granite [13].

The A-CN-K plot (Al_2O_3-(CaO^* + Na_2O)-K_2O) is a dependable measure for evaluating weathering patterns [25]. The weathering tendency tends to be around the A-vertex and toward muscovite and illite (Fig. 4) due to the metasomatism of potassium [15]. The increased concentrations of Al_2O_3 and Fe_2O_3 in all the samples indicate the existence of aluminum silicate minerals such as muscovite [26]. Nearly every sample in the core of the A–CN–K ternary diagram is above the feldspar join line, indicating plagioclase with CIA values ranging from (46–70) during monsoon and (32–74) during summer. The CIA values were >50 (UCC ~50) in almost all samples indicating low to moderate chemical weathering.

The A-C-N diagram was used to depict the molar proportions of (Al_2O_3-K_2O), CaO^*, and Na_2O to observe the plagioclase weathering pattern in the sediments. All samples in the (A–C–N) triangle plot have a distribution field close to the A apex, which may be due to the impact of significant weathering. The majority of the sediments in the study show a single line for the plagioclase weathering trend, indicating that the parent rocks' plagioclases are low to intermediately weathered. The sediments display a linear trend with high CaO values and are enriched in Al_2O_3 suggesting that the sediments gradually reduce albite and are enriched in the weathering of anorthite parent material (Fig. 5). The PIA values of the sediment samples ranged from (46–77) during monsoon and (29–88) during summer.

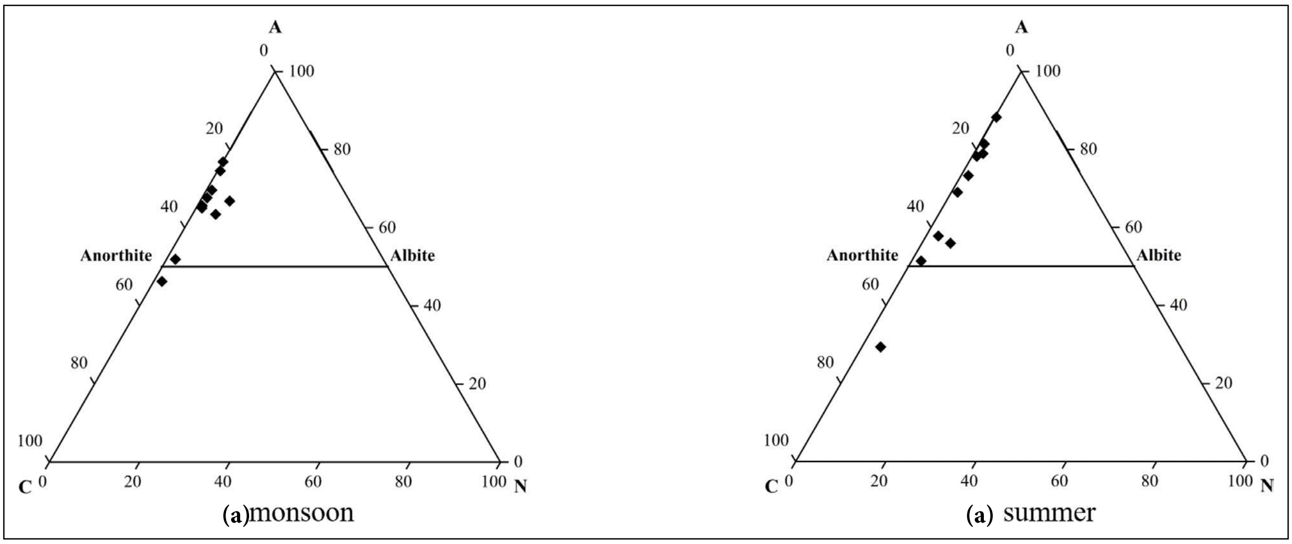

Figure 5. A-C-N ternary diagram of the study area **(a)** monsoon and **(b)** summer.

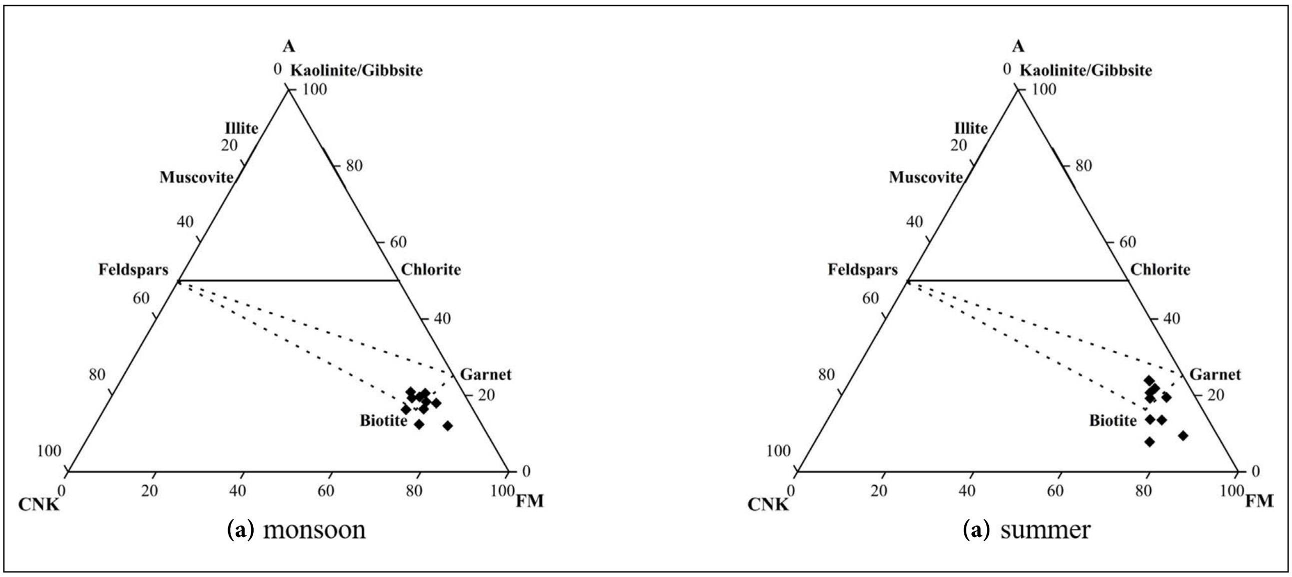

Figure 6. A-CNK-FM ternary diagram of the study area **(a)** monsoon and **(b)** summer.

In the A-CNK-FM (Al_2O_3 - ($CaO + Na_2O + K_2O$) - ($Fe_2O_3 + MgO$)) diagram all the sediment samples lie below the feldspar region indicating the presence of garnet and biotite in the study area (Fig. 6). Gneiss dominates the Noyyal basin's subsurface, reaching its maximum in the center. The southern and southeast regions of Noyyal are home to charnockite and on the eastern edge basic rock are found. Patches of pink granite may be observed in the western, southwestern, and southeast sections. The basin is also encompassed by several types of rocks, including basic and ultra-mafic rocks, garnet-sillimanite graphite gneiss, granite, charnockite, fissile hornblende biotite gneiss, and hornblende biotite gneiss [13]. The A-CNK-FM diagram provides evidence of the existence of these minerals in the studied sediment samples indicating that the underlying rock formations are mostly composed of igneous and metamorphic rocks.

CONCLUSION

The surface sediment of the Noyyal River basin was geochemically analyzed to understand the major oxide geochemistry, weathering intensity, and provenance. Based on the findings and the subsequent discussion of the current study, the following conclusions may be drawn:

- Major element data suggests that the major sources of sediments were mafic and intermediate igneous rocks.
- The CIA and PIA values, CIA and K/Na values, and the sediments' CIA and Al/Na values suggest low to intermediate silicate weathering in the sample locations.
- The average ICV score suggests that rock-forming minerals like plagioclase and alkali-feldspar are more prevalent and fewer clay minerals are present.
- The A-CN-K plot shows that the weathering tendency tends to be around the A-vertex and toward muscovite

and illite. All the samples are above the feldspar join line, indicating plagioclase with CIA values >50.

- The A-C-N plot shows a single line for the plagioclase weathering trend, indicating that the parent rocks' plagioclases are low to intermediately weathered. The sediments display a linear trend with high CaO values and are enriched in Al_2O_3 suggesting that the sediments gradually reduce albite and are enriched in the weathering of anorthite parent material
- The A-CNK-FM shows all the sediment samples lie below the feldspar region indicating the presence of garnet and biotite and provides evidence of the existence of these minerals indicating that the underlying rock formations are mostly composed of igneous and metamorphic rocks.

The Noyyal River basin illustrates the intricate interaction between natural and human-induced processes that control the mobility and accumulation of surface material. The transportation of surface material in the Noyyal River basin from its provenance to its sink is an intricate process that is affected by geological, hydrological, land use, climate, and human variables. Comprehending this process is crucial for efficient river basin management and reducing the consequences of sediment-related problems such as inundation, deterioration of water quality, and accumulation of sediment in reservoirs.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

The relationship between economic growth, population, FDI, globalization, and CO_2 emissions in OIC member countries

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ABSTRACT

The concentration of CO_2 emissions in OIC member countries has decreased over the past decade. The theory of sustainable growth suggests that increased CO_2 emissions can be influenced by various factors such as economic growth, population, FDI, and globalization, and vice versa. However, economic growth, population, FDI, and globalization in OIC member countries have all increased, which contradicts the theory of sustainable growth. Therefore, this study aims to test and analyze the effects of economic growth, population, FDI, and globalization on CO_2 emission concentrations in OIC member countries. This research is quantitative, using data on economic growth, population, FDI, globalization index, economic globalization, political globalization, and social globalization for 53 OIC member countries over the period from 1992 to 2020, obtained from various sources such as the World Bank, UNCTAD, and the KOF Index of Globalization. The data analysis technique used is the System GMM. The results of this study show that economic growth and increased FDI have a significant effect on increasing CO_2 emission concentrations. In contrast, increases in population and globalization have a reducing effect on CO_2 emission concentrations in OIC member countries.

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INTRODUCTION

Over the past 150 years, humans have increased the concentration of carbon dioxide (CO_2) in the atmosphere from about 280 ppm (parts per million) to the current 385 ppm [1]. The increase in CO_2 emissions has caused the global average temperature to rise by about 1 °C since the pre-industrial period, while the oceans have increased in temperature and acidity as they absorb CO_2 and heat [2]. Global resources have depleted since the second half of the twentieth century, and environmental crises have intensified. To address these conditions, a sustainable development strategy was proposed in "Our Common Future" by the World Commission on Environment and Development in 1987. During this period, the concept of the circular economy emerged to reduce the consumption of natural resources and minimize environmental pollution by considering the circulation of resources within social and economic systems [3]. Emissions from burning fossil fuels significantly contribute to today's hotly debated ecological issues. More than half of the contribution to the greenhouse effect is caused by CO_2, primarily released due to the use of fossil fuels, with no economically viable technologies for CO_2 reduction currently available [4]. The continued use of fossil fuels will negatively impact environmental sustainability due to increased CO_2 emissions and may eventually erode the earth's ozone layer.

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The growth of CO_2 emissions in OIC (Organisation of Islamic Cooperation) member countries shows fluctuations from year to year (Fig. 1). From 1992 to 2006, CO_2 emissions produced by OIC member countries continued to increase. However, from 2007 to 2009, they showed a downward trend, which could be attributed to the Subprime Mortgage crisis that negatively impacted the performance of global industries, leading to a reduction in CO_2 emissions. In 2010, CO_2 emissions in OIC countries began to rise again, reaching their peak in 2012. However, from 2013 to 2020, CO_2 emissions generally decreased yearly, indicating growing public awareness in OIC member countries of the importance of sustainability in environmental ecosystems, alongside increased encouragement to adopt renewable technologies over the last decade. The theory of sustainable growth was first coined by Meadows [5] in 1972 in "The Limits to Growth." Meadows revealed that achieving balance in sustainable growth requires consideration of several influencing factors. These factors include population, capital, birth rate, death rate, investment value, depreciation, community values, environmental sustainability, social welfare, and technological progress.

A country's economic growth is one factor that influences the growth of CO_2 emissions. Research on the impact of economic growth on CO_2 emissions has been widely conducted, yielding a variety of findings [6–8]. Anwar's findings show that economic growth significantly increases CO_2 emissions [9]. Meanwhile, Mujtaba's [10] findings show the opposite result, indicating that economic growth significantly reduces CO_2 emissions. By 2022, the total GDP of OIC countries had increased to US$ 8.7 trillion as a result of the ongoing gradual recovery. This economic measure shows that the OIC country group accounted for 8.7% of global GDP that year, up 0.9 percentage points from the previous year. Regarding Purchasing Power Parity (PPP) expressed in international dollars, the total GDP of OIC countries reached 24.4 trillion dollars and accounted for 14.9% of global GDP in 2022, up 0.3 percentage points from 2021 [11]. Based on these data, economic growth may be a factor that plays a role in influencing the increase in CO_2 emissions in OIC member countries. However, some findings suggest that economic growth can also play a role in reducing CO_2 emission levels. Thus, the relationship between economic growth and CO_2 emissions needs further analysis.

Another factor that is thought to influence the growth of CO_2 emissions is the growth of a country's population. As the population increases, new houses, office buildings, malls, and roads are built to accommodate this growth, covering fertile agricultural land and forests that could otherwise absorb CO_2 emissions [12]. By 2021, it is estimated that there will be 1.9 billion Muslims, making up about 25% of the world's population. Over the next decade, the Muslim population is projected to continue growing at twice the rate of the non-Muslim population [13]. Populations in OIC countries are urbanizing more rapidly than the global average. This trend contributes to increased CO_2 emissions in OIC countries, as most economic activity, energy consumption, and greenhouse gas emissions occur in urban areas. Therefore, cities need to reduce their energy consumption and switch to renewable energy sources if they are to lower their carbon footprint significantly [14]. Mendonça's [15] findings show that population growth increases CO_2 emissions. However, Yang's [16] findings indicate that population growth contributes to reducing CO_2 emissions. Thus, based on this and the theory of sustainable growth, there is an indication that population growth plays a role in the growth of CO_2 emissions. More in-depth analyses are needed to determine how this influence is realized.

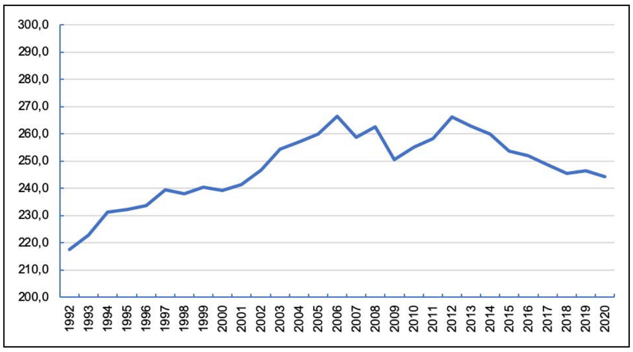

Figure 1. CO_2 emission growth of OIC member countries from 1992–2021.

Source: World Bank Data, 2024.

It is also suspected that Foreign Direct Investment (FDI) is one of the factors that can affect the growth of CO_2 emissions. FDI represents investment in productive assets by a parent company in another country [17]. In 2022, FDI flows in OIC countries reached US$ 2.3 trillion, an increase of 18.4% from the value in 2018 [11]. Several studies reveal a relationship between FDI and CO_2 emission intensity [18–20]. Ali pointed out that the increase in FDI inflows to Organization of Islamic Cooperation (OIC) countries has had a detrimental impact on nature and ecological systems, rather than focusing on technology-oriented resource utilization [21]. This indicates that the growth of FDI in OIC member countries has been partially directed towards advancing environmentally friendly technological innovation, but has primarily focused on exploiting natural resources, which negatively impacts the environment and ultimately results in increased CO_2 emissions in these countries. However, Khan's [22] findings show that FDI has a significant positive impact on the ecological footprint and demonstrates an environmentally friendly effect in lower-middle-income OIC member countries. These findings present an opposite result compared to previous studies, making the impact of FDI on CO_2 emissions unclear.

Globalization is now also an essential factor in reducing CO_2 emissions. Several studies show that globalization influences CO_2 emissions [23–25]. Globalization plays a vital role as a means to spread and adopt technology in managing the digital economy market. Through globalization, opportunities for sustainable economic growth are opening up in several sectors, including renewable energy, sustainable transportation, and clean manufacturing, by introducing products and services based on renewable energy resources [26]. Although there is a general opinion that globalization and economic freedom have many benefits for a country's economy [27], the innovations generated by globalization can support the completion of work more efficiently and reduce costs [26]. An overview of globalization development in OIC countries shows that these countries are still having difficulty catching up with more developed nations. OIC countries still face challenges narrowing the economic and developmental gap with developed nations [28]. Therefore, the impact of globalization, such as the introduction of renewable energy technology that can reduce CO_2 emissions, has not been fully explained, and further analysis is needed to determine its impact.

Based on the previously described background, this study aims to analyze and identify the relationship between economic growth, population, FDI, and globalization on CO_2 emissions in OIC member countries. The research also aims to clarify the role of each of these factors in increasing or decreasing CO_2 emissions, considering the specific conditions in OIC countries. This research will provide deeper insights into effective environmental policies and sustainable development strategies for OIC countries. The implications of this research encompass several aspects, including the potential to serve as a foundation for policymakers in OIC member countries when formulating more effective and targeted environmental policies. By capturing the impact of economic growth, population, FDI, and globalization on CO_2 emissions, this research aids policymakers in identifying the key factors that contribute to increasing or decreasing emissions. Additionally, the findings can assist OIC countries in designing sustainable development strategies that balance economic growth with environmental protection, emphasizing green technologies and energy efficiency. The research can also guide international investment and trade decisions by providing insights into how FDI and globalization affect CO_2 emissions and how to direct investments to support greener technologies and practices.

LITERATURE REVIEW

Economic Growth and CO_2 Emissions

Dadkhah explains that national income is an important indicator reflecting a country's economic condition, encompassing the total output of goods and services produced (GDP) as well as its distribution within society, including wages, corporate profits, rental income, interest, and other forms of income [29]. The relationship between economic growth and the environment has long been discussed, notably since the United Nations report "Our Common Future" introduced the concept of "Sustainable Development." Developing countries, including OIC members, often focus more on poverty alleviation than on adopting advanced technologies for environmental protection, unlike high-income developed countries [30]. Meadows [5] explains that increased energy use as part of economic development is often directly related to rising CO_2 emissions. This is because many energy sources used in the economic development come from fossil fuels, which produce carbon emissions. In other words, the more energy consumed to enhance productivity and efficiency, the greater the potential for CO_2 emissions. Adedoyin [31] also supports this statement by asserting that increasing fossil energy production to support economic growth will exacerbate CO_2 emissions and hinder the achievement of sustainable development.

Previous research on the impact of economic growth on CO_2 emissions has produced mixed results. Some studies indicate that economic growth significantly increases CO_2 emissions, as observed in Osobajo's [32] study of 70 countries from 1994 to 2013. Similarly, Li's [33] findings show that economic growth in China, driven by fossil fuel consumption, has significantly increased total CO_2 emissions. These findings are also consistent with Zhang's [34] study of five Asian countries in the short term. However, other studies have shown different findings, such as those of Namahoro et al. [35], which indicate that economic growth has contributed to reducing CO_2 emissions in 50 African countries. Hdom and Fuinhas [36] found that economic growth decreased CO_2 emissions in Brazil and emphasized the need for more significant investment in sustainable infrastructure to support economic growth while reducing emissions. This finding aligns with Rahman's [37] research, which suggests that investment in green technology can promote greener economic growth. This gap in the literature highlights the uncertainty about how economic growth affects CO_2 emissions in different countries. Therefore, more in-depth studies are needed to understand the relationship between economic growth and CO_2 emissions.

Population and CO_2 Emissions

According to Gluns [38], population growth refers to the increase in an area's population over time caused by a higher birth rate than death rate, as well as immigration into the area. The relationship between CO_2 emissions and population is that the more people there are, the greater the need for transportation, electricity, and consumer goods. This can increase CO_2 emissions due to more intense economic activity, even though pollution control technologies have improved [39]. Meadows [5] states that uncontrolled population growth can lead to increased land and resource use, which can cause environmental degradation and higher CO_2 emissions. Additionally, although technology can extend the growth period, more than technological solutions are needed to overcome the limits imposed by population pressure and industrial activities on the environment, including CO_2 emissions. Khan [40] argues that rapid population growth accelerates the depletion of natural resources. As the population increases, the demand for resources such as fossil fuels also rises to meet growing energy needs. This results in increased combustion of fossil fuels, which is one of the primary sources of CO_2 emissions. In other words, the more energy the population requires, the greater the amount of fossil fuels burned, increasing CO_2 emissions.

Studies conducted in different countries provide a varied picture of how population growth affects CO_2 emissions [16, 41–44]. Some findings show that population growth leads to an increase in CO_2 emissions, as found by Mendonça et al. [15] in 50 countries during the period 1990 to 2015. Anser et al. [45] also found that population growth increased CO_2 emissions in member countries of the South Asian Association for Regional Cooperation (SAARC) from 1994-2013. Chandra et al. [46] further points out that population growth significantly increases CO_2 emissions. With more people, the demand for energy for homes, industries, and businesses also rises. This often leads to constructing more power plants that use fossil fuels such as coal and oil, which produce large amounts of CO_2. Additionally, a larger population means a greater need for goods and services, leading to increased production, transport, and packaging, which contributes to CO_2 emissions [46]. However, some findings show that population growth affects reducing CO_2 emissions, as observed by Rehman [47] in Pakistan from 2001 to 2014. Although many studies have explored the relationship between population growth and CO_2 emissions, its influence on CO_2 emissions is still unclear. Therefore, more in-depth analyses are needed to understand the impact of the population on CO_2 emissions.

FDI and CO_2 Emissions

In the relationship between FDI and CO_2 emissions, Meadows states that sustainable growth focuses on various factors that affect development, such as population, capital, technology, investment value, technological progress, and environmental sustainability. Factors like investment value and technological progress are related to how FDI can impact the growth of CO_2 emissions. FDI can bring more efficient technology or capital that increases economic activity. These technologies and capital can, in turn, affect CO_2 emissions by reducing them through clean technologies or increasing them through more excellent energy production and consumption [5]. Veidenheimer [48] explains that FDI can help reduce CO_2 emissions per unit of output by transferring green technology and exploiting economies of scale. By attracting more FDI, countries can improve efficiency and reduce production costs and CO_2 emissions per unit of output. However, to achieve such benefits, significant initial investments in infrastructure and technology are required. Wang [49] explains that FDI is one of the drivers of increased CO_2 emissions. Meanwhile, Marques and Caetano [50] argues that in developed countries, increased FDI can reduce CO_2 emissions, whereas in middle-income countries, increased FDI tends to increase CO_2 emissions.

Previous studies on the relationship between FDI and CO_2 emissions have shown mixed results. Some findings indicate that an increase in FDI leads to a significant rise in CO_2 emissions, as seen in Ullah's [51] study on Vietnam from 1975 to 2017. Similarly, Huang [52] demonstrated that increased FDI contributed to higher CO_2 emissions in G20 member countries from 1996 to 2018. Asongu and Odhiambo [53] also reported similar results for 49 SSA countries between 2000 and 2012. However, other studies present contrasting results, where an increase in FDI significantly reduces CO_2 emissions, such as Rafique's [54] findings for BRICS countries from 1990 to 2017. Wang's [55] research also revealed that an increase in FDI lowers CO_2 emissions in 28 provinces in China during the period 2000 to 2018. Several other studies align with this view [56, 57]. While theory suggests that FDI should reduce CO_2 emissions through the adoption of clean technology and improved efficiency, empirical evidence indicates that the impact of FDI is highly dependent on country-specific factors, such as environmental regulations, the level of economic development, and the type of technology adopted. Therefore, further research is needed to understand the conditions under which FDI will reduce or increase CO_2 emissions.

Globalization and CO_2 Emissions

Globalization is a key driver, including global price competitiveness and future automation. Communication technology enables companies to expand their reach globally [58]. In the relationship between globalization and CO_2 emissions, Meadows revealed that globalization increases interconnections between countries, accelerating technological progress and investment by transferring knowledge and capital. This fuels economic growth and infrastructure development and pressures the environment and social welfare [5]. Shahbaz [59] states that globalization is vital in reducing CO_2 emissions because it helps developing countries acquire the necessary technology and management experience to reduce pollution earlier in their economic development. Jahanger et al. [60] also mentions that globalization benefits developing countries by improving technology, production, and consumption efficiency, thus allocating more funds to environmentally friendly projects. This suggests that globalization can significantly help reduce environmental pollution. Ting Ma [61] provides evidence that participation in globalization can improve developing countries' performance in protecting the environment by implementing stricter regulations in response to pressure from international norms.

Studies on the effect of globalization on CO_2 emissions have been widely conducted by researchers, with mixed results. Some researchers state that an increase in globalization significantly impacts reducing CO_2 emissions. For example, Xiaoman's [25] study on Middle East and North Africa (MENA) countries from 1980 to 2018 found this effect. Tsimisaraka [62] also reported that an increase in globalization will decrease CO_2 emissions in OBOR countries. Umar's findings show that globalization played a vital role in reducing CO_2 emissions in China in the long run from 1980 to 2017 [23]. Similarly, Muhammad's [63] findings for 170 countries from 1990 to 2018 indicate increased globalization will increase CO_2 emissions. Conversely, Anser's [64] study shows increased CO_2 emissions are influenced by increased globalization in South Asian countries from 1985 to 2019. Other findings are consistent with this view [24, 65]. These studies highlight a gap between theory and reality regarding the impact of globalization on CO_2 emissions. While some studies suggest that

Table 1. Summary of literature review

Author	Year	Region	Period	Variable	Method	Results
Namahoro et al. [35]	2021	Afrika regions	1980–2018	GDP → CO_2	PMG, CCEMG, CS-DL	Negative
Hdom et al. [36]	2020	Brazil	1975–2016	GDP → CO_2	FMOLS, DOLS	Negative
Osobajo et al. [32]	2020	70 countries	1994–2013	GDP → CO_2	POLS, fixed effect	Positive
Li et al. [33]	2021	China	1990–2020	GDP → CO_2	ARDL	Positive
Adedoyin et al. [31]	2020	BRICS	1990–2014	GDP → CO_2	PMG-ARDL	Positive
Zhang et al. [34]	2023	6 Asian countries	1975–2020	GDP → CO_2	AMG	Positive
Rahman et al. [37]	2021	10 countries	1979–2017	GDP → CO_2	DOLS, FMOLS, PMG	Negative
Yang et al. [16]	2021	OCED	1971–2016	POP → CO_2	FMOLS, DOLS, AMG	Negative
Wang and Li [41]	2021	154 countries	1992–2016	POP → CO_2	Panel threshold model	Negative
Mendonça et al. [15]	2020	50 countries	1990–2015	POP → CO_2	Hierarchial regression	Positive
Anser et al. [45]	2020	SAARC countries	1994–2013	POP → CO_2	Fixed effect	Positive
Khan et al. [40]	2021	United States	1971–2016	POP → CO_2	GMM, GLM	Positive
Rahman et al. [43]	2021	Bangladesh	1973–2014	POP → CO_2	ARDL	Positive
Yu et al. [42]	2023	30 Provinces in China	2000–2019	POP → CO_2	Systematic GMM	Negative
Xiaoman et al. [25]	2021	MENA countries	1980–2018	GLB → CO_2	Cup-FM, Cup-BC	Negative
Umar et al.	2020	China	1980–2017	GLB → CO_2	ARDL	Negative
Muhammad and Khan [63]	2021	170 countries	1990–2018	GLB → CO_2	GMM, fixed effect	Negative
Anser et al. [64]	2021	South Asian	1985–2017	GLB → CO_2	FMOLS	Positive
Mehmood et al. [65]	2020	South Asian	1972–2013	GLB → CO_2	ARDL	Positive
Ma et al. [61]	2021	179 countries	1995–2014	GLB → CO_2	Fixed effect	Negative
Ullah et al. [51]	2021	Vietnam	1975–2019	FDI → CO_2	ARDL	Positive
Huang et al. [52]	2022	G20 countries	1996–2018	FDI → CO_2	FGLS	Positive
Rafique et al. [54]	2020	BRICS	1990–2017	FDI → CO_2	AMG	Negative
Asongu et al. [53]	2020	49 countries in SSA	2000–2012	FDI → CO_2	GMM	Negative
Wang and Li [41]	2021	30 provinces in China	2004–2016	FDI → CO_2	VECM	Positive
Lin et al. [56]	2022	China	2004–2015	FDI → CO_2	Two-way fixed effect	Negative
Khan et al. [57]	2023	108 countries	2000–2016	FDI → CO_2	VECM	Negative
Wang and Li [41]	2021	28 provinces in China	2000–2018	FDI → CO_2	Quantile regression	Negative

Source: Author processed, 2024.

globalization can reduce emissions through technology and efficiency, others indicate that it increases emissions due to economic activity and energy consumption. This suggests further research to understand the relationship between globalization and CO_2 emissions.

Gap Research

This study identifies a gap in the literature regarding the relationship between economic growth, population, FDI, and globalization with CO_2 emissions in OIC member countries. Meadows' sustainable growth theory states that increases in CO_2 emissions usually go hand in hand with economic growth, population, globalization and FDI. However, empirical data from OIC countries over the past decade show the opposite trend, where an increase in these variables is accompanied by a decrease in CO_2 emissions. This phenomenon suggests an anomaly that warrants further research to understand other factors that may have contributed to the decline in emissions in OIC countries, which have not been fully explained by existing theories. In addition, most previous studies have focused on developed or developing countries in general, without considering the unique characteristics of OIC countries. This study aims to test the relevance of Meadows' theory in the context of OIC countries, while exploring other factors that may play a role in reducing CO_2 emissions. As such, this study is expected to make a significant contribution to understanding the complexity of the relationship between economic and environmental variables in OIC countries, as well as assist policy makers in formulating more sustainable development strategies.

MATERIALS AND METHODS

Research Approach and Data

This research is a quantitative study utilizing secondary data within the category of dynamic panel data. Quantitative research is an approach that involves the collection, analysis, and interpretation of data in numerical or statistical form to investigate relationships, patterns, or trends within a phenomenon [66]. The data analyzed include annual data on CO_2 emissions, GDP, population, Globalization Index, Economic Globalization, Political Globalization, Social Globalization, and FDI for OIC member countries (Table 3) covering the period from 1992 to 2020. The data sources representing the sample in this study are presented in Table 2. The collected data were processed and analyzed using Stata 17 and Eviews 12 software.

Table 2. Variables and data sources

Variable	Description	Unit	Period	Source
CO_2	CO_2 per capita	Metric tons	1992–2020	World Bank data
Y	GDP per capita	US dollar	1992–2020	World Bank data
P	Population	Million person	1992–2020	World Bank data
FDI	Foreign direct investment	Million USD	1992–2020	UNCTAD
IG	Index of globalization	Scale (1–100)	1992–2020	KOF globalization
EG	Economic globalization	Scale (1–100)	1992–2020	KOF globalization
PG	Political globalization	Scale (1–100)	1992–2020	KOF globalization
SG	Social globalization	Scale (1–100)	1992–2020	KOF globalization

Source: Author processed, 2024.

Table 3. Country list

Country	Period	Country	Period	Country	Period	Country	Period
Afghanistan	1993–2020	Gabon	1992–2020	Malaysia	1992–2020	Sudan	1992–2020
Albania	1992–2020	Gambia	1992–2020	Maldives	1992–2020	Suriname	1992–2020
Algeria	1996–2020	Guinea	1992–2020	Mali	1992–2020	Tajikistan	1995–2020
Azerbaijan	1994–2020	Guinea–Bissau	1992–2020	Mauritania	1992–2020	Togo	1992–2020
Bahrain	1999–2020	Guyana	1992–2020	Morocco	1992–2020	Tunisia	1992–2020
Bangladesh	1992–2020	Indonesia	1992–2020	Mozambique	1992–2020	Türkiye	1992–2020
Benin	1992–2020	Iran	1992–2020	Niger	1992–2020	Turkmenistan	2000–2020
Brunei	1992–2020	Iraq	2000–2020	Nigeria	1992–2020	Uganda	1992–2020
Burkina Faso	1992–2020	Jordan	1992–2020	Oman	1992–2020	UAE	1992–2020
Cameroon	1992–2020	Kazakhstan	1997–2020	Pakistan	1997–2020	Uzbekistan	1995–2020
Chad	1992–2020	Kuwait	1999–2020	Qatar	1995–2020	Yemen	1992–2016
Comoros	1992–2020	Kyrgyzstan	1994–2020	Saudi Arabia	1994–2020		
Cote d'Ivoire	1992–2020	Lebanon	1992–2020	Senegal	1993–2020		
Egypt	1992–2020	Libya	1992–2020	Sierra Leone	1992–2020		

Source: Author processed, 2024.

Model Specifications

In creating the econometric model, we based it on Meadows' [5] statement that the factors affecting pollution are economic growth, population, investment, and globalization. Additionally, we used previous studies to select the variables for the model. The first variable selected regarding its influence on CO_2 emissions is economic growth [32, 33, 35, 36]. This variable was chosen because economic growth is often directly related to the level of energy use and CO_2 emissions. Economic growth is usually accompanied by increased energy consumption, much of which comes from fossil fuels that produce CO_2 emissions. Some studies also mention the effect of population on CO_2 emissions [15, 16, 41, 45]. An increase in population is generally associated with higher energy consumption and transport, increasing CO_2 emissions. Other studies show that FDI influences CO_2 emissions [49, 56, 57]. FDI can impact CO_2 emissions by introducing new technologies and practices that may increase or reduce emissions, so the FDI variable is included in the model. The following variable included in the model is globalization. In this study, the globalization variable consists of the globalization index, economic globalization, political globalization, and social globalization. Globalization can affect CO_2 emissions through increased trade, investment, and cultural exchange, which can lead to higher energy consumption and transportation [23, 25, 63, 64]. We transformed all variables into natural logarithms to obtain elasticity and simplify data processing. Logarithmic transformation also helps reduce heteroscedasticity and address scale issues between variables. Thus, the econometric model can be written as follows:

$$lnco_2=\beta_1\ lnco_{2i,t-1}+\beta_2\ lny+\beta_2\ lnp+\beta_3\ lnfdi+\beta_4\ lnig+\beta_5\ lneg+\beta_6\ lnpg+\beta_7\ lnsg+\varepsilon_{it} \quad (1)$$

Where $lnco_2$ is the natural logarithm of carbon dioxide, *lny* is the natural logarithm of GDP, *lnp* is the natural logarithm of population, *lnfdi* is the natural logarithm of FDI, *lnig* is the natural logarithm of globalization index, *lneg* is the natural logarithm of economic globalization, *lnpg* is the natural logarithm of political globalization, and *lnsg* is the natural logarithm of social globalization. The use of $lnco_{2\ i,t-1}$ indicates the dependence of current CO_2 emissions on CO_2 emissions in the previous period, reflecting the dynamic nature of the CO_2 emission phenomenon. Then the interaction between economic growth, population, and FDI variables with globalization is included in the model to measure the combined effect of these variables on CO_2 emissions, as the effect of one variable may differ when influenced by another variable. Furthermore, globalization drives economic growth by increasing trade, investment, and market efficiency. Increased economic activity often results in higher energy production and consumption, leading to increased CO_2 emissions if the energy comes from non-renewable sources [67]. Some OIC countries still depend on fossil fuels to support their economic growth, and as industrial activity and energy consumption increase, they experience a rise in CO_2 emissions. Therefore, in the model (2), we include the interaction between economic growth and globalization to measure the combined impact of economic growth and globalization on CO_2 emission growth.

$$lnco_2=\beta_1\ lnco_{2i,t-1}+\beta_2\ lny+\beta_2\ lnp+\beta_3\ lnig+\beta_4\ lneg+\beta_5\ lnpg+\beta_6\ lnsg+\beta_7\ lnfdi+\beta_8\ (lny\times lnig)+\varepsilon_{it} \quad (2)$$

Where *lny×lnig* represents the interaction between the economic growth and globalization variables. Furthermore, population growth is usually accompanied by an increase in energy consumption. Globalization, which often drives industrialization and urbanization, also increases energy consumption. If the primary energy source is fossil fuels, this will lead to increased CO_2 emissions [68]. Therefore, model (3) includes the interaction between population and globalization to measure their combined effect on CO_2 emission growth.

$$lnco_2=\beta_1\ lnco_{2i,t-1}+\beta_2\ lny+\beta_2\ lnp+\beta_3\ lnig+\beta_4\ lneg+\beta_5\ lnpg+\beta_6\ lnsg+\beta_7\ lnfdi+\beta_8\ (lnp\times lnig)+\varepsilon_{it} \quad (3)$$

Where *lnp×lnig* represents the interaction between population and globalization variables. Furthermore, developed countries may shift the production of polluting goods to developing countries. Globalization, through foreign investment flows, may accelerate this phenomenon [57]. OIC member countries, mainly developing countries, often have more lax environmental regulations than developed countries. As a result, FDI from developed countries may lead to increased CO_2 emissions in these developing countries. Thus, in the model (4), we also include the interaction between FDI and globalization to measure the combined impact of FDI and globalization on CO_2 emission growth.

$$lnco_2=\beta_1\ lnco_{2i,t-1}+\beta_2\ lny+\beta_2\ lnp+\beta_3\ lnig+\beta_4\ lneg+\beta_5\ lnpg+\beta_6\ lnsg+\beta_7\ lnfdi+\beta_8\ (lnfdi\times lnig)+\varepsilon_{it} \quad (4)$$

Where *lnfdi×lnig* represents the interaction between FDI and globalization variables. So that the interaction effect of FDI and globalization can be seen on the growth of CO_2 emissions.

Data Analysis Method

The method used in this study is the Generalized Method of Moments (GMM). GMM is a statistical method used in econometric analysis to evaluate and estimate parameters in statistical models introduced by Arellano and Bond [69]. In the difference GMM estimator, the instrument uses lagged values of the differences and levels of the endogenous variables to overcome the endogeneity problem under the assumption that the first differences of the instrument variables are uncorrelated with the fixed effects. However, the difference GMM has the limitation of lacking efficiency in estimating parameters, especially when the model considers long-run relationships between variables. In addition, using only the first difference of the endogenous variable as an instrument may ignore important information from the level of the endogenous variable and cause bias in parameter estimation. Therefore, the GMM system was introduced by Arellano-Bover [70] and Blundell-Bond [71] as a development of difference GMM. System GMM is used to deal with endogeneity by extending the difference GMM approach to consider the second difference of the endogenous variables as well as incorporating the exogenous variables as instruments. In the GMM system, lagged values of the levels of endogenous variables are used. It also allows the model to capture the long-run effects of exogenous variables and is more efficient in estimating parameters.

Although the GMM method offers many advantages, some limitations must be considered. Complex endogeneity problems can still occur even though GMM is designed to address endogeneity. Therefore, better instrument selection and rigorous instrument validation are required. Estimation efficiency is also a concern, as Difference GMM may be less efficient at estimating parameters, especially when the model considers long-run relationships between variables. The use of System GMM can improve estimation efficiency by considering second differences of endogenous variables as well as exogenous variables as instruments. In addition, dynamic panel data requires certain assumptions that may not always hold in every case. Alternative techniques such as System GMM can help overcome some limitations. Instrument validity is also fundamental, as invalid instruments may result in biased estimates. The Sargan and Arellano-Bond autocorrelation tests are used to ensure instrument validity and consistency of estimation results.

RESULTS AND DISCUSSION

Descriptive Statistics and Correlation Matrix

Descriptive statistics of the variables in this study are presented in Table 4. The average CO_2 emissions per capita of OIC member countries is 4.50 metric tons, with a standard deviation of 7.72. The minimum value of CO_2 emissions is 0.04 metric tons, indicating that some countries have low CO_2 emissions, while the maximum value is 47.66 metric tons, suggesting that some OIC countries have very high CO_2 emissions. The average value for the GDP per capita variable is 5,584.94$, with a minimum of 137.18$ and a maximum of 98,041.41$, indicating positive economic development in OIC member countries. The average population is 27.80 million, with a minimum of 0.24 million and a maximum of 271.86 million, indicating a medium population size on

Table 4. Descriptive statistics

Variable	Mean	Std. dev	Min	Max
CO_2	4.50	7.72	0.04	47.66
Y	5583.94	10949.78	137.18	98041.40
P	27.80	47.77	0.24	271.86
FDI	1436.18	3219.54	-10176.40	25120.70
IG	49.49	12.14	22.10	81.10
EG	47.73	14.76	7.90	87.70
PG	57.13	17.76	11.90	92.70
SG	43.59	16.61	10.50	83.00

Source: STATA Output, 2024.

Table 5. Correlation matrix of variables from 53 OIC member countries

	$LNCO_2$	LNY	LNP	LNFDI	LNIG	LNEG	LNPG	LNSG
$LNCO_2$	1.0000							
LNY	0.8857	1.0000						
LNP	-0.1933	-0.2358	1.0000					
LNFDI	0.4692	0.5060	0.4246	1.0000				
LNIG	0.6460	0.6948	0.1296	0.7075	1.0000			
LNEG	0.6514	0.6238	-0.2079	0.4770	0.7589	1.0000		
LNPG	0.0420	0.0999	0.6853	0.5428	0.6003	0.0918	1.0000	
LNSG	0.7451	0.7970	-0.2808	0.4995	0.8182	0.6929	0.1456	1.0000

Source: STATA Output, 2024.

average across OIC countries. The Globalization Index variable has an average of 49.49, suggesting that globalization in OIC countries is classified as developing. The average values for Economic Globalization, Political Globalization, and Social Globalization are 47.73, 57.13, and 43.59, respectively. The FDI variable has an average value of 1,436.18$ thousand, with a minimum value of -10,176.40$ thousand and a maximum of 25,120.70$ thousand. This range reflects the inadequate infrastructure in some OIC member countries, which can lead to lower foreign investor interest.

The correlation matrix in Table 5 shows the relationship between the variables studied. GDP per capita shows a robust positive correlation with CO_2 emissions at 88.57%, indicating a significant contribution of economic growth to the increase in CO_2 emissions in OIC member countries. Social Globalization also exhibits a positive correlation, at 74.51%, followed by Economic Globalization at 65.14%. Additionally, the Globalization Index shows a correlation of 64.60%, indicating that the growth of globalization substantially influences the growth of CO_2 emissions in OIC member countries. FDI shows a correlation of 46.92%. In contrast, Political Globalization contributes very little to the growth of CO_2 emissions, with a correlation of 4.20%. Notably, the relationship between Population and CO_2 emission growth is negative, with a correlation of -19.33%, suggesting that population growth contributes very little to CO_2 emissions in OIC member countries.

Unit Root Tests

The stationarity test refers to checking whether the statistical properties of a time series remain consistent over time. In this context, the stationarity test aims to determine whether some trends or patterns may affect the behavior of the time series. In this study, the Augmented Dickey-Fuller (ADF) and Phillips-Perron (PP) tests are used to test the stationarity of the data. The null hypothesis for these tests is that the data is stationary. If the data turns out to be non-stationary, the next step is to transform it to achieve stationarity before further modeling [72]. The results of the unit root or stationarity test are presented in Table 6. The unit root test results using the Augmented Dickey-Fuller (ADF) and Phillips-Perron (PP) methods show that most variables in this study are not stationary at the level but become stationary after first differencing. The variables $LNCO_2$, LNY, LNP, LNSG, and LNIG are not significant at the level but become significant at the 1% level after first differencing. Meanwhile, the variables LNFDI, LNEG, and LNPG are significant at the level and become even more significant after first differencing.

Empirical Results

The System GMM (One-Step) results in Model (1) show that an increase in GDP per capita has a statistically significant positive effect on CO_2 emissions at the 5% level. This indicates that increasing GDP per capita will increase

Table 6. Unit root test results

Variable	Augmented dickey fuller		Phillips-perron	
	Level	First difference	Level	First difference
$LNCO_2$	-0.01328	-15.9269***	-0.32705	-24.3342***
LNY	1.44983	-14.7592***	1.42439	-19.8488***
LNP	6.76055	-7.63735***	6.76320	-5.99558***
LNFDI	-2.95539***	-21.6938***	-7.88638***	-31.0757***
LNIG	-1.31639*	-16.2449***	-2.92135***	-22.5276***
LNEG	-2.87490***	-17.3072***	-5.75709***	-27.5009***
LNPG	-4.52863***	-19.0307***	-8.41432***	-26.5086***
LNSG	0.43378	-11.5910***	0.65713	-20.4595***

Source: Eviews Output, 2024. Significant at 10% (*), 5% (**), 1% (***).

CO_2 emissions in OIC member countries. This finding is consistent with Meadows' sustainable growth theory, which states that economic growth positively and significantly affects CO_2 emissions. It also aligns with the research by Osobajo et al. [32] and Li and Haneklaus [33]. Meanwhile, population has a statistically significant negative effect on CO_2 emissions at the 10% level, suggesting that an increase in population will reduce CO_2 emissions in OIC member countries. This finding is consistent with the research by Yang et al. [16] and Wang and Li [41], though it contradicts the sustainable growth theory, which posits that an increase in population will increase CO_2 emissions. The interaction between FDI and CO_2 emissions shows that FDI has a statistically significant positive effect on CO_2 emissions at the 5% level, indicating that an increase in FDI will lead to higher CO_2 emissions in OIC member countries. This finding aligns with the research by Ullah et al. [51] and Huang [52]. The Globalization Index has a statistically significant negative effect on CO_2 emissions at the 1% level, indicating that an increase in the Globalization Index will decrease CO_2 emissions in OIC member countries. This finding is consistent with the research by Xiaoman et al. [25], Umar et al. [23], and Muhammad and Khan [63]. Furthermore, Economic Globalization, Political Globalization, and Social Globalization have a positive and statistically significant effect on the increase in CO_2 emissions, indicating that an increase in these three variables can contribute to the growth of CO_2 emissions in OIC member countries.

Model (2) shows the interaction between GDP per capita and the Globalization Index on CO_2 emissions. The interaction between these two variables has a statistically significant negative effect on CO_2 emissions at the 5% level, suggesting that their combined effect will reduce CO_2 emissions in OIC member countries, including the interaction between GDP per capita and the Globalization Index results in the Globalization Index having a positive impact on CO_2 emissions, which is statistically significant at the 5% level. This finding aligns with the research by Anser et al. [64] and Mehmood and Tariq [65], which states that an increase in globalization will lead to higher CO_2 emissions. Model (3) shows that the interaction between the Population Index and Globalization has a statistically significant negative effect on CO_2 emissions at the 10% level, indicating that their combined effect will reduce CO_2 emissions in OIC member countries. Including the interaction between Population and the Globalization Index causes the Population variable to have a positive and statistically significant effect on CO_2 emissions at the 10% level. This suggests that increased population will increase CO_2 emissions in OIC member countries. This finding is consistent with the research by Mendonça et al. [15] and Anser et al. [45]. Then, in Model (4), the interaction between FDI and the Globalization Index shows a negative but statistically insignificant effect on CO_2 emissions. The interaction causes the Population variable and the Globalization Index variable to negatively and statistically significantly affect CO_2 emissions in OIC member countries. Meanwhile, Models (1) through (4) constants show negative values.

The System GMM (Two-Step) results in Table 8 show that the variable interactions in Model (1) are the same as in the One-Step GMM, but the constant in Model (1) shows a positive value. Meanwhile, Model (2) shows a different interaction with the Population variable, where Population has a positive but statistically insignificant effect on CO_2 emissions. In Model (3), changes occur in the Population, Globalization Index variables, and the interaction between Population and Globalization Index. Population and Globalization Index shows a positive but statistically insignificant effect on CO_2 emissions. Meanwhile, the combined effect of the Population and Globalization Index shows a negative but statistically insignificant impact on CO_2 emissions. In Model (4), the difference lies in the combined impact of FDI and Globalization Index, where the effect becomes negative and statistically significant on CO_2 emissions in the Two-Step GMM. This suggests that the combined impact of FDI and the Globalization Index will reduce CO_2 emissions in OIC member countries.

Model criteria tests, such as instrument tests and autocorrelation tests, are needed to ensure the model's validity. We use the Sargan [73] test to determine the validity of the instruments in the model, with the null hypothesis stating

Table 7. GMM test results (one-step)

Variable	(1)	(2)	(3)	(4)
$LNCO_{2\,i,t-1}$	0.9296***	0.9291***	0.9282***	0.9294***
	(0.0133)	(0.0133)	(0.0133)	(0.0133)
LNY	0.0234**	8.7011**	0.0238**	0.0237**
	(0.0118)	(3.7450)	(0.0117)	(0.0118)
LNP	-0.0297*	-0.0299*	2.2032*	-0.0294*
	(0.0157)	(0.0157)	(1.2328)	(0.0158)
LNFDI	0.0065**	0.0063**	0.0063*	0.0921
	(0.0032)	(0.0032)	(0.0032)	(0.2535)
LNIG	-1.2248***	7.4779**	1.0255	-1.1405***
	(0.3440)	(3.7696)	(1.2955)	(0.4234)
LNEG	0.4496***	0.4481***	0.4452***	0.4504***
	(0.1114)	(0.1112)	(0.1111)	(0.1115)
LNPG	0.4450***	0.4364***	0.4321***	0.4443***
	(0.1258)	(0.1256)	(0.1258)	(0.1259)
LNSG	0.3472***	0.3391***	0.3456***	0.3475***
	(0.0974)	(0.0974)	(0.0972)	(0.0975)
LN(Y*IG)		-8.6768**		
		(3.7445)		
LN(P*IG)			-2.2322*	
			(1.2323)	
LN(FDI*IG)				-0.0857
				(0.2536)
Constant	-0.1529	-0.1879	-0.1515	-0.1511
	(0.2180)	(0.2183)	(0.2174)	(0.2183)
Obs	1419	1419	1419	1419
Sargan (Prob.)	0.1656	0.1821	0.1496	0.1652
Abond (Prob.)	0.7355	0.6702	0.7474	0.7266
FEM	0.8582206	0.8599803	0.8586164	0.8574561
PLS	0.9812088	0.9812486	0.9811302	0.9810241

Source: STATA Output, 2024. Notes: Significant at 10% (*), 5% (**), 1% (***).

that no overidentifying instruments are used. Therefore, the p-value must be more significant than alpha to accept the null hypothesis. The results of the Sargan test on all models in both the One-Step and Two-Step GMM systems show that the instruments used are valid, with all p-values greater than alpha. For the autocorrelation test, we use the Arellano-Bond [69] test to detect the presence of autocorrelation in model errors in GMM estimation, with the null hypothesis stating that there is no autocorrelation in the model used. The p-value must be more significant than alpha to accept the null hypothesis. The results of the autocorrelation test on all models also show no autocorrelation, indicating that all models are consistent and suitable for use. Additionally, to demonstrate the unbiasedness of the model, the estimation results must lie between the upwardly biased Pooled Least Squares (PLS) and the downwardly biased Fixed Effects. The test results show that all GMM model estimates fall between the PLS and Fixed Effects estimation results, indicating that all models used are unbiased.

In the aftermath of the COVID-19 pandemic, all countries, including OIC member states, are working to recover their declining economies. In 2022, OIC member countries experienced an increase in GDP per capita to US$12,851, a 10.8% increase from the previous year [11]. Economic growth in OIC member countries indicates an increase in economic activity. The analysis shows that economic growth can lead to increased CO_2 emissions. Meadows revealed that massive industrial expansion often drives a country's economic growth [5]. However, industrial growth that relies on fossil fuels can result in higher CO_2 emissions, which have severe environmental impacts. Using fossil fuels tends to be more desirable due to their low cost [74]. To mitigate these impacts, OIC

Table 8. GMM test results (two-step)

Variable	(1)	(2)	(3)	(4)
LNCO2 i,t-1	0.9051***	0.9162***	0.9083***	0.9093***
	(0.0186)	(0.0197)	(0.0233)	(0.0178)
LNY	0.0332***	7.1327**	0.0263***	0.0308***
	(0.0094)	(2.3748)	(0.0068)	(0.0103)
LNP	-0.0766***	-0.0138	2.1523	-0.0579**
	(0.0293)	(0.0466)	(1.5300)	(0.0286)
LNFDI	0.0079***	0.0083***	0.0075***	0.7623**
	(0.0013)	(0.0014)	(0.0012)	(0.3609)
LNIG	-2.2470***	5.0532*	0.5060	-1.7691**
	(0.5272)	(2.6992)	(1.6409)	(0.8987)
LNEG	0.6727***	0.7002***	0.5237***	0.7401***
	(0.1489)	(0.1969)	(0.1618)	(0.2390)
LNPG	0.8404***	0.7472***	0.5886***	0.9397***
	(0.2003)	(0.2515)	(0.2181)	(0.3126)
LNSG	0.6820***	0.5830***	0.5215***	0.7326***
	(0.1640)	(0.1826)	(0.1425)	(0.2345)
LN(Y*IG)		-7.1100***		
		(2.3718)		
LN(P*IG)			-2.1945	
			(1.5265)	
LN(FDI*IG)				-0.7530**
				(0.3605)
Constant	0.1745	0.0023	0.1535	0.3618
	(0.2278)	(0.2014)	(0.2362)	(0.3623)
Obs	1419	1419	1419	1419
Sargan (Prob.)	1.0000	1.0000	1.0000	1.0000
Abond (Prob.)	0.8193	0.6737	0.8871	0.7065

Source: STATA Output, 2024. Notes: Significant at 10% (*), 5% (**), 1% (***).

member states need to intensify the shift to renewable energy by diversifying energy sources, developing green policies, raising awareness and education, and fostering regional and international cooperation. Strategies that can be implemented include investment in renewable energy infrastructure, public-private partnerships, research and development of clean energy technologies, and supportive regulations.

The population of OIC member countries has increased significantly over the past 33 years, reaching more than 1.9 billion in 2020, which accounts for 29.2% of the developing world's population and 24.5% of the global population. According to United Nations projections, this figure is expected to continue increasing [30]. This population increase can have both positive and negative impacts on environmental sustainability. The analysis shows that an increase in population can reduce CO_2 emissions. Ahlburg et al. [75] revealed that population growth drives increased efficiency, economies of scale, and technological innovation. However, population growth can also positively impact environmental sustainability, including a decrease in CO_2 emissions, provided that it is controlled. Therefore, population control policies that lead to sustainable growth must be strengthened to manage CO_2 emissions. OIC member countries should implement effective population control policies to ensure that population growth does not put excessive pressure on natural resources and the environment. Additionally, increasing public awareness through educational campaigns and training programs on the benefits of using renewable energy is necessary to maintain environmental sustainability.

The SESRIC report shows that the value of Foreign Direct Investment (FDI) inflows in OIC member countries was recorded at US$ 98 billion in 2020, increased to US$ 138 billion in 2021, but decreased by 1.7% in 2022 to US$ 135 billion. This value accounts for about 5.3% of total global FDI, down from a contribution of about 6.1% in 2018 [11]. The data shows that while FDI flows in OIC countries are stable, their contribution to global FDI is declining. The analysis shows that increased FDI can lead to higher CO_2 emissions. Mitchell [76] explained that a market-based approach to investment regulation can increase FDI, potentially boosting industrial activity and CO_2 emissions. An increase in FDI can drive industrial growth, including environmentally unfriendly FDI, potentially leading to higher CO_2 emissions. Although FDI flows in OIC countries are relatively stable, CO_2 emissions may also remain stable. Mitchell also emphasizes the need for regulations to reduce investment incentives that could lead to higher CO_2 emissions [76]. To effectively reduce CO_2 emissions, OIC member countries need to develop regulations that decrease investment incentives that increase emissions while providing incentives for green technologies.

Finally, the COVID-19 pandemic and changes in trade policies caused uncertainty in global supply chains, resulting in a decline in globalization within OIC member countries [77]. Post-COVID-19, OIC member countries reached a consensus to discuss policies, foster cooperation, and engage in joint problem-solving. This consensus encouraged OIC countries to plan strategies to harness globalization and capitalize on new opportunities for sustainable development [78]. The consensus highlights that globalization is vital in industrial development within OIC countries. Today, globalization drives market expansion, increased trade, and more excellent production, increasing energy consumption [79]. Increased globalization, especially within OIC member countries, can catalyze innovation in green technologies, contributing to reducing CO_2 emissions. Therefore, OIC member countries need to enhance international cooperation by leveraging globalization by transferring green technologies and sharing knowledge on sustainable industrial practices. OIC member countries should also devise appropriate strategies to exploit globalization's opportunities, including integrating environmental sustainability considerations into development planning.

CONCLUSION

The results of this study show that economic growth can increase the concentration of CO_2 emissions in OIC member countries. However, the combined effect of economic growth and globalization shows a statistically negative effect, indicating that an increase in both economic growth and globalization results in a decrease in CO_2 emission concentrations. Therefore, there is a need for policies that support global economic integration in favor of sustainable development. Population growth shows a statistically negative influence on CO_2 emission concentration. The combined effect of population growth and globalization also shows a statistically negative effect on CO_2 emission concentrations. This suggests that population growth can reduce CO_2 emission concentrations in OIC member countries, which may be due to effective population control measures. This highlights the importance of policies that support sustainable development. Furthermore, FDI has a statistically positive effect on CO_2 emissions, meaning that an increase in FDI can raise the concentration of CO_2 emissions in OIC member countries. An increase in FDI can lead to the expansion of industries that are not environmentally friendly, thereby increasing CO_2 emissions. Therefore, strict FDI regulations are needed to control CO_2 emissions while supporting sustainable development. The interaction between FDI and globalization shows a statistically negative effect on CO_2 emissions. Meanwhile, the globalization index shows a statistically negative effect on CO_2 emissions, indicating that an increase in globalization will reduce CO_2 emissions in OIC countries. Conversely, economic, political, and social globalization each show a statistically positive effect on CO_2 emission concentrations.

Based on the findings of this study, it is suggested that future research should focus more specifically on analyzing the economic sectors that contribute most to increased CO_2 emissions in OIC member countries. Future research should also consider the impact of different types of FDI, such as investments in the energy sector versus manufacturing, to understand better how each sector affects CO_2 emissions. Additionally, it is vital to explore the role of government policies and existing environmental regulations in moderating the relationship between economic growth, globalization, and CO_2 emissions. Further research could also examine the role of green technologies introduced through globalization and FDI and how these technologies can be optimized to reduce emissions. This study has limitations, mainly related to the data covering only 1992 to 2020 due to limited data sources. As a result, the data may only partially reflect the long-term dynamics within OIC member countries. Furthermore, this study has yet to fully isolate other factors that may affect changes in CO_2 emissions, such as climate change, energy policy, and changes in consumer behavior. Therefore, future research should adopt a more comprehensive approach by considering additional relevant variables and utilizing more up-to-date and detailed data to provide a more accurate picture.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Physio-chemical characterisation of dumped solid waste

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ABSTRACT

Landfilling is the most common practice used for the disposal of solid waste since it is the cheapest method of municipal solid waste management. The present study aims to determine the physical and chemical characteristics of dumped solid waste collected directly from the Okhla landfill site (New Delhi, India) which has been declared as exhausted in 2018. These waste samples have been collected having ages beyond 20 years. Further, several laboratory tests were performed on the samples to investigate parameters namely physical composition, moisture content, density, optimum moisture content, pH, electrical conductivity, percentages of carbon (C), nitrogen (N), hydrogen (H), sulphur (S) and C/N ratio. The physical composition of samples was found to be substantially heterogeneous. The mean values for moisture content and optimum moisture content were observed as 10.03% and 22.27% respectively. Moreover, the mean of density, pH and electrical conductivity was obtained as 1323.88 kg/m^3, 6.44 and 3.06 mho/cm respectively. On the other hand, the elemental parameters C, H, N, S mean percentages were evaluated as 5.98%, 0.73%, 0.27% and 0.71%. Consequently, C/N ratio was evaluated as 23.46 for the samples. These results have also been compared with the MSW characteristics of Asian countries.

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INTRODUCTION

Dumped solid waste (DSW) mainly comprises wastes from households, commercial buildings, offices, institutions, parks, streets, construction, and demolition sites. Typical residential and commercial DSWs include clothing, disposable tableware, yard trimmings, cans, office disposable tables, paper, and boxes, whereas institutional and industrial DSWs contain restaurant trash, paper, classroom wastes, wood pallets, plastics, corrugated boxes, and office papers [1]. In India, rapid urbanisation, and the shift of population towards cities has contributed to higher DSW generation in metropolitan cities like Delhi, Mumbai, Kolkata, Bengaluru etc [2–4]. Moreover, more than 92% of these wastes are disposed of directly on open dumping sites in an unsecured manner [5, 6]. Therefore, waste management has become one of the strategic agendas of India's leading mission "Swachh Bharat Abhiyan". Accumulated waste not only affects the public health and environment but also hamper the industrial and socio-economic growth of the country [7, 8].

Delhi is a highly urbanized and closely populated metropolitan city that produces about 9000 MT (Metric Tonnes) of solid waste every day which is expected to reach 17000–25000 Tons per day due to rapid industrial development [9–16]. Also, according to Central Public Health and Environmental Engineering Organization [17] per capita municipal solid

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waste (MSW) generation in Delhi is about 700 g/day which is five times the national average. To have an efficient solid waste management system it is important to initially recognise the physical and chemical attributes of the waste [13, 18–22].

Across the globe, numerous studies have been presented on the physio-chemical characteristics of dumped MSW [22–30, 31]. In general, DSW comprises- recyclable waste (textiles, plastics, glass, metals etc), organic or compostable waste (leaves, wood, food, fruit and vegetable peels etc.), hazardous waste (batteries, medicine etc.) and soiled waste (diapers, syringe, sanitary napkins, pad etc Among these, Gomez et al. [22] reported 12% plastic, 16% paper and 48% organic waste in Mexico City. However, Zhou et al. [30] found 55.86%, 11.15%, 8.52%, 3.16%, 2.94% and 0.84% of food residue, plastics, paper, textiles, wood waste and rubber respectively in MSW in China. Chamem and Zairi [26] found organic waste components between 31–59%, paper 9–10%, textiles 12–16% and plastics, leather and rubber 7–11% in MSW of Gabes City. Saglam and Aydin [31] revealed that MSW generated from educational institutes in Istanbul contains about 36.4% organics, 24% paper, 14.4% plastics, 8.1% glass, 4.8% metals and 12.3% miscellaneous waste. Mushtaq et al. [32] reported a high percentage of organic waste between 10.3%–68.5%, tailed by recyclable waste 12.3%–15.30%, and inert waste 8.27%—9.10% respectively. Swales [33] reported that an average MSW sample contained 53.3% of organic matter, 14.7% of plastic, 13% of paper, 4.2% of glass, 2.7% of metal, 11.6% of others and 0.5% of household hazardous in Brisbane. Yildiz et al. [27] found that the moisture content of waste in Turkey, and Istanbul varies between 46–65%. Furthermore, the chemical characteristics of MSW include pH, electrical conductivity, carbon (C), nitrogen (N), hydrogen (H), Oxygen (O), sulphur (S), Phosphorus (P), Chlorine (Cl), C/N ratio etc. Hla & Roberts [29] performed the chemical analysis of MSW in Brisbane, Australia and measured the presence of C, H, N, O, S and Cl as 52.8%, 6.4%, 1.29%, 31%, 0.18% and 0.73% respectively. Zhou et al. [30] reported the percentages of C, H, O, N, S, Cl as 2.45%, 0.46%, 4.17%, 0.28%, 0.12% and 0.77% respectively in China. Gidarakos et al. [24] determined C, H and N content in MSW in Crete, Greece as 53%, 7.32% and 1.32% respectively.

On the other side, several works of literature from India on the physical and chemical characteristics of MSW have also been testified [6, 13, 34, 35]. The composition of MSW in Bangalore as reported by Ramachandra et al. [6] states that paper, metal, glass and organic content were about 12.69%, 1.67%, 0.65% and 81.96% respectively. Also, Mushtaq et al. [35] identified 12.3–15.3% recyclable waste followed by 10.3–68.5% organic waste in MSW collected from the region of North-western Himalayas. Thaitame et al. [36] observed 61% of organic waste and the remaining was inorganic waste in Sangamner City. It has been perceived that organic waste production is much higher in India (about 40–63% [12]), as contrasted to other developed countries [3, 20, 37].

Furthermore, the physical analysis of DSW has also been assessed by [3, 13, 35]. Kumar and Goel [3] reported 42% moisture content and 58% total solids (20% volatile solids and 80% fixed solid of total solids). Mushtaq et al. [35] found average moisture content varied between 47.6–52.40% in the region of Kashmir.

Also, the chemical analysis of DSW in India has been conducted by [13, 38]. Katiyar et al. [38] stated the following percentages of C, H, O, N, S, P and Potash in MSW collected in Bhopal- 26.6%, 5.9%, 47.7%, 1.1%, 0.98%, 0.84% and 0.93% respectively. Also, a C/N ratio equal to 26.6 was reported. Rana et al. [13] indicated the composition of C, O, H and N as 34.18%, 11.41%, 4.42% and 1.35% in Chandigarh MSW whereas, the same was observed as 33.8%, 10.2%, 4.2% and 1.53% in Mohali and Panchkula, it was found to be 31.9%, 11.1%, 4.2% and 1.1% respectively.

The composition of MSW changes with time. It has been testified that in a landfill it takes less than ten years for heavy metals and several decades for organic pollutants, organic carbon and nitrogen to get stabilised. These stable landfill wastes can be used successfully in various construction works such as subgrade road construction. Therefore, over the years, these physical and chemical analyses of DSW need to be conducted for the proper and efficient operation of waste management systems.

The present study aims to determine the physical and chemical characteristics of DSW collected directly from the Okhla landfill site (New Delhi, India) which was declared as exhausted in 2018. These waste samples have been collected having ages beyond 20 years. The physio-chemical analysis of waste is an essential objective and will serve as the guideline in deciding the waste management techniques by the government. The objectives of the present study are- (a) to collect the waste directly from the landfill dumping site, (b) to determine the components of waste in each sample by segregation, (c) to investigate the physical characteristics of waste samples, (d) to investigate the chemical characteristics of the waste samples.

Description of the Site

Okhla landfill site at Okhla Phase – I, New Delhi is situated close to ESIC hospital. The landfill was authorized in 1996 under the head of South Delhi Municipal Corporation (SDMC), extending over an area of 56 acres. The site received 2000 metric tons of waste per day and was announced exhausted in 2018. Despite this, in the year 2023, the landfill site is still receiving waste from the regions of south and central Delhi due to the unattainability of alternate dumping facilities. As a result of which the mountain of waste is still standing as displayed in Figure 1.

Nevertheless, the government is working in full swing to utilise the decomposed waste (>20 years) as composting material, fillers in road construction etc. The work presented here aims to determine the physical and chemical characteristics of stable DSW collected from the exhausted Okhla landfill site.

MATERIALS AND METHODS

Sampling of DSW

In this study, DSW of the Okhla landfill dumping site were collected eight times from different locations of the landfill.

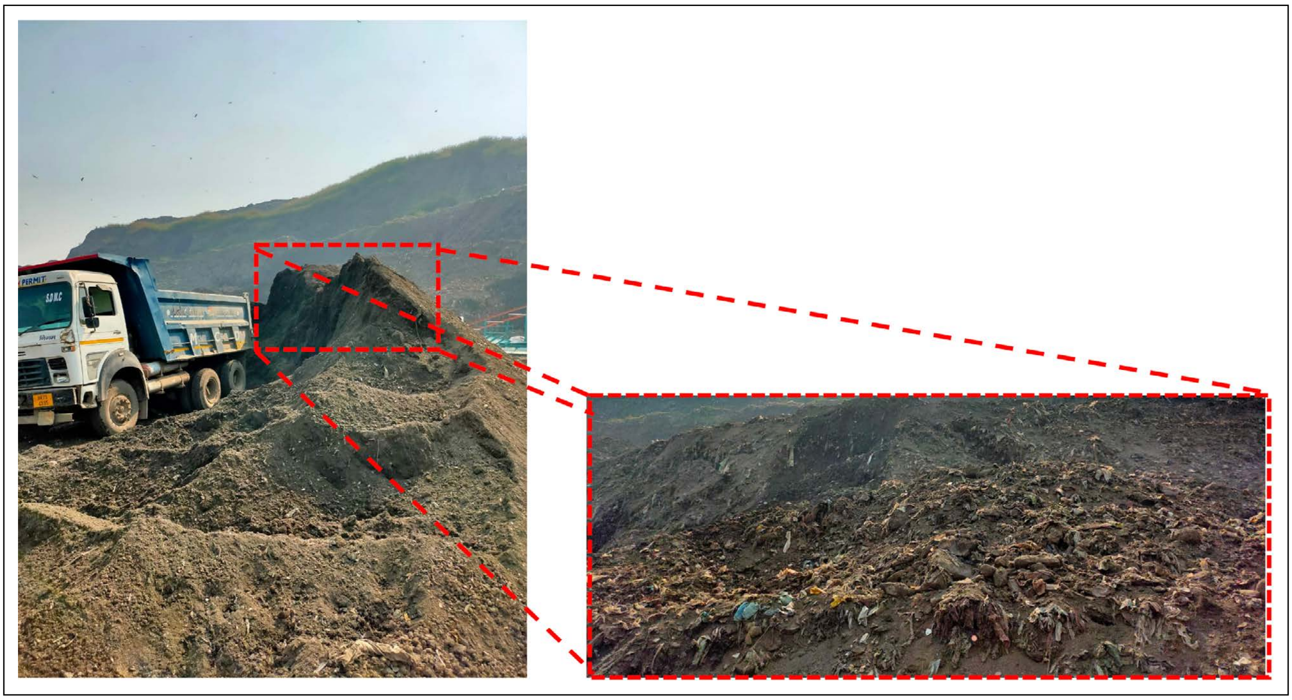

Figure 1. Waste dumped at Okhla Landfill site.

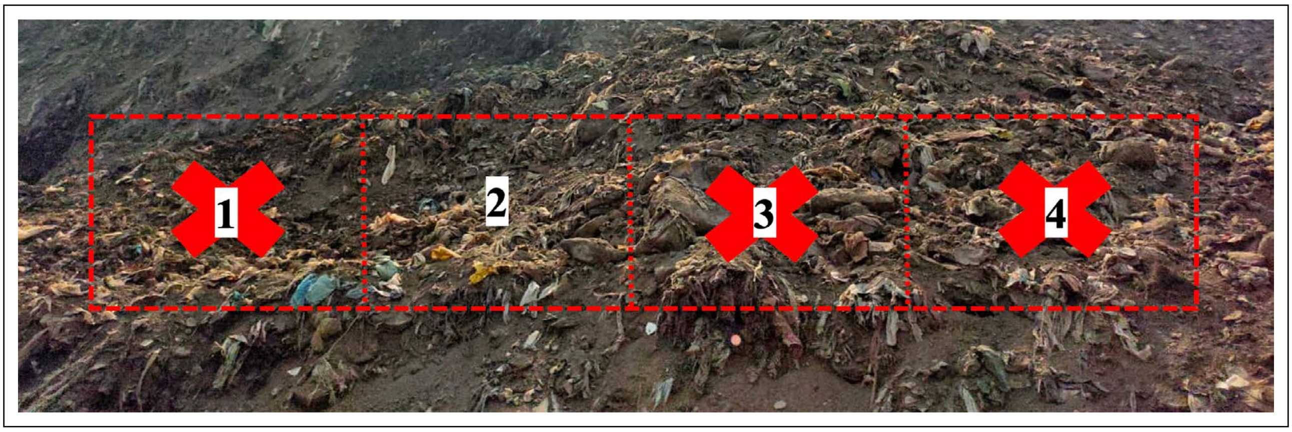

Figure 2. Quartering technique for sampling of waste.

The sampling of each eight samples was performed using the Quartering technique [29, 39–42]. In this technique 20kg of each sample was mixed thoroughly, spread on the ground and quartered approximately. Then one quarter was selected randomly without being biased as shown in Figure 2. These samples were instantly stored in 5kg plastic bags to inhibit any susceptible change in moisture level and carried to the laboratory. The total weight of the collected DSW was approximately 40 kg.

In the laboratory, these collected waste samples of each type were correctly weighed again and composite samples of different samples as per requirement were prepared for the physical and chemical analysis implying the same quartering technique.

Physical Analysis- Laboratory Testing

The physical analysis of DSW has been carried out by performing several laboratory studies. The physical analysis includes the determination of physical composition, moisture content, dry density and optimum moisture content (OMC). The procedures adopted for these tests have been discussed in the subsequent section.

Determination of Physical Composition

Each composite sample of DSW was spread evenly on a clean surface and different types of waste were hand-segregated and grouped into combustible and non-combustible waste categories. The segregated wastes were then weighed and their respective percentages in each sample type were evaluated.

Determination of Moisture Content, Dry Density and OMC

The moisture content of each eight samples was determined using the "Grab sampling without sorting" technique. Initially, 100g of a composite sample of each type was taken in triplicate and oven dried at 110°C for 24 hours. The sample was then cooled and the difference in

Table 1. Physical composition of waste samples I-VIII

Parameters	Waste sample							
	I	II	III	IV	V	VI	VII	VIII
Physical composition (% by weight)								
Combustible waste								
Fine waste (<20 mm)	95.00	94.00	93.00	95.00	48.76	68.79	73.07	31.74
Leaves	0.70	0.60	1.70	1.90	0.23	1.15	2.10	4.19
Textile	–	2.40	–	–	0.03	0.02	1.66	0.09
Wood straps	–	–	–	0.80	0.25	–	–	–
Broken tiles	–	–	–	–	0.20	3.69	6.38	–
Plastic	2.70	1.50	1.30	0.20	8.44	0.19	0.54	4.81
F.A.	1.10	1.50	3.10	2.10	42.07	26.08	16.22	51.58
Non-combustible waste								
Glass	–	–	0.90	–	–	0.05	0.007	5.62
Metals	0.50	–	–	–	–	–	–	1.94

the weight of the sample was recorded. The moisture content (ω_c) of the samples was calculated using Eq. 1;

$$\omega_c\ (\%)=\frac{\text{Difference in the weight of waste sample}}{\text{Initial weight of waste sample}}\times 100 \quad \text{Eq. 1}$$

The dry density of composite waste samples (I to VIII) having natural moisture content was determined according to the Standard Proctor Compaction procedure. A larger compaction mould with a 6-inch inside diameter, 6.1-inch height, with a volume of 1/10 cubic feet with a detachable collar was used. The initial weight of the mould was recorded (say, W_i). Thereafter, the waste sample was filled up to the rim of the mould in three layers, compacting each layer 75 times. A 5.5 lb hammer with a 2-inch face was made to fall from a height of 12 inches on each of the three layers of the sample to achieve the desired compaction. Finally, the weight of the mould along with the compacted waste sample was measured (say, W_f). A similar procedure was adopted for the remaining waste samples. The dry density (γ_d) of waste samples were calculated using Eq. 2.

$$\gamma_d\ (\text{km/m}^3)=\frac{(W_f\text{-}W_i)}{\text{Volume of the mould}} \quad \text{Eq. 2}$$

Chemical Analysis- Laboratory Testing

The chemical analysis of DSW has been carried out by performing several laboratory studies following the guidelines of BIS 9234 [43]. A similar approach to analysis has also been adopted by [42, 44]. Chemical analysis in the present study comprises of determination of pH, electrical conductivity (EC) and elemental analysis.

Determination of pH and EC

The pH of the pulverised waste samples was determined by mixing each sample in water to obtain a 1:10 solution. The solutions were allowed to stand for about 2 hours to ensure maximum dissolution of salts in water. Then pH meter was dipped in each sample and readings were noted [45]. EC of the samples was determined based on the based on the calibration of cell with standard 0.1 N KCl solution of conductivity 14.12 m mhos at 30°C.

Elemental Analysis

Elemental analysis establishes the quantities of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) exhibited in the sample. This evaluation is based on the combustion of samples in a devoted apparatus recognized as an Elemental Analyser. After the combustion compound gases having C, H, N and S elements are liberated and measured using gas chromatography.

RESULTS AND DISCUSSION

Physical Analysis

Physical Composition

The combustible category comprised nine types of waste namely, fine waste, leaves, textiles, wood straps, broken tiles, plastics and F.A (Table 1). In all the samples, fine waste (soil-like material with particle size <20mm) was found to be the major component. The percentage of fine waste varied between 93.00% to 95.00% in samples I-IV whereas, in samples V-VIII the same was obtained to vary between 31.74% to 73.07% by weight. The second major component was found to be F.A. whose percentage varied between 1.10% to 3.10% by weight in samples I-IV. However, its percentage in samples V-VIII was found to be between 16.22% to 51.58% by weight. The third major component was plastic found to vary between 0.20% to 8.44% by weight in samples I-VIII. The other subsequent component was leaves varied between 0.23%–4.19% by weight in samples I-VIII. The textile component was found in samples II and V-VIII with its percentage varying between 0.02%–2.40% by mass. Further, 0.20%–6.38% by weight of broken tiles were found only in samples V-VII. Moreover, wood straps were found to be 0.8% and 0.25% respectively in samples IV and V only.

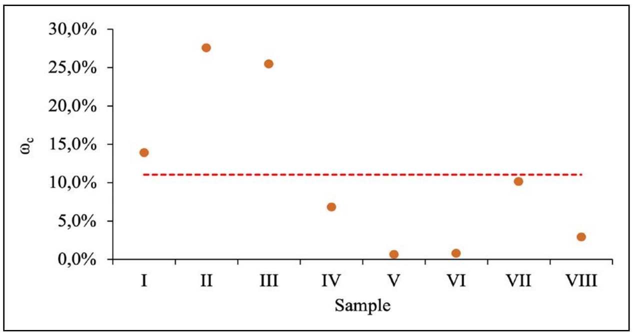

Figure 3. Moisture content in waste samples I-VIII.

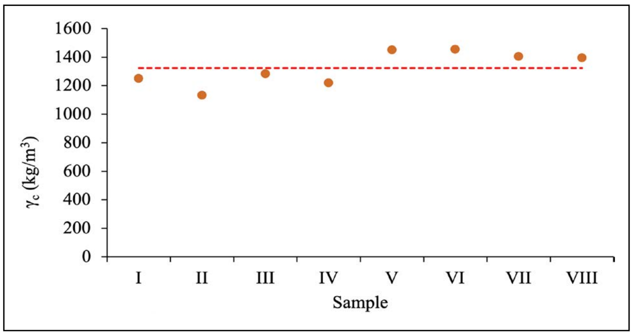

Figure 4. Density of waste samples I-VIII.

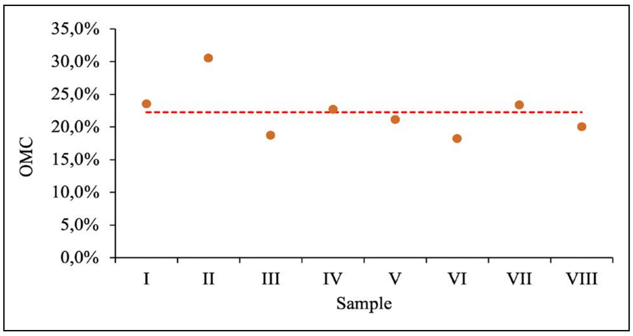

Figure 5. OMC of waste samples I-VIII.

OMC: Optimum moisture content.

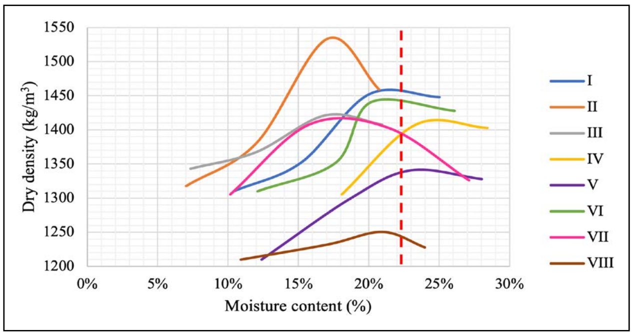

Figure 6. Variation of Dry density wrt moisture content for waste samples I-VIII.

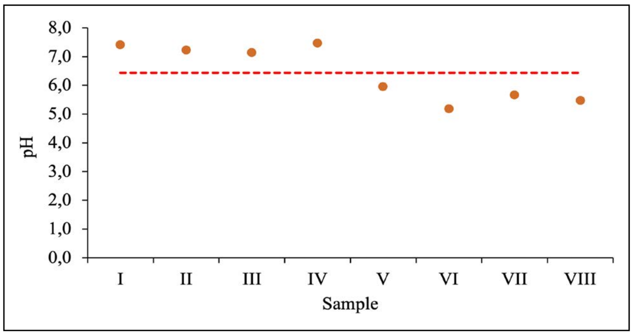

Figure 7. pH of waste samples I-VIII.

In contrast, the non-combustible category comprised metals and glass (Table 1). Metals were found only in samples I and VIII as 0.50% and 1.94% by weight respectively. Glass was found to be 0.90%, 0.05%, 0.007% and 5.62% in samples III, VI, VII and VIII respectively.

Moisture Content, Dry Density and OMC

The moisture contents in samples I-VIII were calculated using the relation given in Eq. 1 and were found as 13.90%, 27.60%, 25.50%, 6.80%, 0.61%, 0.79%, 10.15% and 2.91% respectively. The scatter plot illustrating the variation of moisture content in each sample is shown in Figure 3, depicting a mean value of 11.03%. Saluja et al. [46] also reported an average moisture content of 8.99 ±1.6% for a stabilised landfill site. In contrast, the moisture content in MSW across various cities in India is found to vary between 46–51% [4, 21, 47] and in Asian countries between 17–65% [3, 16, 19, 20]. This low percentage of moisture content in the present case is apparent due to the decomposition and compaction of the landfill site over time.

Using the Standard Proctors Compaction test the density of each sample was determined as mentioned in section 2.3.3. The dry densities evaluated using Eq. 2 are 1250 kg/m^3, 1132 kg/m^3, 1284 kg/m^3, 1219 kg/m^3, 1450 kg/m^3, 1456 kg/m^3, 1406 kg/m^3, 1394 kg/m^3 in samples I to VIII respectively describing the average dry density equal to 1323.88 kg/m^3 (Fig. 4). However, Hazra and Goel [48] stated the average density of MSW in Bhopal (India) as 600 kg/m^3. But then dry density was found to vary between 500–1500 kg/m^3 in China [49].

In samples I-VIII the OMC was obtained as 23.50%, 30.50%, 18.71%, 22.69%, 21.12%, 18.25%, 23.37% and 20% respectively. Thus, the average OMC in samples was found to be 22.27% as depicted in Figure 5. Further, Figure 6 illustrates the variation of moisture content versus dry density. The peak value of each curve indicates the OMC of the respective samples.

Chemical Analysis

pH and EC

The pH of samples I-VIII has been observed to vary between 5.18 and 7.47 as shown in a scatter plot (Fig. 7) indicating 6.44 as the mean value. Further, the EC of each sample I-VIII varied between 2.41–3.59 mho/cm as shown in Figure 8. The average EC of samples was found to be 3.06 mho/cm indicative of a great degree of mineralization in waste samples [50]. Also, Shanthi et al. [42] stated average pH and EC as 7.25 and 3.74 mho/cm for DSW samples of the Coimbatore (India) region.

Elemental Analysis

C and H contents are indicators of the level of oxidation in the waste samples. The percentage of C in I-VIII sam-

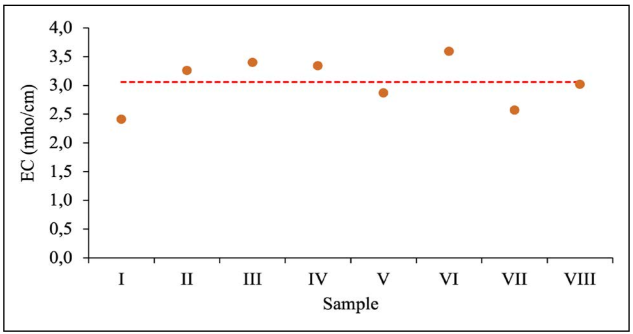

Figure 8. EC of waste samples I-VIII.

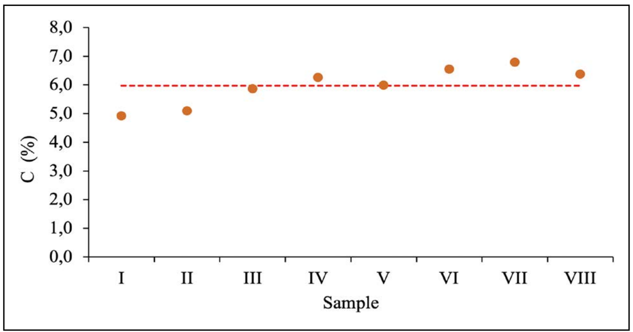

Figure 9. Carbon content of waste samples I-VIII.

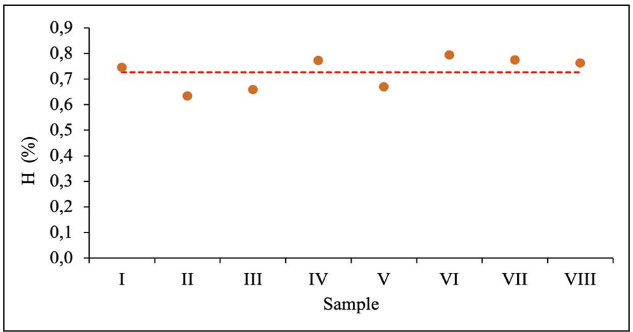

Figure 10. Hydrogen content of waste samples I-VIII.

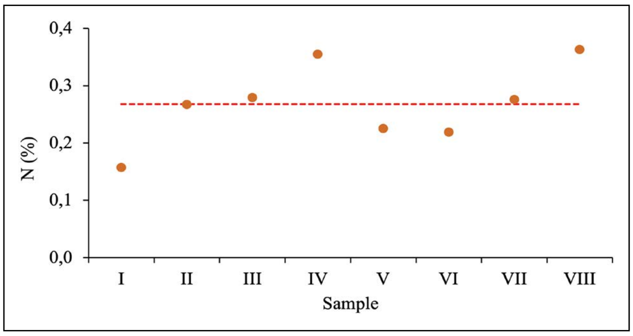

Figure 11. Nitrogen content of waste samples I-VIII.

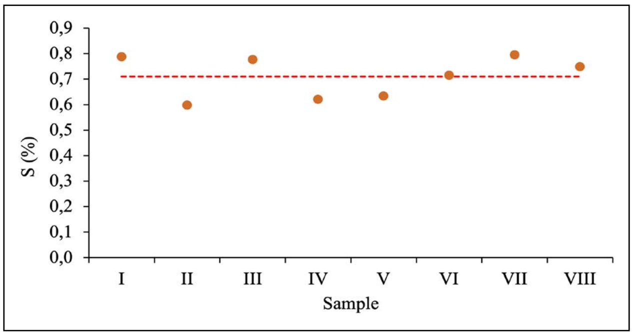

Figure 12. Sulphur content of waste samples I-VIII.

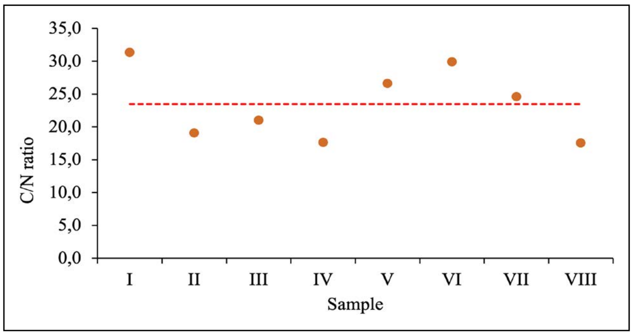

Figure 13. C/N ratio of waste samples I-VIII.

ples varied between 4.92% to 6.79% having a mean value of 5.98% as illustrated in Figure 9. However, H content in samples was found to be between 0.634% to 0.794% with a mean percentage of 0.73% as depicted in Figure 10. Trabelsi et al. [41] and Saluja et al. [46] reported C% as 6.82% and 3.5% respectively and H% as 1.07% and 0.478% respectively in the DSW sample of >20-year-old landfill.

N content in eight samples was found to vary in the range of 0.157% to 3.363% beside the mean percentage of 0.27% (Fig. 11). Likewise, Saluja et al. [46] indicated 0.13% N whereas, Trabelsi et al. [41] reported N content as 0.55% in stable MSW samples. Moreover, the mean S% of eight samples were observed as 0.71% only which varied in each sample between 0.598%–0.795% (Fig. 12). Tracing percentage of S (0.197%) has also been reported by Saluja et al. [46].

The C/N ratio is indicative of rate of biodegradation of waste in landfills and is inversely correlated. In general, the C/N ratio of DSW varies between 20–30 for maximum digestion by microbial action [51]. In the present study, the mean C/N ratio has been obtained as 23.46 (Fig. 13) which is less than 30, indicative of completely decomposed and stable waste samples [52]. Also, Trabelsi et al. [41] and Saluja et al. [46] reported C/N ratio of 12.4 and 36.56 respectively.

CONCLUSION

The present study aims to investigate the physio-chemical characteristics of DSW samples collected from an exhausted Okhla landfill site (about >20years old). The following are some of the major conclusions derived from the study.

i. In all the waste samples fine waste (soil-like material having particle size <20mm) was obtained to be the major constituent about 75%. The other combustible constituents were F.A. > leaves > textile > broken tiles > wood straps whereas, non-combustible constituents-metal and glass were found in traces.

ii. The average moisture content of samples was detected to be 11.03%. On the other hand, mean density and OMC were observed as 1323.88 kg/m^3 and 22.27% respectively.

iii. The pH and EC of the samples were determined as 6.44 and 3.06 mho/cm respectively.

iv. The chemical analysis revealed a good C/N ratio equal to 23.46 (<30) which indicates that the waste has been digested and decomposed effectively.

v. Hence, this decomposed waste can be effectively utilised for construction works such as subgrade in roads, brick manufacturing etc.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Mold development risk assessment in the inner side of a building envelope under varying climate conditions

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ABSTRACT

Mold infestation in buildings can arise due to favorable growth conditions for mold fungi, posing significant health risks and structural damage. This research aims to understand the complex transient building physics processes influencing mold development, focusing on the influence of physical building variables on the transient humidity and temperature behavior of building components in various climates. The study utilizes WUFI, a hydro-thermal simulation software, to assess mold risk in an exterior wall design. The results indicate that a broadly applicable approach can effectively guide safe design practices. The goal is to predict mold development on building materials during the design stage and minimize the risk of mold growth throughout the materials' service life.

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INTRODUCTION

Mold growth in buildings is a pressing issue that has garnered considerable attention due to its adverse effects on both human health and structural integrity. Mold can trigger respiratory problems, allergic reactions, and other health issues in occupants. Moreover, it can lead to significant structural damage, compromising the safety and longevity of buildings. Understanding the conditions that foster mold growth is paramount for developing effective prevention strategies, particularly in the context of varying climatic conditions [1–3].

Importance of Mold Prevention

The inner side of building envelopes, being less visible and often overlooked, can become a hotspot for mold growth if not adequately managed. Factors such as high relative humidity, fluctuating temperatures, and prolonged exposure to moisture can create an ideal environment for mold proliferation [4, 5]. To address this, building scientists and engineers must consider these variables during the design and construction phases [6, 7].

Objectivesof The Study

This study aims to extend the knowledge on mold development risk by:

1. Assessing the influence of physical building variables on the transient humidity and temperature behavior of building components in various climates.
2. Using WUFI to simulate an exterior wall design and evaluate mold growth risk.
3. Providing insights that can guide the design phase to minimize the risk of mold growth over the service life of building materials.

Significance

The outcomes of this research are anticipated to make a substantial contribution to the field of building science by offering a widely applicable method for assessing mold risk.

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This methodology can aid designers and builders in developing safer, more durable structures by integrating mold prevention strategies from the initial design phase [8, 9].

Theoretical Framework

This study's theoretical approach is based on building physics principles, with an emphasis on the complex interactions of heat and moisture movement within building envelopes. Understanding these interactions is critical for forecasting and restricting mold growth, which is affected by several major factors: relative humidity, temperature, and time exposure [10, 11].

Heat and Moisture Transfer

Understanding the interactions between heat and moisture within building envelopes is essential for predicting and mitigating mold growth. Several key processes govern the movement of heat and moisture through building materials, each contributing to the overall behavior of the building envelope under different environmental conditions. The main processes include conduction, convection, radiation, diffusion, and capillarity [12, 13].

Conduction

Conduction is the process by which heat energy is transferred through a material due to a temperature gradient. In the context of building envelopes, conduction occurs through the walls, floors, and roofs as heat moves from the warmer side to the cooler side. The rate of heat transfer by conduction depends on the thermal conductivity of the materials involved and the temperature difference across them [14].

Materials with high thermal conductivity, like metals, transfer heat more efficiently than insulating materials. The thickness of the material also affects the rate of heat transfer; thicker materials slow down conduction [15, 16].

Convection

Convection involves the transfer of heat and moisture through the movement of air. This process can occur within the air spaces of a building envelope or on the surface of building materials. There are two types of convection: natural convection, driven by temperature differences causing air movement, and forced convection, driven by external forces such as fans or wind [17].

Natural convection occurs due to buoyancy effects where warmer, less dense air rises and cooler, denser air sinks. Forced convection is enhanced by mechanical means like HVAC systems. Convection can contribute to heat loss or gain and influence moisture levels in building cavities [18, 19].

Radiation

Radiation is the transfer of heat in the form of electromagnetic waves, primarily infrared radiation. Unlike conduction and convection, radiation does not require a medium to transfer heat. In buildings, radiation can occur through windows, roofs, and walls exposed to the sun or other heat sources [20].

All objects emit and absorb radiant energy. The amount of radiation emitted depends on the temperature and surface properties of the material.Reflective surfaces can reduce radiant heat transfer by reflecting incident energy [21, 22].

Diffusion

Diffusion refers to the movement of moisture (water vapor) through building materials due to vapor pressure differences. This process is critical in understanding how moisture migrates through walls, roofs, and floors, and how it can lead to condensation and mold growth [23].

Moisture moves from areas of high vapor pressure to areas of low vapor pressure. Vapor permeability of materials dictates how easily moisture can diffuse through them. Proper vapor barriers can control diffusion and prevent moisture buildup within the building envelope [24, 25].

Capillarity

Capillarity, or capillary action, is the movement of liquid moisture through porous materials due to the forces of adhesion, cohesion, and surface tension. This process is significant in porous building materials like concrete, brick, and wood, where moisture can travel upwards against gravity [26].

Capillary action can transport moisture from the ground into walls and floors.

The size and connectivity of pores in a material influence the rate and extent of capillary rise. Proper detailing and use of damp-proof courses can mitigate capillary moisture intrusion [27, 28].

Relative Humidity

Relative humidity (RH) is a critical factor in mold development. It is defined as the amount of moisture in the air relative to the maximum amount the air can hold at a given temperature. High RH levels can lead to condensation on building surfaces, creating an environment conducive to mold growth. Laboratory tests have established threshold values for RH above which mold is likely to develop [29]. Effective moisture control strategies aim to maintain indoor RH levels below these critical thresholds [30].

Table 1 categorizes the risk levels for mold growth based on relative humidity percentages. Maintaining RH below 60% is considered safe, while levels above 80% significantly increase the risk of mold development.

Temperature

Temperature plays a significant role in both the rate of mold growth and the moisture dynamics within building materials. Warmer temperatures can accelerate mold growth by providing favorable conditions for spore germination and proliferation. Conversely, cooler temperatures can slow down mold growth but do not eliminate the risk entirely [31]. Temperature also affects the vapor pressure and, consequently, the diffusion of moisture through building materials [32].

Table 1. Mold growth risk based on relative humidity

Condition	Relative humidity (%)
Safe zone	<60
Risk zone	60–80
Critical zone	>80

Table 2. Temperature Influence on mold growth rate

Temperature (°C)	Mold growth rate
0–10	Low
10–20	Moderate
20–30	High
30–40	Very high

Table 2 shows how different temperature ranges influence the rate of mold growth. Higher temperatures typically result in faster mold growth, highlighting the importance of temperature control in preventing mold development.

Time Exposure

The duration of exposure to high humidity and temperature conditions is another vital consideration. Mold does not develop instantly; it requires a sustained period of favorable conditions to grow. Thus, understanding the transient behavior of humidity and temperature within building components is essential for accurate risk assessment [33].

Table 3 summarizes the relationship between exposure time to favorable conditions and the risk of mold growth. Longer exposure times increase the risk, underscoring the need for timely moisture control interventions.

Table 3. Time exposure and mold risk

Exposure time (days)	Mold risk level
<7	Low
7–14	Moderate
>14	High

Combined Effects

In real-world scenarios, these processes do not act in isolation but interact with each other, leading to complex heat and moisture dynamics within building envelopes. For example, solar radiation can increase the surface temperature of a wall, enhancing conduction and potentially

driving moisture diffusion and convection [34]. Understanding these interactions is crucial for accurately predicting the moisture performance of building materials and preventing mold growth (Fig. 1) [35].

Practical Implications

Understanding these fundamental processes allows for the development of effective strategies to manage heat and moisture within buildings. Key strategies include:

- Material Selection: Choosing materials with appropriate thermal and hygric properties to control heat and moisture transfer [36, 37].
- Design Considerations: Incorporating features like vapor barriers, insulation, and ventilation to manage moisture and heat flow [38, 39].
- Climate Adaptation: Tailoring building designs to specific climatic conditions to mitigate the effects of local environmental factors [40].

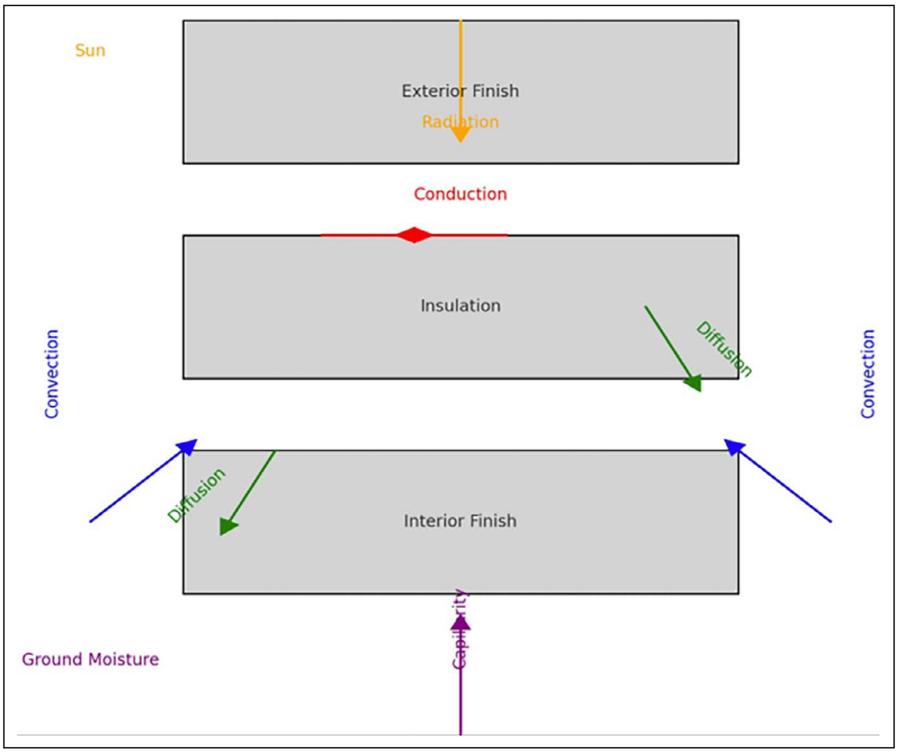

Figure 1. Schematic of heat and moisture transfer processes.

By leveraging the principles of heat and moisture transfer, building designers and engineers can create more resilient and durable structures that minimize the risk of mold growth and ensure occupant comfort and health.

Hydro-Thermal Simulation

To analyze the interactions between heat and moisture and predict mold risk, the study utilizes hygrothermal simulation tools such as WUFI (Wärme und Feuchte Instationär). WUFI simulates the transient behavior of heat and moisture in building components, allowing for the assessment of mold growth risk under varying climatic conditions [41].

Modeling Approaches

1. Steady-State Models: These models assume constant environmental conditions and are useful for understanding basic moisture transport mechanisms. However, they are less effective for predicting mold growth under dynamic conditions.
2. Transient Models: These models consider the time-varying nature of environmental conditions and provide a more accurate prediction of moisture and temperature behavior in building components [42].

Previous Studies

Previous research has highlighted the significance of accurately predicting the moisture behavior in buildings to prevent mold growth. For instance, Sedlbauer (2001) developed models to predict mold formation on building surfaces, emphasizing the need for precise data on humidity and temperature. Similarly, Wang and Brennan (2004) demonstrated the importance of understanding the moisture performance of building envelopes to develop effective mold prevention strategies [43].

MATERIALS AND METHODS

Data Collection

Climate Data involves gathering temperature and humidity data from reliable sources such as meteorological databases or climate models. The data should cover various climatic regions to account for different environmental conditions. Material Properties: Gathering information on the thermal and hygric (moisture-related) properties of materials used in building construction. This includes parameters such as thermal conductivity, specific heat capacity, water absorption coefficient, and vapor permeability.

Model Setup

Wall Assembly Definition: This step involves creating a digital model of the exterior wall in WUFI. The wall assembly includes layers of materials such as exterior cladding, insulation, vapor barriers, and interior finishes.

Inputting Material Properties: Inputting the gathered material properties into WUFI to accurately simulate how each material responds to heat and moisture.

Simulation Execution

Running Simulations: Simulations are run for each climate scenario. This involves setting boundary conditions that reflect the exterior and interior climate conditions, such as temperature, relative humidity, and solar radiation.

Duration: Simulations are often run over extended periods (e.g., one year) to capture seasonal variations and long-term trends in temperature and humidity within the wall assembly.

Analysis

Evaluating Results: Post-processing the simulation data to evaluate how temperature and humidity levels change over time within the wall assembly. This helps identify periods and conditions where the risk of mold growth is highest.

Mold Growth Risk: Assessing the risk of mold growth based on criteria such as the duration of high humidity levels and temperature ranges conducive to mold development.

Sımulation Steps

Climate Data

Profiles: Utilizing temperature and humidity profiles for different climatic regions, such as hot and humid, cold and dry, or temperate climates. This ensures that the simulations are representative of various environmental conditions.

Building Materials

Properties: Inputting detailed properties of commonly used building materials like wood, concrete, brick, and insulation materials. Accurate data ensures reliable simulation results.

Design Elements

Wall Assembly Configuration: Configuring the details of the wall assembly, including the sequence of materials, thickness of layers, and presence of vapor barriers or insulation.

Insulation Types: Testing different insulation types (e.g., fiberglass, foam, mineral wool) to see how they impact moisture and temperature behavior.

Results

Transient Behavior of Humidity and Temperature,

Simulation Data: The results show how humidity and temperature levels within the wall assembly change over time, illustrating the dynamic response to external and internal climate conditions.

Critical Periods: Identifying specific times of the year when the conditions are most favorable for mold growth, such as prolonged periods of high humidity.

Figures and Tables

Figures 2-4 show relative humidity levels within the wall over time for different climate scenarios. This helps visualize how different climates affect moisture levels in the wall assembly.

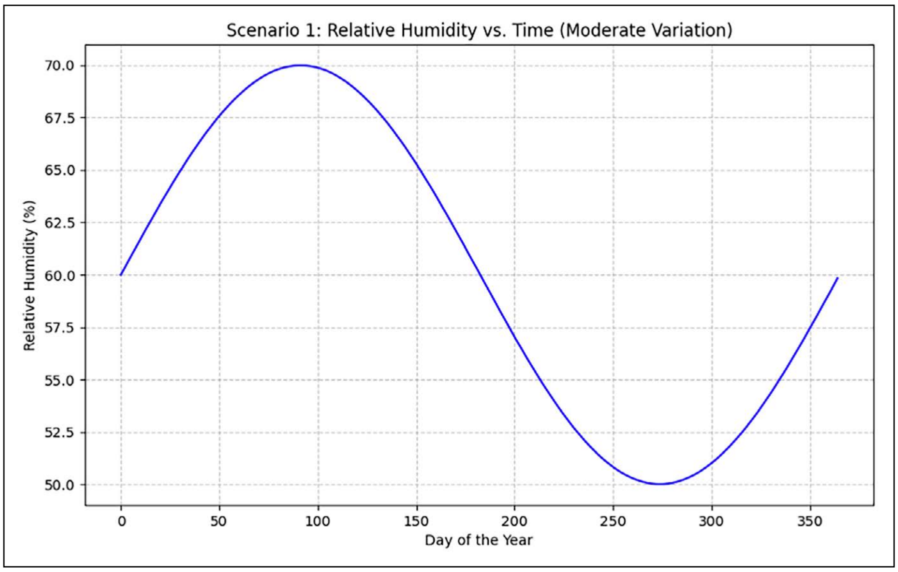

Figure 2. Moderate humidity variation.

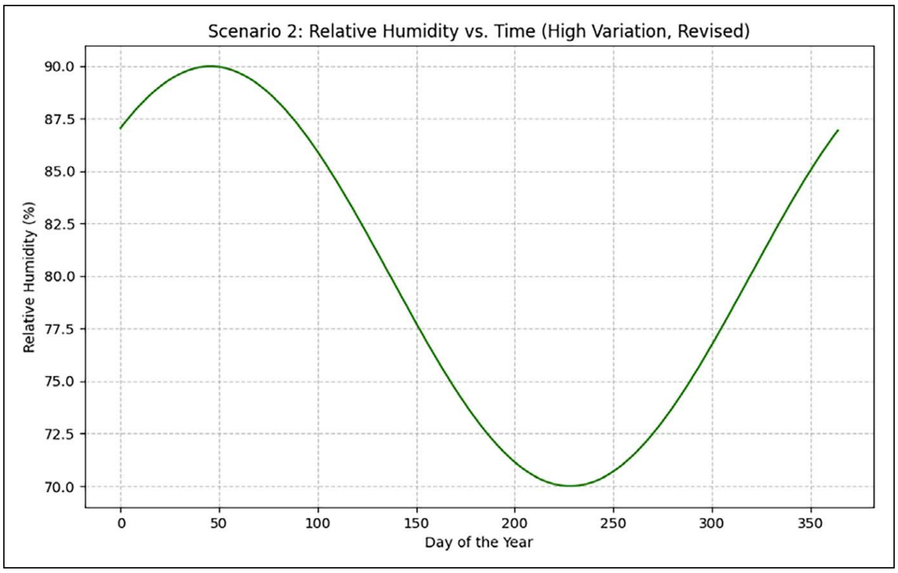

Figure 3. High humidity variation.

Table 4 Summarizes the mold growth risk for various building materials under different climate scenarios. It provides a clear comparison of how each material performs in terms of mold resistance.

Scenario 1: Moderate Humidity Variation

- Description: This scenario shows a moderate variation in humidity levels, fluctuating around an average of 60%.
- Amplitude: The humidity varies by about 10%, ranging from 50% to 70%.
- Seasonal Peaks: Peaks in the middle of the year, indicating a higher risk of mold growth during this period.

Scenario 2: High Humidity Variation

- Description: Represents a climate with significant humidity variation, with an average around 50%.
- Amplitude: The humidity varies by about 15%, ranging from 70% to 90%.
- Phase Shift: The peaks are shifted compared to Scenario 1, showing different seasonal timings.
- Risk Implications: Higher risk for mold growth, requiring advanced moisture control measures.

Scenario 3: Low Humidity Variation

- Description: Shows stable humidity levels throughout the year, with an average of 55%.
- Amplitude: Small variation of about 5%, ranging from 50% to 60%.
- Risk Implications: Lower risk for mold growth, with stable conditions posingminimal threat.

These figures help visualize how different climate scenarios affect moisture levels within the wall assembly, aiding in the assessment of mold growth risk.

To provide a full analysis, it is necessary to define the materials used in each scenario. Materials are often chosen based

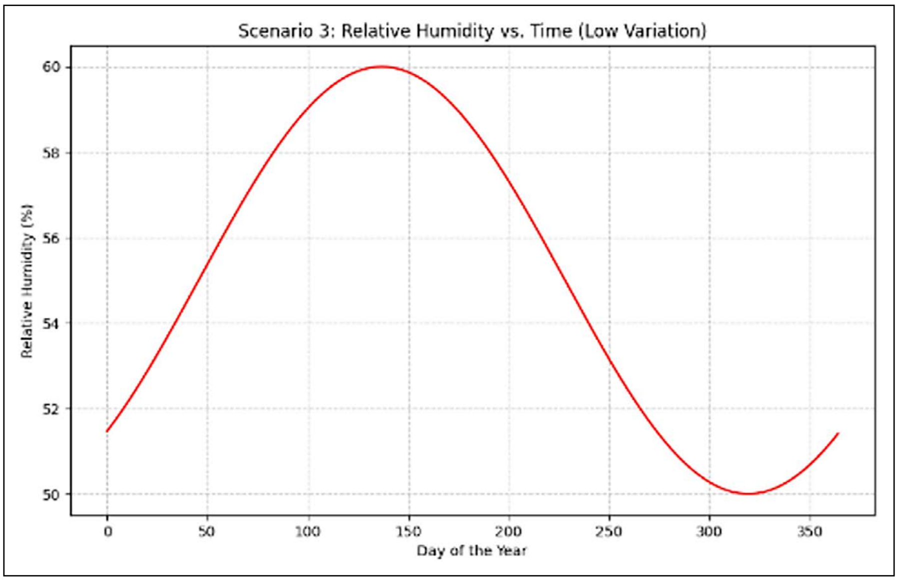

Figure 4. Low humidity variation.

Table 4. Various building materials under different climate scenarios

Material	Climate scenario	Mold risk level
Material A	Scenario 1	High
Material B	Scenario 2	Medium
Material C	Scenario 3	Low

on traditional building procedures and their capacity to resist various climate conditions.

Scenario 1: Moderate Humidity Variation

- Exterior Cladding: Brick veneer
- Insulation: Fiberglass batt insulation
- Sheathing: Oriented strand board (OSB)
- Vapor Barrier: Polyethylene sheet
- Interior Finish: Gypsum drywall

Characteristics:

- Brick Veneer: Durable and provides moderate thermal mass.
- Fiberglass Insulation: Commonly used, provides good thermal resistance but can be susceptible to moisture.
- OSB Sheathing: Standard sheathing material, has moderate moisture resistance.
- Polyethylene Vapor Barrier: Prevents moisture from penetrating the wall cavity.
- Gypsum Drywall: Standard interior finish, can be affected by high humidity.

Scenario 2: High Humidity Variation,

- Exterior Cladding: Stucco
- Insulation: Spray foam insulation
- Sheathing: Plywood
- Vapor Barrier: Smart vapor retarder (e.g., MemBrain)
- Interior Finish: Moisture-resistant gypsum board (green board)

Characteristics:

- Stucco: Breathable material that can handle high humidity but requires maintenance.
- Spray Foam Insulation: Provides excellent thermal resistance and acts as an air barrier.
- Plywood Sheathing: Higher moisture resistance compared to OSB.
- Smart Vapor Retarder: Adjusts permeability based on humidity levels, providing better moisture control.
- Moisture-Resistant Gypsum Board: Better suited for high humidity environments.

Scenario 3: Low Humidity Variation

- Exterior Cladding: Vinyl siding
- Insulation: Rigid foam insulation (e.g., extruded polystyrene)
- Sheathing: Fiberboard
- Vapor Barrier: Kraft-faced insulation (integrated vapor retarder)
- Interior Finish: Standard gypsum drywall

Characteristics:

- Vinyl Siding: Low maintenance and good moisture resistance.
- Rigid Foam Insulation: Provides good thermal resistance and moisture barrier properties.
- Fiberboard Sheathing: Lightweight and has moderate moisture resistance.
- Kraft-Faced Insulation: Provides some vapor resistance, suitable for low humidity variations.
- Standard Gypsum Drywall: Commonly used, suitable for environments with low humidity fluctuations.

Table 5. The mold growth risk for various building materials under different climate

Material	Climate scenario 1	Climate scenario 2	Climate scenario 3
Exterior cladding			
Brick veneer	Low	Medium	Low
Stucco	Medium	High	Medium
Vinyl siding	Low	Low	Low
Insulation			
Fiberglass batt ınsulation	Medium	High	Medium
Spray foam insulation	Low	Low	Low
Rigid foam insulation	Low	Low	Low
Sheathing			
OSB	Medium	High	Medium
Plywood	Medium	Medium	Low
Fiberboard	Medium	High	Medium
Vapor barrier			
Polyethylene sheet	Low	Medium	Low
Smart vapor retarder	Low	Low	Low
Kraft-faced ınsulation	Medium	Medium	Low
Interior finish			
Standard gypsum drywall	Medium	High	Medium
Moisture-resistant gypsum board (green board)	Low	Medium	Low

**: Indicates insulation materials, which play a key role in regulating both thermal and moisture behavior of the wall assemblies.

Comparative Analysis of Materials

- Scenario 1 materials are chosen for moderate conditions, balancing cost and performance with a standard moisture management approach.
- Scenario 2 materials are selected to handle significant humidity variations, emphasizing high moisture resistance and advanced vapor control to mitigate mold risk.
- Scenario 3 materials are optimized for stable conditions, focusing on simplicity and cost-effectiveness with basic moisture control.
- By selecting appropriate materials based on the expected climate conditions, the study aims to minimize the risk of mold growth and enhance the durability and safety of building envelopes.

Table 5 is a detailed table summarizing the mold growth risk for various building materials under different climate scenarios.

Explanation of Risk Levels:

- Low: The material is unlikely to support mold growth under typical conditions for this scenario.
- Medium: There is a moderate risk of mold growth, requiring some moisture control measures.
- High: The material is highly susceptible to mold growth under these conditions, necessitating robust moisture control strategies.

Key Observations:

- Scenario 1 (Moderate Humidity Variation): Most materials have a medium risk due to moderate fluctuations in humidity. Standard materials like OSB and fiberglass insulation show higher risk compared to more resistant materials like rigid foam insulation.
- Scenario 2 (High Humidity Variation): This scenario presents the highest mold growth risk. Materials such as OSB, fiberglass insulation, and standard gypsum drywall are particularly vulnerable, requiring advanced moisture control and careful material selection.
- Scenario 3 (Low Humidity Variation): The stable humidity levels result in generally low mold growth risk for most materials. Even standard materials perform well, with minimal need for specialized moisture management.
- Assessing mold growth risk in various materials under different climates helps designers and builders enhance building durability and safety.

RESULTS AND DISCUSSIONS

Simulation Setup

The hydro-thermal simulations were conducted on a standard exterior wall assembly using WUFI software. Key parameters included:

- Climate Data: Temperature and humidity profiles from hot and humid, cold and dry, and temperate climates.

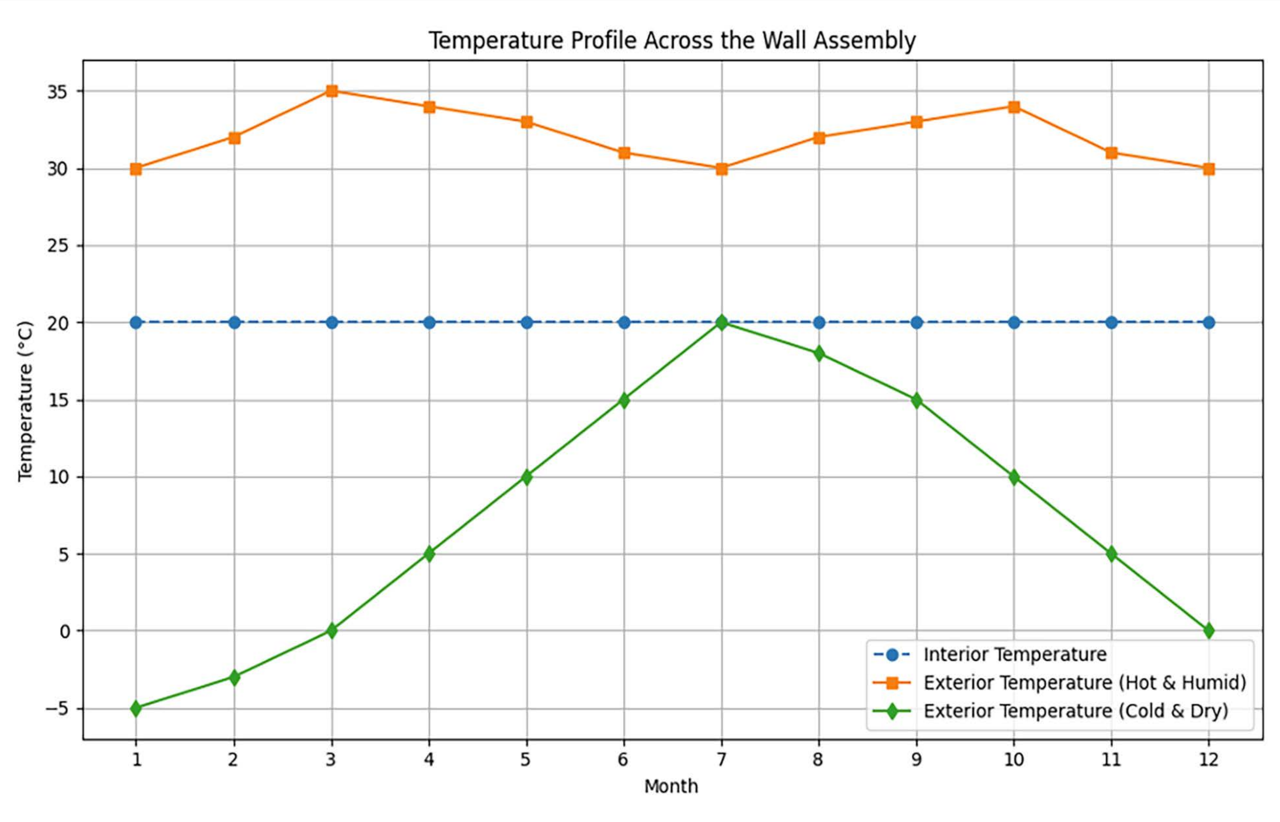

Figure 5. Temperature profile.

- Material Properties: Thermal conductivity, specific heat capacity, vapor permeability, and moisture absorption characteristics.
- Boundary Conditions: Indoor conditions maintained at 20°C and 50% relative humidity (RH), with outdoor conditions varying based on the climate data.

Temperature And Humidity Profiles

The temperature profile across the wall assembly showed significant variation between the interior and exterior surfaces (Fig. 5). In hot and humid climates, the exterior surface temperature reached up to 35°C during peak summer months, while the interior temperature remained stable around 20°C, demonstrating the insulation's effectiveness in maintaining indoor comfort.

The relative humidity profile indicated higher humidity levels at the exterior surface in humidclimates, often exceeding 80% during peak humidity periods. The insulation layer showed moderate humidity levels, while the interior surface maintained a constant 50% RH, highlighting the importance of vapor barriers in controlling moisture ingress.

Moisture Content and Mold Growth Risk

The moisture content analysis revealed that the exterior cladding, particularly in humid climates, experienced the highest moisture content, posing a significant mold growth risk. The insulation layer, although showing moderate moisture levels, still presented a moderate risk, emphasizing the need for effective moisture management strategies (Table 6).

Seasonal Variations

The simulation results highlighted seasonal variations in temperature and humidity, which directly influenced the mold growth risk. For example, during the summer months, higher temperatures and humidity levels at the exterior surface increased the mold growth risk. In contrast, winter conditions with lower temperatures and humidity levels reduced the risk but did not eliminate it entirely.

Impact of Material Properties

The choice of materials significantly impacted the hydro-thermal performance of the wall assembly. Materials with high thermal conductivity, such as metal cladding, showed greater temperature fluctuations and higher moisture content, increasing the mold growth risk. Conversely, materials with low thermal conductivity and high vapor permeability, such as mineral wool insulation, demonstrated better moisture management and lower mold growth risk.

Table 6. Moisture content and mold growth risk

Material layer	Moisture content (%)	Mold growth risk
Exterior cladding	12%	High
Insulation	8%	Moderate
Vapor barrier	2%	Low
Interior finish	3%	Low

Table 7. Recommended design strategies based on simulation results

Strategy	Effectiveness	Recommendation
Use of vapor barriers	High	Essential for all climate conditions
High-performance ınsulation	High	Critical in humid and cold climates
Adequate ventilation	Moderate to high	Important in all climate conditions
Reflective exterior surfaces	Moderate to high	Recommended in hot climates

Effectiveness Of Design Strategies

The simulation results validated the effectiveness of various design strategies in mitigating mold growth risks (Table 7):

- Vapor Barriers: Proper placement and selection of vapor barriers significantly reduced moisture ingress and condensation within the wall assembly.
- Insulation: High-performance insulation materials effectively maintained stable indoor temperatures and reduced humidity levels, lowering mold growth risk.
- Ventilation: Adequate ventilation in wall cavities and indoor spaces helped control humidity levels, further reducing the risk of mold development.

Practical Implications

The findings underscore the importance of considering climate-specific conditions during the design phase to ensure the longevity and safety of building materials. By leveraging hydro-thermal simulations, designers can make informed decisions about material selection, insulation, and moisture control strategies, ultimately enhancing building performance and occupant comfort.

CONCLUSION

The study demonstrates that hydro-thermal simulations are highly effective in assessing mold development risks in building envelopes. By understanding the transient behavior of humidity and temperature, designers can make informed decisions to minimize mold growth risks. The findings emphasize the importance of considering climate-specific conditions during the design phase to ensure the longevity and safety of building materials. Hydro-thermal simulations are crucial in modern building science, providing deep insights into the interactions between heat and moisture within building envelopes. By accurately modeling these interactions, hydro-thermal simulations support the development of resilient, energy-efficient, and healthy buildings. Understanding the results of these simulations enables designers to optimize materials and construction techniques, ultimately leading to cost savings, improved performance, and enhanced occupant comfort.

DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. USE OF AI FOR WRITING ASSISTANCE Not declared.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Environmental Research & Technology

Research Article

Performance evaluation of a simple electrochemical treatment model for saline wastewaters: Part A

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Efficiency; Electrochemical treatment process; Factorial experiments; Factors; Wastewater

ABSTRACT

This paper examined the efficacies of the electrochemical treatment (E_{tt}) technique in the reduction of chloride ion (Cl^-) from saline (salty) wastewaters (brine). Saline wastewaters (Sw) concentrations between 10 g/l and 40 g/l of Cl^- were prepared and subjected to E_{tt} utilising a locally developed composite carbon–resin (as the anode) and aluminium (as the cathode) electrodes. E_{tt} of the simulated brine was conducted on a laboratory scale. The influence of selected factors on the efficacy of the E_{tt} process was monitored utilising fractional factorial experiments. These selected factors were optimized using steepest descent technique (between the minimum and maximum concentrations) and rate change of Cl^- removal efficacy through Microsoft Excel Solver. The optimum values of these selected factors were used to purify typical raw saline water. Efficacies of the E_{tt} process in removing Cl^- from the typical raw saline water was utilised to predict efficacy of the system using typical Cl^- concentration in seawater based on literature, previous and published studies. The study revealed the relationship between chloride removal efficacy (%), initial concentration of chloride, current through the wastewater and separation distance between the electrodes were best in the form of exponentials with coefficient of determination of 0.979, 0.920 and 0.977, respectively. The optimum values of these selected factors such as current, pH, treatment period and separation distance between the electrode (centre to centre of the electrode) were 10.5 A equivalent to 0.795 A cm-2, 6.7, 2.75 hr and 42 mm, respectively. It was concluded that E_{tt} with composite carbon-resin electrodes is among effective tools for removing Cl^- from saline wastewater during E_{tt}. The performance of the treatment technique was between 68.52 and 94.82 %.

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INTRODUCTION

Overall water available on the Earth as a planet has been estimated to be equivalent to 1400×10^6 km^3 [1]. This amount of water on the planet comprises 97 percent of salty water which is filled with a high concentration of salt and other minerals. This indicates that 97 percent of the earth's water is not potable. Out of the total remaining volume of water, 2 percent of the earth's water is glacier ice at the North and South Poles, which are not accessible and usable [1]. It has been reported that fewer than 1 percent of Earth's water is freshwater, which is accessible for human uses (drinking, transportation, heating and cooling, industry, and many other purposes) [2]. With a critical knowledge that water

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is among the primary life force which sustain all the living animals and plants [3], it is important to protect the quality of water. It is well established that sources of typical water (ground and surface) are facing critical deterioration in qualities due to various activities of man such as industrialization, agricultural practices, urbanization, and the relentless expansion of population [3]. This critical deterioration in qualities is aggravated by environmental adjustments and geological moves. Documents and researches have been revealed that aquatic environments are daily threatened by releasing large amounts of synthetic pollutants and industrial chemicals such as arsenic compounds [4], ionizable aromatic pollutants [5], arsenic and chloride contained materials [6, 7], zinc oxide nanocomposites [8], cationic and anionic dyes [9], ciprofloxacin antibiotic [10], tannery industry, and pharmaceuticals such as cefazolin antibiotic and personal care products [11], Bisphenol A, nonylphenols, benzophenones, and benzotriazoles [12]. Among the mentioned pollutants, Cl^-, which is widely utilised as a preservative and stabilizer or antioxidant for many types of plastics (polyvinyl chloride), must be removed from the environment such as water to make it potable [13]. Brine and saline water can be toxic and harmful to the aquatic animals and environment due to the presence of high salinity and other chemical substances [14], which indicates that these type of water and wastewater must be treated. Saline water or brine treatments using adsorption, electrochemical, membrane and electrodialysis are most promising alternatives to seawater treatments and brine disposal. These treatments techniques give an output that reduce the environmental pollution materials and environmental friendly, production of freshwater with extraordinary recovery and minimization of solid or liquid wastes volume [14].

In summary, electrochemical, ion-exchange, reverse osmosis membrane, distillation, adsorption and electrodialysis processes have been identified to be effective for the reduction of Cl^-, but some of these processes such as reverse osmosis membrane, distillation and ion-exchange are not cost-effective treatment processes and produce secondary wastes [4–9]. Some of these conventional treatment processes for the reduction of Cl^- from water and industrial wastewaters have other critical disadvantages [8–11]. Application of the adsorption process only transfers the target pollutant from the liquid phase to the solid phase such as nanoclay [15]; pretreated dried activated sludge [16] and other adsorbents [17]. Over the past few decades, electrochemical treatment technology has attracted great attention among many researchers as an advanced and emerging treatment technology for water and wastewater treatment [18]. Figure 1 presents publications on electrochemical treatment techniques in selected countries between 1977 and 2022. Electrochemical treatment techniques are electrical and voltage-driven technologies that have been utilised successful in saline water and brine desalination [19–167]. The treatment technique is based on the selective transportation of ions in aqueous solutions or electrolyte and utilises an applied electrical voltage gradient, difference, or slope

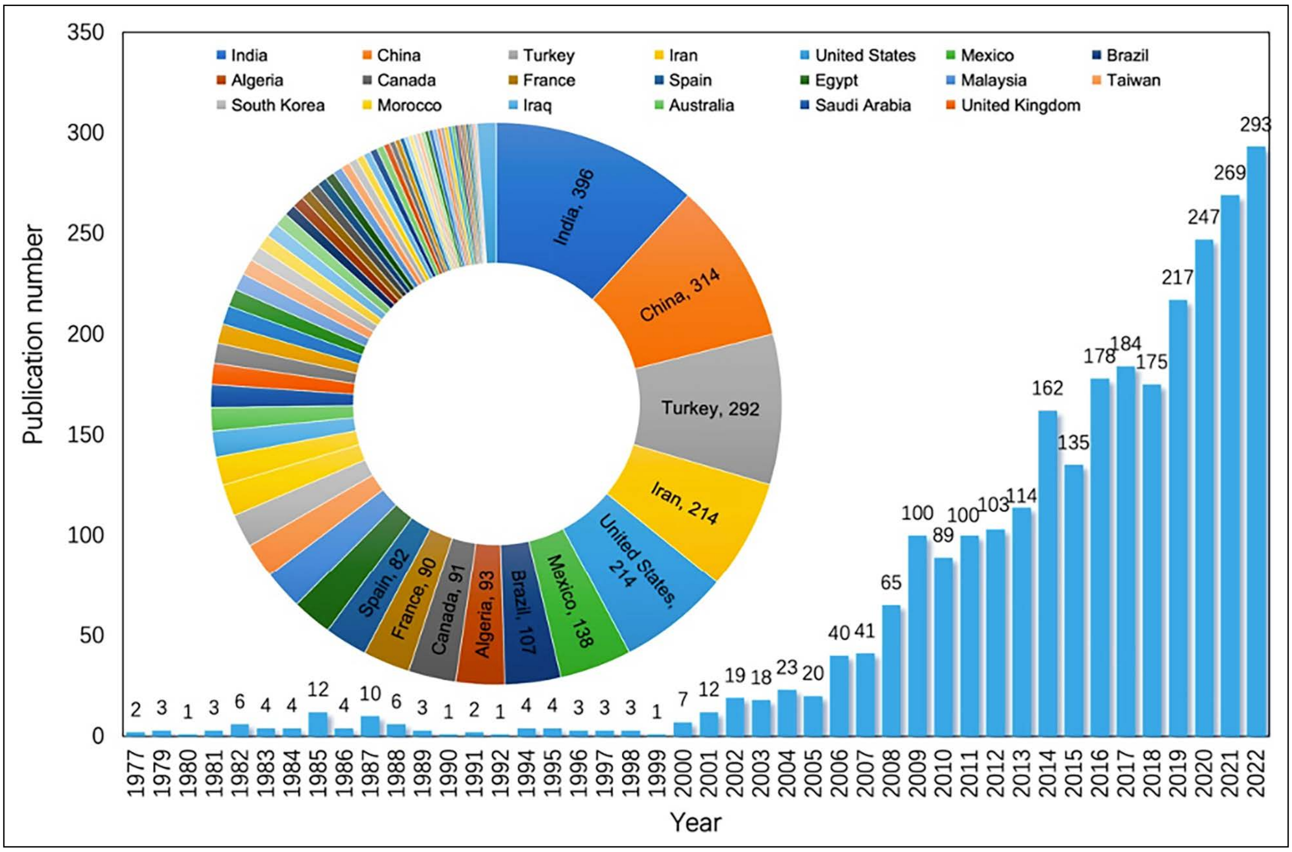

Figure 1. Publications on electrochemical treatment technique from selected countries between 1977 and 2022 (Source: Luciano et al. [131]).

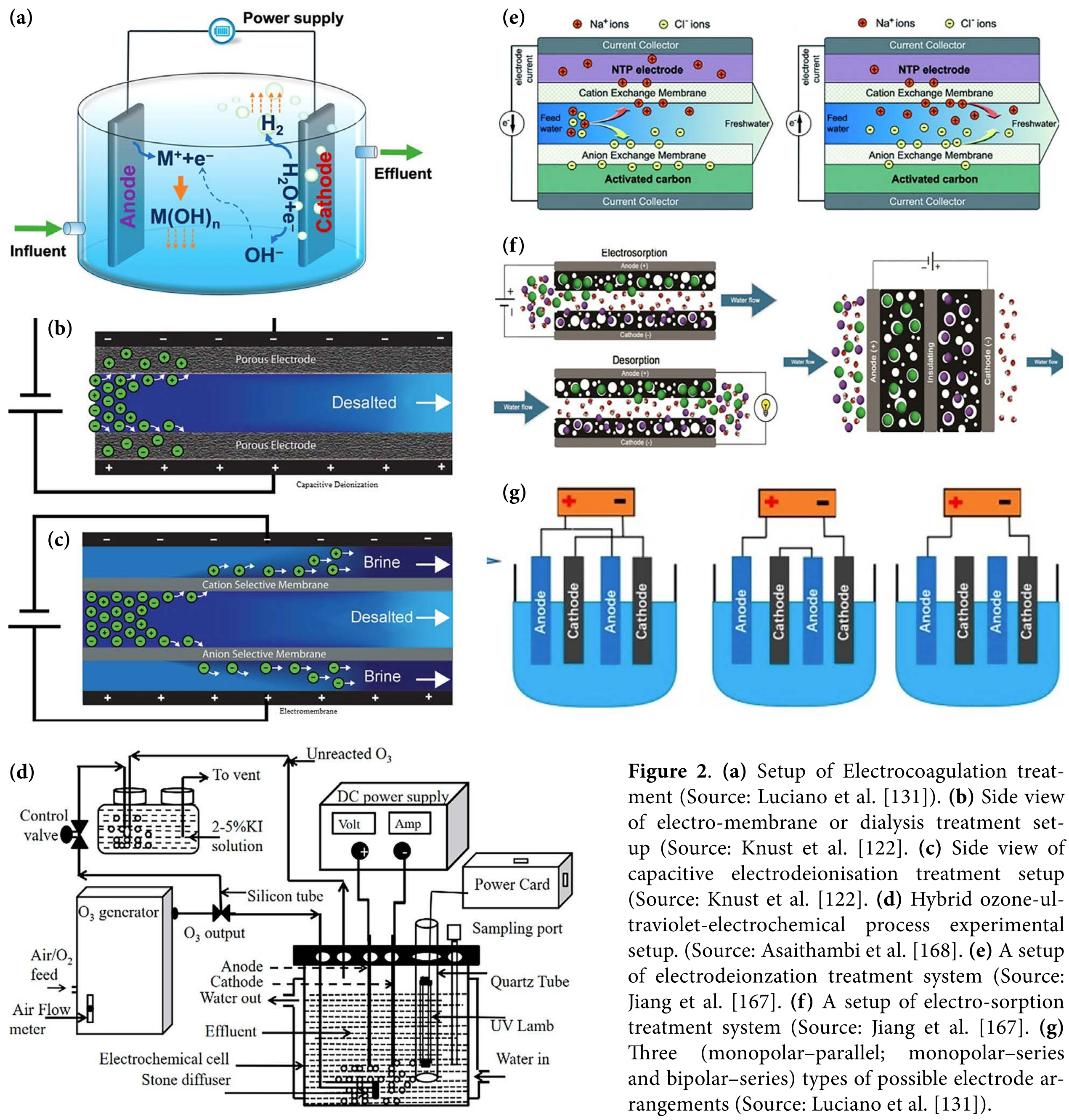

Figure 2. **(a)** Setup of Electrocoagulation treatment (Source: Luciano et al. [131]). **(b)** Side view of electro-membrane or dialysis treatment setup (Source: Knust et al. [122]. **(c)** Side view of capacitive electrodeionisation treatment setup (Source: Knust et al. [122]. **(d)** Hybrid ozone-ultraviolet-electrochemical process experimental setup. (Source: Asaithambi et al. [168]. **(e)** A setup of electrodeionzation treatment system (Source: Jiang et al. [167]. **(f)** A setup of electro-sorption treatment system (Source: Jiang et al. [167]. **(g)** Three (monopolar–parallel; monopolar–series and bipolar–series) types of possible electrode arrangements (Source: Luciano et al. [131]).

to drive anions and cations in opposite directions to the electrode. E_{tt} uses electric current and electrodes to neutralize and aggregate pollutants and contaminants in water and wastewaters [18–21]. Although, Advanced Oxidation Processes (AOPs) are also highly effective for degrading recalcitrant organic pollutants in water and wastewater treatment, E_{tt} processes are adaptable and can be tailored to various types of water and wastewater, addressing specific treatment needs to meet regulatory requirements [21–41, 112]. E_{tt} often complement traditional treatment methods, enhancing overall system performance [41–62]. E_{tt} is relatively inexpensive due to its lower equipment and maintenance costs and because no additional chemicals are required [131].The category and treatment of water and wastewater using E_{tt}, are controlled by several factors, which include nature, and size of reactive species to be generated in E_{tt} processes the type of the treatment technique, electrode or electro catalyst materials, water or wastewater composition, water or wastewater pH settings, and operational constraints [19–170]. E_{tt} can be inform of any of these treatment techniques [19–167]:

i. **Electrocoagulation:** This process uses electric current to dissolve metal electrodes, which produces coagulants in situ that neutralizes and aggregates the contaminants. Wide range of pollutants can be reduced and removed from wastewater using this technique. These pollutants are usually negatively charged such as microorganisms, inorganic colloidal particles, cyanobacteria, organic bacteria and clay [36–58]. Figure 2a presents a typical setup for electrocoagulation.

ii. **Electrooxidation:** The process allows the passage of electric current and a chemical reaction in which an atom or a molecule losses electron or electrons. At the anode (made of the catalytic material needed for conversion) the movement of electrons or molecules allows for oxidation of the pollutants. These oxidation processes can be anodic oxidation where pollutants are oxidized directly on the electrode or indirect oxidation by generation of oxidizing species or agents. The principle of the process can be in the form of [39–71]:
   a. **Anodic Oxidation:** It is possible at low potential differences. The main set back of the process is that the process allows deposition of polymeric layer on the surface of anode, which reduces electrical conductivity.
   b. **Indirect Oxidation:** In this process there is no direct electrons transfer between the anode and the organic matter, which prevents the fouling of anode due to organic particulate.

The process is based on the principle that oxidization of pollutants is conducted in the aqueous solution through oxidizing agents [39–71].

iii. **Electro-flotation:** The process uses electrolytically generated gas bubbles, which are typically hydrogen and oxygen to float and separate suspended solids or particles. It is a gravity separation process. The process is cost effective process for the separation of many inorganic and organic pollutants. The process removes hydrophobic ions from aqueous solutions [79–88].

iv. **Electrodialysis:** This technique utilises ion exchange membrane for the separation of pollutants and electrolytes from the wastewater and water. The process uses an electric field to drive ions through selective membranes, thus separate the pollutants from wastewater and water. It is based on the principle of potential gradient technique or method. It helps to select the ions to pass through the membranes. The main requirement for the process is direct current and ion exchange membranes (anion exchange membrane and the other is cation exchange membrane). The selection of the membrane is based on the function and the purpose of usage [104–145]. Figure 2b shows an arrangement of electrodialysis treatment process.

v. **Electrochemical Advanced Oxidation Processes:** Electrochemical Advanced Oxidation Processes is a combination of electrochemical methods and advanced oxidation processes to generate highly reactive species that degrade pollutants [46–51].

vi. **Electrochemical Reduction:** The process involves reduction reactions at the cathode to remove pollutants or convert pollutants into less harmful substances. [29–35]. In this process one or more electron of an atom or molecule is deposited on the surface of the cathode due to passage of electric current in the electrochemical system. Electrochemical reduction can be used for removal of organic and heavy metals such as Pb, Hg, and similar metals. The system is cost effective, but the process efficiency is very sensitive to wastewater composition or ingredients.

vii. **Electrochemical Desalination or Capacitive Deionization:** The process uses electrochemical techniques or methods to remove salts from water, either through capacitive deionization or through other electrochemical means. It uses direct current power source. In the process current passes through saline water. The ions in the solution are absorbed at cathode and anode. Finally, the ions are de-absorbed form electrodes. This technique is use for the purification of saline water and brackish desalination [24–29]. Figure 2c presents typical arrangement of capacitive deionization systems.

viii. **Electrochemical Peroxidation:** This process is combination of electrochemical oxidation and hydrogen peroxide generation in the process to enhance treatment efficacy [31–35].

ix. **Electrochemical Disinfection:** The process utilises electrochemical techniques to incapacitate microorganisms in wastewater and water. The process is more efficient method than the conventional chemical disinfection techniques or method. The technique works on the principle of the anodic generation of strong oxidizing agents such as O_2, O_3, and hypochlorite during water electrolysis [56]. Categories of electro-disinfection are as follows:
   a. **Electro-disinfection using oxygen gas:** The technique involves formation of anodic oxygen that has capacity of killing germs to some extent. It is usually recommended for the removal odour of water.
   b. **Electro disinfection using chlorine gas and hypochlorite ions:** The process involves activated chlorine for killing the bacteria, fungi, and spores.
   c. **Electro disinfection using O_3:** The technique has high oxidation potential and diffusion through the cell walls of microorganisms [20–35].

x. **Photoelectrochemical Treatment:** This technique combines photocatalysis and electrochemistry for pollutant degradation using light and electrochemical reactions [24–35]. Figure 2d shows the arrangement of photoelectrochemical treatment system.

xi. **Electrochemical Membrane or Electro-Filtration Processes:** This process integrates electrochemical methods with membrane filtration to enhance separation and degradation of contaminants. It is used for the removal of solid suspended particles. This is upgraded by using an electrical field across it for removal of dissolved organic carbon [16–30].

xii. **Electrodeionzation:** This method mainly utilises semipermeable membranes and ion exchange method for wastewater and water purification. The technique has specific semipermeable membranes that allow electrically charged ions to pass through. It is used for high purity of water [130–131]. Figure 2e show a setup of electrodeionzation treatment system.

xiii. **Electro Floto coagulation:** This technique is combination of electrical charges, gas flotations and coagulation process. It is especially deals with the particle size [69–71].

xiv. **Photo Electro Catalysis:** It is a process in which catalyst and light are utilized for the acceleration of the chemical reaction. Catalyst activities are accelerated by utilising light irradiation or solar. The technique efficiently treats wastewater and water containing inorganic ions, organic compounds reduction and for disinfection. The process is based on the principle of photoexcitation. Degradations of organic compounds by this technique are due to simultaneous actions of light and potential difference between the electrodes during the treatment time [130–131].

xv. **Son electro Catalysis:** In this, techniques sound waves having frequency 20kHz to 10^6kHz utilised for treatment of wastewater and water through the series of compression and rarefaction cycles, causing the pressure zone in the medium. One of the key set back of this technique is the polarization and passivation of electrodes due to the reduced mass transfer. In the process gas accumulate at electrode, which resulted in depletion of pollutants to the surface of electrodes boundary layer (Due to polarization). Accumulation of reactants at electrodes critically result in poor efficiency (Passivation) [134–145].

xvi. **Electro-Fenton Process:** The process involves electrochemistry and Fenton reaction. It is an advance oxidation process, which is based on radical reactions. The process has been used for the removal of organic pollutants such as pesticides, pharmaceuticals, phenol, dyes, and phenolic compounds. Electro-Fenton process can be carried out in the cells that can be divided by cation exchange membrane or by not dividing the cell with membrane [51].

xvii. **Electro-sorption:** The process involves combination of electrochemical and adsorption processes. In the process, the electrodes are passive in nature and particles from the electrodes or electrode's surface act as an adsorbent to adsorb the adsorbates which are the pollutants. [150–167]. Figure 2f show a setup of electro-sorption treatment system.

In electrochemical treatment of water and wastewater, electrodes play a critical role in driving electrochemical reactions and end-products. Selection of electrode significantly influences the performance and efficiency, operational cost, longevity and durability of the treatment process [102–170]. Literature listed some of the main categories of electrodes (passive and active or sacrificial) in use as follows: graphite; titanium; titanium coated with mixed metal oxides; Boron-Doped Diamond; stainless steel; Platinum-Coated; Iron and Aluminum Electrodes; Carbon Felt and Carbon Cloth Electrodes; Lead Dioxide (PbO_2) Electrodes, Nickel and Nickel-Based, Zinc and Zinc-Based, and Polymer Composite Electrodes. There are three types of electrode arrangements (Fig. 2g) for electrochemical cells: monopolar–parallel, monopolar–series, and bipolar–series [1–95, 131].

Criteria and factors for the selection of any electrode during the treatment processes are as follows [1–170]:

a) Electrode Material: Must be conductive and compatible with the specific treatment process.

b) Durability, effectiveness and Corrosion Resistance: Important for longevity and cost-effectiveness.

c) Initial and operational Costs: Balance between performance and budget.

d) Electrocatalytic Activity: Determines efficiency in generating desired radicals or intermediates

e) Environmental Impact: Toxicity and disposal considerations.

With reference to the urgent needs for sustainable development goals, based on relationship between economy, environment, society and poverty eradication [171], sustainable water and wastewater management, the importance and performance of E_{tt} techniques in removing pollutants from aqueous solutions, there is a critical need to further evaluate the efficacy of E_{tt} in reducing Cl^- from salty water, which is common as sea water. The main objectives of the current study are to evaluate the efficacy of E_{tt} process (utilising carbon– resin and aluminium electrodes) in removing Cl^- from salty (saline) water, optimise selected operational factors, utilising the optimum values of the selected operational factors for the treatment typical raw saline wastewaters with critical focus on Cl^- removal and simulate the treatment performance.

MATERIALS AND METHODS

All chemicals and reagents used in this research study had a chemical purity of 95% or above. Distilled water was used in the preparations of primary and secondary standard solutions. All equipment used in the experiments were calibrated and the coefficient of determinations of these calibrations (relationship between expected and obtained values) were 96 % or above. This section is breakdown as follows:

a. **Materials:** Development and properties of fabricated composite Carbon (graphite) - Resin electrodes. Carbon (graphite) - resin electrodes were prepared, developed and established from wasted dry cells (dry cells were used based on availability as household solid waste at no additional cost). The discarded dry cells (D R_{20} UM_{-1}) were collected from different dumpsite locations in Nigeria. These collected cells were segmented and carbon (graphite) were removed from these cells, crushed and powdered. Powdered carbon was separated into different particle sizes using British Standard particle sizes. A fixed amount by weight of the powdered carbon was mixed with resin (organic binder), and moulded into 25- millimetre diameter, 100-millimetre long electrode using a fabricated extruder and plunger, and a compaction machine. Microstructures and Energy Dispersive Spectroscopy of the developed Carbon-resin electrode were monitored to ascertain the composition of the electrode using a scanning electron microscope (Carl Zeiss Smart Evo 10 of secondary electron imaging detector, system vacuum of 89e06Torr and WD of 9.14mm at different magnification). Details of the preparation, development, physical and chemical properties of the electrodes were documented in previous studies such as Oke [172, 173]; Oke et al. [174–176]; Oke et al. [177]; Oke et al. [178]; Oke [179], Oke et al. [180]; Oke and Ogedengbe [181]; Olayanju et al. [182] and Oke et al. [183].

b. **Design and Development of Electrochemical Facility (Electrolysing Equipment):** Electrolysing equipment was designed and developed from local materials to convert alternating current to direct current [184]. The design, development, fabrication procedure, performance and properties of the device are as presented in previous publications such as Oke [172] and Oke and Ogedengbe [185].

c. **Preparation of Synthetic Saline Wastewater:** Analytical Sodium Chloride (60.0 grams) was dissolved in 1000 ml of distilled water as a stock solution and working salty wastewaters were prepared from the stock. The synthesised chloride wastewaters (between 10 g/l and 40 g/l) were prepared utilising procedures and methods specified in the Standard Methods for Water and Wastewater Examination such as APHA [186] and Van Loosdrecht et al. [187].

d. **Laboratory Setup and Electrochemical Treatment of synthesised chloride wastewaters (Desalination Experiments):** Salty wastewaters were subjected to E_{tt} utilising developed carbon–resin (anode) and aluminium (cathode) electrodes in a 2000 ml reactor. electro-coagulation and electro-oxidation based on two types of electrodes (aluminum and graphite) The choice of electrode impacts the effectiveness of water and wastewater treatment systems, influencing operational costs, treatment efficiency, and system durability. Fehintola et al. [188] presents the laboratory setup of the E_{tt} of the simulated wastewaters.

e. **Experimental Study of Operational Factors that affects the performance of Electrochemical:** The influence of selected factors (separation distance between the electrodes, volume of the wastewater used, applied current, flow rate, pH, depth of the electrode, initial concentration of the Cl^- and contact surface area of the electrode used) on the efficacy of E_{tt} process were monitored utilising fractional factorial experiment and optimised utilising combination of steepest and Microsoft Excel Solver techniques. Fehintola et al. [188] presents the standard fractional factorial experiments and the factors. The selection of the Microsoft Excel Solver was based on the availability of the software at no additional cost (available in all Microsoft Excel packages). Solver is an Add-in for the Microsoft Excel packages which are typically not enabled during the initial installation of Microsoft Office (Excel). The procedures required in using Microsoft Excel Solver can be summarized as indicated in Fehintola et al. [188]. The choice of these factors to be studied was based on the theoretical data about several factors that determine the performance of an electrochemical treatment process and the knowledge concerning carbon-resin and aluminium electrodes [102–170].

f. **Analysis of Chloride concentrations and Computation:** Chloride determinations in both raw and treated brine were conducted utilising the argenotometric method specified in APHA [186]. Chloride concentration was calculated using equation (1) as follows:

$$Cl^-(mg/l)=35450\left(\frac{(A\text{-}B)N_0P_1}{V_S}\right)C_f \tag{1}$$

Where; N_0 stands for normality of Silver Nitrate used, P1 stands for dilution factor; Vs stands for volume of sample used (ml), A stands for volume of the titrate used for the sample (ml), Cf stands for calibration factor and B stands for volume of the titrate used for the blank (ml). Efficiencies of the process were based mainly on pollutant (chloride) removal (Y,%), which was computed using equation (2). The choice of the argenotometric and instrumentation methods was based on accuracy, type of wastewater (clear aqueous solution) and availability of required reagents.

$$Y=100\left(\frac{(C_0-C_t)}{C_0}\right) \tag{2}$$

Where: C_o stands for initial chloride concentration of the synthetic wastewater (mg/l). Ct stands for final chloride concentration of the synthetic wastewater (mg/l) and Y stands for chloride removed (%) at optimum values of the selected operational factors. These selected operational factors were optimised using steepest descent and rate change in the efficacy of the technique. Optimum values of the selected operational factors were utilised to purify typical raw saline water. The efficacies of the system with typical raw saline water were utilised to simulate efficacy and performance in typical seawater with chloride concentration of 31000 mg/l with reference to Akindahunsi et al. [189]; 35.3779 g/l of chloride ion based on Thabit et al. [190]; 41.80 g/l based on Mehan-Martes and Mertel et al. [191] and 43.6995 g/l of chloride ions based on Lior and Kim [192]. Figure 3 presents the flow chart of the procedures used in the utilization of Microsoft Excel Solver.

RESULTS AND DISCUSSION

Results from this study are presented as follows:

a) Development, Properties, and Stability of the electrodes

The study established that electrical resistance per unit length, density and stability of composite carbon-resin electrode are functions of the following factors particle size, compressive pressure and percentage composition of the binder. Density of the electrode increased from 1.26 to

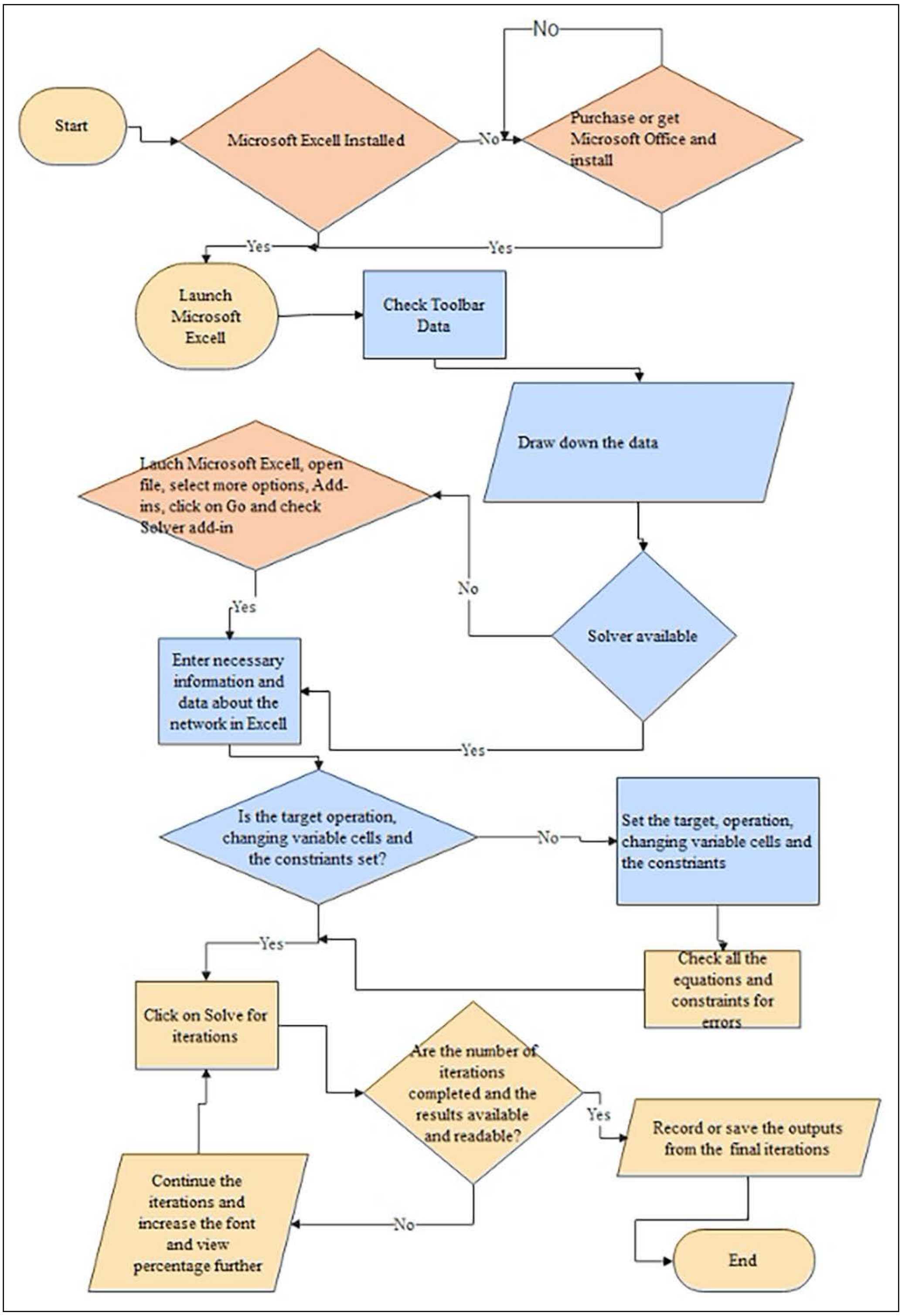

Figure 3. Flow chart of the step required in utilization of Microsoft Excel Solver.

1.65 gcm^{-3} when carbon particle size ranged from 245 to 45×10^{-6}m at 60 MNm^{-2} applied compressive pressure and declines from 1.86 to 1.65 gcm^{-3} with a range of applied compressive pressure from 100 to 60 MNm^{-2}. Electrical resistance per unit length was established to increase with cumulative portion of binder and declines with increasing in applied compressive pressure. The stability of the composite electrode was of increasing order with cumulative applied compressive pressure and declines with increase in current density and carbon particle size [175]. Estimated costs revealed that cost of producing composite carbon-resin electrode was cheaper (\$13.25 m^{-1}) than that of heat-treated electrodes (\$33.33 m^{-1}) [179].

More on the properties of this composite carbon-resin electrode can be established in literature such as Oke [172; 173]; Oke et al. [174, 176]; Oke et al. [177]; Oke et al. [178]; Oke et al. [180]; Oke and Ogedengbe [181]; Olayanju et al. [182] and Oke et al. [183].

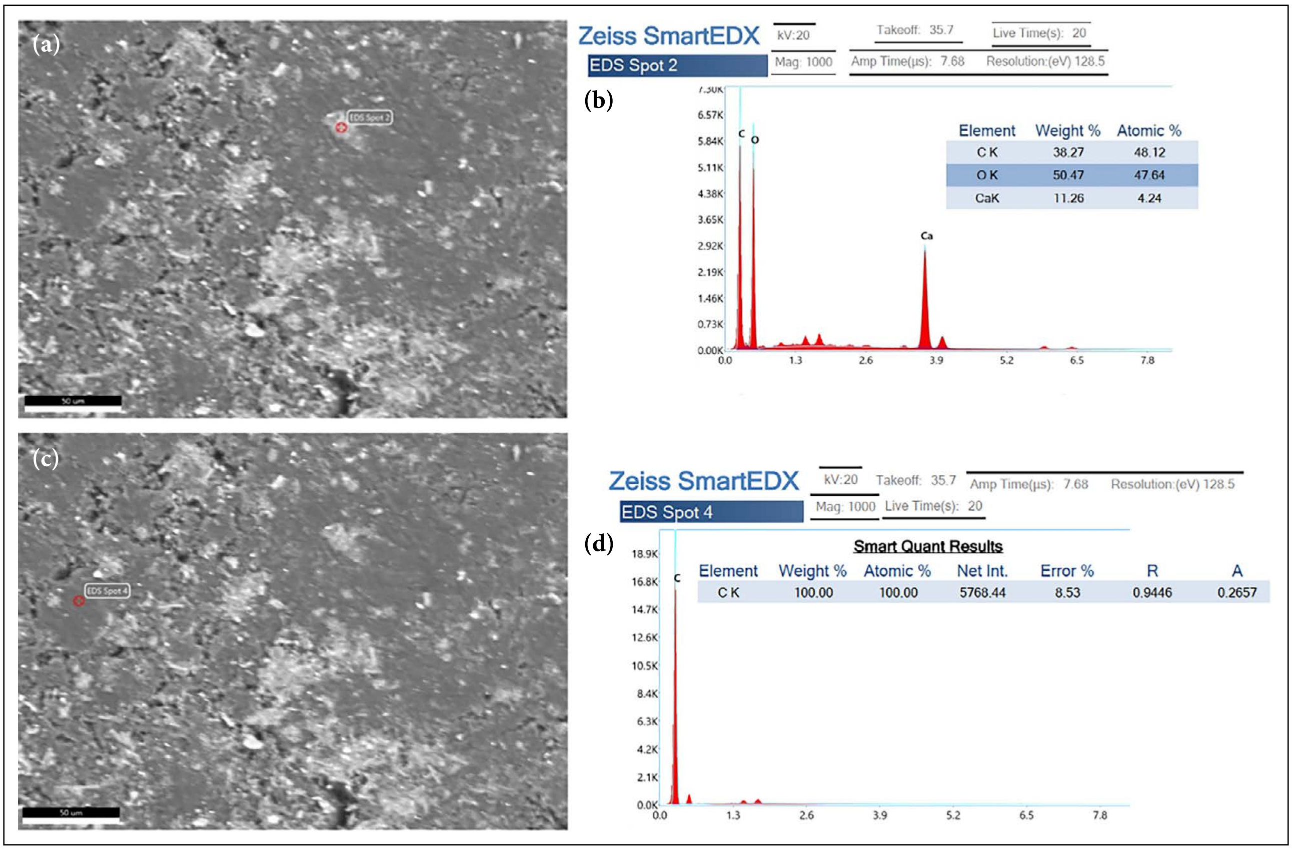

Figure 4. **(a)** The major constituents of the graphite resin electrode at spot 2. **(b)** The Result of zeiss smart EDX for spot 2. **(c)** The major constituents of the graphite resin electrode at spot 4. **(d)** The result of zeiss smart EDX for spot 2.

b) Scanned Electro Magnetic and Energy Dispersive Spectroscopy of the electrodes

Figure 4a-c and d provide the major and key configurations of the selected spots in graphite (carbon) resin electrode. The figure shown that the main components of the electrode are Carbon (between 38.27 % and 100 %) Oxygen (50.47 %) and Calcium (11.26%). The result specified the occurrence of Carbon and Oxygen at spots 2 and 4, as the highest composition of the developed carbon-resin electrode. The occurrence of these two components (carbon and oxygen) can be accredited to the organic binder used, powdered graphite used and likely trapped Oxygen during missing processes. This result of the composition revealed that removal of chloride may be attributed to adsorption by the pores and conversion of some of the components to calcium, carbon and oxygen end products such as $Ca(OCl)_2$ and $CaCl_2$. Figure 5a-c and d show and establish the Scanned Electro Magnetic (SEM) structures of the electrodes at various magnification of 100, 250, 500 and 750. From these figures, it is clearly showed that the powdered particles of the powdered carbon electrode were closely parked and porosity is very low. This lower porosity can be attributed to a lower concentration of binder, higher compressive pressure and nano-particle sizes utilised in the development of the carbon-resin electrode stated in Oke et al. [178]. The figures established that there are two categories of pore with reference to the nature of the pores (continuous and separated or standalone pores). The continuous pores have the tendency to accommodate more concentration of particles at the same time, while standalone adsorb different concentration of particles at different time.

c) Development and Performance of the electrolysing Equipment

The performance of the fabricated equipment converting (electrolysing equipment) alternating current to direct current was 95 % and above. The results of the performance were compared with similar imported equipment and analysed statistically using analysis of variance, total error, coefficient of determination, and model selection criterion. The results of total error, coefficient of determination and model selection criterion analysis were 22.8, 0.244, and 3.312 and 24.3, 0.243 and 3.066 for locally developed and imported electrolysing equipment respectively. The results analysis of variance indicates that there was no significant difference between the two equipment (locally developed and imported electrolysing equipment) at a 95 % confidence level. Detailed data are available in Literature such as Oke [172], Oke and Ogedengbe [185].

d) Desalination of Synthetic Salty Water and Effects of Selected Operational Factors on the Performance

The study established that the maximum values the performance of the system occurred with 94.82% removal of chloride concentration when the surface area of the composite carbon resin electrode was 19.64 cm^2, the flow of the wastewater was 2.0l/hr, the treatment time of 4.0 hr and the current flow through the wastewater was 10.0 A (higher factorial factor levels), which indicated that these mentioned factors

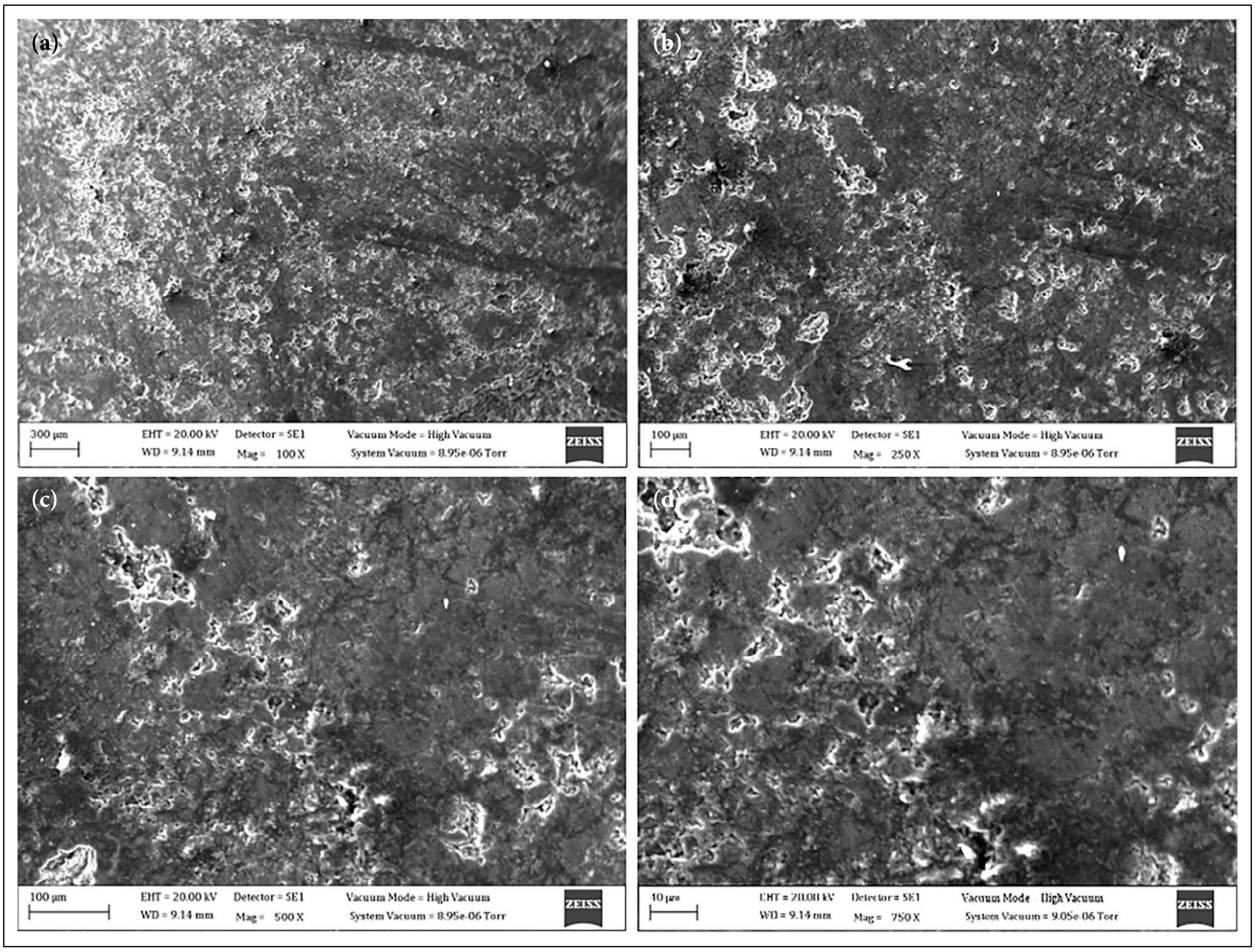

Figure 5. **(a)** Scanned electro magnetic (SEM) structures of the electrode at 300 µm. **(b)** Scanned electro magnetic (SEM) structures of the electrode at 100 µm. **(c)** Scanned electro magnetic (SEM) structures of the electrode at 100 µm. **(d)** Scanned electro magnetic (SEM) structures of the electrode at 40 µm.

had positive influence on the performance of electrochemical treatment of the wastewater. It was revealed that during the treatment process. The lowest value of the performance of the process occurred with 68. 52% removal of the chloride by the treatment process. This level of performance occurred when the initial concentrations of chloride was 40×10^3 mg /l, the separation distances between electrodes was 10.0 cm, the depth of the electrode was 1.0 cm and pH was 10.0 (higher factorial factor levels), which meant that these latter mentioned selected factors contributed negatively to the performance of the treatment process. The cations moved toward the negatively charged cathode, while anions moved toward the positively charged anode. The outcome is the separation of concentrated brine aqueous solutions and freshwater. The detailed efficacy of the E_{tt} process in the current study is presented in another paper specifically such as Oke [172]; Oke et al. [184] and Fehintola et al. [188]. The electrolysis chemistry of the reactions at the developed carbon-resin electrodes and solution are as follows [21, 112, 137]:

Anode: $2Cl^-\rightarrow Cl_2+2e^-$ (3)

Cathode: $2H_2O+2e^-\rightarrow H_2+2OH^-$ (4)

In solution: Cl_2+H_2OÄ $HOCl+Cl^-+H^+$ (5)

$HOCl$Ä H^++OCl^- (6)

Dissociation constants

$$K_3=\frac{[HOCl]\ [Cl^-]}{Cl_2}\approx 2\times10^{-4} \quad (7)$$

$$K_4=\frac{[H^+]\ [OCl^-]}{[HOCl]}\approx 2\times10^{-4}\ at\ 0°C \quad (8)$$

Loss reactions at:

Anode:

$$6OCl^- +3H_2O\rightarrow 2Cl_3^-+4Cl^-+6H^+ + \frac{3}{2}\, O_2+6e^- \quad (9)$$

Cathode:

$$2H_2O\rightarrow\ O_2 4H^++4e^- \quad (10)$$

$$OCl^-+H_2O+2e^-\rightarrow Cl^-+2OH^- \quad (11)$$

Solution:

$$2HOCl+OCl^-\rightarrow ClO_3^-+2Cl^-2H^+ \quad (12)$$

$$2ClO^-\rightarrow O_2+2Cl^- \quad (13)$$

$$H_2+OCl^-\rightarrow H_2O+Cl^- \quad (14)$$

Other likely reactions:

$$Mg^{2+}+2OH^-\rightarrow Mg[OH]_2 \quad (15)$$

$$Ca^{2+}+2OH^-\rightarrow Ca[OH]_2 \quad (16)$$

$$X^{n+}+nOH^-\rightarrow X[OH]_n \quad (17)$$

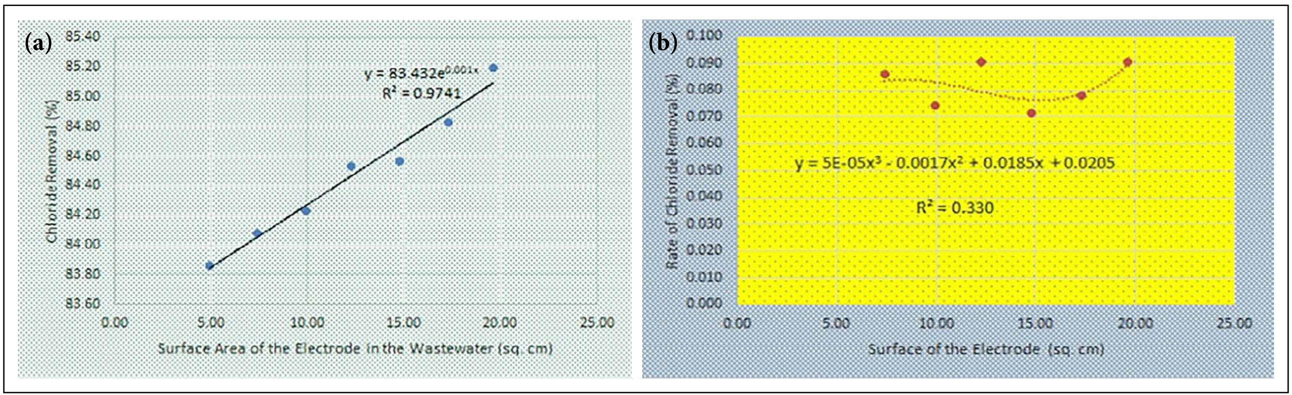

Figure 6. **(a)** Relationship between surface area of the electrodes in the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the surface area of the electrodes in the wastewater and performance of the electrochemical treatment process using steepest descent technique.

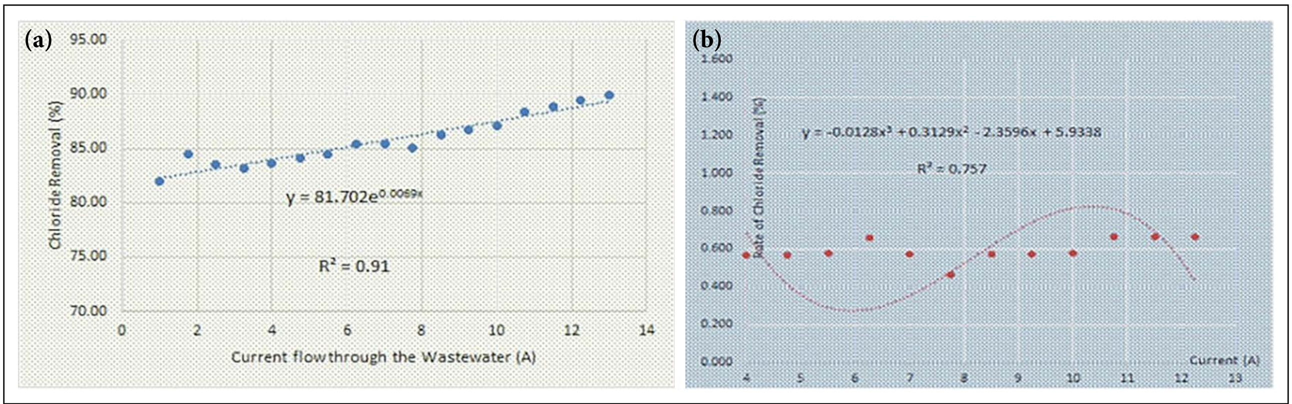

Figure 7. **(a)** Relationship between current flow through the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the current flow through the wastewater and performance of the electrochemical treatment process using steepest descent technique.

e) Optimisation of the Selected factors in the Desalination of Salty water and Simulated Performance

Figure 6a presents relationship between surface area of the developed carbon-resin electrodes in the wastewater and efficacy of the E_{tt} process utilising steepest descent technique. The figure establishes that there is an exponential relationship, which is a positive indicating that surface area of the developed carbon-resin electrode increases the efficacy of E_{tt} process. The figure revealed that at higher surface area of the developed carbon-resin electrode in the wastewater efficacy of E_{tt} process improves greatly. Figure 6b provides information on the optimization and efficacy change in the process due to variation in the surface area of the developed carbon-resin electrode. The figure revealed that the optimum surface area of the developed carbon-resin electrode was 13.2 cm^2 of 2000 ml of the wastewater. The relationship between the surface area of the radius and the depth can be expressed as:

$$S_c=\Pi r_c^2+\Pi r_c d_e \tag{18}$$

Where; de stand for the depth of the electrode in the wastewater; rc represents the actual radius of the electrode and S_c stands for the contact surface area of the electrode. The rate change in the contact surface area can be expressed as follows:

$$\partial(S_c)=\frac{\partial}{\partial r_c}(\Pi r_c^2+\Pi r_c d_e)+\frac{\partial}{\partial r_c}(\Pi r_c^2+\Pi r_c d_e) \tag{19}$$

Mishra and Ram [193] stated that steepest descent technique is among the conventional, oldest, and well-establish explore techniques for decreasing multivariable unrestricted optimization challenges. This technique has performed a vital role in the advance of progressed optimization algorithms. The technique is a first-order derivative numerical and iterative optimization algorithm that convergence or divergence is linear for a situation of quadratic functions. More of steepest descent technique can be established in literature such as efficient numerical method in Wu et al. [194]; numerical technique for multicriteria optimization highlighted in Bento et al. [195]; numerical technique Variable Order Vector Optimization Problems documented in Wang et al. [196]; numerical technique for mining signal transduction network available in Bello et al. [197], numerical technique optimization of mechanical systems in Haug et al. [198] and numerical technique for multicriteria optimization Bento et al. [199]. The observation is similar to previous researches and studies such as Alam et al. [35] statement on treatment on saline wastewater, Korbahti [200] observation on optimization of E_{tt} of textile dye wastewater, Szpyrkowicz et al. [201] conclusions on E_{tt} of tannery wastewater and Deng et al. [202] on the efficacy of E_{tt} of nitrogen- containing organic wastewater by iron filings.

Figure 7a presents relationship between current flow through the wastewater and efficacy of the E_{tt} process util-

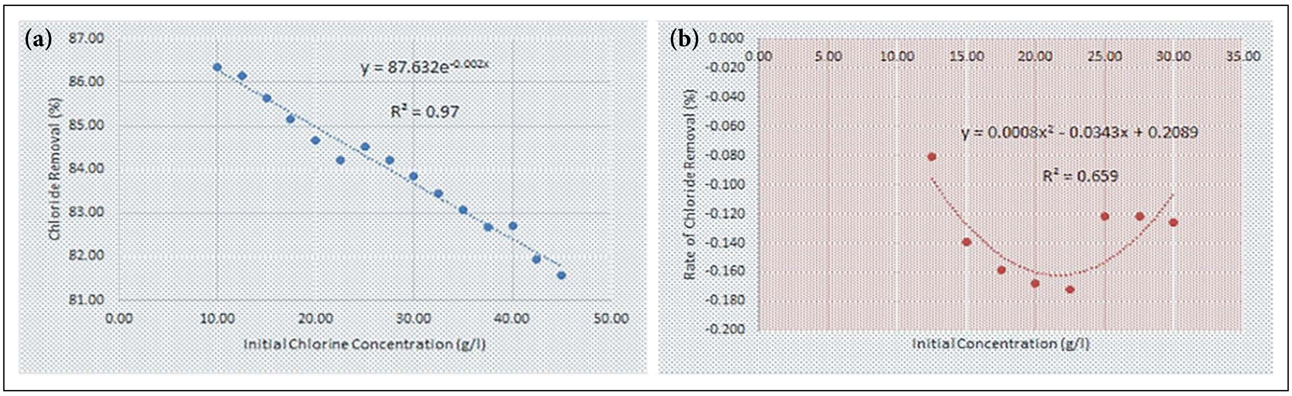

Figure 8. **(a)** Relationship between initial concentration of Chloride ion in the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the initial concentration of chloride ion in the wastewater and performance of the electrochemical treatment process using steepest descent technique.

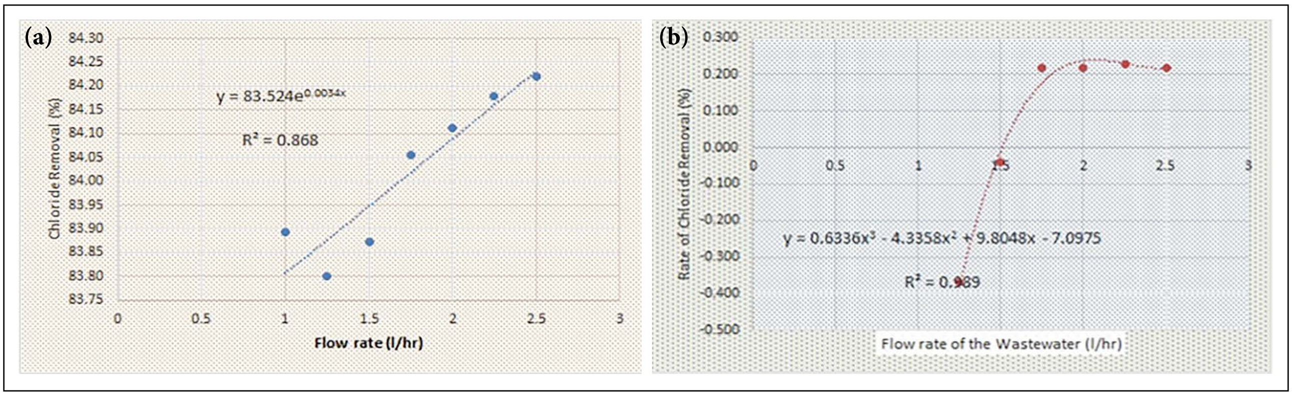

Figure 9. **(a)** Relationship between flow rate of the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the flow rate of the wastewater and performance of the electrochemical treatment process using steepest descent technique.

ising steepest descent technique. The figure establishes that there is a positive relationship, which is exponential form between the flow and efficacy of the process, which indicate that current flow through the wastewater increases the efficacy of E_{tt} process. This positive relationship can be attributed to further influx of chloride ion and flocs formation of the pollutant. The figure revealed that at higher current flow through the wastewater the efficacy of the system improves greatly. The observation is similar to previous researches and studies such as Alam et al.[35] statement on treatment on saline wastewater, Tulin and Serdar [203] observation on efficacy of electrooxidation- E_{tt} of container washing wastewater, Lyvia [204] conclusion on influence of current density of electro-bioreactor treatment on reduction of phosphorus and micropollutants, and reduction or elimination of fouling, Feng et al.[205] on efficacy of two new E_{tt} systems for wastewaters and Li and He [206] on optimizing the efficacy of a membrane bio- E_{tt}. Figure 7b provides information on the optimization and efficacy change in the process due to variation in the surface area of the developed carbon-resin electrode. The figure revealed that the optimum current flow through the wastewater was 10.5 A of 2.0×10^3 millilitres of the wastewater, which is equivalent to current volumetric of 5.25×10^{-3} A per ml and a current density of 0.795 A per cm^2, which is greater than 30 A per m^2 as minimum value stated in previous researches and studies such as Phalakornkule et al. [207], Acosta-Santoyo et al. [208] and Korbahti [200].

Figure 8a presents relationship between initial concentration of chloride ions in the saline wastewater and efficacy of the E_{tt} process utilising steepest descent technique. The figure establishes that there is a negative exponential relationship, which indicates that initial concentration of Cl^- decline, increases the efficacy of E_{tt} process. This efficacy can be attributed to higher concentration load of chloride available at a given time than other times and lower contact area and current at present. The figure revealed that at higher initial concentration of Cl^- in the saline wastewater, efficacy of the E_{tt} system declines greatly. Figure 8b provides information on the optimization and efficacy change in the process due to variation in the initial concentration of chloride ions in the wastewater. The figure revealed that the optimum initial concentration of Cl^- in the saline wastewater was 27.5 g/l. This behaviour of Cl^- reduction is described by the complex composition of the initial concentration of Cl^- in the saline wastewater and the low contribution of both direct and indirect electro-oxidation and electro-adsorption mechanisms [208].

Figure 9a presents relationship between flow rate of the wastewater and efficacy of the E_{tt} process utilising steepest descent technique. The figure establishes that there is an exponential relationship, which is positive indicating

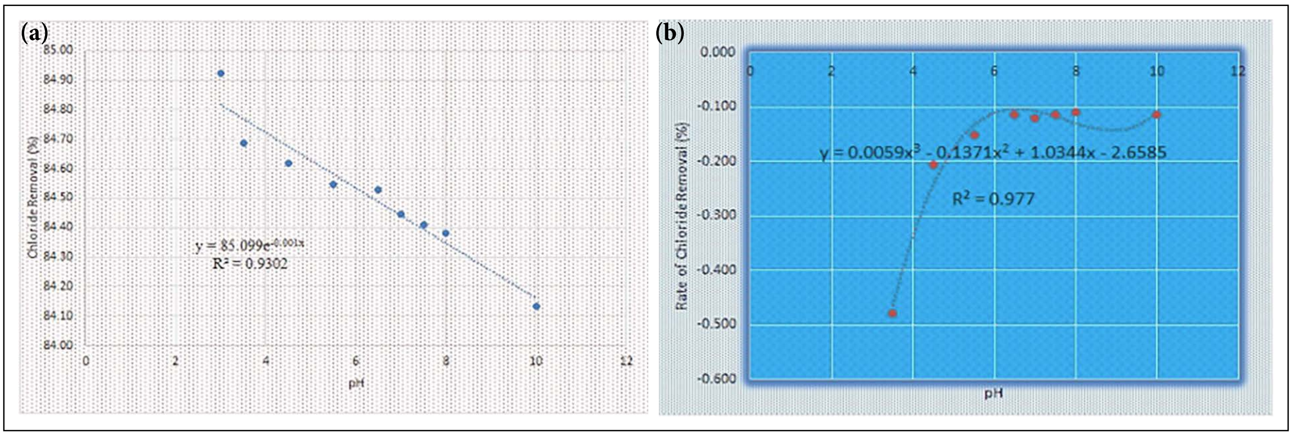

Figure 10. **(a)** Relationship between pH of the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the pH of the wastewater and performance of the electrochemical treatment process using steepest descent technique.

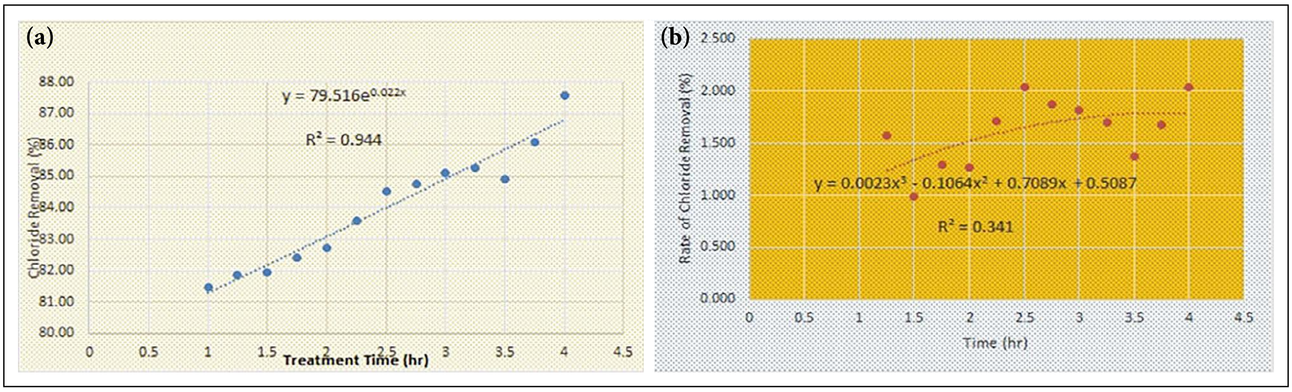

Figure 11. **(a)** Relationship between treatment time of the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the treatment time of the wastewater and performance of the electrochemical treatment process using steepest descent technique.

that flow rate of the wastewater increases the efficacy of E_{tt} process. The figure revealed that at higher flow rate of the wastewater, the efficacy of E_{tt} system improves greatly.

These results, finding and observation of optimum initial concentration is similar to 31000 mg/l based on Akindahunsi et al. [189]; 35.3779 g/l of chloride ion based on Thabit et al. [190]; 41.80 g/l based on Mehan-Martes and Mertel et al. [191] and 43.6995 g/l of chloride ions based on Lior and Kim [192]. These optimum concentrations of saline wastewater are functions of locations, nature of the process and other critical factors. In addition, the observation is similar to previous studies such as Alam et al.[35]; Korbahti [200]; Isaac et al.[209]; Garcia-Seura et al. [210]; Ensano et al. [211] and Meng et al. [212]. Figure 9b provides information on the optimization and efficacy change in the process due to variation in the flow rate of the wastewater. The figure revealed that the optimum flow rate of the wastewater was 1.89 l/hr of the wastewater. This behaviour of flow rate of the wastewater is explained by the complex flow rate of the wastewater, availability and accessibility of the initial concentration of Cl^- in the wastewater, mixing phenomenon and the contribution of both direct and indirect electro-oxidation, electrocoagulation and electro-adsorption mechanisms.

Figure 10a presents relationship between pH the wastewater and efficacy of the E_{tt} process utilising steepest descent technique. The figure establishes that there is a negatively expressed exponential relationship, which indicates that an increase in the pH declines the efficacy of E_{tt} process. The figure revealed that at higher pH of the wastewater, the efficacy of E_{tt} declines or decreases greatly. Figure 10b provides information on the optimization and efficacy change in the process due to variation in the pH of the wastewater. The figure revealed that the optimum pH of the saline wastewater was 6.7. Tulin and Serdar. [203] reported that higher pH of wastewater required low retention time of operation and lower pH value required high detention time to perform the efficacy. Figure 11a presents relationship between treatment time of the wastewater and efficacy of the electrochemical treatment process utilising steepest descent technique. The figure establishes that there is a positive exponential relationship, which indicates that treatment time of increases the efficacy of electrochemical treatment process. This observation agrees with literature and previous studies [203]. Figure 11b provides information on the optimization and efficacy change in the process due to variation in the treatment period of the wastewater. The figure revealed that the optimum treatment time of

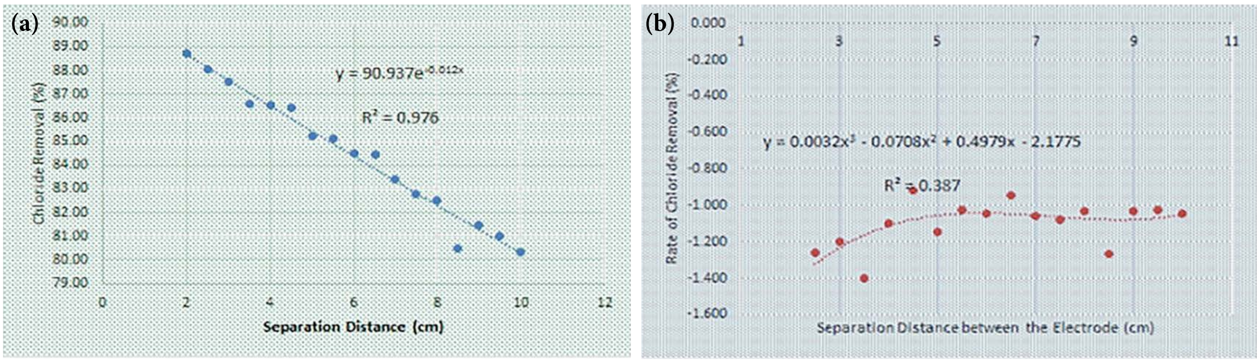

Figure 12. **(a)** Relationship between separation distance between the electrodes in the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the separation distance between the electrodes in the wastewater and performance of the electrochemical treatment process using steepest descent technique.

the wastewater was 2.75 hours. Tulin and Serdar [203] reported a treatment time of 300 minutes (5 hours) for container washing wastewater at pH of 3.0 and 120 minutes for the same wastewater at pH value of 5.0.

Figure 12a presents relationship between separation distance between the electrode in the wastewater and efficacy of the electrochemical treatment process utilising steepest descent technique. The figure establishes that there is a negatively response- exponential relationship, which indicates that separation distance between the electrode declines the efficacy of E_{tt} process. The figure revealed that at higher separation distance between the electrode in the wastewater, the efficacy of the system declines or decreases greatly. Figure 12b provides information on the optimization and efficacy change in the process due to variation in the separation distance between the electrode in the wastewater. The figure revealed that the optimum separation distance between the developed carbon-resin electrodes in the wastewater was 42 mm centre to centre of the aluminium cathode of 20 mm diameter and carbon-resin anode of 25 mm diameter. Phalakornkule et al. [207] obtained 8.0 mm as optimum distance between the electrodes, contact time of at least 5.0 minutes and current density of at least 30 A per m^2 for the treatment of reactive blue 140 utilising iron anode. Obijole et al. [213] obtained a mathematical representation that correlates resistance of an aqueous solution (Rc), the distance or separation space between the developed carbon-resin electrodes during electrochemical treatment of wastewater (X_c), and electrical conductivity of the aqueous solution (E_c) as follows:

$$R_c = \frac{R_c}{E_c} \ln\left(\frac{R_c + X_c}{R_c}\right) \quad (7)$$

Where; rc stands for the radius of the cylindrical electrode in the wastewater.

Although, optimization of E_{tt} salty is limited in literature, but the results were similar to optimization of electrochemical removal of cefazolin antibiotic from hospital wastewater [12], arsenate from aqueous solution by electro-coagulation [38], arsenic removal from groundwater samples utilising iron electrocoagulation treatment [39], optimization of arsenic removal from potable and drinking water by electrocoagulation treatment [49]; arsenic treatment utilising technology of electrocoagulation [58]; arsenite reduction from groundwater samples in a batch electrocoagulation treatment process [61] and optimization of the electrocoagulation treatment process for the reduction of lead from water samples [47]. It is like optimization of the adsorption of a textile dye onto nano-clay utilising a central composite design [15] and optimization of electrocoagulation treatment process for efficient reduction of ciprofloxacin antibiotic utilising iron electrode; kinetic and isotherm studies of adsorption [11]. In line with the efficacy, Feng et al. [202] reported that 4 m^3 per hour flow rate of E_{tt} system was established to reduce between 87% and 91% of Total-Phosphorous, between 74% and 96% of Total-Nitrogen, within 70 % and 94 % of NH4-N, between 88 % and 91 % of Total Organic Carbon and between 75 % and 87% of Chemical Oxygen Demand.

Similarly, for the same wastewater at a flow rate of 0.5 m^3 per hour, the system attained between 62 % and 90 % of Total-Phosphorous, within 83 % and 92 % of Total-Nitrogen, between 90 % and 100 % of NH4-N, and between 75 % and 83% of Total Organic Carbon, with between 80 % and 100 % of Chemical Oxygen Demand. Acosta-Santoyo et al. [207] documented that the efficiency of oxyfluorfen degradation by electro-oxidation treatment process increases with current density meanwhile the degradation of Total Organic Carbon follows an opposite trend. This behaviour or efficacy is explained by the complex composition of the initial sample and the contribution of both direct and indirect oxidation mechanisms. Alam et al. [35] documented that the effect of current density on efficacy of E_{tt} of wastewaters is considered a significant process constraint as it rules the coagulant dosage, which based or related to faradays first and second laws and hydrogen gas as an end product in the system. In addition, reduction of pollutants growths with the intensification of current density as it produces further flocs because of quicker anodic dissolution. Körbahti [200] reported that the optimized situations under specified cost driven constraints in the E_{tt} *of textile dye wastewater* were attained for the highest desirability at 6.7 mA cm^{-2}, 5.9 mA cm^{-2} and 5.4 mA cm^{-2}

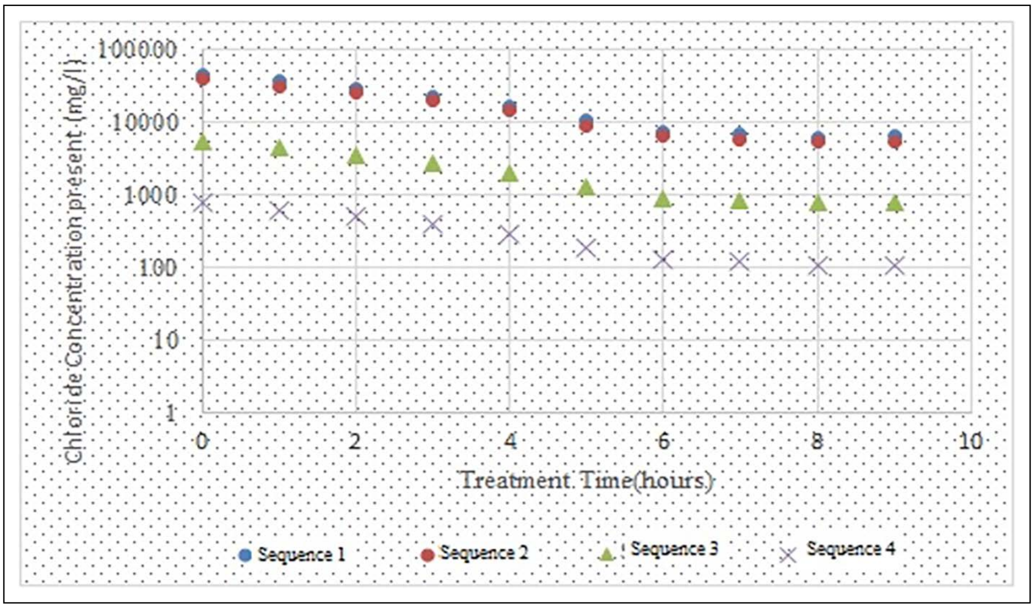

Figure 13. Treatment of typical raw saline wastewater utilising optimum values of operational factors.

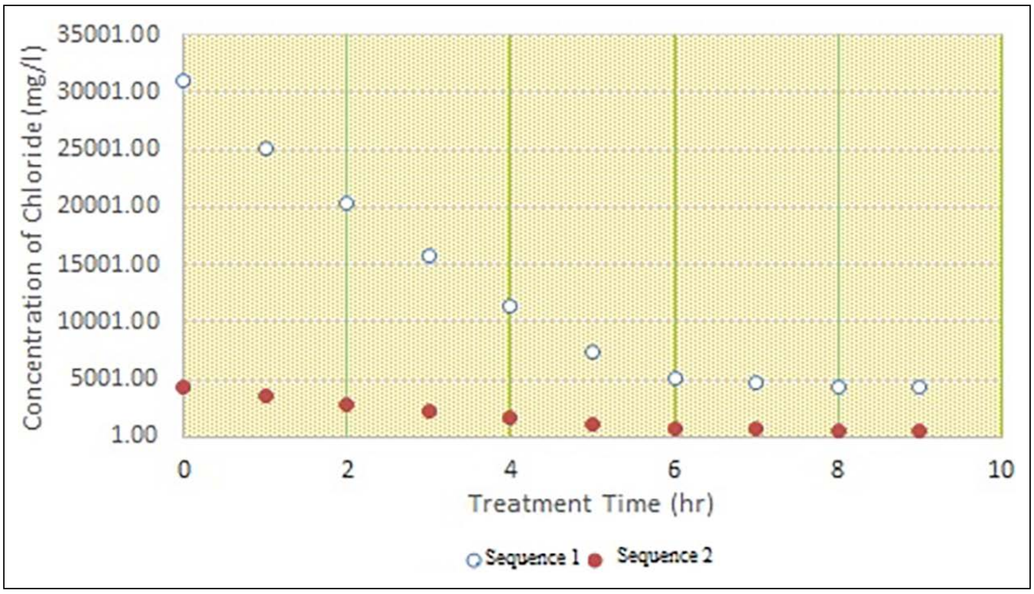

Figure 14. Simulation of typical raw saline wastewater utilising optimum values of operational factors based on Akindahunsi et al. [189].

current density and 3.1 gL^{-1}, 2.5 $g L^{-1}$ and 2.8 $g L^{-1}$ supporting NaCl concentration. Szpyrkowicz et al. [201] showed that selectivity of the removal of deferent pollutants was affected by current density which direct anodic oxidation as an additional process for the destruction of the selected pollutants. The efficacy of the electrochemical of typical raw saline wastewater of 45000 mg/l ranges from 19% after 1.0 hour treatment to 85.9 % after 9 hours of treatment. Figure 13 present the efficacy of the system in respect of treatment time. Simulation with a sequence batch reactor revealed that first sequence ended at 6345 mg/l of NaCl at 9 hours, second sequence ended at 5450 mg/l of NaCl at 9 hours of treatment, third sequence ended at 768.5 mg/l of NaCl and fourth sequence ended at 108.4 mg/l of NaCl. Salt and high concentrations of dissolved solids in water in the leachate of urban sanitary landfill sites, surface runoff, contaminated groundwater, and the wastewaters subsequent from recycling units of gas, mining operations and oil industries [214]. Figures 14-17 present the efficacy of the system in respect to simulated process. These figures revealed that at least second batch sequence treatments are required for seawater. Figure 14 revealed the system require at least two sequences or two treatment systems in series for the seawater (Atlantic ocean) from Nigeria, with 4371.00 mg/l and 616.31 mg/l for first and second sequences, respectively. Figure 15 revealed the system require at least two sequences or two treatment systems in series for the seawater from Qatar, with 4988.28 mg/l and 703.35 mg/l for first and second sequences, respectively. Figure 16 revealed the system require at least two sequences or two treatment systems in series for the seawater from Spain, with 5893.80 mg/l and 831.03 mg/l for first and second sequences, respectively. Figure 17 revealed the system require

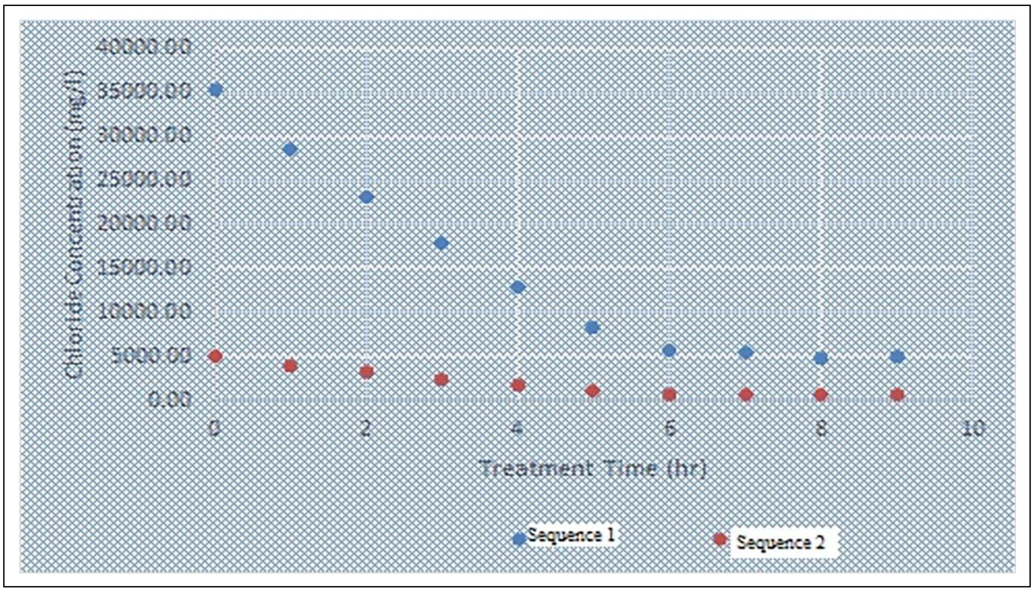

Figure 15. Simulation of typical raw saline wastewater utilising optimum values of operational factors based on Thabit et al. [190].

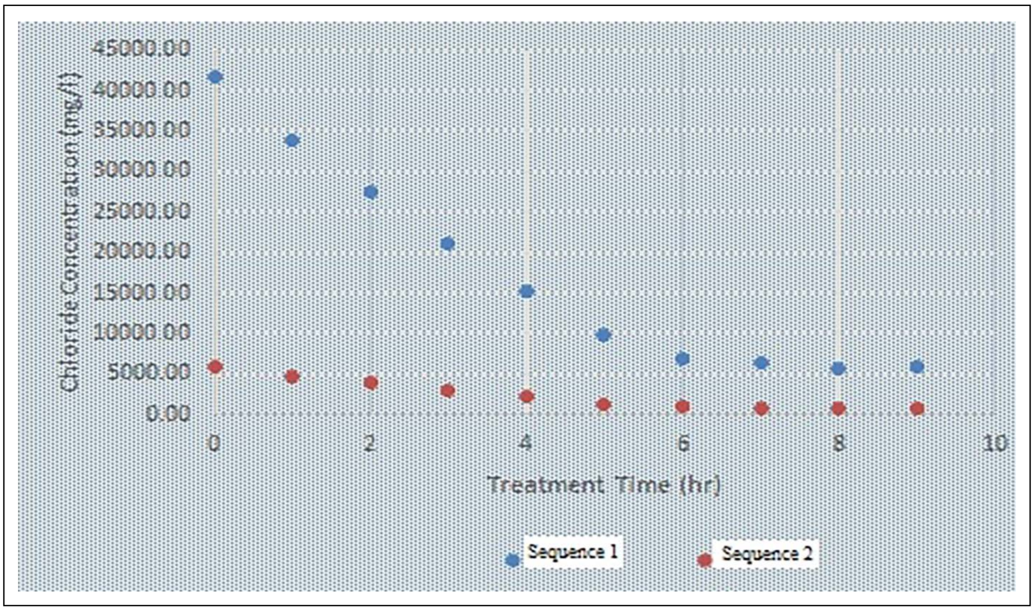

Figure 16. Simulation of typical raw saline wastewater utilising optimum values of operational factors based on Melian- Martel et al. [191].

at least two sequences or two treatment systems in series for the seawater, from United States of America with 6161.63 mg/l and 868.79 mg/l for first and second sequences, respectively. These sequence treatments are commonly experiences, which make electrochemical treatment applicable as an advance treatment or for polishing treated water [215–240]. Further information on electrochemical treatment toward perfecting water treated water can be established in literature such as Liu et al. [241], Xiao et al. [242]; Kakavandi and Ahmadi [243]; Jeddi et al. [244]; Zhang et al. [245]; Yun and Redzwan [246]; Jamal and Pugazhendi [247]; Shahata and Urase [248]; Lu et al. [249]; Ahmad et al. [250]; Eom et al. [251]; Huang et al [252]; Paredez et al. [253]; Jorfi et al. [254]; Maharaja et al. [255]; Formentini-Schmitt et al. [256]; Doltabadi et al. [257]; Ahmadi et al. [258] and Myint et al. [259].

CONCLUSION

It can be concluded based on the study that:

a. The electrochemical treatment with carbon-resin and aluminium electrodes is a direct electrolysis of saline or sea water, which reduce the concentration of chloride to an acceptable level with two or more sequence treatment,

b. The optimum values of these selected factors such as current, pH, treatment period and separation distance between the electrode (centre to centre of the electrode) were 10.5 A equivalent to 0.795 A cm^{-2}, 6.7, 2.75 hr and 42 mm (centre to centre of the developed carbon-resin electrodes equivalent to 19.5 mm space between the electrodes), respectively,

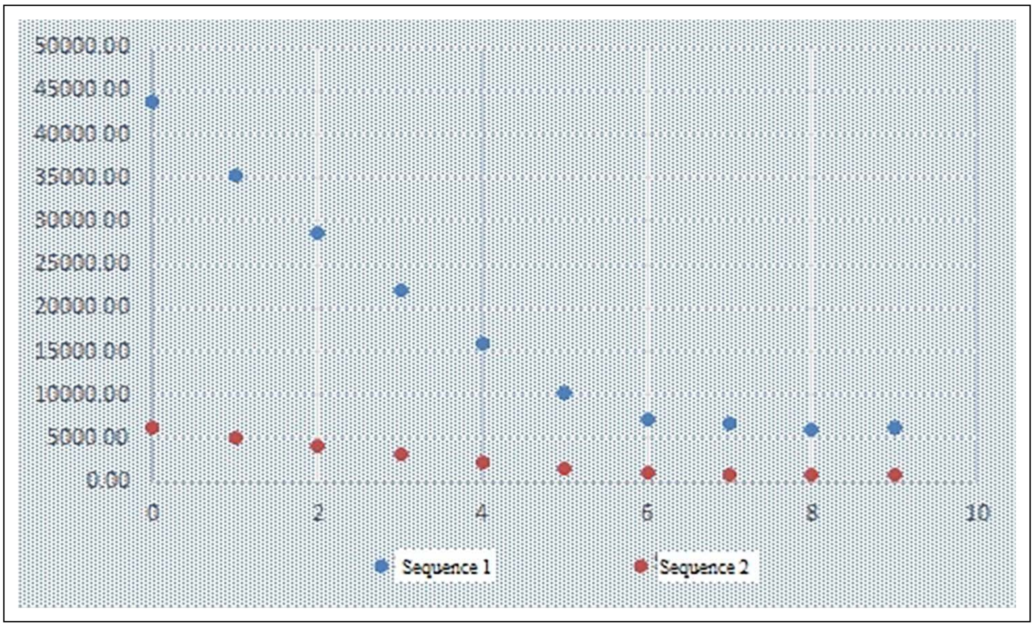

Figure 17. Simulation of typical raw saline wastewater utilising optimum values of operational factors based on Lior and Kim [192].

c. The process is limited to high concentration of salt such as chloride and dissolved solids, treated with graphite-resin and aluminium electrodes,

d. The challenges of the process include cathode passivation, periodic replacement of sacrificial anodes, the need for post-treatment due to high metal-ion concentrations, and high power-consumption costs in areas with limited access to electricity, optimization of operating conditions of electrochemical to achieve both low power consumption with adequate and high removal efficiency,

e. Future perspectives, utilisation of hypochlorite solutions by direct electrolysis of saline or sea water to decrease marine progress is significantly more suitable safer and appropriate exploring the techno-economic feasibility of electrochemical treatment with other treatment techniques,

f. The recommendations from this study include identification of energy pathways and energy application and management of hybrid electrochemical treatment systems; focus efforts on the effective removal of emerging pollutants from the environment utilising hybrid electrochemical treatment systems.

DATA AVAILABILITY STATEMENT

The authors confirm and establish that the data that supports and gives the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon sufficient request.

CONFLICT OF INTEREST

The authors of this article declared no potential or probable conflicts of interest with respect to the study, research, authorship, or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

The authors confirmed that Artificial Intelligence was not utilise in the computation, preparation, writing, editing or as a writing assistant in the development of the manuscript.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Review Article

Industrial symbiosis practices: A case study of Türkiye and Denmark

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ABSTRACT

Industrial symbiosis (IS) is a collaborative strategy where companies share services and physical resources. This promotes resource efficiency and reduces the environmental impact of industrial activities within a network. IS offers numerous benefits, including: (1) reduced greenhouse gas emissions through energy savings, process improvements, and fuel substitution, (2) lower energy costs, (3) less waste sent to landfills, (4) decreased use of virgin materials, (5) minimized transport and logistics costs, (6) lower environmental impact, (7) reduced pollution, (8) decreased water consumption, (9) reduced hazardous waste, (10) economic benefits from waste valorization (adding value), (11) easier compliance with environmental regulations. Consuming large amounts of resources (raw materials, water, electricity, etc.) and generating significant solid, liquid, and gaseous waste, industries in Türkiye and Denmark have increasingly adopted IS to optimize their systems and address sustainability concerns. Concerted efforts over the last decade have advanced IS practices, particularly in process sectors such as chemicals and manufacturing. This study aims to shed light on the current implementation of sustainable practices within the industrial landscapes of these two countries, focusing on key IS initiatives.

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INTRODUCTION

Driven by the use of, among others, conventional energy sources, our planet's health has gradually deteriorated. The modern world now faces many problems arising from past unsustainable practices. One major challenge is the energy crisis, where non-renewable energy sources will be depleted in the coming decades. This will lead to rising energy prices, disrupting the global market and making it difficult for low-income populations to afford it. These are just a few of the challenges facing the modern world [1]. The current situation was the reason for concluding the 2030 Agenda for Sustainable Development (2015) by United Nations (UN). The document presents the 17 Sustainable Development Goals (SDGs) (Fig. 1) and 169 targets to be met by 2030 by the Member States. Agenda is a plan that implements actions for people, planet, and prosperity. It also focuses on cooperation between countries and spreading peace efforts around the world. UN adds that by following the three pillars of sustainable development (social, economic, environmental), human life and the health of our planet will significantly improve [2]. Industrial symbiosis (IS), which focuses on the flows and networks among industrial organizations and aims to build synergistic solutions among resource users and contribute to responsible production and consumption, is an integral part of Sustainable Development Goal 12 under the heading "Responsible Production and Consumption" that promotes resource efficiency and sustainable industrial infrastructure [3].

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Figure 1. The SDGs [4].

IS is a collaborative and sustainable methodology that brings together multiple sectors and businesses to maximise resource use, minimise waste and improve overall economic and environmental outcomes. The idea emphasises the interconnectedness of industrial processes, the partnership here being biologically derived from the term 'symbiosis', creating a system where the by-products of one entity become useful inputs for another, reducing environmental impact and advancing circular economy ideas.

IS could be defined as a situation when the waste or residuals of one entity are transferred to another for utilization in production processes. It is achieved through collaboration between entities for mutual economic and environmental benefits through the exchange of by-products [5]. IS, which is a well-known process, attempts to minimize energy losses by establishing an interconnected network in which materials are constantly circulated. The primary goal is to reduce the negative environmental impact while limiting raw material extraction. It also reduces the growing need for landfill waste disposal. The key principle of IS (Fig. 2) is the physical exchange of materials, energy, and water between two or more companies, turning what is normally seen as waste into a resource.

Ehrenfeld and Gertler [6] have described the Kalundborg IS in Denmark as one of the most prominent cases. This case study illustrates how symbiotic relationships can lead to the effective use of resources and the elimination of waste by examining the growing interdependence between companies in the Kalundborg region. Around the world, efforts of a similar nature have been modeled after the Kalundborg IS.

Boons and Roome [7] look at the link between learning and sustainable development within the broader framework of sustainable development. Although not exclusively focused on IS, their research provides a conceptual structure for understanding the role of education in cultivating sustainable behavior—an idea essential for the implementation of IS projects.

Chertow's [8] research, which provides a thorough overview of IS and insights into its literature and taxonomy, is a seminal work on the subject. The study highlights the essential components of symbiotic relationships, emphasizing the sharing of resources and energy between industries to create partnerships that benefit all parties. The author emphasizes how IS can reduce resource depletion and environmental degradation, which can support sustainable growth.

Symeou and Rossos [9] conducted a thorough literature analysis to analyze the incorporation of IS into planning frameworks and to understand its formation in urban and regional planning. Their study highlights the importance of government support and strategic planning while shedding light on the opportunities and difficulties of integrating IS concepts into broader sustainability initiatives.

These references offer a comprehensive overview of IS, including theoretical foundations, real-world applications, and contributions to sustainable development.

Over the last few decades, the negative environmental impacts of increased urbanisation and industrialization, as well as the intensive use of land and natural resources, have led to a growing interest in the concepts of IS and energy efficiency

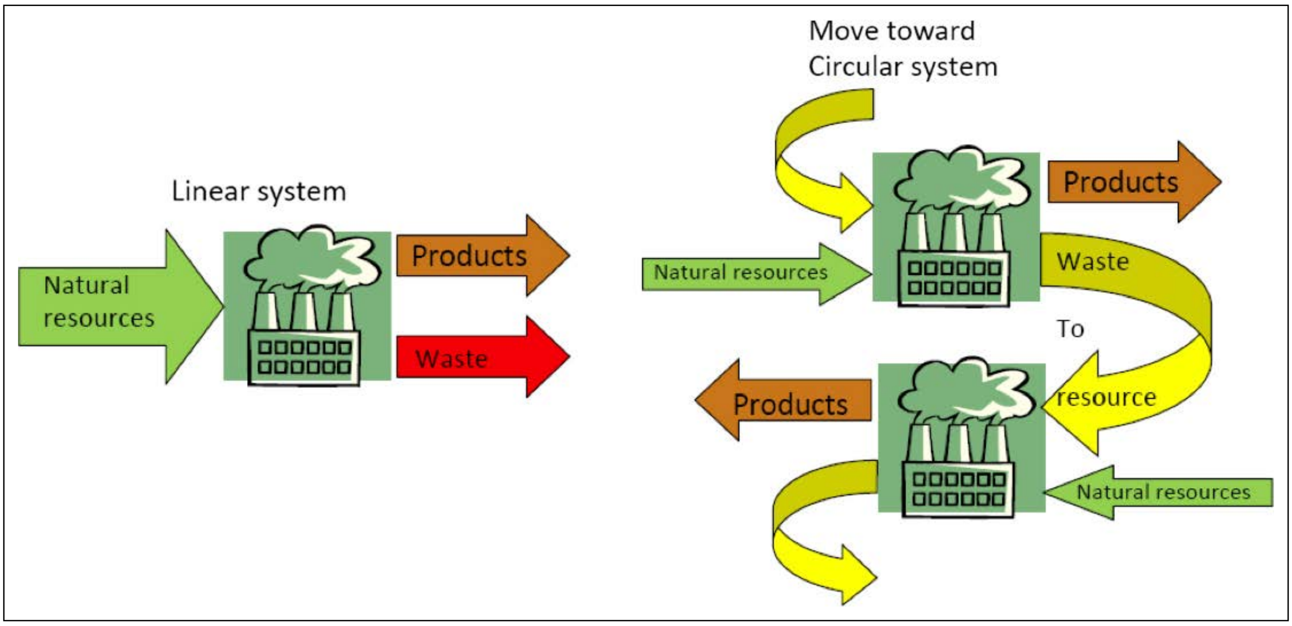

Figure 2. The scheme of IS [11].

and their potential in terms of environmental, economic, and social aspects. Energy-intensive industries are eager to introduce measures to reduce their energy and resource consumption. Smart waste management and efficient water recycling are important complementary measures to improve the efficiency and reduce the environmental impact of production processes. Although IS and energy efficiency case studies have increased over the past decades [10], this trend has only recently increased due to the attention and commitment to sustainability regarding energy consumption. high quality and increasing waste/by-product production [1].

IS is a circular economy strategy (Fig. 2) in which the waste and residues of one or more companies become the resource inputs of another company. It is often found in industrial parks that foster innovation and business collaboration. Municipalities can support the growth of IS, thereby contributing to the achievement of carbon reduction goals and reducing resource needs. At the same time, cities can attract businesses, create jobs, increase tax revenue, reduce waste management costs, and promote themselves through IS [5].

The joint sharing of resources such as energy, material by-products, waste, and water is the focus of IS [10]. Economic and environmental benefits have been central concepts of IS [12] since its inception. According to the widely accepted definition of IS, the economic, environmental, and social benefits arising from the exchange of materials and other shared resource flows between and within industries are numerous [13].

Ensuring prosperity in both developed and developing countries requires a comprehensive approach that integrates social, environmental, and economic development. This integration, exemplified by the concept of sustainable development, is increasingly prioritized, particularly in developed nations. IS is emerging as a crucial approach contributing to sustainable development, highlighting the social and economic impacts of environmental progress. IS not only addresses industry-related environmental issues but also yields economic and social benefits. Through fostering partnerships, IS promotes cooperation and teamwork, enhancing both environmental and economic performance. This collaborative approach, known as co-production, not only improves environmental sustainability but also enhances competitiveness. Thus, IS stands as one of the most effective practices in addressing contemporary issues such as "resource efficiency, conservation of natural resources, and environmental awareness" [14].

The eco-industrial park concept is a novel and sustainable approach to industrial growth, aiming to integrate social, economic, and environmental concerns. These parks are designed to encourage collaboration amongst sectors that share a site in order to reduce waste, improve resource efficiency, and decrease environmental impact. Important features of eco-industrial parks include the formation of circular material flows, shared infrastructure, and the exchange of materials and energy. The concept aligns with the principles of industrial ecology by highlighting the interconnectedness and interdependence of industrial systems.

IS, the subject of important studies in the literature, has been applied in various countries and sectors and social, economic and environmental contributions have been obtained. Studies on the development of IS have been carried out in specific sectors, such as chemicals [15] and energy-intensive production [16], and in various countries, such as Brazil [17], China [18] and Portugal [19]. Most of the IS practices around the world involve (i) reduction of water consumption, (ii) recovery and treatment of wastewater, (iii) reduction of waste and use of waste as raw material, and (iv) waste to energy and use of waste heat from various processes for heating purposes. Examples of important applications in related areas [20–24] are given in Table 1.

Table 1. Some important examples about IS activities

Country	Sector	IS activities	Reference
France	Biorefinery	Energy and material recovery from water, district heating	[20]
Italy	Tannery industries	Establishing shared facilities among similar firms, such as wastewater treatment, energy and material recovery, waste minimization, and biogas plants.	[21]
Mexico	Petrochemical	Major infrastructure (wastewater treatment and material recovery)	[22]
South Korea	Petrochemical, chemical, and metallurgical	Energy and material recovery from water and use of reclaimed water through shared reclamation plant	[23]
Tanzania	Farming, ethanol distillery, energy	Partnership for the production of raw materials from waste, material recovery, waste minimisation and service network sharing and optimisation	[24]

In addition to important examples from around the world, this study aims to compare two countries with different characteristics. These countries are Denmark, which is known for its IS applications, and Türkiye, which has a high potential. The choice of Denmark and Türkiye as focal points for IS in this manuscript stems from a nuanced consideration of various factors that promise a rich and comprehensive exploration. Denmark, known for its advanced sustainability practices and commitment to renewable energy, offers a compelling case study of IS in a highly developed and environmentally conscious context. On the other hand, Türkiye, with its burgeoning economy and diverse industrial landscape, provides a fascinating contrast and an opportunity to examine the applicability and adaptability of symbiotic practices in a dynamic and emerging market. The geographical and economic differences between Denmark and Türkiye provide a unique lens through which to analyze the impact of IS in regions with different challenges and opportunities. Furthermore, the different regulatory frameworks, environmental challenges and cultural contexts in these countries contribute to a holistic understanding of the complex interplay between industry, environment and policy. By selecting Denmark and Türkiye, this manuscript aims to provide insights that are not only locally relevant but also globally significant, contributing to the broader discourse on sustainable industrial practices and circular economies.

INDUSTRIAL SYMBIOSIS PRACTICES IN TÜRKİYE

Türkiye's industrial sectors are becoming increasingly aware of the value of IS in improving resource efficiency and sustainability. The nation has shown a growing interest in promoting symbiotic practices.

The development of eco-industrial parks, where different sectors co-locate to share resources, reduce waste, and reap benefits, is a notable project. The Turkish government has been exploring frameworks and regulations to promote the adoption of IS techniques, although these are not project specific.

An important project in Türkiye that aims to create synergies between sectors in the thrace region is the TR21 Thrace Region IS Project. The initiative aims to improve overall sustainability, minimise waste, and maximise resource utilisation by promoting IS. This initiative is expected to involve cooperation between regional companies, governmental organisations, and possibly even foreign partners.

Similarly, the Antalya Organized Industrial Zone IS and Eco-Efficiency Project focuses on promoting IS and eco-efficient practices within the Antalya region. The project strives to optimise resource utilisation, minimise waste, and improve the environmental performance of industries in the region.

Some of the main IS practices in Türkiye are presented in the subtitles of this section.

Çukurova Region

A feasibility study was carried out for biogas and energy production from corn, chicken, and cattle wastes in the Çukurova region. Waste characterization analyses and biochemical methane potential tests were carried out on the wastes collected from the region and the alternative mixtures of these wastes at different rates. It has been shown that, based on the scenario of establishing a facility with an installed capacity of 1 MW, approximately 5.500 tons of high-added-value organic fertilizer can be obtained annually, as well as approximately 9 million kilowatt-hours of energy from a total of 41.000 tons of agricultural and animal waste [25].

Sütaş Group

One of the most important IS practices in Türkiye is carried out by Sütaş. Animal and vegetable wastes are collected and converted into electrical energy at Enfaş's biogas facilities before being transferred to the grid and used in production facilities. The procedure does not end with the processing and utilization of this waste. Hot water and steam, which are wastes generated by energy plants during waste processing, are also evaluated and used in Sütaş factories. In addition to farm animal waste, Enfaş uses returned products, feed, and organic waste from factories in the production of electricity, hot water, and steam. Furthermore, solid, and liquid fermented products produced in biogas plants are reused as solid and liquid fermented fertilizers for agricultural use. There are three facilities (İzmir-Tire, Aksaray, and Bursa) where the IS project is implemented. Within the scope of the related project, it is stated that 584.205 tons of organic waste were disposed of, 1.8 million kWh of energy savings were achieved, and 98% of waste was recycled. One of the project's major accomplishments is that the energy obtained corresponds to 69% of Sütaş Group's electricity needs, 92% of dairy factory needs, and 21% of dairy factory thermal energy needs [26].

FISSAC Project

The project, in which Türkçimento and Ekodenge are among the partners, was supported by the European Union. Within the scope of the project completed in 2020, calcium sulfoaluminate cement (CSA) was produced using glass waste (Şişecam), ceramic waste (Çanakkale Seramik), and aluminium waste (BEFESA). The produced cement was used in road construction in Adana [27].

MAY & EVSU - Biyorem

The performance of the bioremediation product "Biyorem," which is obtained by the pilot-scale processing of lint waste generated during cottonseed production at the May-Agro production facility by EVSU, was studied. In this context, field trials and laboratory analyses were conducted within 8 months to determine the bioremediation and adsorption potential of the product, which is predicted to clean oil-contaminated soils by the bioremediation method and prevent oil spread by trapping oil in the soil, and successful results were obtained [25].

Ekinciler Inc. - Electric Arc Furnace

Within the scope of the project, it is planned to use the slag obtained in the Electric Arc Furnace (EAF) facilities, where 75% of the iron and steel production in the country is realized, as a by-product in highway construction. It is known that slag falls within the scope of waste in Türkiye and is generally stored. The excess waste volume brings with it space occupation, and environmental, and health problems. In the context of IS, the inclusion of this material in the reproduction cycle will add value to the national economy. Within the scope of the project, the possibilities of using the slag samples taken from Ekinciler Inc. in highway construction were examined across the field of the relevant standards. As a result of the experiments, it was determined that the material gave better results than most natural aggregates [28].

Other IS practices in Türkiye are as follows:

Yünsa creates a new eco-fabric collection by recycling the fabric waste generated during production.

Sütaş uses iron powder from a metalworking (laser cutting) project for H_2S removal in biogas production.

Pepsico uses certain types of processed food waste in the production of biogas together with the waste from chip production, optimizing the efficiency of biogas production.

Anadolu Efes studies obtaining value-added products by further conversion of malt pulp, which is a by-product of beer production.

Roteks Inc. evaluates treatment sludge from the denim washing process in the building materials industry.

Procter & Gamble Inc. conducts a feasibility study for obtaining absorbent material, cellulose, and plastic by recycling diaper waste from production.

Eti Krom Inc. evaluates olivine, which is a by-product from chromite enrichment activities, as a refractory raw material.

Eti Krom Inc. produces low-carbon ferrochrome by using fine-grained chromite ore from ore preparation and enrichment activities as a concentrate.

Bilecik Demir Çelik Inc. produces white fused alumina (WFA) as a secondary raw material from alumina-based refractory wastes from iron and steel production furnaces.

Ekinciler Demir Çelik Inc. produces secondary raw materials from dolomite refractory brick waste from iron and steel production furnaces [29].

INDUSTRIAL SYMBIOSIS PRACTICES IN DENMARK

Selected main IS practices in Denmark are presented below.

Baltic Industrial Symbiosis (BIS)

Since the projects and innovations in an IS are about company collaborations, an important role for the facilitator is to be the link between companies that can be a potential match for the symbiotic exchange [30]. The aim of the BIS project is to combine companies' efforts to use the waste of one partner as a resource for others. The project stipulates peer-to-peer exchange practices between IS managers. It develops new business and financial models [31].

Within the Baltic IS (BIS), which promoted IS and helped boost eco-innovation, the partners involved more than 150 enterprises and used a dialogue approach to acquire information regarding the companies' consumption and under-utilized and lost resources within the production process. IS can also benefit municipalities by attracting companies to locate in and/or remain within the municipality, ensuring jobs and tax revenues, drawing in further partners, creating a strong local brand, and perhaps also assisting in reducing waste treatment costs [5]. Denmark's companies, which are named Symbiosis Center Denmark, Kalundborg Municipality, Kalundborg Symbiosis, Næstved Municipality, and Roskilde University, are the partners of BIS.

Ressource City

The Ressource City is at the heart of the circular economy and the green transition in the Næstved metropolis. As a platform for innovation, knowledge and inspiration, the Ressource City contributes to the growth of local businesses by creating value and supporting local sustainable development. The Glass Cluster is a great example of the Ressource City's work and how a municipality can support sustainable business partnerships [30].

The Glass Cluster symbiosis, in the municipality of Næstved, Denmark, recycles 100.000 tons of glass a year and provides heat for 1.250 households. The recycled material makes up 95% of the glass for packaging, while the remaining dust is used to produce insulation. The municipality's circular economy department, "Ressource City," has embraced the cluster and communicated and shared the success story as part of the Næstved brand. Yet, ironically, glass waste from local households in Næstved is collected in such a way that it cannot be used in the Glass Cluster. This highlights a need for clean waste fractions [32, 33].

The Ressource City was responsible for branding the exchange of secondary glass as "the Glass Cluster" and has communicated the success story far and wide to inspire others to work with the circular economy. Næstved municipality and the Glass Cluster were selected as one of C40 and Realdania's "Cities 100": 100 cities with an innovative and ambitious approach to reducing climate footprints [5].

GreenLab Skive

A local goal for carbon neutrality and energy self-sufficiency by 2029 in Skive, central Jutland, and the vision of a transition to a "Green Energy Valley", called for actions out of the ordinary. With a supportive organizational structure, a willingness to take risks, the earmarking of funding, and creativity in solving legislative barriers, the municipality laid the seeds for and nurtured the growth of an innovative IS [34].

GreenLab Skive is an energy-focused green industrial park that has developed into an IS. As of 2020, nine waste, supply, and private companies are in GreenLab Skive, exchanging energy, excess heat, biomass, and non-recyclable plastic waste. Green-Lab Skive is planned to grow further and attract more energy-demanding companies to take part in the innovative energy symbiosis [5].

Kalundborg Symbiosis

Kalundborg Symbiosis is recognized as the first IS in the world and is considered a best practice example, attracting broad interest from multiple stakeholders [30]. The largest IS facility in Denmark is located in Kalundborg. It is both a city and a municipality, located about 100 km from the capital of Denmark, Copenhagen. The investment in Kalundborg is called the first complete implementation of IS. In this case, it consists of the exchange of goods between participants, which include private and public enterprises. Entities included in the symbiosis are characterized by a high variety of activities [35].

The main entities include, among others:

ARGO is a company responsible for the collection and subsequent processing of waste from the inhabitants of the municipality of Kalundborg. The company's priority is the reuse of a given waste and recycling, which allows for the recovery of raw materials. The final step is to extract thermal energy from the waste, which is converted into electricity.

Avista Green is a company dealing in the processing of waste oils from industrial plants and car workshops. The company has created a permanent loop for the oil by recycling it in a continuous cycle. Avista Green collects used oil and submits it to processes that will enable it to be reused.

Boehringer Ingelheim is a pharmaceutical company focused on improving human and animal health. The plant located in Kalendborg produces feed supplement products with a global reach, exporting its products all over the world.

Kalundborg Rafinery is the largest refinery in Denmark. Thanks to the cooperation between the entities of the symbiosis, the refinery benefits from convenient access to water and biogas. The company is characterized by the fact that residual sulfur from the desulfurization plant is converted into liquid and high-efficiency fertilizer. The result is the production of the cleanest fuel in the world, with a negligible sulfur content.

Saint-Gobain Gyproc is an entity producing gypsum boards made of natural gypsum and recycled gypsum. The company's activities focus on the broadly understood development of the production of recycled gypsum, contributing to the creation of a closed circuit for this material.

Kalundborg Bioenergy is a producer of biogas, from which hydrogen sulfide and carbon dioxide are then removed. The upgraded biogas is sent to participants (IS) and to external recipients throughout the country. The next activity is the recovery of sulfur from hydrogen sulfide, which is then used in fertilizers.

Kalundborg Utility is the main water supply and heat supplier for the residents and local businesses in Kalundborg. The company also deals with innovative wastewater treatment using ozone.

Novo Nordisk is a global manufacturer of pharmaceuticals that are very popular around the world. In Kalundborg, Novo Nordisk produces products for the treatment of severe obesity and diabetes, as well as several biopharmaceutical products.

Novozymes is a company highly associated with the microbiology market, and with enzymes that enable more efficient agriculture, energy savings in production, and washing at lower temperatures. The entity has a positive impact on the environment due to the production of substances that, e.g., allow the use of fewer chemicals while achieving the same result. In addition, the company is an example of the correct creation of a closed loop, benefiting from process steam and treated surface water from Lake Tissø, which is used directly to produce enzymes. The next stage is the processing of biomass obtained from the production of enzymes, which is converted into energy and fertilizers.

Remilk is a company that, thanks to the fermentation process, produces milk proteins. It is a replacement for traditional milk protein derived from animals. The innovative approach of the company allows the creation of any dairy product free from antibiotics, hormones, lactose, and cholesterol. Remilk's breakthrough technology enables the production of a cost-effective dairy alternative on a global scale with negligible environmental impact.

Unibio is a company that produces protein from methane, which is then used as an ingredient in animal feed. The technology used allows for the separation of protein production from agriculture or fishing, thus affecting the natural environment. In addition, the obtained biogas is taken from the entity, which is Kalundborg Bioenergy.

Ørsted is owner of the Asnæs Power Station in Kalundborg. It produces electricity, steam, and heat. Steam is supplied to Novozymes and Novo Nordisk. The power plant uses steam to produce electricity. The heat generated from this production is transferred to residents and businesses in the Kalundborg area. An important fact is the cooperation between Kalundborg Rafinery and Ørsted. The companies exchange the water produced as a by-product. On a large scale, this reduces the demand for water abstraction from the nearby Tissø lake.

Each of the listed exemplary participants cooperates with others, trying to pass on the goods they need. The goods exchanged between the participants include water, information, energy, and broadly understood material goods [36].

Every year, the IS saves the partners and the environment for:

- 4 million m^3 of groundwater by using surface water instead
- 586.000 tonnes of CO_2
- 62.000 tonnes of recycled residual materials

80% of the CO_2 emissions in the symbiosis have been reduced since 2015. The local energy supply is now CO_2-neutral [37].

IS in the municipality of Kalundborg is constantly developing, becoming a leader under the influence of the scale, quantity, and quality of implemented solutions. The project in Kalundborg is a global example of how IS should work [36].

Aalborg: IS North

Another example is the "IS North" project, which takes place in the north of Denmark. The cooperation is focused on the resources of the limestone lake, which is located near the city of Aalborg. IS has its origins in the 1970s, but a significant intensification took place after 2010, when cooperation between entities located in the north of Denmark allowed the effective use of limestone in many mutually beneficial stages of production. From year to year, the number of companies involved in the IS model increases, including both large and small local enterprises. There are more than 25 streams of resource exchange between participants. The concept of resources has no limits because it includes any material whose reuse brings about the desired effect. For some enterprises, a by-product may be a suitable raw material for another entity.

The IS North project demonstrates significant energy savings. Companies participating in this initiative save an average of 264 MWh each. This corresponds to the annual energy consumption of 8 households. On average, companies can avoid 800 tons of CO_2 emissions. This corresponds to the annual CO_2 emissions of 100 Danish people. A typical value for resource exchange symbiosis is between 30 and 50.000 DKK per year for a small company. The average value of such symbiosis is much higher, two SMEs can expect 1-2 million DKK per year in sustainable synergy [38].

The IS North project brings surprising results, and its main goal is constant development. Therefore, new businesses are encouraged to become participants from the very beginning and positively influence the world. As science advances, new flows of material exchange between existing market partners emerge that revolutionize the economic model of the time. The project introduced in northern Denmark fits perfectly into the climate goals of the 21st century. To achieve climate neutrality, it is necessary to change the strategy of economic development. This requires cooperation between companies and joining forces in the development of a circular economy [37].

Water Symbiosis

The increasing pressure on drinking water resources has led to a focus on replacing drinking water with lower quality secondary water in Denmark. Advanced treatment technologies are making it financially viable to upgrade this secondary water for specific purposes. This project investigates and optimizes the use of such treated secondary water in IS between companies [35].

Green District Heat

The Green District Heat project is developing a generic model for utilizing industrial waste heat as district heating in nearby communities, specifically oil refineries or villages associated with them. In the context of reducing fossil fuel use in the Sealand region, the project investigates the possibility of transferring excess heat from factories to the district heating network in a way that is both socio-economically and environmentally sustainable. A similar application has been implemented in the Kalundborg region, where the Statoil refinery, a partner in the Kalundborg Symbiosis, generates enough excess heat to cover 80% of Kalundborg's heat needs [35].

BENEFITS OF INDUSTRIAL SYMBIOSIS PRACTICES

The implementation of IS practices offers several benefits with social, environmental, and economic aspects. IS promotes a circular economy model by sharing resources, such as energy and raw materials, and recycling waste as inputs for other processes. This reduces the need for new resource extraction and minimises disposal costs. Chertow [8] and Ehrenfeld and Gertler [6] highlight the potential for cost-effective collaboration and increased competitiveness between industries involved in symbiotic relationships, which underlines this economic efficiency.

From an environmental point of view, IS is seen as a major contributor to sustainable development goals. It reduces their negative impact on the environment by encouraging the reuse of by-products and reducing the total amount of waste generated. The exchange of materials and energy between companies can reduce pollution, greenhouse gas emissions, and resource depletion. Gibbs and Deutz [39] highlight the possibility of reduced environmental impacts through symbiotic interactions when they discuss these environmental benefits in the context of industrial ecology and eco-industrial development.

IS techniques promote community involvement and cooperation, fostering social cohesion at a societal level. This collaborative strategy can build social cohesion, create jobs, and improve the general standard of living in areas surrounding industrial sites. Boons and Roome [7] emphasize the critical role of collaboration in achieving positive social outcomes in sustainable development.

This manuscript compares key IS applications developed in Denmark with similar practices used in Türkiye. Due to its status as a developed country with diverse infrastructure, Denmark has an advantage over Türkiye in implementing these applications. Additionally, Denmark excels in fostering regional partnerships for IS practices. Compared to Türkiye, Danish applications tend to be more collaborative and have more developed components. In similar practices in Türkiye, deficiencies are noticeable in terms of infrastructure and cooperation, particularly in areas like waste heat, wastewater reuse, and establishing industrial raw material exchange infrastructure between public and private sectors. However, Türkiye has great potential, due to its waste volume and geographical area. To promote IS in Türkiye, the first step is to develop new partnerships and spread awareness about IS nationwide. Water symbiosis and green district heating projects are also recommended for implementation in Türkiye, particularly in Organized Industrial Zones and surrounding areas. These projects hold promise for achieving social, economic, and environmental benefits.

Each of these countries attempts, in its own way, to mitigate the negative effects of industrial development and implement sustainable development practices. Nowadays, Denmark stands out for its advanced cooperative structure, technological infrastructure, and current practices. Denmark, which hosts leading sustainable development applications, is a model country, especially with its eco-park and socio-economic benefits. Meanwhile, Türkiye is improving its achievements in existing applications and realizing its potential through partnerships and investments throughout the country.

The application of IS techniques offers three key benefits: social well-being, environmental sustainability, and economic efficiency. A body of the manuscript underlines this point, highlighting the significant contribution of IS to promoting a more sustainable and circular industrial landscape.

CONCLUSION

IS is an environmental management approach within the framework of an industrial ecology. It is a key enabler of the circular economy, supporting the industry in the transition from inefficient and unsustainable production systems to profitable and environmentally friendly manufacturing concepts. Creating IS in an industrial park can be done by discovering IS, that is, seeing opportunities to change materials, energy, products or water. Potential flows of matter and energy can be constructed by seeing possibilities change depending on the raw materials used, waste or products.

The IS practices, which are becoming more preferred all over the world, will increasingly develop and will no longer be limited to the exchanges or flows of matter such as materials, energy, water, and by-products. In Europe, the inclusion of IS as an example of resource efficiency in Commission policy is helping to pave the way for new programs.

This study addresses different IS practices in two countries, Türkiye and Denmark. The main factors for choosing these two countries are as follows: (i) Denmark is one of the leading regions in the world for IS implementation. (ii) Danish IS studies are implemented regionally (Baltic region), suggesting a similar mission/vision might be possible for Türkiye due to its geopolitical position. (iii) Türkiye has high waste generation and recycling potential, with a significant amount of organic waste. (iv) Türkiye's growing population and developing industries create energy needs that IS could help address. (v) This study compares Denmark, with its world-leading Kalundborg case, to Türkiye's high IS potential. It examines the applicability of Danish practices to the Turkish context. By considering these elements, the study explores prominent IS practices in both countries and offers future suggestions, particularly for Türkiye, to evaluate its IS potential.

This study makes a noteworthy contribution to the existing literature by offering a comparative analysis of IS practices in two diverse contexts, Denmark and Türkiye. Comparing these countries provides a novel perspective on the adaptability and effectiveness of IS strategies,considering varying levels of economic development, industrial diversity, and environmental priorities. The findings are expected to provide valuable insights for policymakers, researchers, and industry practitioners. This will aid in the development of tailored IS approaches that consider local nuances. Additionally, the study contributes to the broader discourse on sustainable industrial practices and circular economies,offering a deeper understanding of how IS can be applied and optimized in different global settings.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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