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Research Article

Treatment of slaughterhouse industry wastewater with ultrafiltration membrane and evaluation with life cycle analysis

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ABSTRACT

Slaughterhouse wastewater is one of the most produced industrial wastewater in the world and has a high pollution potential, and this wastewater can cause a high level of polluting effect when it is given directly to river beds or sewage systems. Wastewater contains proteins, fats, carbohydrates in the treatment of blood, skin and feathers, which results in much higher biological oxygen demand (BOD) and chemical oxygen content (COD). The possibility of using ultrafiltration for slaughterhouse wastewater treatment was investigated. The results showed that ultrafiltration can be an efficient purification method. COD and BOD_5 removal efficiency is around 96% and 95%. In addition to these results, the Life Cycle Analysis (LCA) of the ultrafiltration system was also carried out. Accordingly, the effects of ultrafiltration system on human health, ecosystem quality, climate change and resources were calculated as 0,00000046 Disability-Adjusted Life Years (DALY), 0,134 PDFxm^2yr, 0,336 kg CO_2 eq and 6,937 MJ respectively. As a result of the study, it is thought that slaughterhouse wastewater can be used as irrigation water after passing through the ultrafiltration membrane due to the high content of N and P.

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INTRODUCTION

Global meat production has doubled in the last thirty years, and it is thought that this consumption will continue to increase rapidly with the increase in the income and quality of life of people in underdeveloped countries [1–3]. Slaughterhouse wastewater (SWW) is one of the most produced industrial wastewater worldwide. It is assumed that the European SWW industry produces 145 million m^3 of wastewater per year that must be treated for discharge into rivers or municipal wastewater networks. SWW industries use approximately 29% of the fresh water consumed by the agricultural sector worldwide [4]. In 2004, the United States Environmental Protection Agency (USEPA) listed SWW as one of the most harmful industrial wastes in the agriculture and food category. SWW is characterized by a complex mixture of mostly oil, protein and fiber [5]. These wastewaters cause a highly polluting effect when they are discharged into river beds or sewer systems without any treatment. Due to the high organic, nitrogen (N) and phosphorus (P)

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content of these wastewaters, they cause eutrophication in surface water and pollution of groundwater [6]. Wastewater from the SWW industry needs to be treated and stabilized before it is discharged into the soil to prevent environmental pollution, removing the contents such as blood, manure, hair, oil, feathers and bones [7].

Due to the rapid population growth of developed Asian countries such as Saudi Arabia, Japan and South Korea, the need for more and quality water has increased. Developed Asian countries such as Singapore, Japan, and South Korea have adopted large-scale Ultrafiltration membranes (UF) membrane water purification systems to partially fulfill their drinking water requirements and through distribution networks. UF have made their way into wastewater treatment methods quickly, thanks to their environmental friendliness and easy installation of advanced devices [8]. It has been reported that membrane technologies fulfill multiple sustainability criteria in terms of flexibility, adaptability, minimal footprint and environmental impacts [9, 10]. UF membrane systems have received a lot of notice in the water treatment industry as they can provide stable filtrate quality by removing colloids, particles and microorganisms. Compared to conventional treatment methods, UF membrane provides better quality purified water. Compared to conventional treatment methods, UF membrane provides better quality purified water. Removal of pathogens and particles can be achieved with a UF membrane, which significantly increases the biological safety of drinking water. Particles and macromolecules in the range of 0.001–0.1 μm are usually removed in these systems [11]. Dissolved salts and small molecules in water pass through the membrane. Substances removed include colloids, proteins, microbiological contaminants and large organic molecules. In UF membrane systems, molecules with molecular weight greater than 1000–100000 Da are removed. The application pressure in the membrane is in the range of 1–7 bar on average [12].

Life Cycle Analysis (LCA), in the simplest terms, is an innovative and holistic approach that aims to reduce the energy, waste and emissions that any product, system or service consumes during the process from the raw material and preliminary design stage to the recycling and disposal stage. LCA is a scientific and comparative analysis and evaluation process of the environmental effects of a product, system or service. LCA differs from traditional methods with the terms "cradle to grave" and "functional unit" [13]. There are four concepts in the concept of LCA, namely target and scope definition (ISO 14040), inventory analysis (ISO 14041), impact assessment (ISO 14042) and interpretation (ISO 14043), and these four concepts should be combined with others for the healthy execution and implementation of the LCA method [14]. In this study, the treatment performance of SWW with UF membrane was evaluated. In addition, the reuse potential of treated water was investigated according to current water quality standards. These treatment performance values were analyzed with LCA and their effects on the ecosystem were examined.

Table 1. Chemical analysis results

Parameter	Raw wastewater (mg/L)	UF membrane removal efficiency (%)
COD	4150	96
BOD_5	3120	95
TDS	2320	94

MATERIALS AND METHODS

The raw wastewater used in this study was taken from the integrated meat plant in Aksaray, which produces approximately 5 tons of wastewater per day. The effluent samples obtained were characterized based on the pollutant concentration. Samples were preserved by storing them in a cold room at 4°C and brought to room temperature only 2 hours before the start of the experiment. COD was performed using the closed reflux method (5220-D) and BOD_5 was determined according to the 5-day BOD test method (5210-B). The Chemical Oxygen Demand (COD) of the raw wastewater was measured as 4150 mg/L, and the Biological Oxygen Demand (BOD_5) was measured as 3120 mg/L.

Membrane System

Details of membrane system design the study have been summarized in earlier study [15]. UP150 (Microdyn-Nadir, Germany) was used in this study. The membrane assembly was operated under a pressure of 3 bar. The experimental setup of the membrane module consists of a nitrogen gas system for constant pressure filtration. The filtered water was weighed and collected using a personal computer to calculate the data flow. All experimental sets were repeated 2 times.

LCA System

In this study, SimaPro 8.2.3.0 package program and Ecoinvent 3 library in this program and IMPACT 2002+ method were used for LCA calculations. IMPACT 2002+ was developed by the Swiss Federal Institute of Technology in 2002 and was designed to link 14 intermediate categories with 4 damage categories. Damage categories, on the other hand, make it possible to qualitatively understand the damage of the product, system or service to human health and the environment.

RESULTS AND DISCUSSIONS

Most of the wastewater from the SWW is of organic origin and contains high amounts of COD and BOD_5. The results in Table 1 reveal that there is significant removal of certain pollution indices (ie BOD_5, COD) after ultrafiltration of SWW. BOD_5, COD, TDS (Total Dissolved Matter) removal was 94%, 96% and 94%, respectively. In the microfiltration membrane, the removal of BOD_5, COD and TDS is 66%, 64% and 71%, respectively.

SWW cause pollution of water resources and emerge as a large pollutant load in the treatment plant. Bohdziewicz and Sroka (2005) analyzed SWW with RO membrane and showed a removal efficiency of 85.8%, 50.0%, 97.5% and 90.0% for COD, BOD_5, Total Phosphorus (TP) and TN, respectively [16]. Gürel and Büyükgüngör (2011) investigated the performance of membrane bioreactors (MBRs) for the treatment of SWW. It achieved 44%, 65%, 96% and 97% removals for Total Kjeldahl Nitrogen (TKN), TP, Total Organic Carbon (TOC) and COD, respectively [17]. Although organic matter was successfully removed, a high nitrate concentration remained in the treated wastewater. Also, membrane processes may face major fouling problems when processing high concentration feed streams such as the abattoir industry, which can greatly limit the rate of permeability across membranes due to the formation of thick biofouling layers on thick surfaces [18, 19].

Flux Graphs of Membranes

Membrane fouling is stated as the main disadvantage of membrane technology in the face of widespread application. Contamination reduces the permeability because of the deposition of colloids, particles, macromolecules and salts on the surface of the membranes, thus reducing the flux, shortening the membrane life and increasing the cost due to frequent chemical and physical cleaning. Operating at higher membrane flows results in increased system costs. On the other hand, higher flux treatment can increase surface contamination by increasing the convective force towards the membrane, since flux is also directly related to the driving force and the total hydraulic resistance offered by the membrane. Flux graph of UF membrane was given in Figure 1.

When Figure 1 was examined, it was observed that the flux in UF membrane decreased over time.

LCA Results

In this study, the analysis of the environmental effects of the system was completed by performing the LCA analysis of the parts of the UF membrane system. Table 2 presents the damage category values obtained as a result of the LCA analysis of the ultrafiltration membrane system.

DALY is defined as the healthy life span lost as a result of various processes [20]. In DALY calculations, each individual has a healthy life span, which is assumed to be in his hands at birth. This period may decrease over time due to various factors. DALY is an expression of this loss of healthy life expectancy [20]. PDF x m^2 x yr unit is an expression of the species that are expected to disappear in 1 m^2 of soil over a year. While the Kg CO_2 eq value is a unit in which

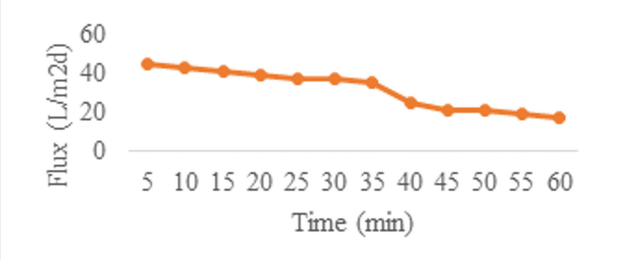

Figure 1. Flux graph of UF Membrane.

Table 2. LCA analysis results

Damage category	Value	Unit
Human health	0,00000046	DALY
Ecosystem quality	0,134	PDF x m^2 x yr
Climate change	0,336	kg CO_2 eq
Resources	6,937	MJ

the climate change effects of various gases are measured in terms of CO_2, the MJ unit is the expression of the energy spent while extracting or processing resources [21].

At these values, it seems that the ultrafiltration membrane system steals 0.00000046 years from the healthy life of a person. The same system causes the extinction of a total of 0.134 species in one m^2 of soil in a year and produces 0.336 kg of CO_2 equivalent greenhouse gas. The total energy spent for the creation of the membrane system, including the extraction and processing of raw materials, was calculated as 6,937 MJ.

In addition, the production of the ultrafiltration membrane system releases 320.097 g of CO_2, 1.16 g of methane (CH_4) and 1.44 g of sulfur dioxide (SO_2) into the air. The same system deposits various types of petroleum-derived products and 12.76 g of calcium waste onto the land. Similarly, 13.62 g silicon and 7.69 g Sulphate (SO_4^{2-}) lead the way in wastes to water. These values belong to the waste products that are released the most, and in fact, much more waste products are released into the environment. The total effects of all these wastes and emissions are already presented in Table 2.

CONCLUSIONS

Agricultural water is defined as water used to grow fresh produce and sustain livestock. Due to the effects of urbanization, industrialization and climate change, there will be more competition among agricultural water resources. For these reasons, countries have started to use pre-treated waste water as irrigation water in agriculture. Wastewater contains rich nutrient material and fertilizer consumption can be less than 50% when this wastewater is applied to the soil after a pre-treatment. SWW contain a high percentage of nutrients. With this study, it is thought that SWW can be used as irrigation water after passing through ultrafiltration membrane, since it contains high amounts of N and P. In addition to the environmental benefits of SWW, the environmental damage caused by the processing of these waters was also examined, and the product life cycle was completed and a full environmental performance review was carried out. The LCA technique can be used to integrate environmental considerations holistically into the water recycling technology selection. Accordingly, while the environmental damage of membrane systems occurs in very small amounts, it is estimated that the benefits of the treated wastewater will be much more than the damage to the environment.

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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.

ETHICS

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

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Research Article

The effect of sustainable product design on corporate sustainability: The example of manufacturing enterprises in Türkiye

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ABSTRACT

Companies must meet the requirements and expectations of their customers to ensure their existence. In this sense, the main goal of this study is to show the impact of sustainable product design on corporate sustainability. The universe of the study consists of business managers who work in the metal products and machinery industry. They operate in Şanlıurfa province, which is located in the south-eastern region of Türkiye and is the second-largest city in the region and is an industrial city. We used random sampling method in the study. We collected data from the participants by meeting face to face with the help of the questionnaire we created. We analysed the collected data by applying quantitative research methods and statistical analysis techniques. We found that there is a positive and significant relationship between sustainable product design and the sub-dimensions of corporate sustainability. We also reported that sustainable product design has an impact of approximately 16% on corporate sustainability. In 2022, we encountered some difficulties while collecting data due to the effects of the Covid-19 outbreak. It is prepared for that the findings gained in this investigation will contribute to the literature by shedding light on studies planned for the future. In addition, the study was limited to correlation and simple regression analyses. It is recommended that other methods of analysis be used in future studies.

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INTRODUCTION

To increase sustainability, companies strive to have a structure with a strong strategy and planning method that complies with current and future policies and actions related to environmental regulations. Scientists and entrepreneurs are constantly striving to reduce global warming and resource depletion. In the design stage, which is one of the most significant stages to make sure product sustainability, the environmental impact of the product should be minimized [1]. Companies in the position of industrial consumers reinforce environmental concerns with their sustainability

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goals. Making sustainability environmentally friendly in the design phase can help create a livable world [2]. Management policies for sustainability goals have played an important role in raising awareness through various programs and designs [3]. In recent years, middle-income consumers are known to be more sensitive to environmental issues. This is reflected in various studies. For example, [4] found that consumers are choosing to purchase environmentally friendly products, but among the 17 countries studied, Indian consumers have the highest percentage of respondents who are skeptical about sustainable products. In today's world, where consumer desire to buy eco-friendly products is increasing, industrial companies need to develop their sustainable policies in this direction. The need for sustainable product design has been studied by many researchers, especially to reduce the carbon footprint. Sustainable design and planning play an important role in reducing energy costs, reducing greenhouse gas emissions, and controlling waste and pollution. In the light of all this information, the main objective of this study is to identify companies' thoughts on sustainable product design. For this purpose, the province of Şanlıurfa, which is located in the southeast of Türkiye and is one of the most important industrial cities in the region, constitutes the universe of the study. It is assumed that the results of applied research will contribute to the literature. Moreover, it is assumed that conducting such a study in Şanlıurfa for the first time will provide direction for various studies to be conducted on this topic in the future.

CONCEPTUAL FRAMEWORK

Sustainable Product Design

The concept of sustainable product design refers to the development of the product by taking into account the economic, social, and environmental functions during the design of the product [5]. Product performance: durability, reliability, the purchase should be considered not only in terms of aesthetics but also in terms of criteria such as global warming, reduction of energy consumption and reuse, recycling, and remanufacturing [6, 7]. A sustainable product requires solutions that meet both functional and environmental requirements to achieve operational, economic, and social goals [8, 9].

Explain the concept of sustainable product design in one of the studies [10]. Corresponding to them, substantial aspects should be picked up into detail at the construction stage. In addition, the terms "design for the environment, eco-design, eco-efficient design, environmentally friendly production, green design, and life cycle design" are explained in the corresponding study. In a scientific research, sustainable product design is examined in three sub-dimensions. These; classified as environmental, social and economic dimensions. For companies to have sustainable products, these three dimensions should be considered throughout the life cycle of the products.

Managers need accurate information and product life cycle data to realize the design of a sustainable product. Life cycle assessment tools are costly and time-consuming [11]. It will be difficult to use this method at an early stage of design when detailed information about the final product is not available. Therefore, it is difficult to assess the environmental impact of the design phase of a product, a particular material, or a production process [12]. Assessing the environmental impact of products requires knowledge of material properties, product form, size, and manufacturing processes. However, these data are difficult to obtain in the conceptual design process when there is no reference [6]. The current research suggests that products are limited to considering the general functional characteristics of products rather than the detailed design parameters because it is difficult to access detailed information in the early design stage [13]. Sustainable design is an approach that encourages companies to minimize their environmental impact through product design while increasing their market advantage and innovation [10].

Corporate Sustainability

The concept of sustainability has been defined as "meeting the needs of a business's direct and indirect stakeholders (such as shareholders, employees, customers, pressure groups, communities, etc.) without compromising its ability to meet the needs of future stakeholders". Businesses carry out environmental, social and economic activities to be sustainable [14]. The fact that wastes become unmanageable and natural resources are consumed or damaged has revealed the concept of sustainability within businesses [15]. The concept of corporate sustainability has become something that needs to be worked on for organizations today and its existence is not even considered. However, the mentioned sustainability phenomenon is more about strategic management than how conflicting logics can coexist [16]. In its most general form, corporate sustainability refers to the capacity of businesses to sustain any situation or process for a certain period of time [17]. Sustainability-oriented strategies in businesses take into account all possible environmental, social and economic factors that affect stakeholders and sustainable development. Strategies focused on corporate sustainability, businesses for the environment; It covers preferences that aim to create long-term value and competitive advantage by considering ecological, social and economic factors [18].

Environmental Sustainability

The concept of environmental sustainability was first used by the World Bank. The term "environmentally responsible development" was used [19]. Next, the notion became current as "environmentally sustainable development" [20]. The notion of environmental sustainability is today used. For example, P. Sutton, Environmental Sustainability Commissioner for the Australian state of Victoria, defined environmental sustainability as "the ability to maintain valued qualities of the physical environment" [21]. The OECD Environmental Strategy for the First Decade of the 21st Century has contributed importantly to the concept of environmental sustainability [22]. These are first, reconstruction (renewable resources are used and their use should not exceed long-term natural reclamation rates). Second, substitutability (non-renewable resources are used efficiently and their use is replaced by renewable resources or other types of capital). By taking third, assimilation (the release of hazardous or polluting substances into the environment does not exceed the absorption capacity). Finally, it is possible to explain it as removing the barriers to recycling.

Ecological sustainability is an approach based on the notion of ecosystem services. These are both renewable and non-renewable resources and the ability to absorb wastes that benefit people and thus enhance their well-being. In order to enjoy and use these services for centuries, humanity must learn to live within the limits of the biophysical environment. Unlike the economic or social spheres, environmental sustainability implies open to the development and application of goals that are hard tied to the biophysical properties of the system. The borders of the ecosystem serve as a fixed series of highly special pressures at local and universal scales [23].

Economic Sustainability

Economic sustainability is more adopted by many firms on an international scale. It means that companies should consider the economic, environmental, and social effects of their activities [24]. The dimension of economically sustainable consumption raises another question about whether a product should be purchased. To some extent, consumption benefits the economy and consumer welfare. [25]. However, it has been shown that purely materialistically motivated consumption does not contribute to personal happiness [26]. Moreover, lowering consumption levels can bring benefits to businesses, society, and the environment that are detrimental to consumers' well-being in some situation [27]. Lembet, explained the concept of economic responsibility in his scientific study as "being profitable for shareholders, creating good employment opportunities for employees, producing quality products for customers" [28]. In another empirical study, it was mentioned that economic sustainability is most emphasized to incorporate sustainability and is the focus in achieving these types of sustainability [29].

Cultural Sustainability

Innovative sustainability solutions that benefit the environment, society, and businesses depend on the willingness of leaders to develop a "culture of sustainability" within their companies. Research has shown that an organization's culture operates at multiple levels, and developing and sustaining a culture of sustainability requires leaders to address each of these levels. The first level consists of visible artifacts and behaviors. These are the tangible and specific parts of the system that can be observed by those who are not part of the system. The second stage of culture includes the values that the system embraces. These are plainly set forth values and methods of treatment that show how the organization chooses to present itself privately and externally. The final stage of managerial culture. It consists of shared basic assumptions that guide the behavior of organizational members. These assumptions are often implicit and operate at an unconscious level, but are thoroughly embedded and easily integrated into the life of the organization [3].

The complex nature of corporate culture presents managers with unique challenges as they seek to create awareness among their employees that sustainability can not only reduce the company's impact on the natural environment but also significantly impact the company's long-term health and success. Research has shown that changing a culture is an extensive undertaking and that managers must use multiple tools to change the decision-making framework in which managers and employees evaluate and ultimately generate solutions to the challenges facing the organization [30]. Despite the complexity and time involved, cultures can be changed through the diligent efforts of the organization's leadership team [3].

Social Sustainability

In now's earth, firms are progressively seeking to gain a competitive advantage by incorporating sustainability into their business strategies. Sustainability discourse usually focuses on triple bottom line standards with targets for economic, social, and environmental purposes [31]. Companies focus on building organizational resources and capabilities in ways that are difficult to imitate and then building the foundations for a lasting, sustainable competitive advantage. In theory, its application is very intuitive as it shares certain terms with other common sustainability studies, such as "resources" and "sustainable" [32]. Social sustainability is directly related to gaining a place in the middle of society.

The means of social sustainability; first, using social sustainability as a source forces industry officers to change from a short-term to a longer-term context. Second, a multidimensional view of social sustainability allows managers to improve corporate social sustainability. It shows that employees, customers, and other corporate stakeholders play a significant role in effectively improving social sustainability. So, it becomes the possible to reduce the perception of the lack of benefits of social sustainability [33].

Managerial Sustainability

Sustainable management is the integration of management and environmental management principles and their development in a seamless relationship between environ-

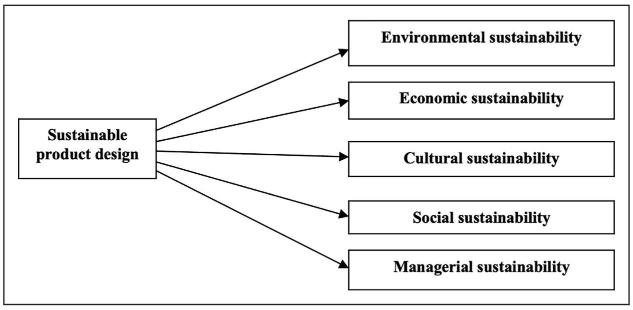

Figure 1. Conceptual model of the study. Source: Authors' Construction.

ment and management. Sustainable management is not a pure structure, because it requires some components intertwined with environmental and management processes [34]. Sustainable management requires the internal development of environmental and social measures and external contribution to sustainability in society and economy [35]. Sustainability management tools enable managers to operationalize sustainability-oriented strategies and coordinate activities within a company. He points out that companies pursuing corporate sustainability need practical decision-making tools to facilitate the design and selection of sustainable products, processes, and programs. In addition, such management tools can be useful for the corporate change and learning process [36]. In this study, we showed our research model, which we developed in accordance with the literature, in Figure 1.

METHODOLOGY

Within the scope of the study, sustainable product design was used as an independent variable. Dependent variables consist of 5 variables. These are respectively; environmental sustainability, cultural sustainability, social sustainability, economic sustainability, and managerial sustainability. The study is based on the quantitative research method. To collect data, a questionnaire consisting of two parts, based on the original scale and covering demographic information, was created. Before collecting data, on 9 December 2021, Adıyaman University Social and Human Sciences Ethics Committee was applied and permission was requested. By its decision dated March 2, 2022, and numbered 222, the relevant unit allowed the collection of information using a questionnaire. First of all, the validity and reliability of the scale were tested for the collected data.

H1: Sustainable product design has a positive and significant impact on the environmental sustainability of the company.

H2: Sustainable product design has a positive and significant impact on the cultural sustainability of the company.

Table 1. Distribution of businesses by industry

Business line	Frequency distribution (%)
Metal kitchen	71
Communication machines	2
Electrical machines	6.3
Vehicle machinery	3
Elevator machines	10
Car repair	3
Other machines	4.7

H3: Sustainable product design has a positive and significant impact on the social sustainability of the company.

H4: Sustainable product design has a positive and significant impact on the economic sustainability of the company.

H5: Sustainable product design has a positive and significant impact on the business sustainability of the company.

Population and Sample of the Research

In the organized industrial zone of Şanlıurfa, 95 firms in the metal goods and machinery industry work. With a share of 11% in the amount industry of Şanlıurfa, it ranks third after the metalware and machinery, ceramics, glass, and non-metalware industries. The managers of 90 of the 95 companies in the metalware and machinery industry in Şanlıurfa were examined using a questionnaire.

Scales

The scale we used in this study was taken from a previously validated and reliable study. In this line, the managerial sustainability scale established by [37] was utilized to measure managerial sustainability. The scale consists of 39 items and five sub-dimensions. We used 5-point Likert type in the original scale. We asked the participants to mark the most appropriate option among the options "1=I strongly disagree, 5=I strongly agree". In the study, sustainable product design, i.e., expressions related to the independent variable, was adopted by [38] from their study.

Descriptive Analysis

There are two analyses in this part of the study. These consist of the distribution of companies by business sector and the demographic characteristics of the participants. We have shown the results for descriptive statistics in Table 1 and Table 2.

As seen in Table 1, we found that the highest participation was in the "Metal Kitchen" section with 71%.

We have shown the information on the demographic characteristics of the participants in Table 2. When examining Table 2, the highest number of participants

Table 2. Demographic information

	Frequency distribution (%)
Gender	
Male	73
Female	23
Age	
≤25	12
26–35	28
36–40	19
41–45	20
≥46	21
Education	
Primary education	15
High school	24
Associate degree	23
Graduation	25
Past graduate	13
Duty period	
≤5	13
6–10	20
11–15	24
16–20	23
≥21	20
Status	
Business owner	12
Business partner	20
General director	27
Departmental manager	23
Other	18
Level of Income	
≤10. 000 TL	12
10001–15000 TL	20
1501–20000 TL	19
20001–25000 TL	23
≥25001	26

consists of men, the highest number of participants is in the age group "26-35", the educational level consists of participants at the highest level "undergraduate", when examining the working hours, workers between "11-15" years have the highest weight. When the professional position is measured, we have determined that the highest participation includes the "General Manager" position and eventually, when we look at the income level, the highest participation belongs to the income group of "≥25.001 TL".

FINDINGS

In this part of the research, we have had the results of the analysis we have made regarding the factor reliability analysis. Then, we performed correlation analysis to determine the relationship between the variables we included in the research model. We included the findings of multiple regression analyzes to test the validity of the hypotheses.

Factor and Reliability Analysis

We applied factor analysis to determine how many dimensions the questionnaire items used in the research were and what their factor loads were. For factor analysis, we used the principal component analysis method and varimax rotation method. From the data obtained as a result of factor analysis, we noticed that the scale has a 6-dimensional structure.

As a result of the analysis we have made, we have revealed that the scale used consists of 6 dimensions as in the original scale. Factor loading values of sustainable product design; Values ranging from 0.602 to 0.865 and factor loads of environmental sustainability; We found that it took values ranging from 0.678 to 0.926. In addition, the factor loads of cultural sustainability; It has values between 0.681 and 0.911, and the factor load values of economic sustainability; We found that it took values between 0.679 and 0.915. Factor loads of social sustainability; Factor loads of corporate sustainability and values between 0.598 and 0.954; We found values varying between 0.596 and 0.965.

We noticed that the value we obtained as a result of factor analysis in terms of model factor loads varied between 0.596 and 0.965. Also, the percentages of variance of the factor loadings were determined: Values between 58% and 68%. The fact that the variances of the factor loadings are above 50% indicates that the validity of the analysis is quite high [39].

We used Cronbach's alpha internal reliability coefficients to measure the reliability of the research model. As a result of the analysis of the data we obtained, we noticed that the Cronbach alpha coefficients were greater than 0.7. We found that this result is compatible with the literature [40]. We have shown the factor analysis results of the study in detail in Table 3.

Correlation Analysis

Correlation analysis was performed to test the presence of the relationship between dependent and independent variables in the research model.

When Table 4 on sustainable product design is examined, there is a low and significant relationship between environmental sustainability (r=0.234), a positive, low, and significant relationship between cultural sustainability (r=0.223), and a positive relationship between economic sustainability (r=0.42). We revealed the existence of a significant and

Table 3. Factor and reliability analysis results of variables

Variables	Statement	Factor loading	Varicance %	Cronbach's Alpha
Sustainable product design	1	0.865	63.652	0.821
	2	0.775		
	3	0.844		
	4	0.621		
	5	0.602		
Environmental sustainability	1	0.865	62.520	0.860
	2	0.678		
	3	0.921		
	4	0.796		
	5	0.768		
	6	0.926		
Cultural sustainability	1	0.713	58.980	0.768
	2	0.745		
	3	0.865		
	4	0.681		
	5	0.911		
Economic sustainability	1	0.813	63.942	0.742
	2	0.796		
	3	0.679		
	4	0.915		
Social sustainability	1	0.598	58.624	0.786
	2	0.678		
	3	0.741		
	4	0.753		
	5	0.852		
	6	0.954		
	7	0.856		
	8	0.854		
Managerial sustainability	1	0.852	68.920	0.892
	2	0.874		
	3	0.965		
	4	0.869		
	5	0.961		
	6	0.941		
	7	0.875		
	8	0.652		
	9	0.624		
	10	0.762		
	11	0.742		
	12	0.751		
	13	0.596		
	14	0.623		
	15	0.711		

moderate relationship. We found a low and positive relationship between sustainable product design and social sustainability (r=0.236). Finally, we reported a moderately positive and significant relationship (r=0.381) between sustainable product design and corporate sustainability.

Regression Analysis and Testing Hypotheses

We used multiple regression analysis to determine the relationship levels between sustainable product design and environmental, cultural, economic, social, and corporate sustainability variables. We used SPSS 15.0 analysis program for all statistical analyses. We show the results of multiple regression analysis in Table 5. We have shown the regression equation below to test the hypotheses of the independent variables in the research model.

$$Y=\beta 0 ++ \beta 1+ÇS + \beta 2+KS + \beta 3+ ET + \beta 4SS+ \beta 5+YS$$

We included sustainable product design (ST) in the model as an independent variable in the multiple regression equation. We used the concepts of environmental sustainability (ES), cultural sustainability (CS), economic sustainability (ES), social sustainability (SS), and corporate sustainability (TS) as dependent variables. The β value in the equation is the standardized beta coefficient. The β-coefficients and significance levels (p) of the variables as a result of the regression analysis are shown in Table 5.

As seen in Table 5, we found that sustainable product design has a positive and significant effect on environmental sustainability with a β-coefficient of "0.396" and a significance level of "0,000". In its working model, "H1: Sustainable product design has a positive and meaningful impact on the company's environmental sustainability." hypothesis was supported.

We found that the effect of sustainable product design on cultural sustainability has a positive and significant effect with the significance level of "0.405" and the β coefficient "0,000". In this case, the hypothesis "H2: Sustainable product design has a positive and significant impact on corporate cultural sustainability" was supported.

In addition, we found that the effect of sustainable product design on social sustainability has a positive and significant effect with a β-coefficient of "0.398" and a significance level of "0.004". The hypothesis "H3: Sustainable product design has a positive and significant impact on corporate social sustainability" was supported.

We found that sustainable product design has a positive and significant effect on economic sustainability, with a β-coefficient of "0.425" and a significance level of "0.003". In this case, the hypothesis "H4: Sustainable product design positively and significantly impacts economic sustainability" was supported.

We found that "0,426" and β coefficient "0,000" have a positive and significant effect on the impact of sustainable product design on corporate sustainability. In this case, the hypothesis "H5: Sustainable product design has a positive

Table 4. Mean, standard deviation and correlation values of the variables

Variables	1	2	3	4	5	6
Sustainable product design	1.000					
Environmental sustainability	0.234*	1.000				
Cultural sustainability	0.223*	0.211*	1.000			
Economic sustainability	0.420**	0.398**	0.463**	1.000		
Social sustainability	0.236*	0.324**	0.520**	0.542**	1.000	
Managerial sustainability	0.381**	0.376**	0.216*	0.541**	0.452**	1.000
Average	3.210	2.980	3.520	3.230	3.620	3.260
Standard deviation	0.720	0.563	0.765	0.820	0.924	0.886

**: Correlation is significant at the 0.01 level (double tail); *: Correlation is significant at the 0.05 level (single tail).

Table 5. Regression analysis results for sustainable product design in research

	Dependent variables	Std. β	t	p	Tolerance	Variance insertion factor
Independent variable	Environmental sustainability	0.396	3.966	0.000**	0.702	2.975
	Cultural sustainability	0.405	3.485	0.000**	0.694	1.957
	Economic sustainability	0.425	2.986	0.003*	0.698	2.001
	Social sustainability	0.398	2.997	0.004*	0.689	3.260
	Managerial sustainability	0.426	3.432	0.000**	0.735	1.650
	F			3.342**		
	R^2			0.159		

*: Correlation is significant at the 0.05 level (single tail); **: Correlation is significant at the 0.01 level (double tail).

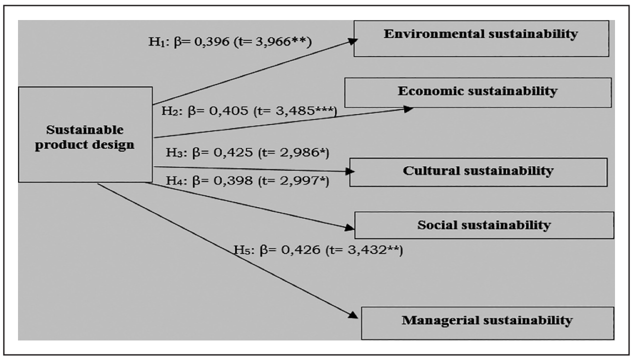

Figure 2. Structural path model results. Source: Authors' Construction.

and significant impact on corporate sustainability" was supported. When the F (3.342) and R2 (0.159) values were analyzed in the regression analysis, it was found that the model was at the "0.000" significance level and explained 15.9% of the variance in sustainable product design. According to this result, 15.9% of corporate sustainability is explained by sustainable product design. We have shown the findings regarding the statistical analysis of the hypotheses we developed within the scope of the study in Figure 2.

DISCUSSION

In this study, we examined the effects of sustainable product design on corporate sustainability. Customer satisfaction is the first priority in today's manufacturing companies. In this direction, the most important goal of the companies is to produce in accordance with the beliefs, attitudes, and expectations of the individuals who make up the society. In an academic study, the concept of sustainability mentioned that the competitive opportunities of companies are not limited to the goods and services they produce. In this context, the performances of companies are evaluated not only according to their economic performance but also according to their performance against the environment and society. In this direction, today's companies have started to adopt a structure that is sensitive to environmental and social problems. There are factors such as organizational culture, innovation, human resources, value creation for customers, supply chain and business ethics, and social responsibility that affect the concept of sustainability in companies [41]. There are many studies in the literature that talk about the impact of social, environmental, societal, social, and environmental criteria in ensuring corporate sustainability [42–44].

Mentioned sustainable product design in their studies. In the related study, it was emphasized that functionality, cost, and environmental impact should be considered in the design of the product [3]. It is mentioned that this situation constitutes approximately 70% of the production and cost. Three criteria were addressed in product design. These; It was listed as "cost-benefit analysis, maximizing the number of reusable parts and minimizing the amount of waste". In this study, we examined whether the sustainable design has an impact on corporate sustainability. We noticed that there was a research gap in the literature. We have not come across a study directly investigating the relationship between sustainable product design and corporate sustainability.

In the model created in this study, we revealed the effect of the independent variable of sustainable product design on the dependent variables of environmental, cultural, social, economic, and corporate sustainability. We applied factor analysis to determine the variables that make up the research model. As a result of the analysis, we found that the sub-dimensions supported the model, that is, we reached results that are compatible with the original scale. The variables we used within the scope of the study; We looked at the mean, standard deviation, and correlation values and used regression analysis to test the hypotheses established in the model. The results of the analysis we have done within the scope of the study show parallelism with the research findings [45, 46]. On the other hand, the finding that sustainable product design positively and significantly affects social sustainability is consistent with the study [47]. Another result obtained in the study was the conclusion that sustainable product design affects economic sustainability. When the studies in the literature are examined, our study is consistent with similar results to the study of [48]. Again, having similar findings to our study, [49] mentioned that sustainable sourcing and product designs can improve the overall performance of companies and reduce social and financial risks.

To sum up, all hypotheses developed in this study, which examined the effects of sustainable product design on corporate sustainability (environmental, cultural, economic, social, and managerial), where supported. It has been supported that sustainable product design carried out by businesses has a positive and meaningful effect on corporate sustainability. Results consistent with similar studies in the literature were obtained. Considering that sustainable product design has environmental, economic, and social aspects, the relationship between corporate sustainability sub-dimensions was supported in this study. Today's modern businesses should carry out their production by considering social and environmental factors. Profit maximization logic alone does not seem sufficient for business continuity today. Considering the social and environmental stakeholders of the enterprises, in other words, mutual interests come to the fore according to the social change theory. Enterprises that lack environmentally friendly production; face negative reactions from society, that is, consumers and customers. Today's customer profile is more healthy and in the production phase; climate change, zero waste, businesses that use recyclable energy prefer their products and services more. Business owners and managers must consider environmental criteria at every stage of production. Today's customer profile is more healthy and in the production phase; climate change, zero waste, businesses that use recyclable energy prefer their products and services more. Business owners and managers must consider environmental criteria at every stage of production. Today's customer profile is more healthy and in the production phase; climate change, zero waste, businesses that use recyclable energy prefer their products and services more. Business owners and managers must consider environmental criteria at every stage of production.

Contribution

Evidence gathered during the study revealed that sustainable product design affects the sustainability of businesses in general. For companies to survive, they need to develop products with sustainable product design in mind. In other words: If companies want to ensure their existence, they must consider factors such as cost, quality, and efficient use of time, as well as customer, social and natural environmental factors. On the other hand, the study found that sustainable product design has an impact on environmental, cultural, social, economic, and corporate sustainability. In addition, it has been determined that there is a positive and significant relationship between sustainable product design and the sub-dimensions of corporate sustainability.

Practical Implications

Within the scope of the study, it is possible to make some suggestions for market actors, namely practitioners.Firm partners and supervisors should carry out by getting into charge the attitudes of the public and consumers before moving into manufacture. Especially in today's world, global warming, the Covid-19 epidemic and the resulting loss of life and the problems in the supply of raw materials have caused the purchasing power of customers to decrease. At the same time, the Covid 19 pandemic has negatively affected the character of the men who make up the society. Global warming, earthquakes, hot conflicts on a raund scale affect the activities of manufacturing companies. To reduce these effects, it is suggested to focus on customer expectations and requirements in product design. Sustainable product design; Considering that they should carry out their environmental, production activities by taking into account the social and individual effects, this should be considered important for the acceptance of companies and for them to carry out their activities in a healthy way. In short, customer satisfaction, environmental factors (waste management, waste disposal, use of recyclable energy), taking an active role in social projects (for example, building schools and places of worship, participating in cultural events, supporting employment projects), planned employment activities, supporting sports activities. It is assumed to support a number of socially oriented projects such as making donations.

CONCLUSIONS

We have obtained some results in this study, in which we investigated the effect of sustainable product design on corporate sustainability. First, we examined whether there is a relationship between sustainable product design and corporate sustainability and whether this relationship is meaningful. As a result of the statistical analysis, we determined that there is a positive and significant relationship between sustainable product design and the sub-dimensions of corporate sustainability (environmental, cultural, social, economic and management). When we examined the relationship levels between sustainable product design and the sub-dimensions of corporate sustainability, we noticed that the highest correlation was between sustainable product design and economic sustainability sub-dimension (r=0.42). We found the lowest correlation between sustainable product design and cultural sustainability (r=0.223). We developed 5 hypotheses within the scope of the research and all of these hypotheses were supported by statistical analysis. On the other hand, sustainable product design explained about 16% of the change in corporate sustainability. We realized that sustainable product design has an impact on all sub-dimensions of corporate sustainability. It is recommended that companies show the necessary sensitivity about sustainable product design in order to maintain their existence. Within the scope of the research, 5 hypotheses were developed and all of these hypotheses were supported. In other words, sustainable product design was found to explain about 16% of the change in corporate sustainability. In addition, it has been determined that sustainable product design has an effect on all sub-dimensions of corporate sustainability. In order for companies to survive, they need to show the necessary sensitivity about sustainable product design.

Limitations

In this study, we examined the thoughts of the managers of companies operating in the metal products and machinery industry in the organized industrial zone of Şanlıurfa, one of the most important industrial cities of the region, in the southeastern region of Türkiye, on sustainability and sustainability product design. The main limitation is that the study was carried out at a single point in Türkiye and in a sector operating in a certain sector. Another limitation is that the data collected in the study is based on statistical correlations and simple regression analysis. Coinciding with the year 2022, when the severity of the Covid 19 pandemic is felt most, emerges as the biggest limitation that prevents data collection in different business sectors. On the other hand, we consider it an important limitation that the study is based on a cross-sectional questionnaire. We limited the statements in the questionnaire to the variables of sustainable product design and corporate sustainability.

Future Research

In this study, we investigated the thoughts of manufacturing company managers on sustainable product design and corporate sustainability. We mentioned in the previous section that there are some limitations of the study. In this direction, it would be appropriate to make some suggestions for future studies. Since the research is only about managers, it is suggested that future studies should also be done on employees, business owners and customers. Since the study is a longitudinal study, the cross-sectional design of future studies will contribute to the literature. In addition, we consider it an important shortcoming that the present study was carried out in only one region. We recommend that prospective planned studies be carried out in different regions and in different countries. In addition, the survey method was used in the study. It would be appropriate to use other research methods such as interview methods and observation management in future studies. In this study, we examined the effects of corporate sustainability on sustainable product design. In future studies, it is recommended to examine various mediation effects such as corporate social responsibility, organizational support, employee motivation, stakeholder relations and customer loyalty.

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.

ETHICS

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

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Research Article

Enhance modelling predicting for pollution removal in wastewater treatment plants by using an adaptive neuro-fuzzy inference system

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ABSTRACT

Biological and physical treatment in wastewater treatment plants appears to be one of the most important variables in water quality management and planning. This crucial characteristic, on the other hand, is difficult to quantify and takes a long time to obtain precise results. Scientists have sought to devise several solutions to address these issues. Artificial intelligence models are one technique to monitor the pollutant parameters more consistently and economically at treatment plants and regulate these pollution elements during processing. This study proposes using an adaptive network-based fuzzy inference system (ANFIS) model to regulate primary and biological wastewater treatment and used it to model the nonlinear interactions between influent pollutant factors and effluent variables in a wastewater treatment facility. Models for the prediction of removal efficiency of biological oxygen demand (BOD), total nitrogen (TN), total phosphorus (TP), and total suspended solids (TSS) in a wastewater treatment plant were developed using ANFIS. Hydraulic retention time (HRT), temperature (T), and dissolved oxygen (DO) were input variables for BOD, TN, TP, and TSS models, as determined by linear correlation matrices between input and output variables. The findings reveal that the developed system is capable of accurately predicting and controlling outcomes. For BOD, TN, TP, and TSS, ANFIS was able to achieve minimum mean square errors of 0.1673, 0.0266, 0.0318, and 0.0523, respectively. The correlation coefficients for BOD, TN, TP, and TSS are all quite strong. In the wastewater treatment plant, ANFIS' prediction performance was satisfactory and the ANFIS model can be used to predict the efficiency of removing pollutants from wastewater.

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INTRODUCTION

As the population grows and companies flourish, wastewater treatment becomes increasingly important due to the increased volume of wastewater generated by facilities each year. As a result, low-cost techniques that give accurate results for predicting treatment efficiency in wastewater treatment plants (WWTP) must be developed. WWTP entails a number of sophisticated and unpredictably unpredictable procedures. The treatment plant's smooth and effective operation, on the other hand, is dependent on a proper model capable of accurately representing the

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system's dynamic character. Previously, the majority of models were utilized in industrial wastewater treatment plants. WWTP operation includes physical, biological, and chemical features of wastewater streams, as well as biological and degrading mechanisms. Improved process control algorithms based on artificial intelligence (AI) technologies have received a lot of attention as a result of growing environmental and economic concerns [1].

According to the literature, suspended solids (SS_{eff}) and chemical oxygen demand (COD_{eff}) in the effluent from a hospital wastewater treatment facility were forecasted using three distinct adaptive neuro-fuzzy inference systems (ANFIS) and artificial neural networks (ANN) and in terms of effluent prediction, the results showed that ANFIS surpasses ANN statistically [2]. The ANFIS model is used to forecast effluent pH quality and artificial neural network is used as a comparison [3]. Another study used five process variables to predict the effluent chemical oxygen demand load from a full-scale expanded granular sludge bed reactor (EGSBR) treating corn processing wastewater, including influent chemical oxygen demand, influent flow rate, influent total Kjeldahl nitrogen, effluent volatile fatty acids, and effluent bicarbonate. The proposed ANFIS model was created using a hybrid learning approach, and its performance was assessed using a set of test data randomly selected from the experimental domain. The ANFIS-based predictions were validated using a variety of descriptive statistical metrics, including root-mean-square error, index of agreement, a factor of two, fractional variance, the proportion of systematic error, and so on [4]. Using daily data, feed-forward neural network (FFNN), support vector regression (SVR), and ANFIS black box artificial intelligence models (AI) were used to estimate effluent biological oxygen demand (BOD_{eff}) and chemical oxygen demand (COD_{eff}) of Tabriz wastewater treatment plant (WWTP). In addition, the BOD_{eff} and COD_{eff} parameters were predicted using the autoregressive integrated moving average (ARIMA) linear model to compare the linear and non-linear models' abilities in complicated process prediction [5]. In another research, the non-linear system of the activated sludge process in an industrial wastewater treatment plant was identified using the ANFIS and generalized linear model (GLM) regression. Predictive models of effluent chemical and 5-day biochemical oxygen demands were developed based on previously assessed inputs and outputs. From a list of possibilities, the least absolute shrinkage and selection operator (LASSO) and a fuzzy brute force search were employed to choose the best regressor combination for the GLMs and ANFIS models, respectively [6]. Furthermore, ANFIS allows direct inverse control of the substrate in an activated sludge system and the performance of the suggested controller is proven by tracking the substrate setpoints then the result of that reveal that the proposed controller can efficiently and precisely manage the substrate concentration level and the proposed inverse controller could be a beneficial control mechanism for the WWTP [7]. In another prior study support vector machine (SVM) and adaptive neuro-fuzzy inference system (ANFIS) models were used to evaluate the removal efficiency of Kjeldahl Nitrogen in a full-scale aerobic biological wastewater treatment facility and the input variables used in the modeling process include pH, COD, total solids (TS), free ammonia, ammonia nitrogen, and Kjeldahl nitrogen then the results of model development was provide an adaptable, functional, real-time, and alternate approach of replicating Kjeldahl nitrogen removal efficiency [8]. In another study, too, the use of successfully ANFIS modeling have employed to increase the output of anaerobic digesters [9]. The ANFIS model also was used to remove carbon and nitrogen. As a comparison, a feed-forward neural network is used. All of the variables investigated, including COD, suspended solids (SS), and ammonium nitrogen (NH4-N), were found to have increased prediction power using the ANFIS model [10].

According to prior research, most of them are focused on figuring out how to eliminate pollutants from wastewater during the biological treatment stage. Artificial intelligence models were used to analyze industrial and domestic wastewater treatment plants.

As a result, Biological and physical treatment in wastewater treatment plants appears to be one of the most important aspects of water quality management and planning. This crucial characteristic, on the other hand, is difficult to quantify and takes a long time to obtain precise results. Scientists have sought to devise a number of solutions to address these issues. Artificial intelligence models are one technique to monitor the pollutant parameters more consistently and economically at treatment plants and regulate these pollution elements during processing. Therefore, the fundamental goal of this research is to use the ANFIS model to apply, predict, and develop the pollutant removal efficiency for primary and biological treatment in WWTPs. This modeling study employed MATLAB APPDESIGNER model data for training, testing, and predictions. BOD, TN, TP, and TSS were the parameters investigated. Before running the simulation for prediction, the data was standardized. The output of the model was compared to actual training data and ANN data, and the error was minimized to produce the best operating points.

MATERIALS AND METHODS

Probabilistic reasoning, fuzzy logic, neural networks, and evolutionary computation are examples of intelligent technology. As can be observed, each of these technologies has its own set of benefits and drawbacks, and in many real-world applications, researchers will need to mix several intelligent technologies and learn from other sources. Hybrid intelligent systems have emerged as a result of the requirement for such a combination [11].

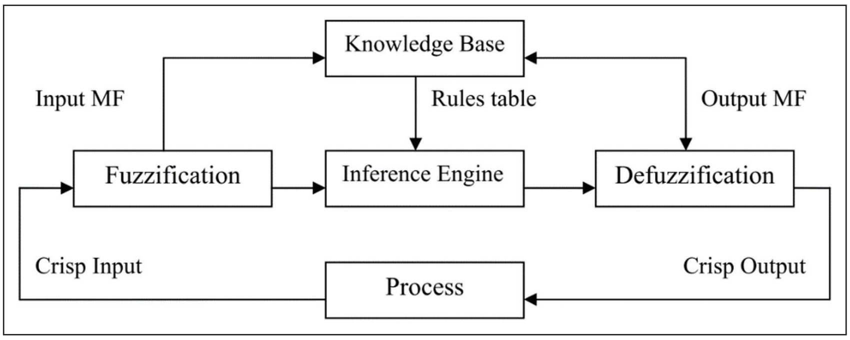

Figure 1. The fuzzy logic controller's basic structure [12].

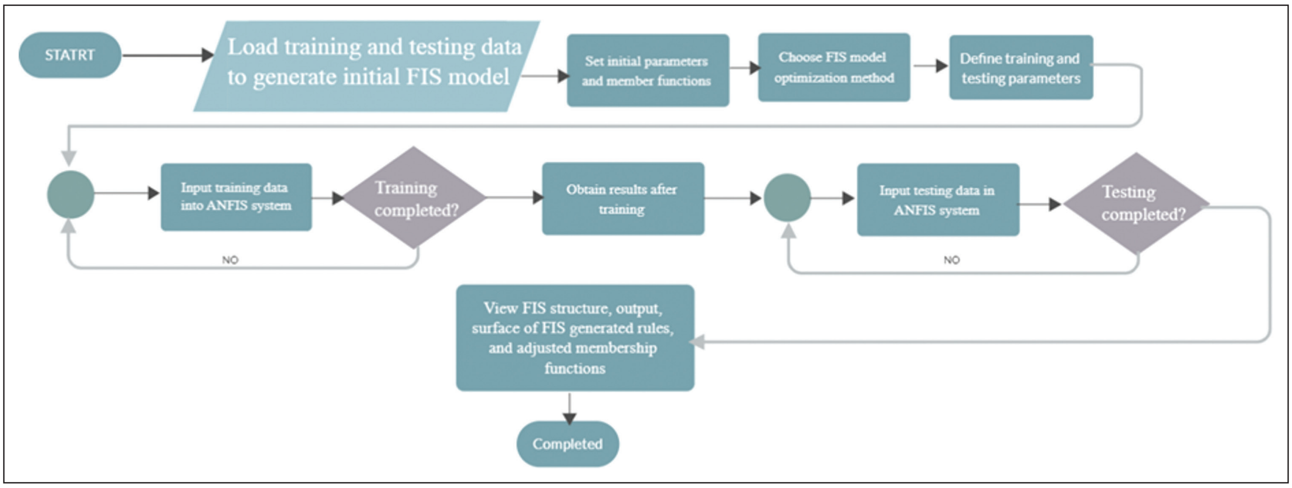

Figure 2. Flow chart of ANFIS test step [9].

The term "hybrid intelligent system" refers to a system that incorporates at least two intelligent technologies. Combining a neural network with a fuzzy system, for example, produces a hybrid neuro-fuzzy system.

Soft Computing (SC), an emerging technique to constructing hybrid intelligent systems capable of reasoning and learning in an uncertain and imprecise environment, is based on a combination of probabilistic reasoning, fuzzy logic, neural networks, and evolutionary computation.

Fuzzy Logic and Fuzzy Inference System

Fuzzification, fuzzy rule base, fuzzy output engine, and defuzzification are the four steps of a fuzzy system, as depicted in (Fig. 1) [12]. The input unit contains the input variables, as well as any information about the input variables that will affect the scenario under investigation [13]. The information with respect to the input variables is generally referred to as a database. The variables in the input can be numerical or textual [14]. Fuzzification is a method of assigning numerical values to linguistic adjectives and calculating the number of membership functions in fuzzy system sets. The fuzzy rule base is made up of all logical rules that connect the input and output variables, as well as any possible intermediary connections. The input variables are converted to their appropriate outputs by the fuzzy output engine. This is accomplished by considering the numerous relationships established in the fuzzy rule base. Finally, defuzzification is the process of converting the fuzzy system's language outputs into numerical values.

At the end of the information and fuzzy rule base interaction, the output unit generates variables. (Fig. 2) depicts the general ANFIS process for developing the ANFIS prediction model.

Model Architecture and Components

When a neural network is combined with a fuzzy system, a strong hybrid system capable of tackling complicated issues is created. This hybrid system's behavior may be defined in terms comparable to human rules, making it an accurate tool for simulating non-linear functions [15]. ANFIS employs a hybrid learning technique that specifies how the weights should be updated to reduce the error between the actual and desired output, adjusting the fuzzy inference system's parameters and structure in the process (FIS). (Fig. 3) depicts the structure of ANFIS, which is a Sugeno fuzzy model.

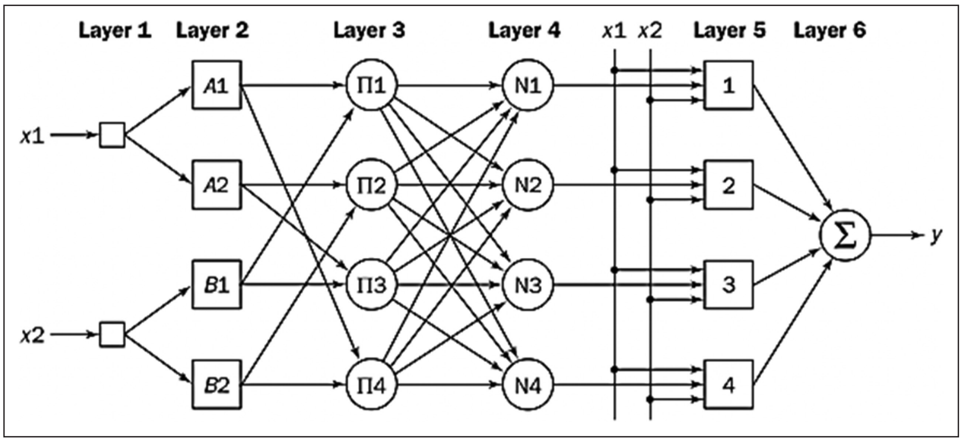

Figure 3. ANFIS structure.

ANFIS is an adaptive network that uses supervised learning on the learning method, similar to the Takagi-Sugeno fuzzy inference system [16]. Inputs and outputs, database and pre-processor, fuzzy system generator, fuzzy inference system, and adaptive neural network are the five major components of the model [17]. In most cases, the input and output parameters are chosen or derived from the system description parameters. The database and pre-processor are required for model creation and contain information about system performance. This information is normally gathered by collecting data on parameters that the system monitors on a regular basis. MATLAB is regarded a good tool for this study and is utilized to create system performance information.

A Sugeno fuzzy inference system and associated adaptive networks, as well as an ana adaptive network-based fuzzy inference system, are used (ANFIS). The input and output variables are chosen or generated from the variables that are typically used to describe the system. Model development necessitates the creation of a database containing system performance data. In most cases, it is created by gathering parameters from the APPDESIGNER model. For the model to produce accurate information on the system, the training database must be of high quality. The database must include sufficient and reliable information on the system for the model to accurately characterize it. A raw database, on the other hand, is likely to contain some duplicated and contradictory data. As a result, the raw training database may need to be pretreated to reduce duplicates and resolve data conflicts. Because the ANFIS is normally launched with a prototype fuzzy system, a fuzzy system generator is required. This function is provided by the software MATLAB (Matworks Inc.). Jang [17] utilized MATLAB to program the model, demonstrating that the language is adequate for model programming.

In order to achieve the lowest possible error, the model will be used to determine the relationship between the APPDESIGNER MATLAB model and the ANFIS model.

ANFIS is a multilayer feed-forward network that maps inputs into outputs with the use of neural network learning techniques and fuzzy reasoning. It's an adaptable neural network-based fuzzy inference system (FIS). The architecture of a typical ANFIS for the first order Sugeno fuzzy model, with two inputs, two rules, and one output (MFs). For a first order Sugeno fuzzy model [18], the following is an example of a rule set containing four fuzzy if–then rules:

Rule 1: If x is A1 and y is B1 then $f_1 = p_1 x + q_1 y + r_1$

Rule 2: If x is A2 and y is B2 then $f_2 = p_2 x + q_2 y + r_2$

where A1, A2, B1 and B2 are the MFs for the inputs x and y, respectively, p_{ij}, q_{ij} and r_{ij} (i,j =1,2) are consequent parameters [19].

The architecture of a typical ANFIS, as shown in Figure 3, consists of five levels, each of which performs a different function in the ANFIS and is described below.

Layer 1: This layer's nodes are all adaptive nodes. They assign membership scores to the inputs. This layer's outputs are determined by

$$O_{Ai}^{1} = U_{Ai}(x) \quad i = 1,2$$
$$O_{Bj}^{1} = U_{Bj}(x) \quad j = 1,2 \tag{1}$$

where x and y are crisp inputs, and Ai and Bj are fuzzy sets characterized by appropriate MFs, which could be triangular, trapezoidal, Gaussian function, or other shapes, and Ai and Bj are fuzzy sets characterized by appropriate MFs, which could be triangular, trapezoidal, Gaussian function, or other shapes. The generalized bell-shaped MFs (Eq. (2)) defined below are used in this investigation.

$$U_{Ai}(x) = \frac{1}{1 + (\frac{x - c_i}{a_i})^{2b_i}} \quad i = 1,2$$
$$U_{Bj}(x) = \frac{1}{1 + (\frac{x - c_j}{a_i})^{2b_j}} \quad j = 1,2 \tag{2}$$

where $\{a_i, b_i, c_i\}$ and $\{a_j, b_j, c_j\}$ are the parameters of the MFs, governing the bell-shaped functions. Parameters

Table 1. Modeled primary and secondary treatment techniques

System number	Processing	Inputs	Outbuts				Processing
			a	b	c	d	
ANFIS1	primary treatment	HRT, T	BOD	TN	TP	TSS	Mechanical screen + primary sedimentation tank
ANFIS 2	primary treatment	HRT, T	BOD	TN	TP	TSS	Mechanical screen + Grit removal + Grease trap + primary sedimentation tank
ANFIS 3	Secondary Treatment	HRT, T	BOD	TN	TP	TSS	Facultative pond+ Secondary sedimentation tank
ANFIS 4	Secondary Treatment	HRT, T	BOD	TN	TP	TSS	Anaerobic ponds + Facultative Pond+ Secondary sedimentation tank
ANFIS 5	Secondary Treatment	HRT, T, DO	BOD	TN	TP	TSS	Aerobic ponds (Partial Mixing) + Facultative Pond+ Secondary sedimentation tank
ANFIS 6	Secondary Treatment	HRT, T, DO	BOD	TN	TP	TSS	Aerobic ponds (Complete Mixing) + Facultative Pond+ Secondary sedimentation tank
ANFIS 7	Secondary Treatment	HRT, T	BOD	TN	TP	TSS	Anaerobic ponds+ Secondary sedimentation tank
ANFIS 8	Secondary Treatment	HRT, T, DO	BOD	TN	TP	TSS	Aerobic ponds (Partial Mixing) + Secondary sedimentation tank
ANFIS 9	Secondary Treatment	HRT, T, DO	BOD	TN	TP	TSS	Aerobic ponds (Complete Mixing) + Secondary sedimentation tank
ANFIS 10	Secondary Treatment	HRT, T, DO	BOD	TN	TP	TSS	Anaerobic ponds + Aerobic ponds (Partial Mixing) + Secondary sedimentation tank
ANFIS 11	Secondary Treatment	HRT, T, DO	BOD	TN	TP	TSS	Anaerobic ponds + Aerobic ponds (Complete Mixing) + Secondary sedimentation tank

in this layer are referred to as premise parameters or antecedent parameters.

Layer 2: The nodes in this layer are fixed nodes with the number 2 next to them, indicating that they act as a simple multiplier. This layer's outputs are expressed as

$$O_{ij}^2 = w_{ij} = U_{Ai}(x)U_{Bj}(y), \;\; i,j = 1{,}2 \tag{3}$$

which represents the firing strength of each rule. The degree to which the antecedent element of the rule is satisfied is referred to as the firing strength.

Layer 3: The nodes in this layer are also fixed nodes with the label, indicating that they play a role in network normalization. This layer's outputs can be expressed as

$$O_{ij}^3 = \overline{w_{ij}} = \frac{w_{ij}}{w_{11}+w_{12}+w_{21}+w_{22}}, \quad i,j = 1{,}2 \tag{4}$$

which are called normalized firing strengths.

Layer 4: The output of each node in this layer is just the product of the normalized firing strength and a first-order polynomial (for a first order Sugeno model). As a result, Eq. (5) gives the outputs of this layer.

$$O_{ij}^4 = \overline{w_{ij}}\, f_{ij} = \overline{w_{ij}}\left(p_{ij} + q_{ij}y + r_{ij}\right), \quad i,j = 1{,}2 \tag{5}$$

Subsequent parameters refer to the parameters in this layer.

Layer 5: This layer's single node is a fixed node labelled ∑ that computes the total output as the sum of all incoming signals, i.e.,

$$z = O_1^5 = \sum_{i=1}^{2}\sum_{j=1}^{2}\overline{w_{ij}}\, f_{ij} = \sum_{i=1}^{2}\sum_{j=1}^{2}\overline{w_{ij}}\left(p_{ij}x + q_{ij}y + r_{ij}\right) = \sum\sum(\overline{w_{ij}}\,x)p_{ij} + (\overline{w_{ij}}y)q_{ij} + (\overline{w_{ij}})r_{ij} \tag{6}$$

When the values of the premise parameters are fixed, the result is a linear combination of the subsequent parameters. The ANFIS design may be seen to have two adaptive layers: Layers 1 and 4. to the input MFs. Layer 4 has modifiable parameters $\{p_{ij}, q_{ij}, r_{ij}\}$ Layer 1 has modifiable parameters $\{a_i, b_i, c_i\}$ and $\{a_j, b_j, c_j\}$ related pertaining to the first-order polynomial. The learning algorithm for this ANFIS architecture's task is to tune all the changeable parameters to match the training data in the ANFIS output. The hybrid learning algorithm is a two-step procedure for learning or altering certain adjustable parameters. The premise parameters are held constant in the forward pass of the hybrid learning algorithm, node outputs advance till Layer 4, and the subsequent parameters are determined using the least squares approach. The subsequent parameters are held constant in the backward pass, the error signals flow backward, and the premise parameters are updated using the gradient descent algorithm. Jang provides a detailed algorithm and mathematical basis for the hybrid learning approach [18].

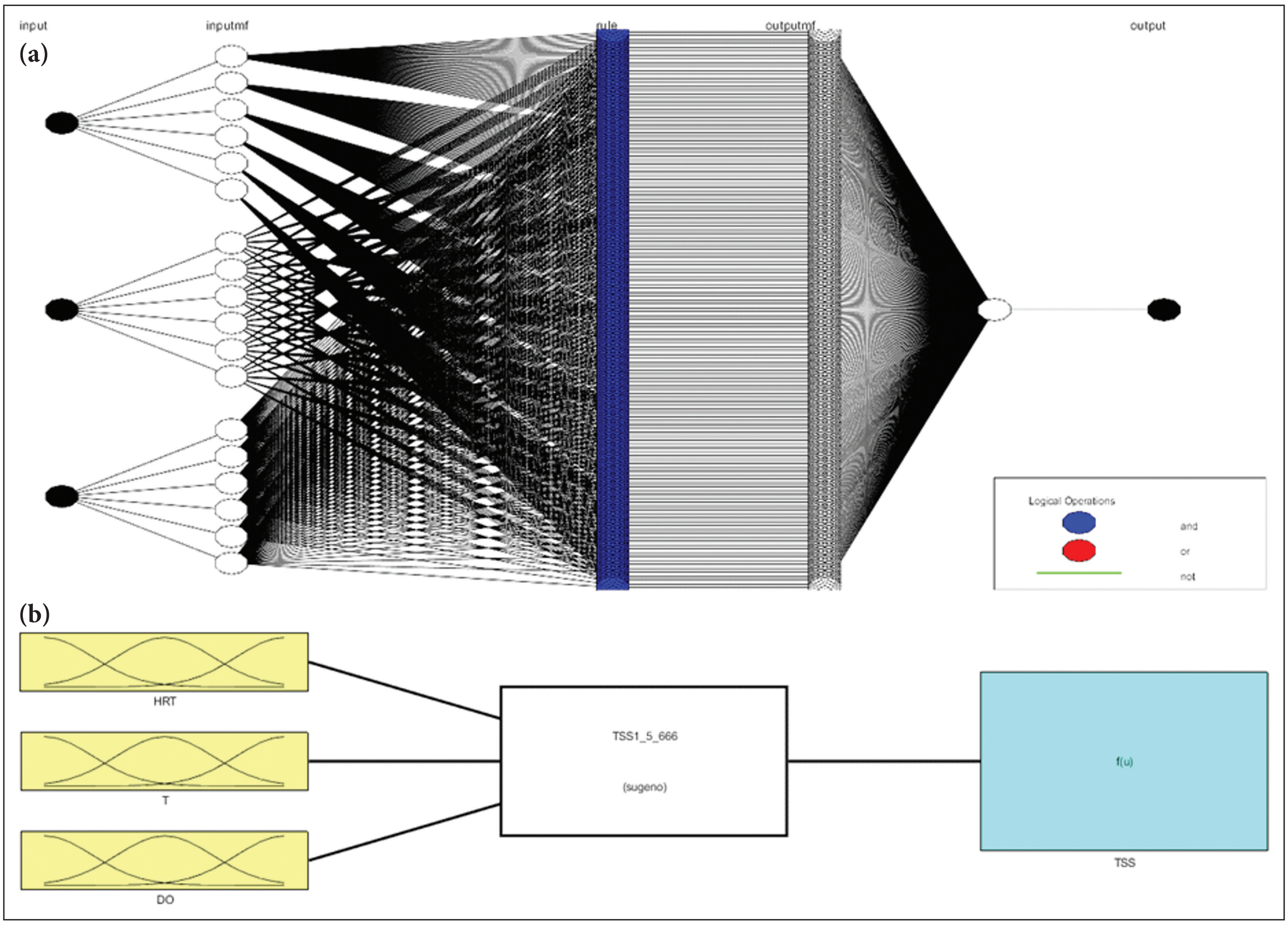

Figure 4. Schematic diagram of **(a)** ANFIS models with all input variables and **(b)** input–output mapping structure of ANFIS models with input variables.

To evaluate the prediction power of ANFIS and ANN trained by each data set, performance indices such as mean square error (MSE), root mean square normalized error (RMSE), mean absolute percentage error (MAPE), and correlation coefficient (R) are utilized. The MSE performance index was established as follows:

$$MSE = \frac{1}{n}\sum_{i=1}^{n}(\hat{y} - y)^2 \tag{7}$$

The RMSE performance index was defined as

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}-y)^2}{n}} \tag{8}$$

where y is the measured values, $\hat{y}$ the corresponding predicted values and n is the number of samples.

Mean absolute percentage error (MAPE):

$$MAPE = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{A_t-F_t}{A_t}\right| \times 100 \tag{9}$$

Where $\bar{A} = \frac{1}{N}\sum_{t=1}^{N} A_t$ and $\bar{F} = \frac{1}{N}\sum_{t=1}^{N} F_t$ are the average values of A_t and F_t over the training or testing dataset. The smaller RMSE and MAPE mean better performance.

Correlation coefficient (R):

$$R = \frac{\sum_{t=1}^{n}(A_t-\bar{A})(F_t-\bar{F})}{\sqrt{\sum_{t=1}^{n}(A_t-\bar{A})^2 . \sum_{t=1}^{n}(F_t-\bar{F})^2}} \tag{10}$$

The Plant Description

The ANFIS model was tested as an artificial intelligence model to operate a MATLAB-modeled wastewater treatment system.

The wastewater treatment plan's major processing techniques were several types of primary treatment (two models) and secondary treatment (nine models).

Mechanical screen and primary sedimentation tank are one sort of primary treatment procedure, while mechanical screen, grit removal, grease trap, and primary sedimentation tank are the other.

In terms of secondary treatment, nine different models were compared and clarified in Table 1. The inputs to the ANFIS1 (a) model, for example, are HRT and T, and the output is BOD.

The influent variables include hydraulic retention time (HRT), temperature (T) and dissolved oxygen (DO) and the effluent variables include the removal efficiency of bio-

Table 2. The detailed information of the models

Model	Training data	Testing data	Number of input MF for the following outputs				Rules for the following outputs			
			BOD	TN	TP	TSS	BOD	TN	TP	TSS
ANFIS1	120	18	46	86	86	84	24	48	48	32
ANFIS2	120	18	86	108	106	106	48	80	60	60
ANFIS3	144	25	88	1010	99	1010	64	100	81	100
ANFIS4	144	22	106	88	66	98	60	64	36	72
ANFIS5	576	84	866	888	1086	666	288	512	480	216
ANFIS6	576	93	686	868	888	1086	288	384	512	480
ANFIS7	205	41	86	88	108	88	48	64	80	64
ANFIS8	576	107	688	787	677	856	384	392	294	240
ANFIS9	576	107	865	888	777	699	240	512	343	486
ANFIS10	576	105	878	988	789	567	448	576	504	210
ANFIS11	576	98	668	985	867	644	288	360	336	96

logical oxygen demand (BOD5), total nitrogen (TN), total phosphorous (TP) and total suspended solids (TSS).

Model Implementation

The ANFIS (Adaptive Neuro-Fuzzy Inference System) editor of the Fuzzy toolbox in MATLAB was used to create a model in Sugeno structure (R2021 version, The MathWorks Inc., USA). The membership functions were extracted from the APPDESIGNER system's data set, which had been standardized and divided into training and testing data. The model's parameters were estimated using a hybrid learning method, and the model was validated using APPDESIGNER model data effluent parameters like output BOD, TN, TP, and TSS.

Figure 4a, b shows the topology of the ANFIS network that was employed. In the creation of a fuzzy system, eleven ANFIS structures with varying input correlation (Fig. 4a) and consisted of five layers were established (Fig. 4b). The following are the meanings of each layer in (Fig. 4b), as well as their counterpart in the ANFIS structures:

Input layer: In the ANFIS inputs layer, state variables are nodes: There are three input variables in total: HRT, T, and DO are all acronyms for hormone replacement therapy (from the influent) Layer with the membership function: Each state variable's term sets are nodes in the ANFIS values layer, which compute the membership value.

For each input variable:

Membership: triangle mf or gauss mf Membership number.

Rules layer: Each rule in the fuzzy class is a node in the ANFIS rules layer, with the rule matching factor xi computed using soft-min or product. Layer of the output membership function: In the function layer, each weighs the result of its linear regression fi, resulting in the rule output.

Table 3. Excel data from APPDESIGNER model

	Inputs		Outputs			
HRT	T	DO	BOD	TN	TP	TSS
30.00	-5.00	0.10	5.00	1.00	1.00	50.00
37.39	-4.00	0.31	5.65	1.17	1.11	50.43
44.78	-3.00	0.53	6.30	1.35	1.22	50.87
52.17	-2.00	0.74	6.96	1.52	1.33	51.30
59.57	-1.00	0.95	7.61	1.70	1.43	51.74
66.96	0.00	1.17	8.26	1.87	1.54	52.17
30.00	-5.00	1.38	8.91	2.04	1.65	52.61
37.39	-4.00	1.59	9.57	2.22	1.76	53.04
44.78	-3.00	1.80	10.22	2.39	1.87	53.48
52.17	-2.00	2.02	10.87	2.57	1.98	53.91
59.57	-1.00	2.23	11.52	2.74	2.09	54.35
66.96	0.00	2.44	12.17	2.91	2.20	54.78
30.00	-5.00	2.66	12.83	3.09	2.30	55.22
37.39	-4.00	2.87	13.48	3.26	2.41	55.65
44.78	-3.00	3.08	14.13	3.43	2.52	56.09
52.17	-2.00	3.30	14.78	3.61	2.63	56.52
59.57	-1.00	3.51	15.43	3.78	2.74	56.96
66.96	0.00	3.72	16.09	3.96	2.85	57.39
30.00	-5.00	3.93	16.74	4.13	2.96	57.83
37.39	-4.00	4.15	17.39	4.30	3.07	58.26
44.78	-3.00	4.36	18.04	4.48	3.17	58.70
52.17	-2.00	4.57	18.70	4.65	3.28	59.13
59.57	-1.00	4.79	19.35	4.83	3.39	59.57
66.96	0.00	5.00	20.00	5.00	3.50	60.00
74.35	-5.00	0.10	20.65	5.17	3.61	60.43
81.74	-4.00	0.31	21.08	5.30	3.70	60.85

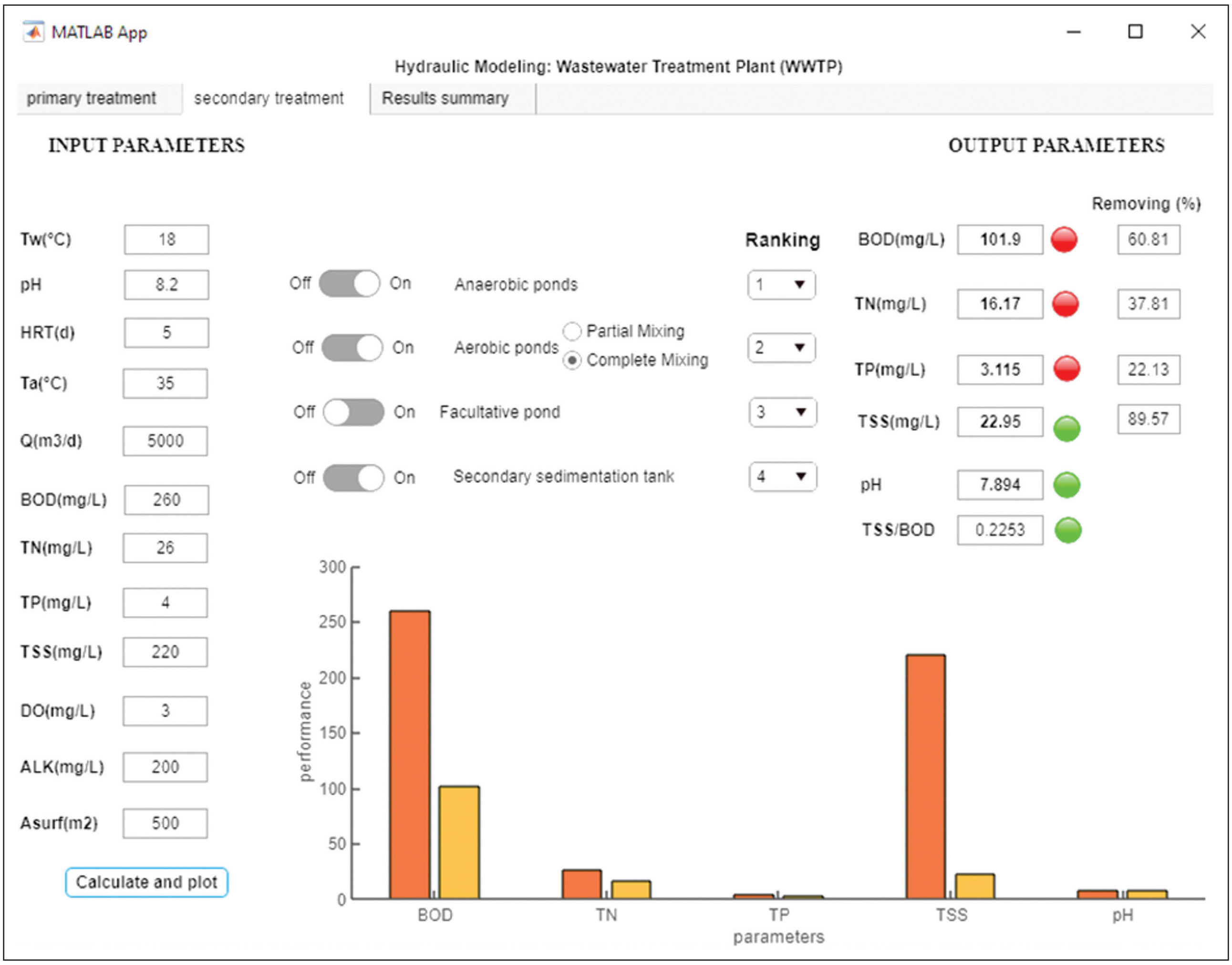

Figure 5. APPDESIGNER model interface.

Normalization layer:

Each xi is scaled into the normalization layer Normalization

Normalization is performed with the equation:

$$x_{norm} = (x_{value} - x_{min})(x_{max} - x_{min}) \quad (11)$$

Output layer: Each rule output is added to the output layer.

Outputs: BOD, TN, TP and TSS (effluent).

Results and Discussion

As shown in (Fig. 5), the data from the APPDESIGNER model was used to create eleven different ANFIS models. As an example of data, the data generated from the APPDESIGNER model has been organized in tables for usage in ANFIS, as seen in Table 3. The effluent BOD, TN, TP, and TSS were monitored in the system as indicators of treatment performance and stability using the ANFIS models applied to the APPDESIGNER model.

The ANFIS model in this paper was created using Matlab's fuzzy function. The data was first examined using Matlab's fuzzy subtractive clustering tool, and the cluster centers were determined. The initializing parameters were determined using the cluster centers, which indicate the initial value of premise parameters.

To identify a suitable ANFIS model, the types and numbers of MFs in ANFIS were investigated, including Gaussian, generalized bell-shaped, triangular, and trapezoidal-shaped functions, as well as the parameters. The values of RMSE and R between the model output values and observed values were used as selection criteria for the optimal final architecture. All ANFIS models with generalized bell-shaped MFs for each input variable showed the best results with diverse input variables. BOD, TN, TP, and TSS were all predicted using these models. Thus, monitoring the BOD, TN, TP, and TSS dynamics for the l wastewater treatment process, which was optimized by trial and error during the training phase, was adequate. The hybrid approach was used to train the network after selecting the initial value of the premise parameter and the design of the predictive model. The network's prem-

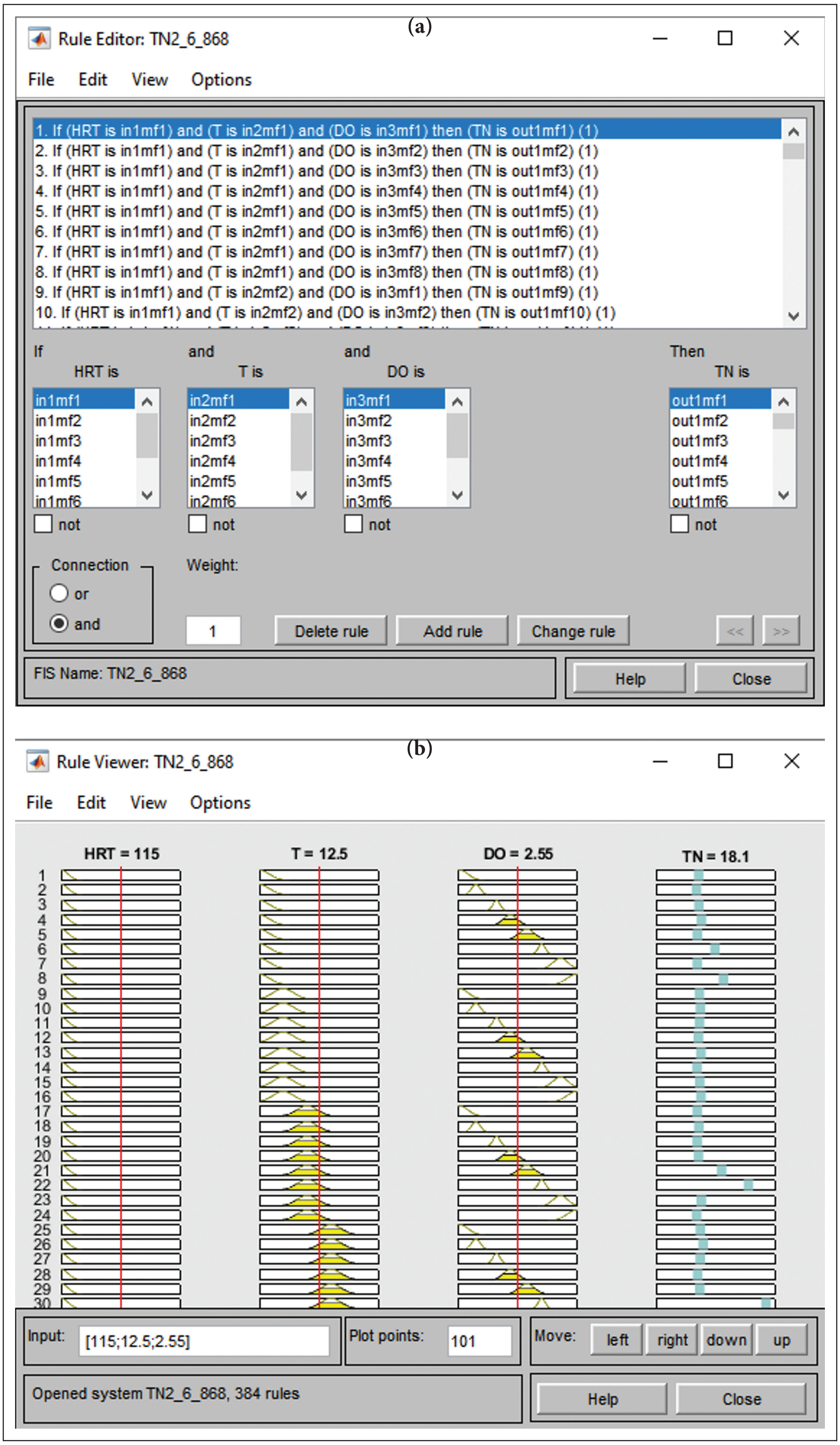

Figure 6. **(a)** Rule editor of Matlab fuzzy logic toolbox **(b)**Rule viewer screen to obtain defuzzified.

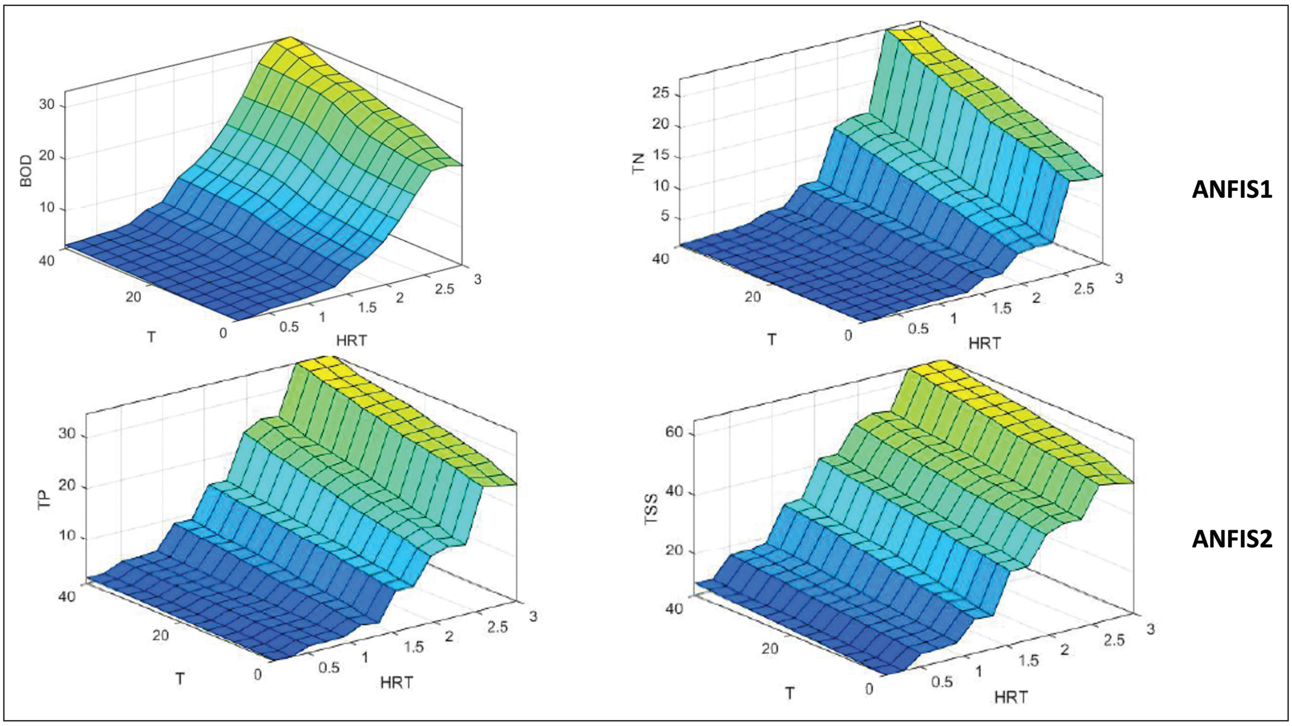

Figure 7. 3D response surface graph.

ise and associated parameters were then trimmed. After obtaining the premise parameter, membership functions for the variables were drawn.

Following the training of the model, inference was done using fuzzy language rules (Fig. 6a). After the network had been trained, those rules were obtained. In terms of comparing output values to input values, several additional heuristic criteria were also introduced. Defuzzified findings and graphical outputs can also be generated. (Fig. 7) shows an example of a Surface Viewer screen generated by the Fuzzy Logic Toolbox. Variable outcomes can be plotted and compared in two or three dimensions. According to the mass center of variables, (Fig. 6b) displays the outcomes of applied rules and their related outputs. Defuzzified values for output variables can be determined manually using the interface by changing input values. The Rule Viewer can produce a variety of output values depending on the input data. Using the interface to acquire defuzzified output values for all of the genuine input values is not flexible. As a result, a program using Matlab codes is built to drive defuzzified output outcomes in line with real-world input values.

RESULTS

The influence of the ANFIS model inputs (temperature, dissolved oxygen, and hydraulic retention time) on the model outputs is also shown in Figure 7 (BOD, TN, TP and TSS).

The ANFIS 1 model, for example, indicates that raising the temperature and lengthening the hydraulic retention time improves the efficiency of pollutant removal in wastewater.

All R-square and RMSE values for the removal efficiency of BOD, TN, TP and TSS are also shown in Table 4. When training, R value was 0.9782 using ANFIS but when validating, R value was 0.9888 using ANFIS.

When training and validating, the RMSE values for ANFIS2 was 0.28 for BOD and 0.0266 using ANFIS was lower than that of 1.7289 and 1.6172 using ANN. The RMSE value of 0.0318 using ANFIS was also lower than that of 1.7398 using ANN when predicting for TN. Figure 8 show the training and predicting results using ANFIS and APPDESIGNER model.

The architecture of ANFIS combines ANN and fuzzy logic, as well as linguistic expressions of MFs and if–then rules, to overcome the limitations of traditional neural networks, such as the risk of becoming trapped in a local minimum and model architecture selection, and to improve predicting performance. As a result, ANFIS is an excellent alternative for simulating wastewater treatment performance. Furthermore, ANN is a black box in nature, with difficult to interpret links between inputs and outputs, whereas ANFIS is clear, with simple to understand and interpret if–then rules. The ANFIS model's prediction performance in the wastewater treatment plant was excellent, and the ANFIS model may be used to estimate the efficiency of eliminating contaminants

Table 4. Determination of the appropriate ANFIS, APPDESIGNER and ANN models

System number	RMSE				R-square value(APPDESIGNER-ANFIS)							
					BOD		TN		TP		TSS	
	BOD	TN	TP	TSS	Training	Testing	Training	Testing	Training	Testing	Training	Testing
ANFIS1	1.3838	0.0995	0.2020	0.3414	0.9782	0.9888	0.9998	0.9999	0.9995	0.9999	0.9996	0.9996
ANN1	1.0476	0.9313	1.0402	2.1390								
ANFIS2	0.2800	0.0266	0.0318	0.1009	0.9992	0.9995	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999
ANN2	1.7289	1.6172	1.7398	2.8112								
ANFIS3	1.2242	0.3460	0.4186	0.6890	0.9968	0.9992	0.9995	0.9998	0.998	0.9967	0.9984	0.9998
ANN3	3.1565	2.3511	1.4402	2.9541								
ANFIS4	1.2582	1.1756	1.1975	1.8257	0.9944	0.9957	0.9935	0.9828	0.9837	0.9906	0.9886	0.9721
ANN4	2.8542	2.3733	1.7433	2.8592								
ANFIS5	1.4918	0.1276	0.1784	0.9143	0.9925	0.9911	0.9998	0.9992	0.9996	0.9984	0.9898	0.9907
ANN5	0.9486	0.5106	0.6192	0.6485								
ANFIS6	2.4545	0.4452	0.1838	0.1289	0.9777	0.972	0.9967	0.9978	0.9996	0.9991	0.9998	0.9995
ANN6	2.2790	1.2215	1.7855	1.4524								
ANFIS7	1.5691	1.3102	0.4659	0.1036	0.9947	0.9973	0.9948	0.996	0.9979	0.998	0.9999	0.9999
ANN7	2.4422	2.0268	1.2311	0.6645								
ANFIS8	0.9822	0.8183	1.0491	0.0650	0.9979	0.9977	0.9901	0.9854	0.9879	0.9873	0.9999	0.9999
ANN8	3.5613	1.3684	2.0934	0.4360								
ANFIS9	1.9230	0.1842	0.6866	0.0326	0.9919	0.9899	0.9995	0.9994	0.9948	0.9953	0.9999	0.9999
ANN9	3.0028	1.1767	1.8458	0.3803								
ANFIS10	0.8467	0.4560	0.1174	0.0523	0.9984	0.998	0.9991	0.9968	0.9998	0.9998	0.9999	0.9999
ANN10	0.1673	0.1656	0.1835	0.0722								
ANFIS11	1.3892	1.3254	0.8686	0.1254	0.996	0.994	0.9942	0.9926	0.9943	0.9947	0.9997	0.9995
ANN11	3.9526	3.5289	2.5361	1.0930								

from wastewater. As a result, based on the artificial intelligence model, it is possible to build physical and biological treatment units in wastewater treatment plants, reducing the high costs and time necessary for wastewater treatment plant design.

CONCLUSIONS

Eleven models based on adaptive neuro-fuzzy inference system (ANFIS) were constructed in this research to predict biological oxygen demand (BOD), total nitrogen (TN), total phosphorous (TP), and total suspended solids (TSS) removal efficiency for a primary and biological wastewater treatment process. The developed models were trained and tested using data from the APPDESIGNER Matlab model for BOD, TN, TP, and TSS. For comparison, the ANN was also used. The neural network models generated good estimations for the BOD, TN, TP, and TSS data sets, which span a wide range of data for training and testing. ANFIS was able to anticipate the variation in removal efficiency based on the findings. Minimum root means square errors (RMSEs) of 0.1673, 0.0266, 0.0318, and 0.0523 were also attained for BOD, TN, TP, and TSS, respectively. For the BOD, TN, TP, and TSS data sets, which span a wide range of data for training and testing, the neural network models generated good estimations. Overall, the results showed that the simulated removal efficiency of BOD, TN, TP, and TSS closely matched observed concentrations, as seen by the low RMSE and very high R values. Given the high level of complexity in the wastewater treatment process, the significant amount of variable information dispersed over the dataset, and the wide concentration ranges, ANFIS models' excellent prediction results for both effluent parameters are particularly relevant. As a result, the ANFIS modelling approach could serve as a generic foundation for modelling different treatment procedures. Furthermore, the ANFIS modelling approach could be used to anticipate and control the performance of treatment processes in treatment plants.

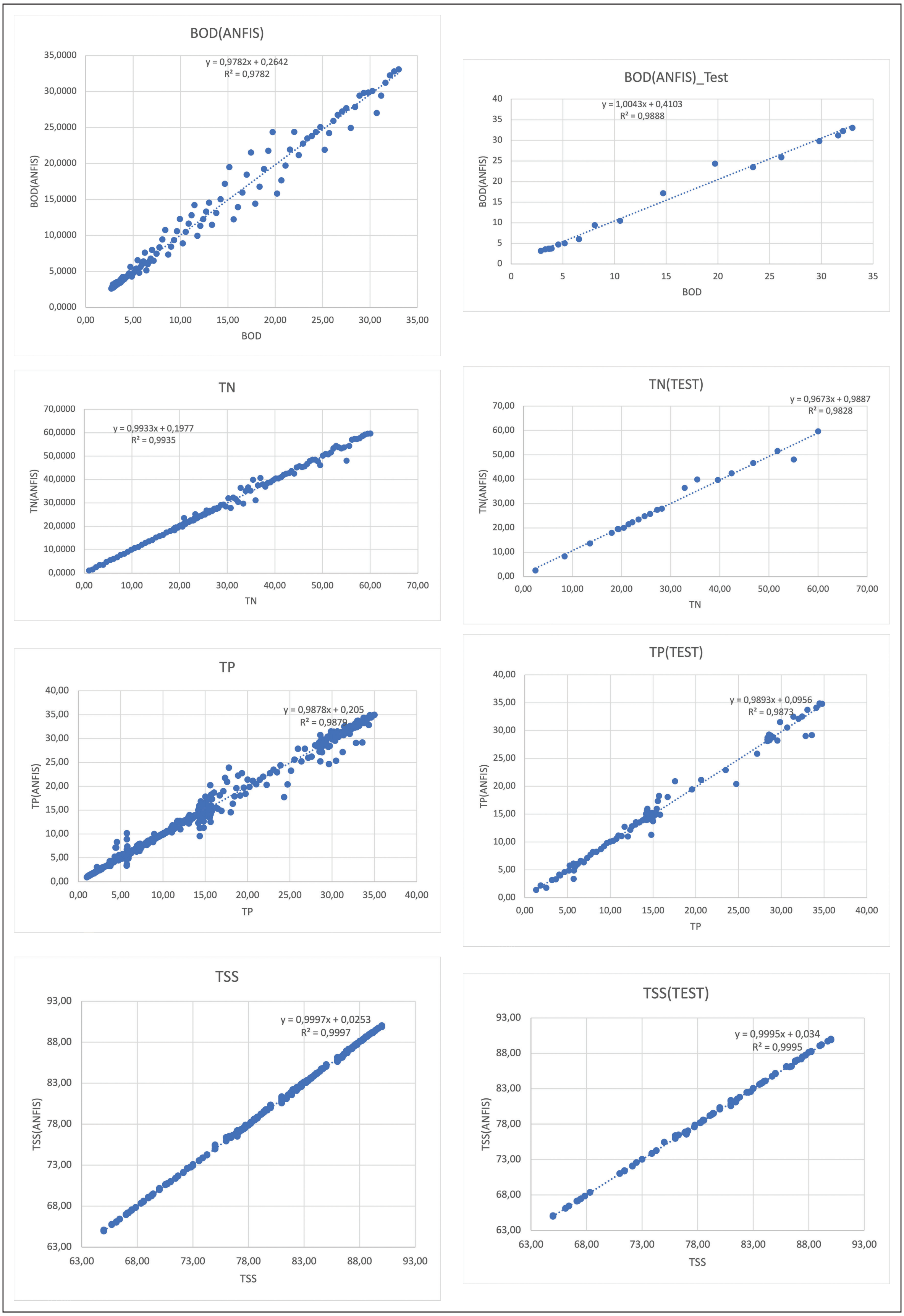

Figure 8. Prediction results of BOD, TN, TP and TSS for ANFIS model.

The proposed ANFIS outperformed Artificial neural network (ANN) in terms of performance and generalization ability. The RMSE and R^2 values for forecasting the removal efficiency of BOD, TN, TN, and TSS using ANFIS were considerably improved. Overall, the findings suggest that ANFS can be used to predict pollutant removal mechanisms in wastewater treatment systems.

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.

ETHICS

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

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Environmental Research & Technology

Review Article

Global commercial aviation policies in the context of the climate crisis and an analysis of these approaches from the perspective of Türkiye

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ABSTRACT

The climate crisis is becoming more visible day by day and is affecting the ecological system more and more. However, despite such a visible threat and its severe effects, efforts at the national and international levels are far from tackling the climate crisis. Especially with its rapid growth and ever-increasing emission rates, the commercial aviation sector remains inadequate in combating the climate crisis. This study discusses the global and Turkish commercial aviation sectors' struggles with the climate crisis. As a result, both international and domestic commercial aviation sectors follow an unrealistic attitude in the fight against the climate crisis, and there is still a long way to go.

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INTRODUCTION

Commercial airlines carrying billions of passengers employ millions of people and contribute to the world economy with their tourism and trade connections. It also contributes large sums to the global gross domestic product [1]. However, the commercial aviation sector negatively affects the environment. In terms of the climate crisis, the share of emissions of the commercial aviation sector is increasing day by day with its rapid growth potential compared to other transportation sectors. These emissions from airplanes are especially greenhouse gases such as carbon dioxide (CO_2), nitrogen oxide (NOx), and water vapor (H_2O) [2]. While the average impact rate of the aviation industry in the climate crisis is 3.5% today, this impact is expected to increase rapidly in the coming years [3].

Towards the end of the 20th century, the global climate crisis displaying environmental symptoms turned into an international security problem that requires international consensus and a joint struggle. The United Nations Framework Convention on Climate Change (UNFCCC, 1992) has drawn a comprehensive roadmap that allows global combat against climate change. However, this convention did not force the parties to reduce emissions, which is the major problem in the climate crisis. Later, the Kyoto Protocol was signed in 1997 and came into effect hardly in 2005 after the necessary conditions were met. However, just like the convention, the protocol also did not contain any enforcement for aviation emissions. Likewise, no explicit reference was made to aviation in the Paris Agreement signed in 2015 [4].

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European Union Emissions Trading System (EU ETS), the Carbon Offset and Reduction Scheme for International Aviation (CORSIA), and local Carbon/fuel tax restrictions are market-based chief practices to reduce aviation emissions against climate change. European Union implemented the ETS, the world's first emissions trading system [5], in 2005 to reduce aviation emissions in Europe. The second practice -Carbon Offset and Reduction Scheme for International Aviation- was launched by the International Civil Aviation Organization (ICAO) to combat aviation emissions globally [6, 7]. In addition, various countries locally enforce carbon/fuel tax to reduce emissions from aviation. When first established, the EU ETS structure did not include aviation emissions. However, because of the rapid increase in aviation emissions, the EU has published the 2008/101/EC Directive for this system to cover commercial aviation activities from 2012. At the outset, the EU ETS system covered all flights to and from the European Economic Area (EEA). But later, airlines operating outside the EEA were excluded from the scope of the EU ETS because of the global political backlash and concerns about complying with global practices to be carried out by ICAO [7].

Although the contribution of the commercial aviation sector to the global economy and ease of human life is quite remarkable, its negative effects on the climate crisis cannot be denied. In order to reduce these adverse effects, various improvements in aircraft efficiency have been made as well as market-based applications. Some operational applications such as efficient airplane routes or fuel-efficiency applications such as biological or hydrogen fuels are (or will be) in progress. However, the recovery rate is slower than the market demand, and plan end dates are later than the critical deadlines predicted for the climate disasters (Airbus stated that they would launch their first hydrogen-powered zero-emission commercial aircraft in 2035) [8]. Therefore, greenhouse gas emissions in the commercial aviation sector are growing and will continue to increase if no action is taken. In Türkiye, both the sectoral investments and the country's geographical location contributed to the development of the commercial aviation sector. While there were 162 active aircraft in 2003, the number amounted to 558 in 2021 in the Turkish airline sector. While the number of flights was 529,205 in 2003, it reached 1,461,577 in 2021. While 34,443,000 passengers were transported in 2003, Turkish aviation companies carried 128,565,706 passengers in 2021. In parallel with global commercial aviation, the rapidly growing Turkish commercial aviation sector also bears certain responsibilities for the climate crisis [9].

In today's world, as in the past, environmental problems are under the shadow of economic development. The main reason for the outbreak of the climate crisis is the greed for continuous growth and production. This strategy of the neoliberal system is particularly influential in the field of aviation. New aircraft models and technologies, the constant expansion of the commercial aviation sector, and intense intercontinental travels are the factors that support the uninterrupted growth of the sector. For this reason, although there are global initiatives against the climate crisis, the main reason underlying the climate change crisis is the ambition for more growth. Considering the nearly 30 years of efforts to combat the climate crisis, there has been no real success; greenhouse gas emissions and global temperatures have increased exponentially during this time. All policies that facilitate the operation of the system established by neoliberalism prevent the combat against the climate crisis [10, 11].

Within this theoretical framework, the current study discusses the fight against commercial aviation emissions, which will pose a significant problem in the future with its rapid growth -although it has a small proportion of global emissions today- and examines environmental practices from the perspective of global, regional, and Türkiye-based studies. This study aims to reveal whether the carbon footprints left behind by the commercial aviation industry, which provides fast, reliable, and comfortable transportation services, pose an exponentially increasing risk in terms of the climate crisis, whether the technology and efficiency improvements applied to the aircraft provide an overall success, whether the result of global and regional carbon reduction initiatives is rational, and whether these initiatives are efficient at the desired level. In addition, this study determines whether the environmental investments made in the rapidly growing Turkish commercial aviation sector comply with the international practices and whether any other different applications exist. The current study dealing with the climate crisis issue and global and Turkish commercial aviation together is unique. Especially in this period, when environmental concerns increase, examining a sector that overlooks these problems will guide future studies.

MATERIALS AND METHODS

The current study, using online databases, benefited from previous literature studies dealing with the world and Türkiye and thoroughly examined the practices against the climate crisis in the commercial aviation sector, and developed a classification covering market-based policies, efficiency and fuel policies, and Turkish commercial aviation's situation and practices. The study divided Market-based strategies into three -regional, global and national- and discussed EU ETS (regional), CORSIA (global), and jet fuel tax application in Japan (national). While the study evaluated efficiency applications and fuel policies in terms of technological improvements and biofuel, hydrogen, and electric aircraft initiatives, it collected the original data on the Turkish aviation sector from The General Directorate of Civil Aviation, Turkish Airlines, and Pegasus Airlines activity reports. The study handled all these data separately in the discussion section and evaluated the results and progressive projections from the climate crisis perspective.

RESULTS

Market-Based Policies

European Union Emissions Trading System

The UN set a negotiation environment considering the global concern about the climate crisis in 1992. In these negotiations, parties agreed on the UN Framework Convention on Climate Change. However, the paucity of this convention to eliminate the concerns about the climate change crisis paved the path to the adoption of the 1997 Kyoto Protocol bringing contracting countries the emission reduction-related obligations [12]. In this regard, the European Greenhouse Gas Emissions Trading Plan, initiated by the EU in 2005 [13, 14] to realize the 8% CO_2 reduction commitment in the Kyoto Protocol [15, 16], is the world's largest market-based and first multi-country trading scheme on greenhouse gas emissions [15, 17, 18]. The system applies to EU member states' large and fixed emitters of greenhouse gases in the energy and industrial sectors [18]. The first ETS phase (pilot phase) started in 2005 and ended in 2007. The second phase began in 2008, which coincided with the Kyoto Protocol, and ended in 2012. The third phase started in 2013 and ended in 2020 [13, 15, 18, 19]. As a cap-and-trade scheme, the EU ETS sets a peak emission amount and distributes allowances. Companies that do not declare the right amount of emissions face severe sanctions [13, 18]. The primary purpose of the EU ETS is to create an environment in which prices increase while allowances decrease [15].

The launch of the EU ETS in 2005 as a product of the flexible mechanisms of the Kyoto Protocol is considered a turning point in this field [12]. In the first stage in 2005, a significant carbon price formation (a price close to zero) could not be achieved. However, this period can be considered a learning or preparation phase for the EU ETS. Initially, the EU ETS included all CO_2 emissions but the commercial aviation sector [20]. During this period, the facilities in the EU ETS system were allowed to release 2.1 billion tons of CO_2 emissions per year. Companies included in the EU ETS system with emission permits have been trading emissions between each other since 2005. At the outset, the allowance price was around €8 but increased to €30 per tonne in June 2005. The prices, which fell to roughly €20 until the end of the year, decreased to €0 towards the end of 2007. In the second period covering 2008–2012, allowances were traded at €20 per ton [12, 19]. Unlike other periods, the third period of the EU ETS also included CO_2 emissions from the commercial aviation sector. The integration of the commercial aviation sector into the EU ETS has been evaluated as a significant step in reducing aviation-related emissions considering climate change. The EU ETS inclusion cost for the aviation companies varies according to airline companies' fuel consumption per flight, operational and efficiency practices, the number of passengers, and the amount of cargo. In other words, more efficient airlines will face lower costs than less efficient airlines. On 9 July 2008, the European Parliament released Directive 2008/101/EC on the integration of aviation into the EU ETS. According to this directive: a) As of 1 January 2012, all commercial airlines operating within the EU will join the EU ETS. In other words, third-country commercial airlines that land and depart from airports within the EU are also in this scope [13, 20, 21]. b) The EU ETS will be implemented within the borders of the EU, considering past CO_2 emissions of companies. In 2012, airline operators will receive a quota of 97% of their average greenhouse gas emissions between 2004 and 2006. This cap will be reduced to 95% annually from 2013 to 2020. c) The allowances will be distributed to the airline companies based on the ton-kilometers performed on the flights in the relevant year. d) The distribution of allowances will be non-discriminatory and applied to all member states. Of the allocations determined, 85% in 2012 and 82% between 2013 to 2020 will be free of charge, and the remaining part will be traded by auction. e) A special reserve of 3% will be allocated for airlines newly included in the EU ETS [13, 20–23].

ICAO and the International Air Transport Association (IATA) reacted strongly against the EU, which supports market-based emission reduction programs and seeks to cover all commercial aviation CO_2 emissions of all countries into the EU ETS system. Furthermore, many developed countries and airline companies, especially the United States (USA), objected to the EU ETS, claiming it was both an unfair practice and contrary to the Chicago Convention. At the same time, several airline companies, such as US-based aviation company Airlines for America, filed a lawsuit against the European Court of Justice for the EU ETS. Some countries, such as China, requested exemptions from the EU ETS [13]. However, the EU, which enacted the ETS, defended itself, claiming that the system neither violates the Chicago Convention nor requires permission to implement the application [24]. After this defense, the Airlines for America opened a case to the European Union Court of Justice for the cancellation of the civil aviation application of ETS. However, the decision rendered by the court did not satisfy the objecting party because the court ruled out that the EU ETS did not violate the sovereignty rights of states, the Chicago Convention, the Kyoto Protocol, and the US-EU Open Skies Agreement [25]. Then, some severe objections arose from the international community to the court decision. Reconsidering the situation, the European Commission issued a stay of execution (Stop-the-Clock), with the decision numbered 377/2013/EU [26], by approving the implementation of the ETS only for civil flights within EU and EEA member countries [27].

To Miyoshi [15], EU ETS has assessed a price for the CO_2 emissions of aviation. The estimated cost of emissions from aviation was around 20 billion Euros in 2020. This source provides large amounts of economic activity to the commercial aviation sector. However, the EU ETS poses an enormous challenge for airlines. For this reason, airline companies need to economically internalize aviation-related CO_2 costs. Airline companies included in the EU ETS receive allowances in proportion to CO_2 they emit. This allowance is a kind of working license for airline companies, and each company has its own specific amount of allocation. Each year in March, all aviation companies must accurately turn in their verified CO_2 emissions to the authorities from which they receive allotments. Companies can trade allowances between each other throughout the year [19].

Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA)

Although there was no specific statement regarding the control of the commercial aviation sector emissions in the Kyoto Protocol on the climate crisis (1997), the duty and responsibility of aviation emissions have been given to ICAO. ICAO is a United Nations specialized agency on international air navigation techniques and the planning and development of international air navigation. The Kyoto Protocol is an agreement that aims to combat global greenhouse gas emissions by imposing binding obligations on the party countries in the fight against the climate crisis since the UNFCCC has no sufficient regulations to combat the climate crisis. However, the protocol did not include the commercial aviation sector, which emits many emissions and requires precautions [4, 28]. As in the Kyoto Protocol, the Paris Agreement, which is active in the fight against the current climate crisis, does not explicitly include emissions from the commercial aviation sector [4].

Since then, ICAO has been working on policies to reduce global aviation emissions within the framework of its responsibility under the Kyoto Protocol (1997). However, as with other UN agencies, the efforts of ICAO have been hampered by the slow progress of negotiations. The parliamentary decisions signed by ICAO in 2010 (A37–19), 2013 (A38–18), and 2016 (A39–3) are significant steps that have been agreed upon. According to the ICAO A37–19 parliamentary decision taken in 2010, the 2020 Carbon Neutral Growth Target (CNG) was agreed upon and aimed to reduce the carbon footprint of global aviation [28]. Regarding this target, which was also agreed upon at the 38th Assembly meeting, ICAO decided to take a market-based measure to reduce global aviation emissions at the 39th Assembly meeting. The reason ICAO has turned to a market-based mitigation policy is that biofuel-like alternative fuels to current jet fuels do not seem to meet future carbon-neutral targets [4, 29].

At the 39th Assembly meeting of ICAO in 2016, the offset program called "Carbon Offsetting and Reduction Scheme for International Aviation" which is a market-based action was accepted and became official [29, 30]. The working principle of the carbon offset program is as follows: In CO_2 offset programs, the emitter party uses carbon credits for compliance. While these credits represent the right to emit tonnes of CO_2 equivalent (or CO_2e), they are also tradable certificates or emission permits. Adopted in the ICAO assembly, CORSIA has targeted to support carbon-neutral targets from 2020 [4]. According to Resolution A39–3 of the ICAO assembly, CORSIA functions as follows [29]:

a) First of all, CORSIA is a carbon offset program. Parties offset emissions by investing in carbon credits or CO_2 reduction projects in other countries [4, 28].
b) Airline companies can also meet the carbon offset requirement by using sustainable alternative fuels [29].
c) The CORSIA program basically covers international flights between participating states. Therefore, flights between non-participating states or between a state party and a non-party state are exempt from CORSIA [4, 29].
d) CORSIA consists of three phases: The pilot phase covering 2021 to 2023, Phase-1 covering 2024 to 2026, and Phase-2 covering 2027 and 2035 [4, 29–31].
e) Participation in the pilot phase and phase-1 of CORSIA is voluntary. As of 6 July 2021, the number of countries included in the voluntary CORSIA program is 104 [32].
f) In the second phase, which will begin in 2027 and continue until the end of 2035, CORSIA will be mandatory for all ICAO members except (1) Small emitters (airlines with less than 10,000 tons of CO_2 share), (2) Flights with aircraft with a Maximum Takeoff Mass (MTOM) of less than 5.7 tons, (3) Humanitarian/medical and firefighting operations, etc. [4, 30, 33].

Taxes on Jet Fuel

Emissions from the commercial aviation sector are increasing rapidly within the general transport sector. For this reason, it is essential to reduce aviation emissions. Many carbon pricing initiatives are carried out to save fuel used for aircraft jet engines and improve emissions. The tax on jet fuel is one such initiative. The tax on jet fuel is an effective practice to reduce the fossil fuels used by airline transportation and emissions. Implementing a tax on jet fuel may pass on savings in fossil fuel usage, and tax revenues can contribute to technological improvements to reduce carbon emissions [34]. More precisely, a fuel-based tax method effectively reduces emissions, as it burdens more costs to airline companies and more ticket fees to passengers [35]. Taxation on aviation is more applied to domestic flights because the Chicago Convention and ICAO do not support it in international flights [36]. In this context, charging a carbon tax on jet fuel to reduce emissions yielded impressive results in Japan. Therefore, the jet fuel tax applied on domestic routes in Japan to diminish civil aviation emissions covered all air transport vehicles, including helicopters [37]. In this application, fuel taxpayers are required to submit a declaration and also pay monthly taxes for the fuel purchased. The aviation fuel tax applied in Japan is an application that exempts international flights as per the Chicago Convention. The Japanese government transfers 1/13 of the revenue from the aviation fuel tax from the state treasury to the Airport Construction and Improvement Account through Social Infrastructure Improvement Special Accounts. The remaining 12/13 of the tax revenue is transferred to local governments to meet the needs of airports. The aviation fuel tax in Japan has been levied to improve aviation and airports rather than the environment. The aviation fuel tax imposed by Japan in the 1970s and 1980s proved to be a significant step forward. The tax collection has provided substantial developments in infrastructure and self-sufficiency in the Japanese aviation network. In other words, with this system, the aviation network can respond to its own needs autonomously [38]. Studies show that the aviation fuel tax applied in Japan has reduced CO_2 emissions [39]. On the other hand, after the tax cut between 2004 and 2013, fuel consumption increased by 246 million gallons in Japan, which caused 2.4 million metric tons of CO_2 emissions. For this reason, more countries adopting the fuel tax system implemented by Japan will yield more effective results [40]. Japan, which stands out with its environmental studies and efforts to reduce greenhouse gas emissions, is a significant role model for the countries offering cheap flights in its region [38].

EFFICIENCY AND FUEL POLICIES

As environmental demands increase, “Greenwashing” efforts in the commercial aviation industry are also doubling. This situation raises unrealistic technological change proposals for “greener” flights. This part of the study covers improvement efforts for civil aviation emissions. There are various initiatives of aircraft manufacturers and airline companies to reduce emissions in civil aviation. The current study discusses efficiency improvements, electric flights, hydrogen-powered flights, and biofuels among these initiatives [41–45].

Productivity Improvements

Aircraft efficiency refers to an aircraft's burnt fuel amount (and released emissions) to carry its payload (passenger or cargo) to a certain distance (for example, one kilometer). Efficiency improvements—i.e., reductions in fuel consumption rate—are achieved by making the aircraft design, engines and airline operations such as flight routes- more efficient and by increasing the number of passengers/cargos carried onboard [44, 46]. A common misconception about the commercial aviation industry is that airplanes are getting more efficient, and emission rates are falling with each passing year. There are even misleading statements announcing an 80% reduction in aviation emissions since the beginning of jet technology. Efficiency improvements reduce per capita emissions for each flight, but tax breaks, subsidies, and rising purchasing power double air traffic and CO_2 emissions every 15 years, far beyond the efficiency-related savings [41, 44, 47].

Electric Flights

Electric aircraft propulsion systems (propeller or fan blades) are driven by electric motors. In all-electric airplanes, these engines are powered by electrical energy supplied directly from batteries or hydrogen fuel cells. In hybrid-electric aircraft, these electric motors run in series or parallel with jet fuel combustion engines [44, 48, 49]. All-electric airplanes run on batteries. If these batteries are rechargeable with renewable power, then the operation of the aircraft can be called “zero emissions” [44, 48, 50, 51]. However, it has not yet become possible to decarbonize electricity production. In addition, batteries have significant social and environmental impacts because essential materials such as lithium and cobalt are extracted from the earth by mining, and other components are manufactured in factories. Therefore, even all-electric aircraft are not yet considered zero emissions. In addition, it is foreseen that this type of aircraft will not become electrified in the short or even medium-term, but only miniature and short-range aircraft may become electrified in the future. Besides, unlike an airplane fuel tank, where its poundage decreases during flight, the battery keeps its weight during the journey. These issues further affect the payload and range capability of the aircraft [44, 52].

Hydrogen-Powered Planes

There are plans and studies to use hydrogen instead of jet fuel as a power source for aircraft. Hydrogen can be burned in a jet engine or utilized for powering a fuel cell to generate electrical energy to turn a propeller [53]. While producing hydrogen from other energy sources, a significant amount of energy gets lost. The produced hydrogen is usually stored in liquid form at -253°C. Airbus worked on hydrogen planes in the 2000s, but they shelved the project in 2010 because they could not overcome some technical problems. In 2020, the company announced its plan to develop a new hydrogen-powered aircraft that could be operational by 2035. This plan includes four concept aircraft, of which the company will select one by 2025 [54].

The hydrogen plane does not meet the climate and environment targets set under the Paris Agreement in terms of time and quantity. Even if the program targets announced by Airbus in 2020 are achieved, it will be too late to meet the actual climate targets [44]. According to the United Nations Environment Program (UNEP), worldwide greenhouse gas emissions must be reduced by 55% by 2030 so that the global warming limit will not exceed 1.5°C as agreed in the Paris Agreement. When the design of the entire aircraft and the conversion of the fleet to hydrogen begins late, these targets will take too long to achieve [55].

Biofuels

Alternative jet fuels or Sustainable Aviation Fuels (SAF) are liquid hydrocarbon fuels used in existing aircraft instead of kerosene, produced from fossil fuels [42]. The leading motive of the SAF investments in the commercial aviation industry is the expectation that biofuels will reduce aviation emissions by substituting or being blended with conventional fossil fuels [56, 57]. Biofuel production uses various sources of biomass (renewable organic material from plants and animals) as inputs [58]. While first-generation biofuels use agricultural products, second-generation biofuels use industrial, agricultural, or domestic wastes such as waste cooking oil, shortening, corn husks, forest resources, or food waste [59, 60]. The sustainability and availability of biomass severely constrain biofuel use [61].

It is often claimed that aviation will only use second-generation biofuels obtained from "waste" sources, thus avoiding direct or indirect impact on sustainability [62]. However, no one can ignore the industry using first-generation biofuels from crops or even whole trees. There are plans for a massive SAF refinery in Paraguay to process soybeans as a feedstock [44] under the permission of CORSIA, the only internationally accepted aviation policy valid until 2035 [63]. The strong political emphasis particularly placed on the presumed benefits of SAF causes increased soy or palm oil usage in fuel production, posing a risk of deforestation [44].

Seber et al. [64] argued that biofuels would reduce aviation emissions in comparison with fossil fuels, while Ganguly et al. [65] claimed that SAF could reduce aviation-related emissions only by up to 78% during its entire life cycle. Even if the SAFs usages are widespread, aviation biofuels will still cost much more than kerosene [44]. Biofuel from waste oil is the most cost-competitive but still doubles the cost [66]. These rising costs will undermine the industry expansion plans [67]. The only way the aviation industry can continue to grow using larger quantities of alternative fuels is to provide alternative fuel producers (such as biofuel makers) with massive government subsidies [44]. The 2016 report by ICAO has documented that it is necessary to build 328 new large bio-refineries each year by 2035 with an average annual cost of $29 billion to $115 billion to produce enough biofuels for international use [68]. This situation suggests that aviation biofuels can not be sustainable, and future investments will be severely risky for public finances [44].

TURKISH COMMERCIAL AVIATION AND INITIATIVES FOR EMISSION REDUCTION

Air transportation, which stands out among other modes of transportation because of its speed, reliability, and comfort, is rapidly increasing its share in the sector. Transportation is the action of transporting someone or something from one point to another. Airline transportation is significant for a country's economy and people's welfare. The statistical studies conducted on the transportation sector show that aviation contributes to preparing the infrastructure of globalization in cultural, economic, and political activities. Civil air transportation which is fast, comfortable, and safe, has been the highest growing transportation type in the 20th century [69].

The commercial aviation industry has entered a rapid growth process with technological developments since the beginning of the 20th century. Especially in the 1970s, the liberalization movements in the commercial aviation sector of the USA went beyond this country's borders and affected many countries. With the global hegemony of neoliberalism, the beginning of a new era in the commercial aviation sector has also influenced the domestic market of Türkiye. The 1983 Turkish Civil Aviation Law No. 2920 has allowed private airline companies to engage in civil aviation activities. This period was marked by the liberalization policy aimed at reducing the role of the state in the markets. While tourism has come to the fore in the liberalization movement, the most critical role in the efforts to revive tourism has fallen to the aviation sector. Meanwhile, the civil aviation sector has gained a broader movement opportunity with liberalization. The Turkish Civil Aviation Law No. 2920 was a significant step in this direction, and it paved the way for the sector on domestic and international routes [70].

The Turkish commercial aviation sector has increased more than the international growth rates. The rapid development, especially over the last 17 years, has made regional and global contributions to the aviation sector in Türkiye. Various reports have supported that the growth in Türkiye's commercial aviation sector will steadily continue [71–73].

According to the General Directorate of Civil Aviation [69], special attention has been paid to the development of civil aviation within the global integration framework for Türkiye's economic and social development. Furthermore, the diversity stemming from Türkiye's geographical location has contributed to developing the commercial aviation industry and becoming one of the fastest-growing countries. The rapidly growing Turkish civil aviation has established a flight network connected to almost any point worldwide. According to the Airports Council International (ACI) 2019 Airport Connectivity Report, Türkiye ranked 5th among European countries with the indirect, direct, airport, and central connection numbers in 2019 by increasing its direct connections by 2.5%, indirect connections by 13.7%, airport connections by 8.1%, and central connections by 18.1%. In the period between 2009 to 2019, it has become the most developing country with its direct and indirect civil aviation connections in "new flight lines" and "new flight destinations." According to the data of the last ten years, it has increased its direct connections by 159.9%, indirect connections by 144.5%, airport connections by 151.5%, and central connections by 386% [74].

The Turkish commercial aviation sector is rapidly growing in Europe and the world, and thus its climate-change-related activities are of significance. The General Directorate of Civil Aviation 2012–2021 annual reports show that operational practices aimed at improving efficiency, in general, come to the fore rather than market-oriented approaches. For example, the Green Airport Project implemented in the 2013 Annual Report of the General Directorate of Civil Aviation awards airports the title of Green Airport and particular discounts on some fees when they meet the necessary conditions. This practice would significantly contribute to disseminating environmentally friendly practices in the sector [75]. Another example was the Flexible Use of Airspace Project, which was deliberated in the 2016 Activity Report of the General Directorate of Civil Aviation. This project aimed to shorten flight paths, instantly establish additional flight paths, save fuel and time, reduce maintenance costs, reduce the impact of global warming and environmental pollution and increase efficiency in the commercial aviation sector [76].

In its 2020 Corporate Sustainability Report, Pegasus Airlines, a private Turkish commercial aviation company, has announced that its operations are within the market-based CORSIA and EU ETS framework. In this context, while they record and report emissions as a requirement of being included in the CORSIA, they fulfill the obligations of the EU ETS for the few flights performed within the EU Economic Area. In addition, they carry out operational activities that increase efficiency and reduce fuel and emissions [77].

Turkish Airlines, the locomotive of the Turkish commercial aviation industry with its largest flight network and fleet, positively increased its efficiency (fuel-saving, operational activities, etc.) initiatives to combat the climate crisis and environmental sensitivities compared to ten years ago. Turkish Airlines works in close cooperation with navigation service providers, especially on domestic and international flights, to improve air traffic management for efficiency [78]. Like Pegasus Airlines, Turkish Airlines is a member of CORSIA and is subject to EU ETS for flights within the European Economic Area [79]. As reported in Turkish Airlines 2018 Sustainability Report, Turkish Airlines carries out an efficiency project to produce bio-fuel (Micro-Jet) from micro-algae in cooperation with Boğaziçi University [80]. In addition, the use of sustainable aviation fuel in the flight Istanbul (IST) - Paris (CDG) on 02 February 2022 is an exceptional practice. Turkish Airlines also stated that sustainable aviation fuel usage would be a regular-weekly practice. The Turkish Airlines flight with sustainable aviation fuel between Istanbul Airport to Paris Charles de Gaulle Airport was also featured on TRT News, Milliyet News, and Turkish Airlines Blog webpages [81–83].

DISCUSSION

Although the initiatives in aviation from the past to the present were individually productive, they were not efficient collectively. Because while making a single aircraft or fleet efficient contributes to fuel savings and natural emission reduction, an increasing number of passengers, flight points, cargo, and aircraft wipes out all efficiency improvements. Because the growth of the commercial aviation industry is demand-driven, reducing the volume of travel today is the most effective way to limit the impact of industry on the climate. For this reason, it would be more reasonable to evaluate environmental sensitivities by looking at aviation practices from a broad framework and building the future rather than saving the day. Therefore, the current study discusses whether the initiatives from past to present regarding the improvement and market-based developments in the commercial aviation sector have positively developed global and domestic aviation in terms of climate change. So, the discussion part is discussed under three headings for better understanding.

Market-Based Applications

First, EU ETS covers CO_2 emissions from flights within the EEA, while CORSIA covers international flights. The EU ETS, which has been in force for nearly 17 years, has considerably decarbonized various sectors of the European Union. It has accelerated the transition from coal to natural gas and renewable energy sources in the energy industry. However, the EU ETS could not achieve the same success in carbon emissions in other sectors other than energy. In particular, the fact that it only includes flights within the EEA shows that it deals with the tip of the iceberg only. Besides, granting too many free allowances has led to more supply, thus distracting the EU ETS from its climate crisis objectives [84]. Anger & Köhler [85] has stated that the EU ETS should reduce aviation carbon emissions and encourage new technologies for the future because aviation emissions have covered a small share of the EU ETS, and the EU ETS determined carbon pricing lower than expectations after 2012.

As for CORSIA, which is more important in terms of international aviation, Atmosfair [86] states that even the name of CORSIA is misleading. Although the letter R in the name denotes the word reduction, the program did not set any emission reduction targets about emissions reduction. Mandatory measures to reduce emissions are insufficient, especially for airlines. Besides, if ICAO honestly tried to reduce aviation emissions, it wouldn't have bothered with a makeover like declaring CORSIA, 19 years after the Kyoto Protocol. Another criticism is toward the requirement that airlines balance their emissions within the framework of carbon-neutral targets starting from 2020. However, avoiding the impact of carbon dioxide formation alone will not make the commercial aviation industry carbon neutral. This is because the contrails and the gases that cause ozone formation released into the atmosphere by the aircraft also harm global warming. Therefore, this structure is not expected to take an effective measure in the fight against the climate crisis [86]. Magdalena Heuwieser, the cofounder of the Stay Grounded activist group, states that CORSIA is irreparably-damaged wreckage because it diverts resources and the policy-making trajectory away from real solutions to climate change; and its existence is worse than doing nothing [87]. Waiting whether CORSIA will be fruitful will result in "too little, too late" in tackling the climate crisis. After 2020, the commercial aviation sector cannot reduce global aviation emissions and achieve “carbon neutral” targets even with the comprehensive implementation of CORSIA and initiatives such as sustainable aviation fuels [6]. The fact that 1% of the world population who use the airlines harm climate than other people of 99% who never use airlines reflects a large inequality among people. Because this 1% of the world population is the least affected, despite their severe influence on climate change. The following question occurs for CORSIA when considering all these criticisms: If flying conditions are not proper environmentally yet, why do more and more people continue to board the planes? [87].

Another topic discussed to reduce aviation emissions is the taxation system. This application is a matter to which the Chicago Convention and ICAO show massive opposition. Therefore, while international flights remain tax-free, local taxation on aviation emissions applies in some countries that take the climate crisis seriously and have strong willpower to make an effort. Governments need to stop subsidizing airline practices, especially given the rapid increase in emissions from the commercial aviation sector. For this purpose, it will be more effective for governments to reflect the cost of all environmental effects arising from aviation to airlines and introduce quotas to reduce fuel use gradually. The fuel tax implemented by Japan has been a significant step in reducing the commercial aviation sector emissions. If a fuel/carbon tax application is implemented globally, it will yield more effective results than other market-based applications. Because the primary objective in the commercial aviation sector, as in other sectors, is profit. Therefore, the emission tax imposed on the commercial aviation sector will naturally drop the profits, slow the growth, and thus decrease emissions. Besides, it would be beneficial, especially in terms of the individual carbon footprints, to impose additional taxes on passengers who use airlines frequently [87].

Efficiency and Fuel Policies

Improvements to efficiency in the commercial aviation sector are largely pseudo efforts to gloss over and ignore reality. When we look at all "so-called" improvements made from past to present, it is clear that they did not affect the total emission rate in the commercial aviation sector, and the emissions steadily increased. On the other hand, depending on increasing aircraft efficiency, some airlines cause a decreasing efficiency per seat by simultaneously increasing the number of business seats or first-class seats, which are more profitable. Furthermore, using private and business jets is also advancing worldwide. These jets are 5 to 14 times more pollutants than commercial aircraft because of their lower number of passengers and higher flight speeds. Despite the decline in air traffic due to COVID-19, the industry is still expected to grow at around 4% annually from 2024 to 2038. For this reason, despite the lowering aviation emissions per capita, the total emission rate is increasing rapidly, negatively affecting the climate system. Therefore, efficiency gains alone are not enough to decarbonize the industry; air traffic should be limited by regulations [44].

Large electric aircraft will not operate in the commercial aviation sector soon because the weight of the batteries still poses an obstacle and disadvantage [57]. Unless a radical and yet uninvented paradigm shift emerges in energy storage today, hydrocarbon fuels will continue to be used in the future [44]. The Net Zero by 2050 report, published by the International Energy Agency (IEA) in 2021, has predicted that commercial battery-powered electric and hydrogen aircraft will be adopted from 2035 but that these aircraft will account for just less than 2% of the global aviation energy consumption in 2050 [88].

Along with many technically incomprehensible aspects, hydrogen flight also has security problems [89]. Accordingly, Airbus stated that hydrogen flight could not be widespread before 2050, and airplanes with only 50 to 100 seats might fly in the 2030s [90]. Eventually, since these aircraft will hold a minor market share, this situation will not reduce global emissions. Furthermore, getting these hydrogen aircraft operational will cause a need for rebuilding many infrastructure elements, such as fuel supply and airport infrastructure design [91]. Hence, the future prevalence and efficiency of hydrogen flight are still uncertain [44].

Innovative technologies are offering alternatives to fossil-based jet fuels, but each option faces challenges, such as cost, investment, market formation, political support, and consumer acceptance. Although forestry residues are the potential raw material for SAF production, high costs, lack of production facilities, limited government subsidies, concerns about the sustainability and competitiveness of raw materials, and customer willingness to pay less are decisive factors for their usage [92]. The aerospace industry has promised a scale-up of biofuel use for more than a decade, but this promise is still unfulfilled. For example, in total fuel consumption, the biofuel aim of IATA in its 2015 report was 10% by 2020 [93], and the Air Transport Action Group (ATAG) aimed at 6% by 2020 [94]. However, at the end of the day, biological fuel uses by 2021 were at a negligible level (less than 1%) compared to the rate of jet fuels [67].

Turkish Commercial Aviation

At present, the Turkish commercial aviation sector does not integrate with the EU ETS, one of the market-based applications, but pays their fixed fees when performing flights within the EEA. However, the sector has participated in the CORSIA system, which is more comprehensive, and agreed to fulfill its obligations regarding future applications. As seen in the activity reports of the General Directorate of Civil Aviation, Turkish Airlines, and Pegasus Airlines, the sector institutions carry out more efficiency-oriented studies to combat the climate change factors. For example, Turkish Airlines has started experiments on biofuels in cooperation with Boğaziçi University, and it performed the first biofuel flight from Istanbul to Paris in February 2022, also as stated in TRT News, Milliyet News ve Turkish Airlines Blogs. The Turkish commercial aviation sector aims to prevent the aviation-related climate crisis, but the measures are far from the existing reality. There is no market-based carbon/fuel tax application in Türkiye. It is anticipated that the Turkish aviation industry will continue to grow under global CORSIA measures, which are far from solving high emission releases in the commercial aviation industry. As for the fuel studies, despite the Turkish Airlines reports declaring ongoing Biofuel studies, it is almost impossible to carry out a cost-effective agricultural production for biofuel use in Türkiye while the system has not proven itself on a global scale.

Turkish Airlines has stated sustainable aviation fuel usage in flights, but it has not specified the most vital information, namely, the amount of sustainable fuel planned. For this reason, it should be well understood that announcing sustainable aviation fuel uses in flights does not mean that we have effectively eliminated environmental impacts. Considering the increasing applications of "Greenwashing" [43], especially in the commercial aviation sector, it is significant to know how much biofuel was used in the Turkish Airlines flight or how much of it was blended with the existing jet fuel, and this information was not available on news sites (TRT News, Milliyet News, and Turkish Airlines Blog). Using biofuel during just one flight does not mean becoming successful in the struggle against the climate crisis, as many global airlines already operate flights through a blend of biofuel and jet fuel. However, at this point, it has not been possible to free the commercial aviation industry from fossil fuels.

As a result, the measures in the commercial aviation sector, whose impact on the climate crisis is increasing rapidly, are implicit methods of continuing to grow rather than combating this crisis. For this reason, a sector that does not give up on growth will not care about environmental concerns, and the findings indicate this. The ever-increasing fleets, passenger numbers, fuel consumption, and emissions are profound indicators of this.

CONCLUSION

As the first Emissions Trading System, EU ETS has been operating since 2005. It has covered the aviation sector since 2012, but it has a narrow scope. Over these years, the EU ETS has reached no significant success in reducing emissions stimulating climate change. The existing emissions have not decreased in these years; on the contrary, they have increased. CORSIA, on the other hand, is far from reducing aviation emissions, although it has, with great hope and a big advertisement, claimed that it would neutralize aviation emissions. In terms of aviation, carbon/fuel tax offers a more effective solution than other applications. Of course, considering that the best aviation is the one generating no emissions, even if this solution is insufficient, it is the one that will contribute to solutions more than other applications. For this reason, local carbon/fuel tax practices should be allowed to spread globally as soon as possible.

It should be recalled that the emissions of each extra flight will erase all gains of the efficient activities like flying over the shortest possible route, flying at the most efficient altitude, maximizing the airplane's load factor, using minimal fuel enough to complete the flight safely, minimizing non-profitable flights, and keeping the hull and engine clean. As everybody knows, as long as there is no extraordinary situation in the commercial aviation sector, the demand will continue to increase.

As the world population increases, the use of natural resources will synchronously increase at the same rate, even many times more compared to the past. Hence, considering the global danger of insufficient agriculture and starvation, using agricultural products as aircraft biofuel seems to be an unlikely solution. For this reason, the commercial aviation sector approaches, which are practically based on dreams and greenwashing, should review its practices on the climate crisis and be more effective and solution-oriented. The most alternative solution for the commercial aviation industry is to cancel short-haul flights immediately and adopt rail systems supported by renewable energy sources. Thus, a more effective step will be taken for the future of the world and humanity.

The Turkish commercial aviation industry has undergone a rapid growth process since the 2000s. New international and domestic routes and flight destinations have been the booster of this growth. The sector has topped in air transportation regionally and globally, using modern airway technologies and fleets. The growth trend in the Turkish commercial aviation sector has coincided with a period when people worldwide have started to voice environmental problems more. The Turkish aviation sector, integrated into the global aviation system, has also taken precautions against the environmental sensitivity within the available possibilities. However, its continuous growth and domestic expansion targets require the Turkish commercial aviation sector to take urgent action against the climate crisis. But, it is unrealistic to expect some positive outcomes for local purposes by following the same already-tried global practices, introducing no additional innovation, and appearing environmentally sensitive.

In conclusion, people either will make this world livable for today and the next generations or cause it to become more unlivable for their extreme pleasure and needs. This election will determine the course of aviation emissions and even the fight against the global climate crisis. Because, as stated in the Climate Change 2022: Climate Change Mitigation Report by Intergovernmental Panel on Climate Change [95], global warming will continue towards the end of the century unless solution-oriented political steps are taken and Existing Nationally Determined Contributions (NDCs) are updated. In this case, global warming will go up towards 2.1–3.4°C, exceeding the 1.5°C-threshold. The commercial aviation industry has the most destructive role in the world climate crisis. Instead of supporting huge polluters such as airlines and airports, spending the public's taxes on more climate-friendly and efficient alternatives, such as rail systems in Türkiye and worldwide, will be a more sustainable approach.

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.

ETHICS

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

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Research Article

Assessment of the highway logistics on carbon footprint

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ABSTRACT

Developing the quality of the types of greenhouse gasses used within the global environment and reducing carbon emissions are recognized as the main of current logistic changes policies. The paper aims to evaluate the contribution of the impact of highway logistics activity, one of the most important causes of carbon dioxide emissions, on the carbon footprint of the Southern Central Anatolian provinces. In this context, multiple regression analyses were conducted in three locations in the Southern Central Anatolian (Antalya, Kayseri, Konya) involving a total of 12 monthly highway logistics activities and carbon emissions. Before analysis, summarized the status of all logistic activities in the study area and collected data related to carbon emission in these regions. However, the coupling relationship between carbon emissions and logistic conditions in regions was calculated by the regression model. The carbon footprint linked to logistics, for Antalya was 87% (R=0.87), for Kayseri was 94% (R=0.94), and for Konya was 63% (R=0.63). It can be seen that, in the multiple regression analysis, Kayseri has a higher carbon footprint than Antalya and Konya when an estimation of the quantile was carbon footprint. The main academic contribution of this study brings a new perspective to the future assessment of environmental policies and prepares a quantitative principle for the implementation of future carbon footprint policies.

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INTRODUCTION

With the improvement of global economics, the nugatory environmental conditions by increased industrial activities are accelerating significantly. The logistics industry has also rapidly developed in the last few years with the serial growth of the global economy [1]. As the main activities of the logistics industry, transportation, warehousing, and handling act for the energy consumption cause intense carbon emissions. Highway logistics is not only important to economic growth, but it also causes an increase in carbon emits. Therefore, decreasing greenhouse gas emissions (especially carbon-derived gases) from logistic activities was deliberated to be an impressive approach to reducing the side-effects of carbon footprint [2–4].

A carbon footprint is the greenhouse gas emissions caused which are explained as carbon dioxide or equivalent gases emitted. A carbon footprint resulting from carbon emission consists of gases—primarily carbon dioxide and monox-

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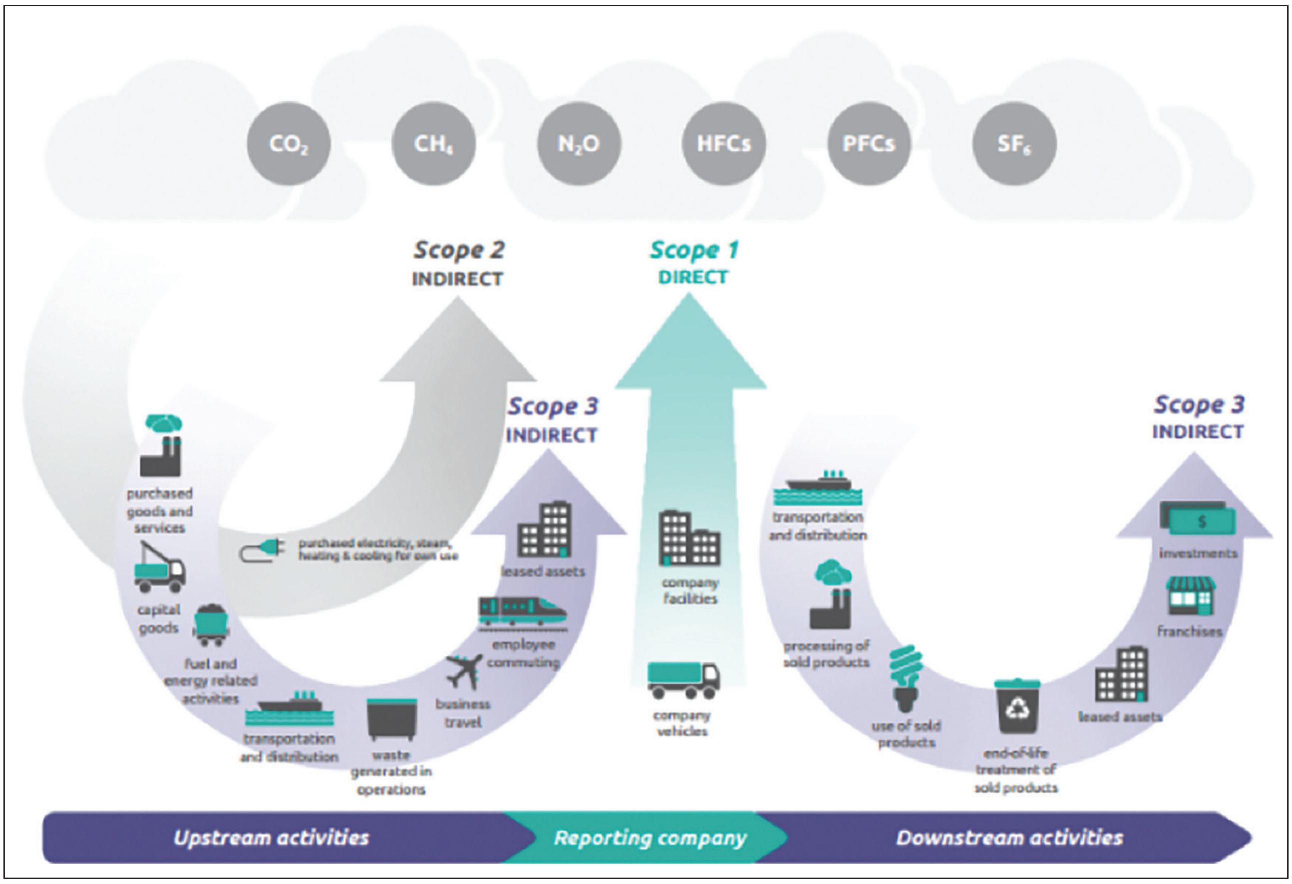

Figure 1. Greenhouse Gas – Protocol Standard [6].

ide—dismissed into the atmosphere by specific humans' actions. Carbon emits are caused by the burning of fossil fuels in the surrounding. Any action to accomplish a human need causes the emissions of carbon. Carbon emissions are recognized as one of the world's largest air-polluting and continue to expand ratio [5]. In order to deal with the negative impacts of carbon footprint, standardization organizations around the world have issued ISO 14064 (standard of greenhouse gas) policies to curb the harm to human health and the destruction of natural resources caused by it. Overview on Scopes according to the Greenhouse Gas-Protocol Standard is given Figure 1.

Figure 1 reporting on scopes 1, 2, and 3 involves collecting data about greenhouse gas output from various sources and compiling it according to the standards of the ISO 14064 equivalent international standard. The ISO 14064 standard provides businesses with data to quantify, report, and verify greenhouse gas emissions. The ISO 14064 standard is included in the ISO 14000 International Standard for environmental management [6].

As an important transport way of the global economy, highway logistics has more and more significance in serving other industries. To evaluate the carbon footprint highway's length is widely used, represented by the carbon emission of highway logistics tools. Thus, the carbon footprint can be regarded as an indicator of highway logistics, and it involves the extent of carbon emission in the air pollution [7].

Environmental and economic impacts of carbon footprint were various and reflected in logistic aspects. In this context, this study attempted to suggest a new framework to evaluate the double-faced efficacy and rate of carbon footprint policies from the perspectives of both environmental and economic. This study aimed to contribution the impact of highway logistics activity, one of the most important causes of carbon dioxide emissions, on the carbon footprint of the Southern Central Anatolian provinces.

After the introduction, chapter 2 first presented the carbon footprint of highway logistics. Nevertheless, after a literature review on this subject, in chapter 3 the method is explained. Chapter 4 presents the study carried out to findings. The impact of the information gathered in the study is discussed, and future studies suggested were discussed in the result chapter.

LITERATURE REVIEW

Carbon footprint is one of the essential standards for all kinds of transport because of its essential role in harming the environment of the companies as well as the preserva-

Table 1. Literature review

Author	Year	Definition
Krstanoski [11]	2006	Estimation of CO_2 emissions from the road transport sector over a 25-year period. He developed a model for the impact of CO_2 gas emissions. As a result of the study, it was estimated that CO_2 emissions will decrease by 32% by 2030 if use implementation of the foreseen measures.
Yang et al. [12]	2009	They investigated how to reduce greenhouse gas emissions from transport by 80% by the 2050 year in California. They focused on three issues based on sub-sectors. It has been stated that there are serious difficulties in practice, those were increasing vehicle efficiency, reducing fuel carbon intensity, and reducing travel demands.
Piecyk and McKinnon [13]	2010	They were investigated the environmental impact. They examined their environmental impacts in the coming years with the help of a questionnaire.
Mondal et al. [10]	2011	They studied carbon emissions from the transportation sector. They found that only highways while CO_2 emissions from transportation were 4.8 in 2007, in 2030 it is predicted that it will increase to 6.9.
Bouchery et al. [14]	2012	They investigated modifying the classical EOQ model as the sustainable order quantity model. The research was for carbon emission regulation. The kinds of literature above developed an inventory model by taking into carbon footprint, environmental or social criteria.
Chavez-Baeza and Sheinbaum-Pardo [15]	2014	They studied greenhouse gases and some pollutants. The estimated future emissions are based on the past situation. The study aimed to detect all kinds of vehicle-related types in the metropolitan areas of the city and reduce emissions.
Quiros et al. [16]	2017	They were investigated, the effects of diesel transport vehicles on the atmosphere. In this study, the weight created by the goods loaded on diesel vehicles and the emission. The relationship between the changes in weight was examined, the direct greenhouse gases of the weight changes were examined.
Gür and Furuncu [17]	2017	In their study they have seen the increase in the regulation's sensitivity to the environment also affecting different countries in the automotive sector. They predicted measures CO_2 gas emission values for the next years.
Argun et al. [18]	2019	They conducted a study to determine the carbon footprint of the district of Konya Province. In the study used the Tier method, the effects of transportation, accommodation, and afforestation were taken into account. As a result of the study emission data were compared with Türkiye and various countries.
Bogacki and Bździuch [19]	2019	They conducted a study in Poland. The effects of buses on emissions were investigated. In the study, only pollutants not only that emissions, direct and indirect greenhouse gases have also increased.
Bilgili et al. [20]	2022	They have been calculated to account for the production processes of the aircraft and passenger trains, the LCA cycle was completed and total emissions were calculated.

tion of environmental values [8]. The trend primarily took off in the 1990s when increased cognize and consciousness about the "carbon footprint" is evidenced. This evidence with The Kyoto Protocol in 1997 asked to decrease greenhouse gases, and 150 countries approved to adopt of the protocol [9]. The number of greenhouse gases emitted to the environment due to direct or indirect acts called the carbon footprint is one of the initial reasons for air pollution and the consumption of natural resources.

With the increase in the level of air pollution caused by greenhouse gases, respiratory diseases can occur in living things. Changes in weather conditions and air pollution impact caused an increase in the nugatory effects on human health.

In addition, globally originating from vehicles created by the logistics industry carbon emissions are known as a

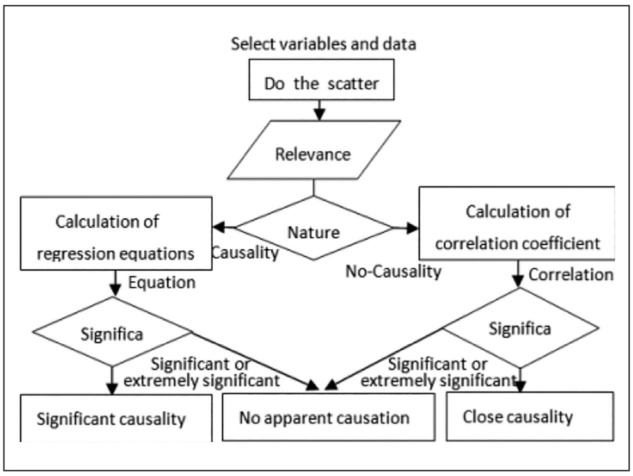

Figure 2. Regression model [21].

Table 2. Number of carbon emission and trucks

2021	Carbon emission (μg/m³)			Number of truck		
	Antalya	Kayseri	Konya	Antalya	Kayseri	Konya
January	22.755	39.907	54.379	24.918	17.193	38.175
February	22.675	39.887	54.499	25.042	17.257	38.252
March	22.694	39.911	54.437	25.165	17.261	38.432
April	22.710	39.927	54.455	25.343	17.288	38.580
May	22.723	39.936	54.463	25.412	17.307	38.606
June	22.741	39.945	54.475	25.519	17.329	38.743
July	22.766	39.955	54.488	25.603	17.381	38.864
August	22.784	39.967	54.494	25.643	17.392	38.951
September	22.801	39.982	54.490	25.727	17.420	39.051
October	22.818	40.009	54.447	25.841	17.461	39.128
November	22.838	40.060	54.493	26.038	17.482	39.206
December	22.859	40.110	54.557	26.139	17.530	39.219

Resource: South Central Anatolia Clean Air Center Directorate and Turkish Statistical Institute - 2021.

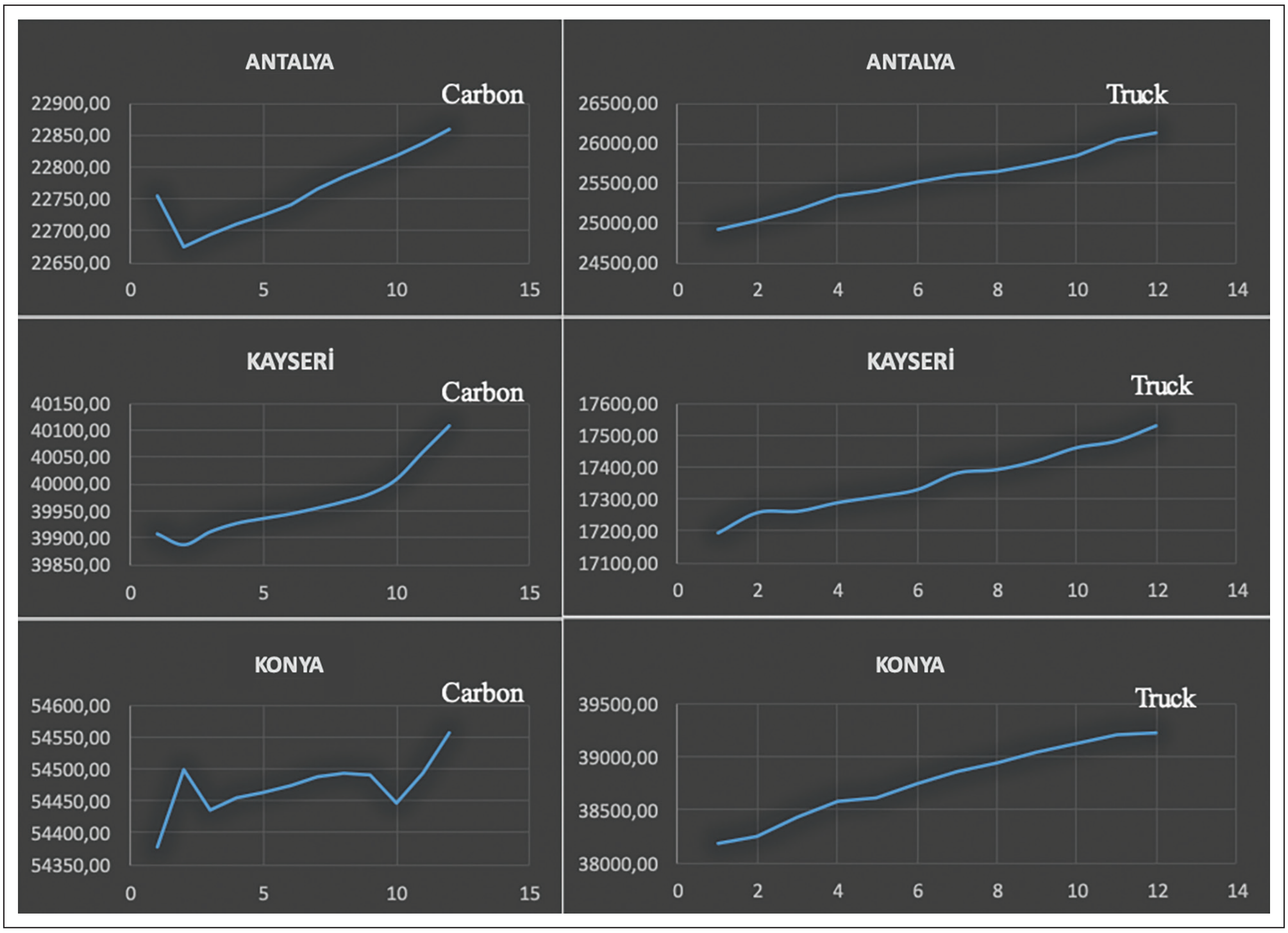

Figure 3. Trends of carbon and trucks.

world problem. Last decades, there has been a continuous increase in the production and logistics of commercial vehicles. The logistic industry is the fastest-growing one of sector in the world. Carbon emissions from fossil fuels are responsible for 22–24% of the greenhouse gas resulting from the highway [10].

Table 3. Multiple regression results

Regression statistics	Antalya	Kayseri	Konya
Multiple R	0.874032182	0.936860144	0.625062621
R square	0.763932255	0.877706929	0.390703281
Adjustable R square	0.740325481	0.865477622	0.329773609
Standard deviation	29.66614999	24.08495931	35.29803351
Observation	12	12	12

Table 4. ANOVA results

	df	Sum of square	Mean square	F	Significance
Antalya					
Regression	1	28480.03857	28480.03857	32.36072156	0.000201428
Difference	10	8800.804555	880.0804555		
Total	11	37280.84312			
Kayseri					
Regression	1	41633.17302	41633.17302	71.77078191	0.000710409
Difference	10	5800.852648	580.0852648		
Total	11	47434.02567			
Konya					
Regression	1	7989.493364	7989.493364	6.412364753	0.029755153
Difference	10	12459.5117	1245.95117		
Total	11	20449.00506			

ANOVA: Analysis of Variance.

In the literature, different researchers define the relationship between carbon footprint and logistics in their ways. The related literature is given in Table 1.

There are many studies in the literature on the carbon footprint for theoretical. In addition, this study is due to a lack of literature includes multiple regression for the local regions. Multiple regression analyses were applied and analyzed to the carbon emission levels where the greenhouse gasses, and the number of trucks. Based on the regression analysis findings, the article presents suggestions for the relationship between carbon footprint and highway logistics. From this viewpoint, of its approach, this research can be an addition to the literature.

MATERIALS AND METHODS

This research aimed to relationship a series of baseline trends in carbon footprint and highway logistics in 2021. In this context, this study to determine the impact of highway logistics activity, one of the most important causes of carbon dioxide emissions, on the carbon footprint of the Southern Central Anatolian provinces. In the first stage of the research, a series of data analyses were held in three locations in the Southern Central Anatolian (Antalya, Kayseri, Konya) involving a total of 12 monthly highway logistics activities and carbon emissions.

The regional logistics were measured in terms of carbon emission, then further multiple regression analyses. In the regression analysis, the multi-correlation coefficient shows the strength between the dependent and independent variables. The predicted value calculated by the regression is a specific coefficient called a point estimate [21]. The regression model is shown in Figure 2.

Based on these two indicators, the relations between carbon emission and highway logistics development were analyzed. Through the evolution trends of these indicators were investigated whether there is that certain convergence exists. Table 2 shows the results of the number of carbon emissions and trucks for the 12 months of 2021 for three provinces.

Specifically, multiple regression was based on variables such as carbon emissions and highway logistic trucks obtained from Table 2 data. In this context, the 95% confidence interval was provided from the multiple prediction values at each of the data points for three regions. According to Table 2, carbon emission and truck graphics in the regions given in Figure 3.

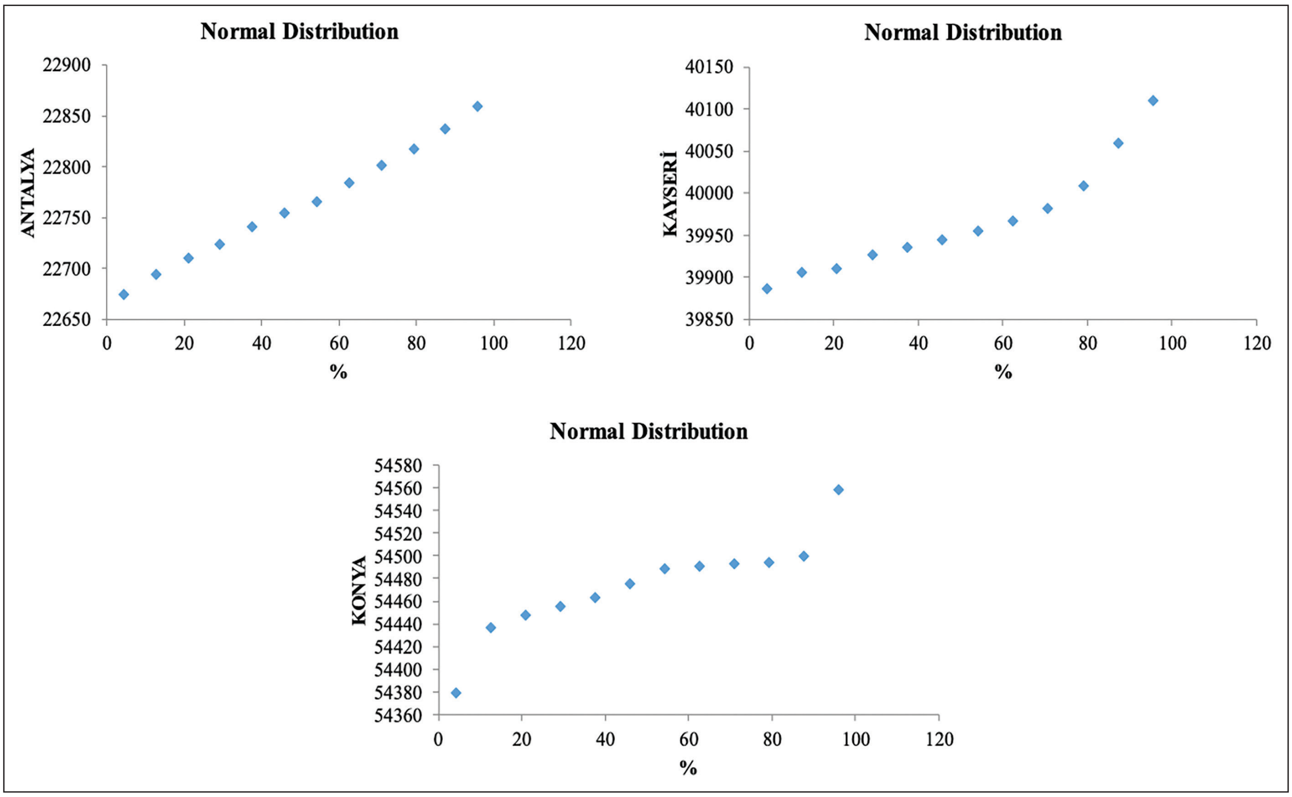

Figure 4. Normal distributions.

The Antalya, Kayseri, and Konya carbon emit and trucks are shown in Figure 3 to compare rates after one year of data is collected. Antalya and Konya's graphs have fluctuated in terms of carbon emissions Kayseri's graph increased at certain rates. However, in logistics, the situation is the same for all three cities.

RESULTS AND DISCUSSION

The regression results helped to identify carbon footprint linkages with carbon emits and highway logistics. The purpose of multiple regression analysis is to explain and predict the effect of change in independent variables on the dependent variable. In the study, the analysis results of the relationship between the number of carbon emissions and highway logistic trucks are expressed with tables and figures. The multiple regression analysis results are given in Table 3.

Multiple regression analysis has been applied with a number of carbon emission variables in order to analyze highway logistics. Furthermore, the significance of the multiple regression models was verified with three samples ($p<0.05$) [22]. As it shows that Table 3 are the adjusted determinations of the multiple regression model per the relationship between carbon emission and highway logistics in Antalya, Kayseri, and Konya. The explanatory ability of the model for Antalya was 87% (R=0.87), Kayseri was 94% (R=0.94), and Konya was 63% (R=0.63). In the multiple regression analysis, Kayseri has a higher determination than Antalya and Konya when an estimation of the quantile was carbon footprint. It was observed that the impact of the carbon footprint was severe on most of the parameters. The multiple R values exceeded the tolerable limits at almost all the stations.

The same data were analyzed according to ANOVA for the 12 monthly periods as Table 4.

This research is a one-way analysis of variance (ANOVA), which is a method of testing differences between three groups and carbon footprint. In a one-way analysis of variance, the same principle is used, with sample homogeneous rather than significant difference being used to measure variability. When the findings were examined, the samples were homogeneous. In all three samples, it was observed that the increase in carbon footprint from the use of carbon emissions and highway logistics significantly. The test statistic F is equal to the "carbon footprint" mean square divided by the error mean square [23]. In this context, the results according to the critical value of F, it was determined that all sample means were comparable at the same time. Moreover, normal distributions in the regions given in Figure 4.

According to the Figure 4, it has been determined that the sample variables are symmetrical and therefore fit the normal distribution. It has been observed that there is a positive relationship between the variables. In other words, it was stated that as the number of vehicles increased separately within the three provinces, the carbon emission values increased.

In similar studies in the literature, it has been seen that logistic modes are largely dependent on fossil fuels. With high fossil fuel consumption, the logistic sector is responsible for 28% of the total carbon footprint emissions in the USA [24]. In this context, reducing carbon footprint emissions is the most important issue in the modern world and especially, for oil and logistic gas enterprises [25]. From this perspective, this study's findings were appropriate to the related literature, which the carbon footprint with the highway logistics. Due to its original approach, the present research study is a contribution to the industry and literature.

CONCLUSION

Improving the quality of the types of greenhouse gasses used within the global environment and reducing carbon emissions are recognized as the main of current logistic changes policies. Measures to minimize the factors that cause emissions are the priority of all countries. Many national and international studies on the subject have been carried out, while countries determine their social and economic development plans, the environment started to show sensitivity to the issue of sustainability.

In this study, paper aims to evaluate the contribution of the impact of highway logistics activity, one of the most important causes of carbon dioxide emissions, on the carbon footprint of the Southern Central Anatolian provinces. The information about the current situation of changes, especially greenhouse a large amount of carbon, which is the most effective greenhouse gas in the emergence of gas emissions attention to logistic transportation.

In this study multiple regression analysis has been applied with a number of carbon emission variables in order to analyze highway logistics.Also, the significance of the multiple regression models was verified with three samples ($p<0.05$) [22]. As it shows results the adjusted determinations of the multiple regression model per the relationship between carbon emission and highway logistics in Antalya, Kayseri, and Konya. The explanatory ability of the model for Antalya was 87% ($R=0.87$), Kayseri was 94% ($R=0.94$), and Konya was 63% ($R=0.63$).

It can be seen that, in the multiple regression analysis, Kayseri has a higher carbon footprint than Antalya and Konya when an estimation of the quantile was carbon footprint. Considering the density of logistics vehicles passing through the provinces, it has been determined that there is a linear increase in carbon footprint rates. Furthermore, the multiple R values exceeded the tolerable limits at almost all the stations. Fuel consumption depend on the increasing number of vehicles increases and causes a remarkable increase in greenhouse gas emissions. According to the data of the General Directorate of Highways, these provinces are the highest volume provinces of logistic draws attention. The fact that the determined they are so prominent in terms of highway logistics, the trade originating from the provinces own industrial production potentials has been effectiveness. The logistic sector, which is necessary for the continuity of the economic process, due to released emissions, has a structure that threatens environmental sustainability. However, the need for the sector should require development in non-destructive methods is the sector's contribution to the ecosystem.

As a precaution, to reduce the environmental damage scope of highway logistics to spread emission-reducing measures, green logistics practices in activities should be done. In this context, especially environmentally friendly alternative fuels should be developed and used. Based on this study, similar and comparative studies can be carried out in other provinces. The main academic contribution of this study brings a new perspective to the future assessment of environmental policies and prepares a quantitative principle for the implementation of future carbon footprint policies.

Future work can be suggested, for highway logistics cases in which the other provinces measure carbon footprint. As another suggestion, future work can be suggested using methods other than regression analysis. Regarding the limitations of the research concerned, it should be mentioned has been conducted within three locations only and highway logistics.

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.

ETHICS

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

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Research Article

Characterisation of aluminium industrial wastewater and investigation of recovery alternatives

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ABSTRACT

Aluminium industry is one of the largest sectors and wastewater generated from this industry could cause crucial environmental problems due to its high heavy metal concentration and conductivity. Therefore, this study aims to determine the characterisation of the wastewater discharged from the two aluminium facilities by considering water recovery potential. While Facility-A produces stainless steel kitchenware, such as pots and pans, In Facility-B, anodised coating takes place from secondary aluminium and wastewater is generated from the units where anodised coating baths and control processes are carried out. For the analyses, the wastewater composite samples from different sections, such as washing, sand-blasting and dyeing in Facility-A were taken in 2 and 24 hours. In Facility-B, three 2-hour composite influent water samples and an effluent sample from chemical wastewater treatment were taken to determine conductivity, pH, chemical oxygen demand (COD), total suspended solids (TSS), etc. As a result of the analyses made, a high value of TSS was detected at all sampling points in Facility-A. It was also seen that the conductivity after demineralisation process in Facility-A was below 30. In Facility-B, it was determined that while the pH obtained from two influent samples was below the discharge limits and showed acidic characteristics, one sample was very basic with a pH value of 12.19 and exceeds the upper limit of discharge. All influent samples in Facility-B show high TSS content in comparison with discharge limits specified in the regulation.

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INTRODUCTION

Aluminium is one of the most widely used metals due to its high strength, corrosion resistance, heat and electrical conductivity [1, 2]. Depending on the development of the aluminium industry, facilities processing aluminium are increasing worldwide. However, the wastewater discharged from these facilities remains an important environmental problem [3, 4]. Significantly, high water costs,

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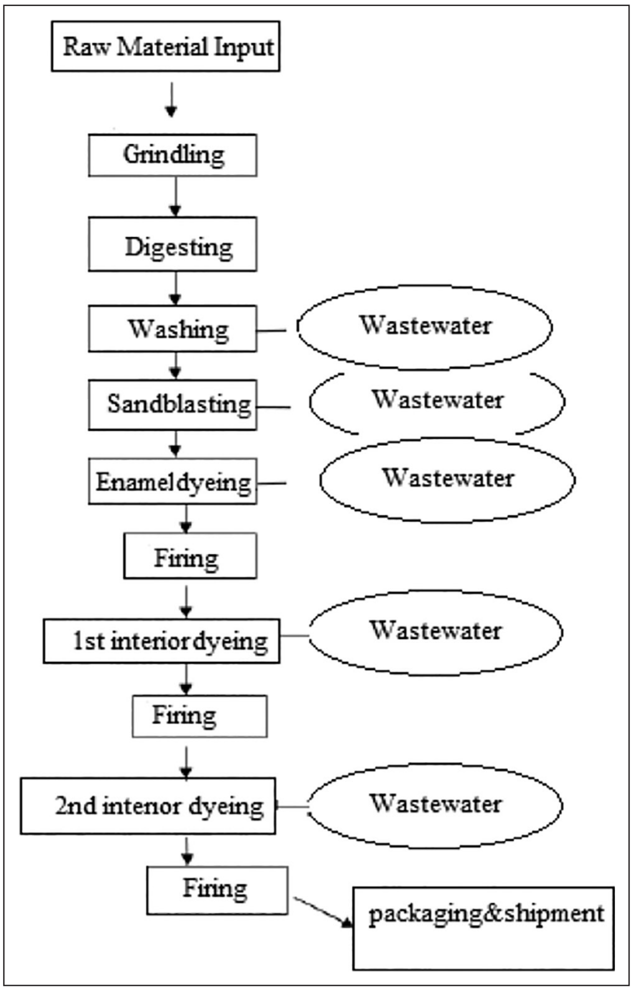

Figure 1. Flow chart of Facility-A.

restrictions on water use, and sanctions to improve environmental conditions have also made water recovery systems attractive to be used efficiently in the industrial sector [5–8].

In aluminium industry, heavy metal content, pH, colour, conductivity, total suspended solids (TSS) and chemical oxygen demand (COD) of the wastewater vary depending on an applied process and amount of aluminium coating [7, 8]. As wastewater produced from various stages (such as washing, dyeing, anodising etc.) has toxic and complex characteristics, it requires the development and use of efficient treatment methods [8–14].

In the aluminium industry, coating and matting are the stages which result in the generation of wastewater rich in aluminium, zinc and chromium [9]. So far, various methods have been used to remove metals from wastewater discharged from the aluminium industry, such as membrane filtration, chemical precipitation, electro-dialysis, electro-deionisation, valorization, and nanotechnology [9–11]. Various shells were also investigated for the efficient removal of aluminium from water [12]. However, it was proven that the efficiency of these methods is based on the determination of the characteristics of the wastewater [15–19]. For example, characteristics of treated effluent from several wastewater treatment plants in the UK were investigated to assess whether differences in nutrient export could be detected by these plants [20]. Two different wastewater samples were characterised to explore the potential for their recovery [21]. Accordingly, the characterisation of wastewater discharged from the pharmaceutical industry was carried out to evaluate the efficiency of bioremediation as a sustainable technique [22]. However, in the national literature, the aluminium sector-based studies usually focus on the determination of characteristics of red mud which is produced in large amounts and could be reused in various sectors, such as cement production [23–26].

Therefore, this study aims to determine the characterisation of the wastewater discharged from the aluminium sector by considering water recovery potential. In this study, the wastewater discharged from two different aluminium facilities was characterised by using the parameters such as conductivity, pH, COD, TSS, etc. To evaluate recovery potential, the applicability of various treatment methods, such as demineralisation, ultrafiltration and reverse osmosis for the removal of pollution in the wastewater was discussed. The content of this manuscript includes the introduction, methods and materials which include the details of the facilities where the work is carried out, the results and discussion in which the analysis results are presented and discussed and then the conclusion part.

MATERIALS AND METHODS

Facility-A produces stainless steel kitchenware such as pots and pans. During the production of non-stick kitchen utensils, after the forming process is completed, the products are taken to the washing line (Fig. 1). In this stage, an average of 11 m^3/day of water is used. The water coming out of the washing section accumulates in the balancing pool and from there it is sent to the settling tank for chemical treatment. In addition, water is used for cleaning the dyeing units (1st and 2nd interior dyeing), which are cleaned every ten days. The wastewater generated from the dyeing process is sent to the treatment plant. It is taken to the industrial wastewater collection pool through the wastewater collection channels within the facility. The wastewater is then pumped into the chemical reactor with the centrifuge. After the chemical treatment process is carried out in the chemical reactor tank, the wastewater is taken to the pre-storage tank. The wastewater is passed from this tank through the sand and active carbon filter tanks, respectively, by a booster pump. After this, the treated wastewater is taken to the clean water tank.

Figure 2. Demineralisation unit in Facility-A.

In Facility-A, water recovery is carried out by demineralisation method as it is both economical and reduces conductivity efficiently. In the demineralisation unit, filter tanks made of different types of materials are applied depending on the characteristics of the water. In addition, multi-way valves (SIATA or FLEG), manual, pneumatic diaphragm valves are employed. Granular activated carbon, anionic and cationic resin are used as filling materials in demineralisation filters. Demineralisation units work automatically as in all other treatment systems. The automation of these filters is provided by different ways and equipment.

This system within Facility-A is automatically controlled by the control panel as shown in Figure 2. The control panel of the system allows manual intervention to the desired equipment and/or unit. There is a manual start button on the control panel of the system so that the filters can start the manual regeneration and a manual phase bypass button is available to enable the filters to pass to the next phase during regeneration. If any unit fails for any reason, the system is automatically disabled. The control panel of the system gives a visual warning in case of malfunction and the description of the malfunction is indicated on the operator panel. In addition, there is a reset button on the control panel of the system.

The demineralisation unit consists of two columns. The first column includes cationic resin and removes positively charged metal ions such as Ca^{+2}, Mg^{+2}, Na^{+1}, Fe^{+2} and Mn^{+2}. When charged ions adhere to the exchange material, they leave as many hydrogen ions as their charge. Due to the increase of hydrogen ions, the amount of acid in the solution increases. At this point, half of the deionisation process is completed. The positively charged metal ions are purified and this leaves hydrogen ions and anions in the solution. In the second column, there is an anionic resin which absorbs the negative ions, such as HCO_3^-, Cl^-, SO_4^{-2} in the solution. When the resin is saturated (it can be understood immediately from the conductivity value in the effluent), the regeneration process is performed with a base. As a result of regeneration, hydroxide is released into the resin. In this case, H^+ ions remain from the first stage and OH^- ions emerging in the second stage in the solution. These combine to form a water molecule. As a result, mineral-free water is obtained at the end of this process.

In Facility-B, anodised coating takes place from secondary aluminium and wastewater is generated from the units where anodised coating and control processes are carried out (Fig. 2). Grid systems are placed at the entrance of the balancing pools for industrial wastewater coming from different points originating from the facility. Wastewater is collected in the balancing pool after passing through the screen. In the three existing balancing pools, the flow oscillations in the wastewater are balanced and the treatment plant is fed at an equal flow rate throughout the day. Figure 3 gives a schematic view of Facility-B.

Facility-B produces 600 m^3 of wastewater per day. The wastewater produced from the use of employees is collected in a separate balancing pool and treated in the biological treatment unit. 1000 people work in the facility and the wastewater produced from internal activities within the plant is approximately 200 m^3 per day.

In Facility-B, before the anodising process, the profiles are subjected to a series of processes such as sanitation and digesting in matting baths. Matting baths provide a satin/mattified appearance on the surface of the profiles.

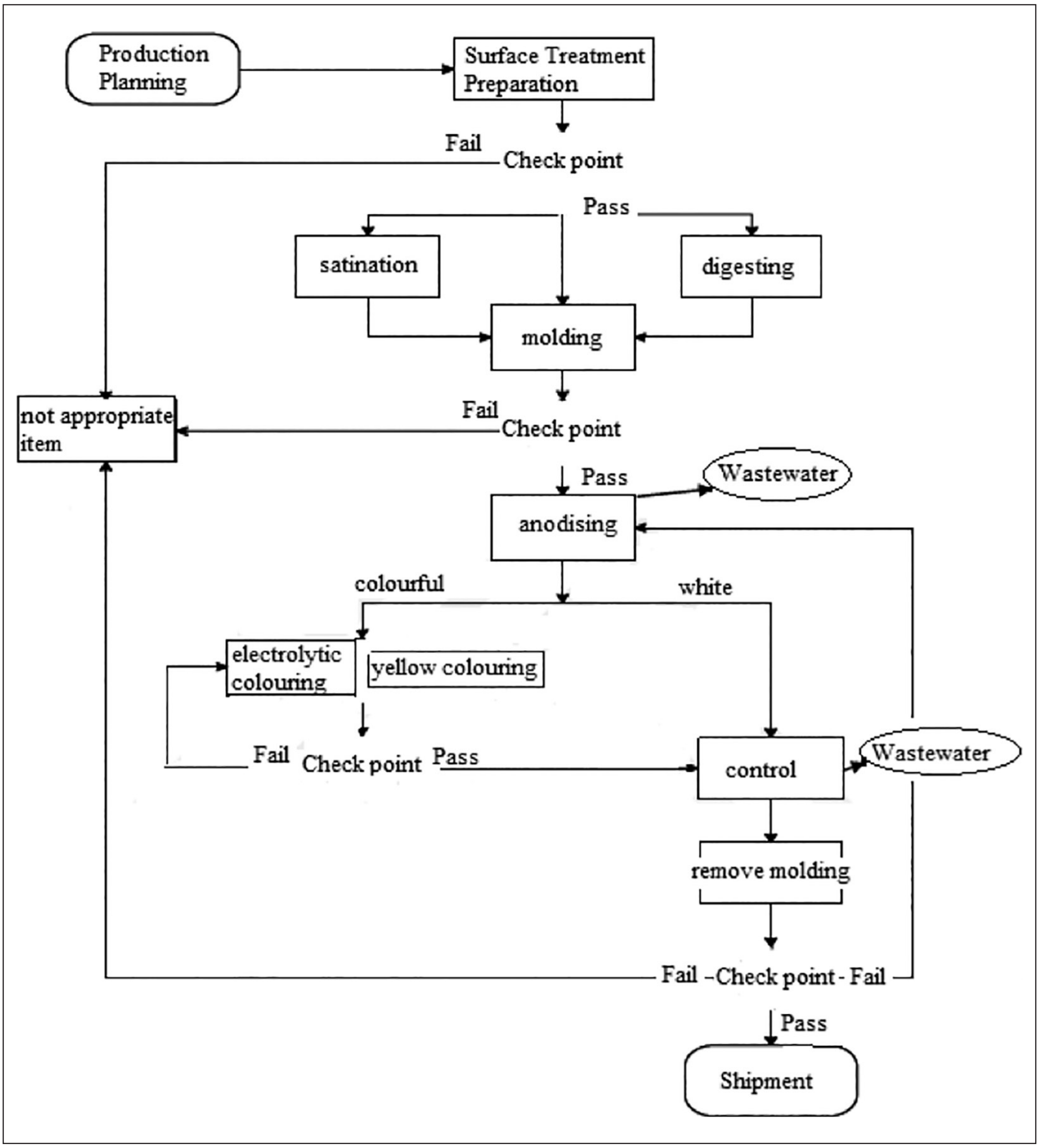

Figure 3. Flow chart of Facility B.

For the analyses, the wastewater composite samples from different sections, such as washing, sand-blasting and dyeing in Facility-A were taken in 2 and 24 hours. In Facility-B, three 2-hour composite influent water samples and an effluent sample from chemical wastewater treatment were taken to determine conductivity, pH, COD, TSS, etc. The values of the parameters were determined by using various methods provided by the Turkish Standards (TS EN ISO 10523), Standard Methods for the Examination of Water and Wastewater (SM 2540 D and SM 5220 B) as detailed in the Results and Discussion section.

RESULTS AND DISCUSSION

The wastewater composite samples from washing, sand-blasting and dyeing in Facility-A were taken in 2 and 24 hours and the values of the parameters, such as colour, pH, conductivity, COD, TSS, etc. were determined and shown in Table 1. As a result of the analyses made, high TSS was detected at all sampling points as shown in Table 1. It is known that ultrafiltration and reverse osmosis methods could be beneficial to eliminating TSS efficiently from wastewater [27]. However, these methods also inherit a high cost for treatment [28].

Table 1. Results of the wastewater analyses in Facility-A

Parameters	Analysis method*	Wastewater from washing section	Wastewater from sand-blasting	Wastewater from 1st interior dyeing	Wastewater from enamel dyeing	Wastewater from 2nd interior dyeing
Colour	–	Dark brown	Black	Grey	Pink	Yellow
Appearance	–	–	Dense and particulate	Dense and particulate	Particulate and turbid	Oily
pH	TS EN ISO 10523	7.35	9.5	7.8	9.8	11.7
Conductivity (μS/cm)	pH meter**	3100	1375	3000	1423	7250
COD (mg/L)	SM 5220 B	>10000	>10000	>10000	464	>3500
TSS (mg/L)	SM 2540 D	541	>750	>750	-	164
Total ferrous (mg/L)	EPA 200.7:2001	29.5	>50	>50	1.4	20
Nickel (mg/L)	EPA 200.7:2001	10.6	>50	>50	2.9	5.5
Aluminium (mg/L)	EPA 200.7:2001	1.2	>6	7.8	4.75	5.65

*: EPA: Environmental Protection Agency; SM: Standard Methods for the Examination of Water and Wastewater; **: Water Quality Meter Temp Log 8603.

Table 2. Results of the further wastewater analyses in Facility-A

Parameters	Influent in settling tank	Effluent of chemical reactor	Effluent after demineralisation	Limits for reusability [29]
Conductivity (μS/cm)	2250	2000	15	<30
COD (mg/L)	187	87.96	45	<50
Ferrous (mg/L)	<10	<10	<10	<10
Aluminium (mg/L)	0.55	0.1	<0.1	<0.1
pH	8.85	7.31	7.05	6–9

Table 3. Results of the wastewater analyses in Facility-B

Parameters	Analysis method*	Sample 1	Sample 2	Sample 3	Sample 4	Discharge limit values [29]
Conductivity (μS/cm)	pH meter**	25000	26123	24261	20400	–
pH	TS EN ISO 10523	4.08	12.19	3.62	6–9	6–9
COD (mg/L)	SM 5220 B	202.6	232.0	247.4	114	100
TSS (mg/L)	SM 2540 D	4886	5270	5716	98	125
Oil-Grease (mg/L)	SM 5520 D	<10	<10	<10	<10	20
Nitrogen (mg/L)	SM 4500 NO2 B	0.03	0.2	0.025	<5	5
Active chlorine (mg/L)	SM 4500 CI-G	0.03	0.03	0.033	<0.5	0.5
Total chrome (mg/L)	EPA 200.7:2001	0.054	0.018	0.163	<1	1
Chrome (mg/L)	SM 3500 Cr:B	<0.02	<0.02	<0.02	<0.02	0.5
Aluminium (mg/L)	EPA 200.7:2001	277679	350125	686549	<3	3
Fluoride (mg/L)	SM 4500 F-D	<0.1	0.53	<0.1	<0.1	50
Ferrous (mg/L)	EPA 200.7:2001	2.553	0.014	5.677	<3	3
Nickel (mg/L)	EPA 200.7:2001	0.082	<0.003	0.154	<0.003	2
Zinc (mg/L)	EPA 200.7:2001	0.056	<0.0006	0.166	<0.0006	3
Colour (Pt-Co)	SM 2120 C	<5	18.5	8	<5	280

*: EPA: Environmental Protection Agency; SM: Standard Methods for the Examination of Water and Wastewater; **: Water Quality Meter Temp Log 8603.

As a further step, the analyses of the wastewater taken from the various sampling points, such as the settling tank, chemical reactor, demineralisation unit were made to measure conductivity, COD, pH, etc. The results are shown in Table 2. For evaluation, the discharge standards of metal industry wastewater to the receiving environment specified in the Water Pollution Control Regulation are taken as a basis [29].

Since the high conductivity creates a stain on the metal surface, it is necessary to reduce the conductivity for reuse. In the metal sector, the conductivity must be <30 so that there is no problem in the surface area of the metal [30]. It is seen that the conductivity after demineralisation is below 30 in Facility-A (Table 2). As the demineralisation method is both economical and reduces conductivity efficiently, it is efficiently used in Facility-A.

In Facility-B, three 2-hour composite influent water samples (Sample 1, 2 and 3) and an effluent sample from chemical wastewater treatment (Sample 4) were collected for the analyses to determine conductivity, pH, COD, TSS, etc. The results are given in Table 3.

As is seen in Table 3 while the pH (4.08 and 3.62, respectively) obtained for Sample 1 and 3 is below the discharge limits (6–9) and shows acidic characteristics, Sample 2 is basic with a pH value of 12.19 and exceeds the upper limit of discharge. Table 3 also shows that TSS in Sample 1, 2 and 3 (4886, 5270 and 5716 mg/L respectively) is quite high in comparison with discharge limits specified in the regulation [29]. Importantly, the COD value of Sample 4 (114 mg/L) does not fall into the range of the discharge limits [29]. In this case, efficient reduction of COD in wastewater treatment could be provided by the application of microalgae [31].

There are also different methods which are particularly based on membrane technology for the elimination of heavy metals from wastewater discharged from aluminium industry. For instance, it was found that commercial membranes could reduce conductivity in the anodising baths significantly [32]. Accordingly, the application of the membrane crystallisation technique to wastewaters discharged from an anodising industry in Denmark provided more than 80% fresh water from the wastewater [33].

In another wastewater characterisation study, membrane experiments were carried out with ultrafiltration, nano-filtration, and reverse osmosis membranes for the aluminium anodic oxidation wastewater discharged from a manufacturing facility in Kayseri, Türkiye [34]. The wastewater from this facility show very low pH and high aluminium content. It was determined that the water treated by both nano-filtration and reverse osmosis could be reused in the process. This provides economical profits as well as environmental benefits.

CONCLUSION

Methods such as supplying water to be used in such facilities in Türkiye from nearby wells reduce the cost of water. The low cost of water and difficulties of establishing water recovery systems could cause stakeholders from various industries not to deal with the issues of wastewater recycling. The high operating and investment costs of wastewater recovery systems and the doubts about their efficiency make these systems not very common. In addition, since the establishment of these recovery systems is not a legal requirement, facilities tend to supply well water for their processes. However, the rapid depletion of clean water resources and the necessity of going deep for the water to be drawn from wells could make wastewater recovery a great necessity soon.

In this study, the analyses were carried out to determine characteristics of wastewater discharged from Facility-A and Facility-B which produce stainless steel kitchenware and make anodising from secondary aluminium. The wastewater discharged from these two different aluminium facilities was characterised by using the parameters such as conductivity, pH, COD, TSS, etc. It was seen that the conductivity after demineralisation process in Facility-A is below 30, which proved that demineralisation method is effectively used in this facility to reduce conductivity efficiently. In Facility-B, while the pH obtained from influent water samples (Sample 1 and 3) is below the discharge limits and shows acidic characteristics, Sample 2 is basic and exceeds the upper limit of discharge [29]. It was also seen that the TSS of influent water samples is quite high in comparison with discharge limits specified in the regulation [29].

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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.

ETHICS

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

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Research Article

Adsorption performance of Pb(II) ions on green synthesized GO and rGO: Isotherm and thermodynamic studies

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ABSTRACT

Graphene oxide (GO) and reduced graphene oxide (rGO) are efficient and low-cost adsorbent carbon-based materials for removing Pb(II) ions from wastewater. In this article, the adsorption performance of environmentally friendly graphene oxide and reduced graphene oxide, which shows high adsorption capacity for Pb(II) ions, has been compared for the first time to our knowledge. Besides, the various characterization techniques are used such as X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy and scanning electron microscopy with energy dispersive X-ray spectroscopy and described in detail as well. In addition, adsorption isotherms and thermodynamic studies are discussed to comprehend the adsorption process as well. From the adsorption isotherms, the maximum adsorption capacities of Pb(II) ions on GO and rGO calculated from the Langmuir (117.6 mg/g) and Dubinin–Radushkevich isotherms (138.5 mg/g), respectively, higher than reported studies in the literature. By thermodynamic investigation, it was found that the adsorption of Pb(II) ions on GO and rGO was spontaneous and exothermic. This study will be established as a basis for future studies and will be especially valuable in understanding the potential of graphene-based materials, which are rising stars that can be considered as promising and effective adsorbents in the removal of heavy metal ions from large volumes of aqueous solutions.

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INTRODUCTION

Water is an indispensable part of the life cycle so that must need to be protected and conserved. Lead (Pb) ion is one of the most toxic heavy metals that pollutes water through the manufacture of paints, mining, fuels, storage batteries etc. [1]. Pb(II) ions, which threatens human health such as neurological disorders, kidney damage, anemia, and can even lead to death, is also very harmful for the environment and ecosystem [2, 3]. According to the United States Environmental Protection Agency (EPA), the allowable concentrations of lead in drinking water has been reported as 15 ppb [4].

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Graphene is an extraordinary material. It has a two-dimensional layer of carbon atoms arranged in a hexagonal crystal structure. Graphene and graphene-based materials have managed to attract the attention of researchers thanks to its magnificent properties such as high surface area, electron and thermal mobility, and mechanical strength [4]. Graphene oxide (GO) and reduced graphene oxide (rGO) and graphene-based composites, have recently attracted utmost attention in adsorption studies of in the removal of dye [5], heavy metal and radionuclide pollutants [6–8]. GO can be synthesized using various approaches such as Brodie [9], Staudenmaier, Hummers [10] by exfoliating the graphite via high oxidizing reagents. These procedures produce the toxic gases such as NO_2, N_2O_4 and also being explosive. In addition to these methods, in 2010 Tour's et al. [11] reported an improve method of GO, in which the amount of $KMnO_4$ was doubled, included H3PO4 as well as H2SO4. The biggest advantage of the Tour method is that it does not use $NaNO_3$, which causes to the formation of toxic substances. GO has various oxygen-containing functional groups such as epoxy, hydroxyl and carboxyl in its basal plane and at its edges. These oxygen-containing groups combine metal ions and organic pollutants by coordination, electrostatic interaction, hydrogen bonding and this allows their use in pollution control [7].

It has been reported that most of the previous studies on the adsorption of heavy metals, GO synthesized by Hummer's method which produced toxic gases during the synthesis, and rGO synthesized with toxic reducing agent such as hydrazine and its derivatives [12, 13]. Although hydrazine is considered a good chemical reagent for rGO, in recent studies vitamin C (ascorbic acid) is considered to be an environmentally friendly and inexpensive reducing agent that can be used instead of hydrazine [14]. Also, the reduction performed by ascorbic acid is highly efficient and provides an advantage for large-scale production. Another advantage of using ascorbic acid is that the risk of incorporating heteroatoms into the structure is minimized, since it consists only of carbon, hydrogen and oxygen [14–16].

Researchers have reported extensive studies for the removal of Pb(II) ions from aquatic environments and various methods such as ion exchange, membrane filtration, electrodeposition, and coagulation have been studied [17, 18] Adsorption is one of the most preferred methods among them thanks to its simple operation, low cost and applicable in large scale [19, 20]. Various type of adsorbents has been used to remove Pb(II) ions from aquatic environments such as zeolites [21], activated carbon [22], carbon aerogel [23], manganese oxide-coated carbon nanotubes [24], chitosan/magnetite composite beads [25], olive cake [26] etc.

Nowadays, cheap, effective and at the same time environmentally friendly adsorbent materials are needed to remove pollutants from aqueous solutions. Here, for the first time our knowledge, GO was obtained by Tour method which is environmentally friendly method, and rGO was synthesized with non-toxic natural reducing agent L-ascorbic acid, and used as adsorbent materials to remove Pb(II) ions from the aquatic environment and their adsorption behavior was investigated. With this study, it was possible to obtain a green and economical adsorbent for the removal of Pb(II) ions from water. Characterizations of the resulting products were done by XRD, SEM-EDS, FT-IR and Raman spectroscopy. Adsorption experiments were investigated in detail under variable operating conditions such as pH, contact time, initial Pb(II) concentration and temperature of Pb(II) solutions. The obtained results were studied by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. In addition, thermodynamic studies (enthalpy, entropy and Gibbs free energy) were calculated by experimental data for the both materials.

MATERIALS AND METHODS

Materials

Synthetic graphite powder (<20 μm) was purchased from Sigma Aldrich. All chemical reagents, 95–98% sulfuric acid (H_2SO_4), 85% phosphoric acid (H_3PO_4), potassium permanganate ($KMnO_4$), 30% hydrogen peroxide (H_2O_2), 37% hydrochloric acid (HCl), Nitric acid (HNO_3), ammonia solution, L-ascorbic acid (L-AA), lead(II) nitrate ($Pb(NO_3)_2$), sodium hydroxide (NaOH), absolute ethanol, were analytical grade and purchased from Merck.

Preparation of Adsorbents

The GO was synthesized by chemical oxidation of graphite powder using Tour' method [11]. Briefly, 9:1 mixture of concentrated H_2SO_4 and H_3PO_4 (360:40 mL) were prepared and stirred for 15 minutes before adding graphite powder (3.0 g) with ice bath. After that, KMnO4 (18.0 g) were gradually added into the mixture under the continuous stirring. Then the mixture was heated at 50 °C and stirred for 12 h. After the reaction was cooled to room temperature and the mixture was poured onto ice (400 mL). Then, 30% H_2O_2 (3 mL) was added until the color of the reaction mixture turned to bright yellow. The brilliant yellow mixture was then repeatedly centrifuged at 4000 rpm and washed with HCl, deionized water, and ethanol. The final product of GO was dried an oven at 70 °C.

The as-dried GO sheet (0.45 g) was added into 500 mL deionized water and ultrasonicated for 1.0 h to homogenize the dispersion. As a reducing agent, L-ascorbic acid (4.5 g) was added to this solution and stirred with a magnetic stirrer for 1.0 h at room temperature. Afterward, pH of the suspension was adjusted to 9.5 using ammonia solution (25% w/w) to provide colloidal stability of GO sheet through electrostatic repulsion in alkaline conditions [27]. Then the mixture was heated at 70 °C under magnetic stirring

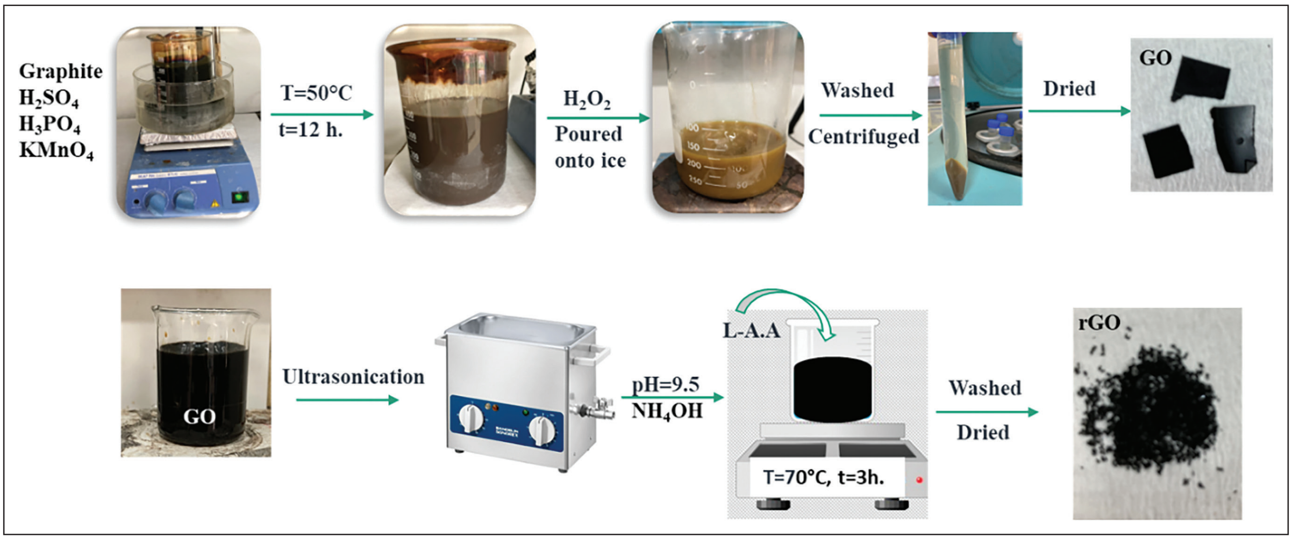

Figure 1. Photographs and schematic diagram for the preparation of GO and rGO.

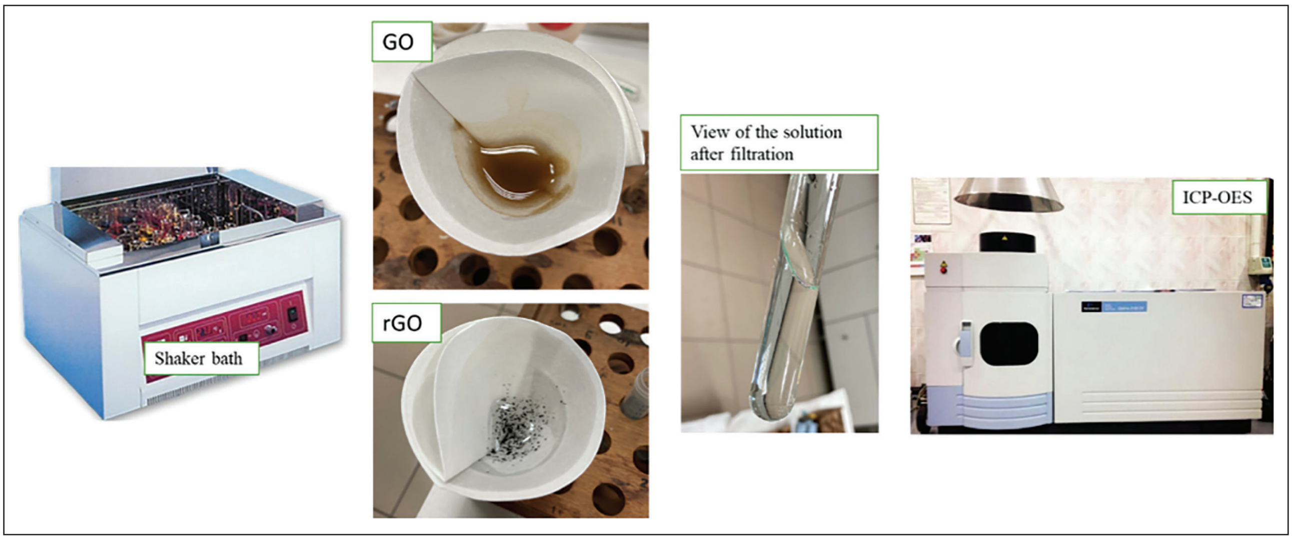

Figure 2. Photographs and schematic diagram of a batch adsorption process.

and kept for 3 h to obtain rGO. The reduced product was repeatedly centrifuged at 4000 rpm for 30 min to remove the supernatant and washed by deionized water to remove residual L-AA. Finally, rGO was dried an oven at 70 °C. Preparation steps of GO and rGO are shown in Figure 1.

Batch Experiment

In this study, initial pH of the solution, initial concentration, contact time and temperature were investigated for the removal of Pb(II) ions by using GO and rGO as adsorbents during the batch adsorption experiment. Generally, the pH of 10 mL solution of known lead concentration was adjusted by adding dropwise with negligible amount of 0.1M NaOH and/or HCl. Then, adsorbent (0.01 g) was added into the solution and transferred into the electronic shaker bath. After achieving the adsorption equilibrium for a certain period of time, the solid parts were removed from the liquid part immediately by the aid of a filter.

Figure 2 shows the scheme of batch experimental stage. After adding GO to Pb(II) solutions, GO is dispersed in the solution due to the hydrophilic nature of GO although rGO does not disperse because it is hydrophobic. After the filtration, a clear and transparent solution was observed for both and the remaining Pb(II) ion concentration was measured by ICP-OES.

The adsorption capacities and removal percentage rate were calculated as follows:

$$q_e = \frac{C_i - C_e}{m} \text{ x } V \tag{1}$$

$$\text{removal percentage rate}(\%) = \frac{C_i - C_e}{C_i} \text{ x } 100 \tag{2}$$

where C_i and C_e in mg/L represent the initial and equilibrium Pb(II) concentration, respectively; V (L) is the volume of the solution in the adsorption study; and m (g) is the mass of adsorbent used.

Analysis Methods

X-ray diffraction (XRD) analysis was carried out on an X-ray diffractometer (Malvern Panalytical Empyrean) with Cu Kα radiation (λ=1.5406) at 45 kV and 40 mA with a step size of 0.01 and recorded in the 2θ range of 5–60°. The chemical characterization of the samples was analyzed by Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) spectrophotometer (Perkin Elmer) and Raman spectra (Renishaw Raman spectrometer) with a 532 nm laser wavelength. It was recorded at the wavenumber region of 4000–450 cm^{-1} and the Raman Shift region of 3000–1000 cm^{-1} corresponding to FTIR and Raman spectrums. The morphological characterization of the samples was captured from a scanning electron microscopy (SEM) (Carl Zeiss 300VP) and elemental compositions were determined by energy-dispersive X-ray spectroscopy (EDS). The operational details of characterization methods can refer to the literature [28, 29]. All batch adsorption experiments were carried out in a thermostated electronic shaker bath (GFL 1083). The pH values of aqueous solutions were measured by a Hanna Instrument, model 8521, pH meter. The measurements of residual Pb(II) concentration were performed using inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima DV 2000).

RESULTS AND DISCUSSION

Characterization of Synthesized Adsorbents

In this study, Tour method was used to synthesize graphene oxide by using graphite as a starting material. After the oxidation process, GO was reduced by using L-ascorbic acid as a non-toxic reducing agent.

XRD analysis was used to understand phase formation and verify the interlayer spacing of graphite, GO and rGO samples.

The interlayer spacing of samples can be calculated according to the Bragg law:

$$n\lambda=2d\sin\theta \tag{3}$$

where n is an integer, λ is wavelength of X-ray for the copper target, θ is angle between the incident and reflected rays and d is the interlayer distance or d-spacing of Miller indices.

The crystallite size of the sample can be calculated using the Debye-Scherrer equation from the following equation:

$$D=\frac{K\lambda}{\beta\cos\theta} \tag{4}$$

where D is the crystallite size of the sample, K is the Scherrer constant (0.94), λ is the wavelength of Cu-K_α (1.54 Å), β is the half-width (rad) of the X-ray diffraction peak (FWHM), and θ is the Bragg's diffraction angle.

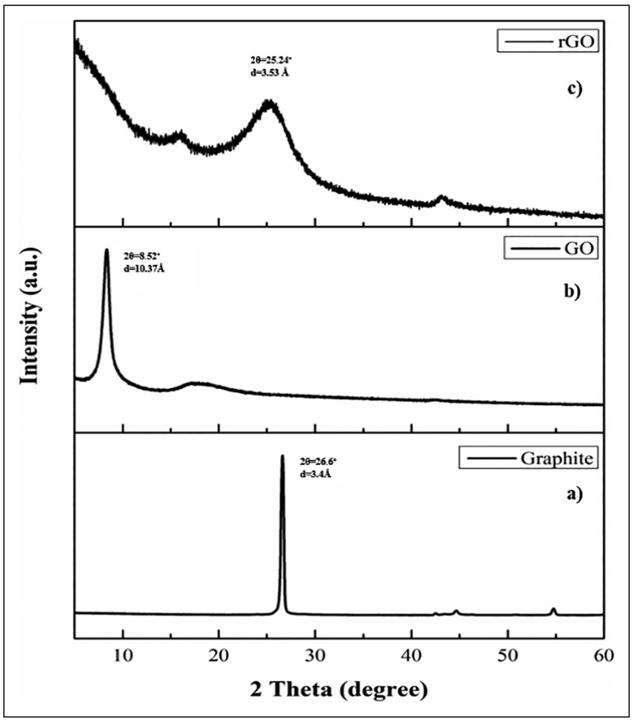

Figure 3. XRD patterns of graphite **(a)**, graphene oxide **(b)** and reduced graphene oxide **(c)**.

Figure 3a shows the XRD spectra of graphite as a starting material. The interlayer spacing of graphite was calculated from the characteristic peak where is a very sharp peak at 2θ=26.6° along with the orientation at (002) plane comes out to be 3.4 Å which is similar in literature [30]. The characteristic graphite peak is disappeared after oxidation process in the synthesized GO as shown in Figure 3b. The characteristic peak of GO at 2θ=8.52° from the diffraction of the (001) plane comes out to be 10.37Å which is in good agreement with the literature [31]. By comparing graphite and GO, the reason of shifting 2θ values from the 26.6° to 8.52° is that the d-spacing between carbon layers increased with the addition of functional groups in oxidation process and graphite is fully oxidized to GO [31]. It can be seen that the characteristic peak position 2θ=25.24° from the diffraction of the (002) was the confirmation of reduction of graphene oxide in Figure 3c. The d-spacing of rGO was calculated using Bragg's law to be 3.53 Å. After the reduction process, the interlayer distance of rGO was lower than GO that infers oxygen containing functional groups were removed efficiently [32]. This result clearly indicate that L-ascorbic acid is an effective reducing agent for GO reduction.

Results from the XRD patterns and Debye-Scherrer equation, the average number of layers was calculated equation 5. In our case, synthesized GO has ~9 scattering layers while rGO has ~5.

$$n=D/d \tag{5}$$

Table 1. Results of XRD analysis for graphite, graphene oxide and reduced graphene oxide samples

Sample name	2 Theta (°)	Interlayer distance (Å)	FWHM (°)	Crystallite size (nm)	Number of layers
Graphite	26.6	3.4	0.34	25.02	74.7
GO	8.52	10.37	0.86	9.68	9.33
rGO	25.24	3.53	5.13	1.65	4.69

where n is the number of layers, D is the crystallite size of the sample calculated using the Debye-Scherrer equation and d is the interlayer distance between the planes.

XRD analysis results which are including 2θ, interlayer spacing, FWHM, crystallite size and number of layers of graphite, GO and rGO are given in Table 1 Results of XRD analysis for graphite, graphene oxide and reduced graphene oxide samples.

FT-IR spectrum give the information of functional groups in graphite, GO and rGO. In Figure 4a, the FT-IR spectrum of graphite is given and clearly seen that do not show any peaks means no oxygen bonds are observed [33]. After the oxidation process, it is seen that FT-IR spectrum of GO in Figure 4b show that oxygen-containing functional groups are introduced in the structure. The FT-IR peaks of GO at 1040, 1219, 1383, 1622, 1729 and 3220 cm^{-1}, which are vibration of alkoxy C–O, epoxy C–O, attributed to the O–H deformation vibration of COOH group, C=C skeletal stretching, carboxylic acid –C=O, and hydroxyl –OH groups, respectively [34]. The FT-IR spectrum of GO show that the existence functional groups designate that graphite has been oxidized and the polar groups particularly hydroxyl groups, made the GO form hydrogen bonds with water molecules and provide hydrophilic nature. The reduction of the oxygen-containing groups in GO by L-AA was also proven by FT-IR spectroscopy as shown in Figure 4c.

After the reduction of graphene oxide, intensities of the peaks corresponding to the oxygen functionalities such as hydroxyl–OH peak at 3660 cm^{-1} were reduced significantly and some peaks were disappeared such as-COOH stretching vibration peak at 1741 cm^{-1}. These results indicates that the GO has been reduced by ascorbic acid. Similar results have been reported in the literature [35, 36].

In Figure 5, surface morphology and elemental composition of graphite, GO and rGO was examined by SEM and EDS spectrum, respectively. Graphite is shown in a platelet-liked stacked sheets (Fig. 5a) while GO has wrinkle, layered and folded morphology (Fig. 5b). The reason for the formation of these morphology is due to the oxygen-containing functional groups formed during the GO formation and the consequent structural defects [37]. SEM images of rGO in Figure 5c show wrinkled, wavy and aggregated morphology. According to EDS results as shown in Figure

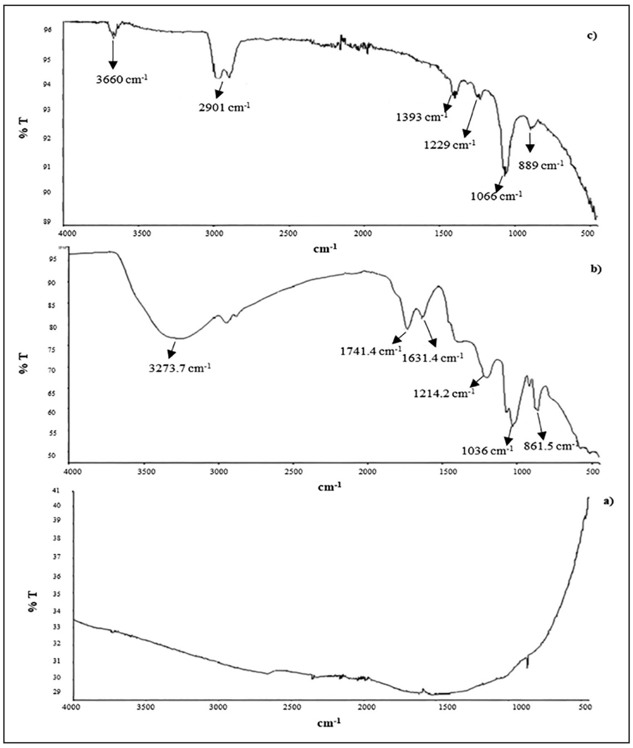

Figure 4. FT-IR spectrums of graphite **(a)**, graphene oxide **(b)** and reduced graphene oxide **(c)**.

5d, graphite contained almost only C (98.4%) by weight. After the oxidation process, GO (Fig. 5e) consisted of both C (44.8%) and O (51.4%) peaks with carbon/oxygen (C/O) ratio was calculated to be 0.87. In comparison, rGO (Fig. 5f) contained larger amounts of carbon (76.8%) relative to oxygen (23.2%). It is understood that with the reduction of GO to rGO with ascorbic acid, the functional groups deteriorate and the C percentage increases and the C/O ratio increases from 0.87 to 3.31. C/O ratios may differ according to synthesis and reduction methods [38].

Raman spectroscopy is a very useful technique to characterize carbon-based materials. The typical Raman spectrum of carbon materials composed of D, G and 2D bands. While D band is appeared in near 1350 cm^{-1}, G and 2D bands are appeared in near 1580 cm^{-1} and 2700 cm^{-1}, respectively. Those Raman bands give different information. Briefly, D band is related to defects vibrations of sp^3 carbon atoms of defects and disorder in the material, G band is related to vibration of sp^2 carbon atoms in a graphitic 2D hexagonal lattice and 2D band is related to number of graphene layers [39].

The Raman spectrum of graphite, prepared GO and rGO is shown in Figure 6. D band of graphite has a low-intensity compared to the G band which is related with nanocrystalline carbon in presented Figure 6a. Besides, graphite has a high intense of 2D band. The I_{2D}/I_G ratio=0.36 indicates the presence of multilayers of graphite as reported similar

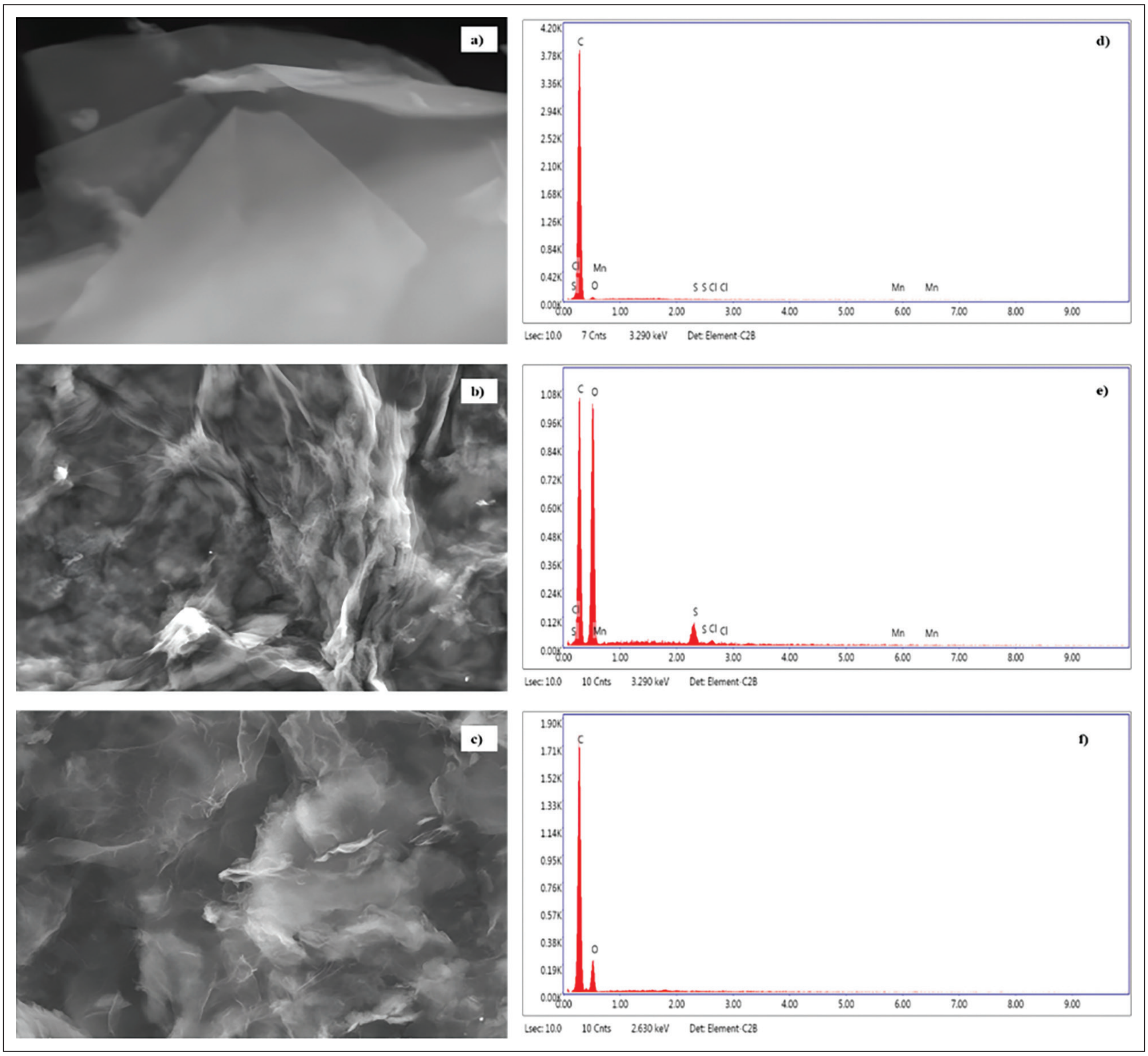

Figure 5. SEM images of graphite **(a)**, graphene oxide **(b)** and reduced graphene oxide **(c)** and EDS spectrum of graphite **(d)**, graphene oxide **(e)** and reduced graphene oxide **(f)**.

[40]. By comparing graphite and GO, it is obviously seen that more intense D band observed in Figure 6b. A common way to describe the defect density in a material is the ratio of the intensities of the D-band to the G-band. A value of the I_D/I_G=0.91 indicates greater disorder of the basal planes of the GO due the functional groups present on the surface of each layer. This is an indication of the increment of disordered phase in the GO in consequence of the oxidation of graphite and related to the formation of sp^3 hybridized bonds. In addition, flat and low intensity of 2D band observed. These properties support the disorder of the material layers and show that GO is composed of multilayers according to I_{2D}/I_G=0.04. After the reduction process, it was found that the intensity ratio D band to G band (I_D/I_G=1.11) increased significantly. This result indicates that most of the oxygenated groups vanished during the reduction process. Similar results have been reported in the literature [35].

Pb(II) Adsorption Evaluations on Synthesized Adsorbents

The influence of initial pH, concentration, contact time and temperature on the adsorption of Pb(II) ions was studied by adding 0.01 g of GO and rGO as adsorbents and 10.0 mL of sample solution into the tubes. The solutions prepared to be studied at different pH values, initial concentrations, different time intervals and temperatures were transferred to the tubes and shaken in a temperature-controlled shaker. Experiments were performed with other conditions held constant.

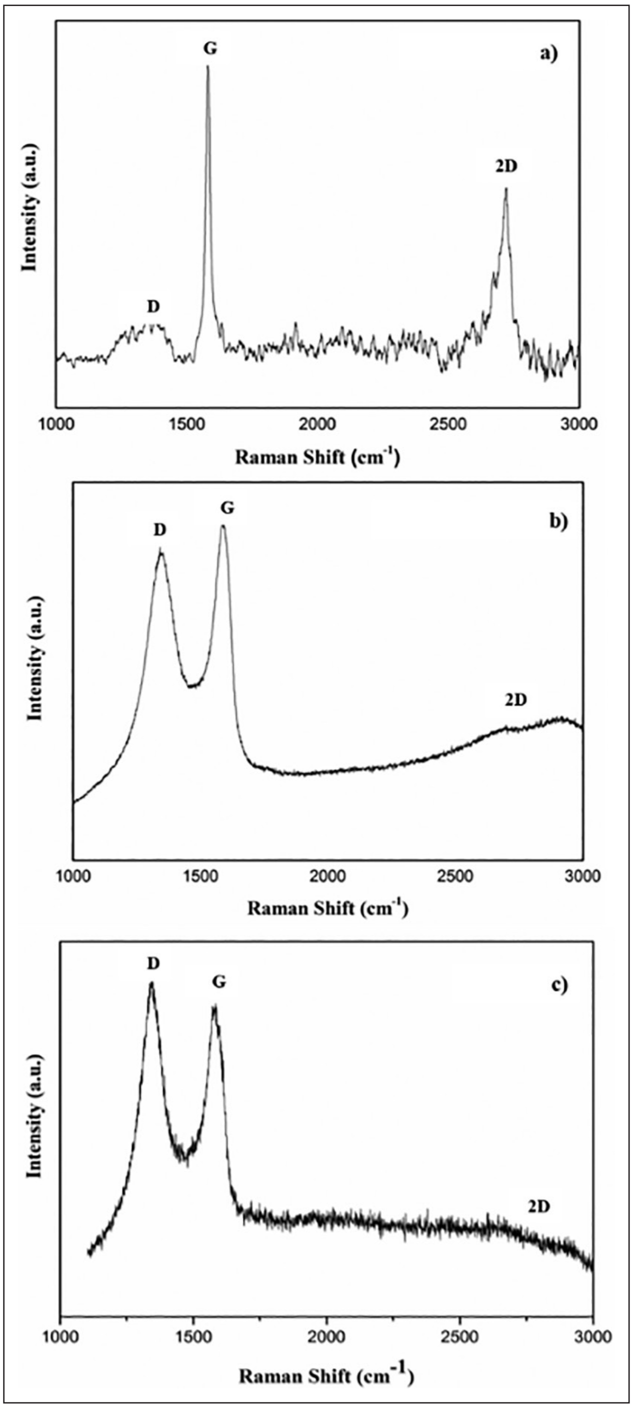

Figure 6. RAMAN spectra of graphite **(a)**, graphene oxide **(b)** and reduced graphene oxide **(c)**.

The role of solution pH is very important to remove the adsorbents from aqueous solutions. Because it affects the surface charge of the adsorbent and states of the functional groups of adsorbents as well as the adsorbate [41]. To study the influence of pH upon % removal rate of Pb(II) of synthesized materials, the experiments were conducted in the pH range of 3–6 at room temperature with 100 mg/L lead and the equilibrium time was kept 30 minutes. Equilibrium solution pH of adsorbent was measured by a portable pH meter. In the Pb(II) adsorption process, alkaline pH should be avoided as precipitation occurs instead of adsorption, therefore above the pH 6.00 were not studied [42].

The results of the experiment are shown in Figure 7. Maximum removal rate was obtained 69% and the adsorption capacity (69.3 mg/g) was the highest at pH 4.0 for GO. On the other hand, Pb(II) removal rate for rGO was higher than GO. rGO has 89% removal rate with the adsorption capacity was calculated 88.94 mg/g at pH 4.0. Since the values obtained at pH 5.0 and 6.0 were very close to pH 4.0, the studies were continued with pH 4.0 for rGO. In the current study, pH value of 4.0 was chosen as optimum.

Figure 8 shows the effects of different initial concentration of Pb(II) on the adsorption of the GO and rGO surface. Throughout the study, the initial lead concentration was studied from 25 to 250 mg/L at room temperature and the equilibrium time was kept 30 minutes at pH 4.0. The removal rate of Pb(II) decreases and the adsorption capacity increases with an increase in initial Pb(II) concentration. It may be due to an increase in the number of Pb(II) ions for the fixed amount of adsorbent. The decrease in percentage removal can be clarified that all the adsorbents had a limited number of active sites, that would have become saturated above a certain concentration. The amount of Pb(II) adsorbed per unit mass of GO and rGO increases with increase in Pb(II) concentration, may be due to the complete utilization of adsorption surface and active sites available which is not possible in low concentration. For the rGO, the optimum values of Pb(II) removal and adsorption capacity are found to be 89% and 88.94 mg/g, respectively, with the initial Pb(II) concentration value of 100 mg/L. For the GO, the optimum values of Pb(II) removal and adsorption capacity are found to be 70.9% and 35.48 mg/g, respectively, with the initial Pb(II) concentration value of 50 mg/L.

Adsorption is highly a time dependent process. When the adsorbent and adsorbate are contacted for a sufficient time, the adsorption performance will increase as the interaction between the ions will ensure the completion of the adsorption process. For this reason, it is very important that the adsorbent and Pb(II) ion have sufficient contact time and reach equilibrium in order to complete the adsorption reaction [2, 42]. In order to study the effect of contact time on adsorption of Pb(II) on GO and rGO was investigated to determine the equilibrium contact time shown in Figure 9.

Removal efficiency was observed to increase as the contact time was increased from 5 to 240 minutes. The uptake of Pb(II) onto GO was rapid within the first 60 minutes due to the availability of binding sites and greater concentration gradient. However, no considerable increase was observed on the removal efficiency as the contact time was further

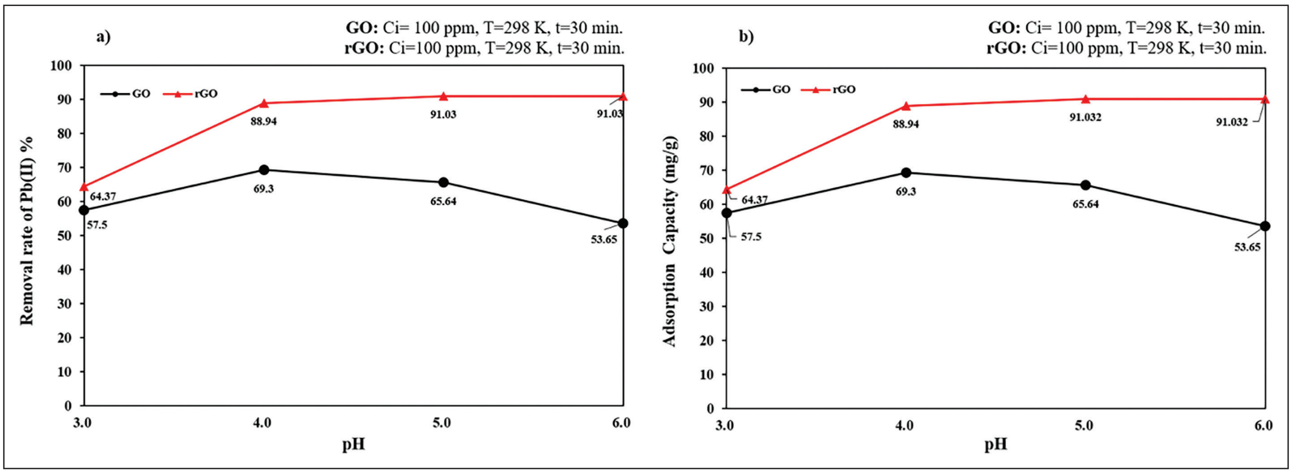

Figure 7. Effect of pH on removal rate **(a)** and adsorption capacity **(b)** onto the GO and rGO materials.

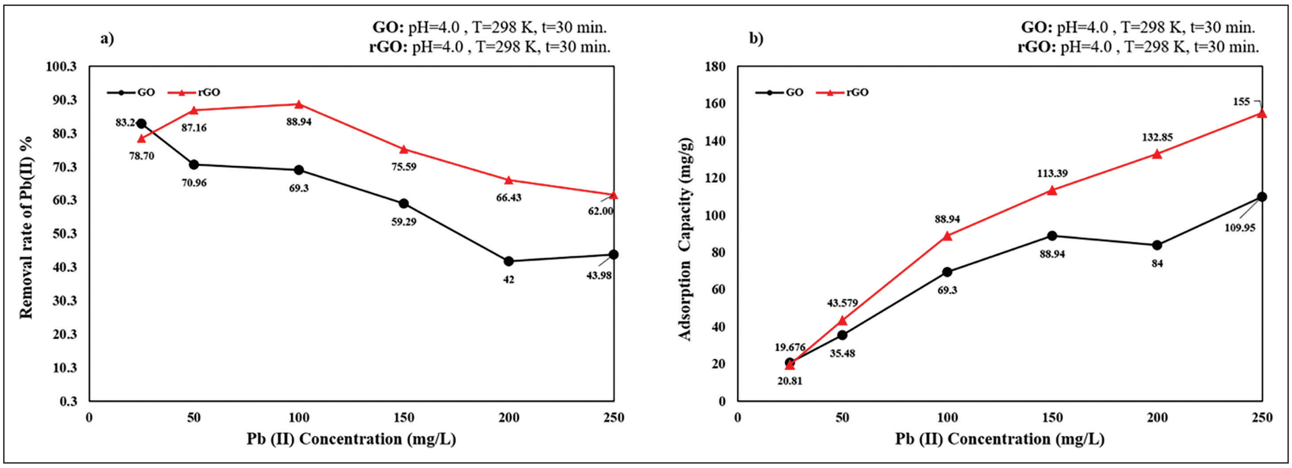

Figure 8. Effect of initial Pb(II) concentration on removal rate **(a)** and adsorption capacity **(b)** onto the GO and rGO materials.

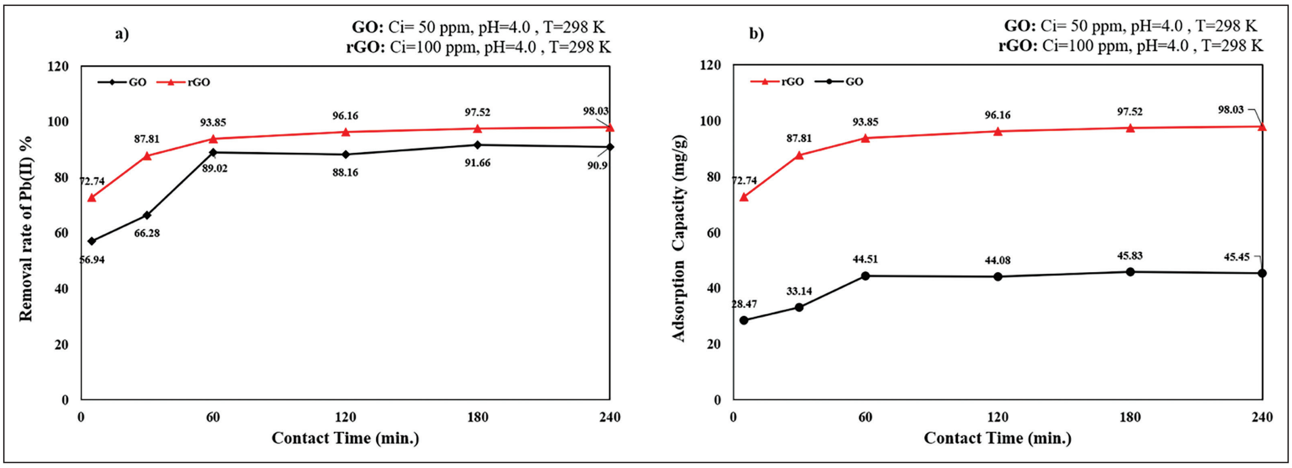

Figure 9. Effect of contact time on removal rate **(a)** and adsorption capacity **(b)** onto the GO and rGO materials.

increased from 60 to 240 minutes. Equilibrium was attained at 60 min. with maximum removal efficiency 89% with the adsorption capacity was calculated 69.3 mg/g for GO while 94% with the adsorption capacity was calculated 93.9 mg/g for rGO. In the present work, 60 min was selected as the contact time to ensure equilibrium.

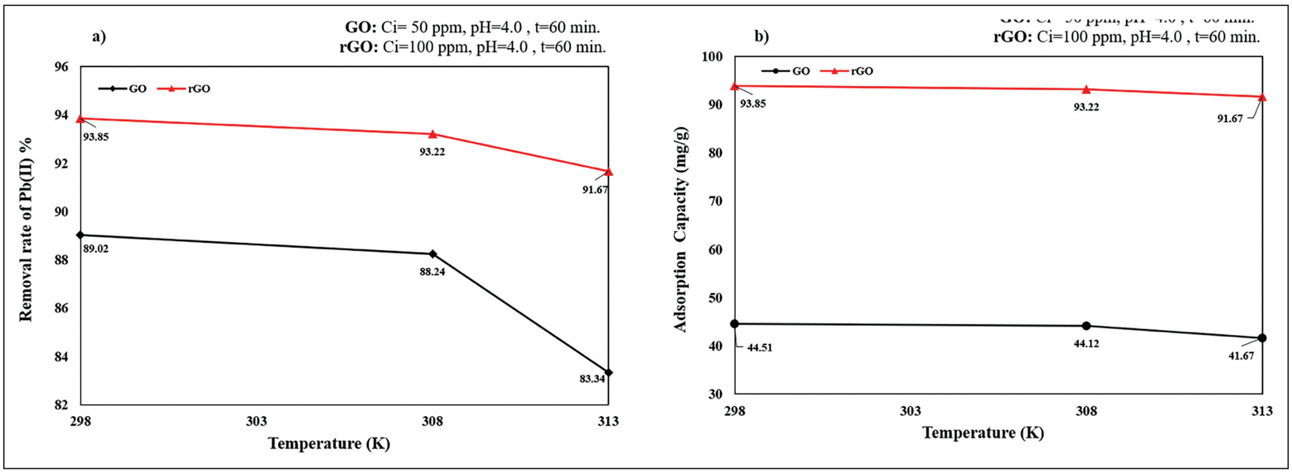

Figure 10. Effect of temperature on removal rate **(a)** and adsorption capacity **(b)** onto the GO and rGO materials.

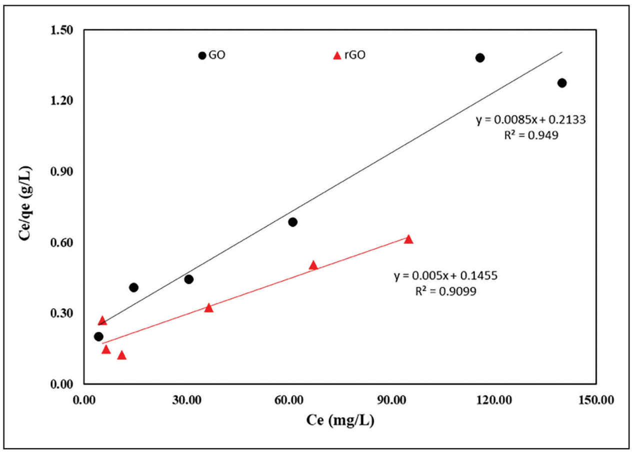

Figure 11. Langmuir plots for adsorption of Pb(II) by the GO and rGO materials.

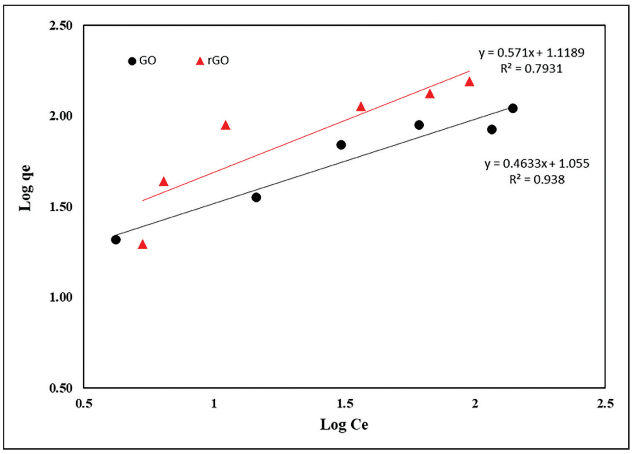

Figure 12. Freundlich plots for adsorption of Pb(II) by the GO and rGO materials.

To understand the effect of temperature, experiments at 298, 308 and 313 K were conducted and the results are shown in Figure 10. It has been seen that removal percentage of Pb(II) slightly decrease when the temperature increase. The adsorption process is more favorable at room temperature for both adsorbents.

Adsorption isotherms can be used to understand the interactions between an adsorbate and sites on the sorbent surface [43]. The Pb(II) solutions in the range of 25–250 mg/L was used to study the adsorption isotherms. Adsorption isotherms are represented by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models with the results shown in Table 2.

The Langmuir isotherm (Fig. 11) is widely used model that describes adsorption on homogeneous surface by monolayer sorption without interaction between adsorbed molecules [26, 44].

The linear form of Langmuir equation can be expressed as follows:

$$\frac{C_e}{q_e}=\frac{1}{K_L q_m}+\frac{C_e}{q_m} \tag{6}$$

where C_e (mg/L) is the equilibrium concentration, K_L (L/mg) is the Langmuir constant and qm (mg/g) is the maximum adsorption quantity.

The favorability of adsorption can be expressed by factor R_L in equation 7. The R_L values indicate that the adsorption process is favorable when $0< R_L <1$, unfavorable when $R_L >1$ and irreversible when $R_L=0$ [45].

$$R_L=\frac{1}{1+K_L C_i} \tag{7}$$

The Freundlich isotherm is based on heterogeneous adsorption process calculated by the equation 8 when plotted as Log q_e versus Log C_e (Fig. 12).

$$\log q_e=\log K_f+\frac{1}{n}\log C_e \tag{8}$$

where K_f and 1/n are the Freundlich constants. The value of n ranging from 1 to 10 indicated that the adsorption process is favorable [46].

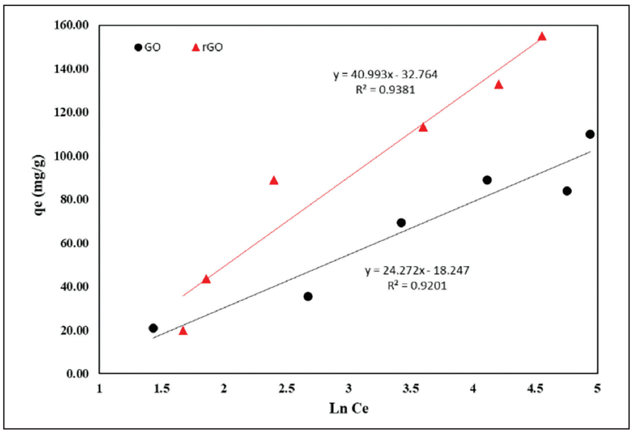

Figure 13. Temkin plots for adsorption of Pb(II) by the GO and rGO materials.

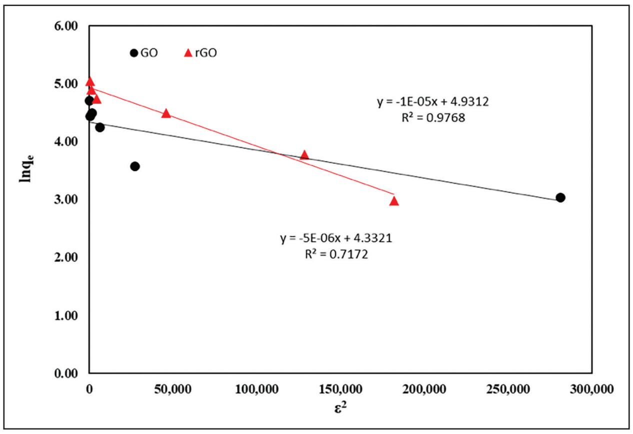

Figure 14. Dubinin-Radushkevich plots for adsorption of Pb(II) by the GO and rGO materials.

Table 2. Adsorption isotherm parameters of Pb(II) adsorption on GO and rGO

Isotherm models	Parameters	GO	rGO
Langmuir	q_m (mg/g)	117.647	200.000
	K_L (L/mg)	0.040	0.034
	R_L	0.334	0.225
	R^2	0.949	0.910
Freundlich	n	2.158	1.751
	K_f	11.350	13.149
	R^2	0.938	0.793
Temkin	b_T (J/mol)	24.272	40.993
	K_T (L/mg)	0.472	0.450
	R^2	0.920	0.938
Dubinin–Radushkevich	K_{DR} (mol/KJ)^2	0.00000500	0.00001014
	q_m (mg/g)	76.104	138.540
	E (kJ/mol)	316.228	222.014
	R^2	0.717	0.971

The Temkin isotherm (Fig. 13) is related to adsorbate and adsorbent interaction and based on this model, the temperature-dependent heat of adsorption of all molecules on the sorbent surface decreases linearly due to interactions with represent the following equation [43].

$$q_e = B\ \ln K_T + B\ \ln C_e \tag{9}$$

$$B = \frac{RT}{b_T} \tag{10}$$

where b_T is the Temkin constant related to the heat of adsorption [J/mol] and K_T represents the Temkin isotherm equilibrium binding constant [L/mg] corresponding to the maximum binding energy.

Dubinin–Radushkevich (D–R) (Fig. 14) is another model which is used to apparent free energy of adsorption, adsorption mechanism based on potential theory which assumes the porous structure and heterogeneous surface of the sorbent [47]. The linear form of D-R isotherm equation is given at the following [46].

$$\ln q_e = \ln q_m - K_{DR}\varepsilon^2 \tag{11}$$

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{12}$$

$$E = \frac{1}{\sqrt{-2\beta}} \tag{13}$$

where q_m (mg/g) is the adsorption capacity, K_{DR} (mol K/J)^2 is a constant related to energy, ε is the Polanyi potential, R is a gas constant (8.314 J/mol K), T is the absolute temperature (K), E is the adsorption mean energy. Plotting $\ln q_e$ against ε^2, the values K_{DR} and q_m can be calculated from the slope and intercept, respectively.

It can be seen from the Table 2 in accordance with the value of R^2, GO is fitted well by Langmuir isotherm with a maximum monolayer adsorption capacity 117.6 mg/g, while Dubinin–Radushkevich model shows a good agreement for rGO with a maximum adsorption capacity 138.5 mg/g. From the data calculated in Table 2, the R_L value of both GO and rGO are between 0–1 indicating that Langmuir isotherm is favorable. In addition, it is observed that the values of the Freundlich isotherm constant "n" are greater than 1, that means Pb(II) is favorably adsorbed onto GO and rGO. The calculated E value is used to predict the reaction mechanism of the adsorption process. If the E value is less than 8 kJ/mol, it indicates a physical adsorption, while the E value is higher than 8 kJ/mol, the adsorption process is chemical in nature [48]. In our cases, E value is 222 kJ/mol that means adsorption process is chemical in nature for rGO.

In Figure 15, the adsorption capacities obtained from the experimental and isotherm models are plotted. As seen in Figure 15a, Langmuir model shows better fit for GO while D-R model can be considered more proper for rGO in Figure 15b.

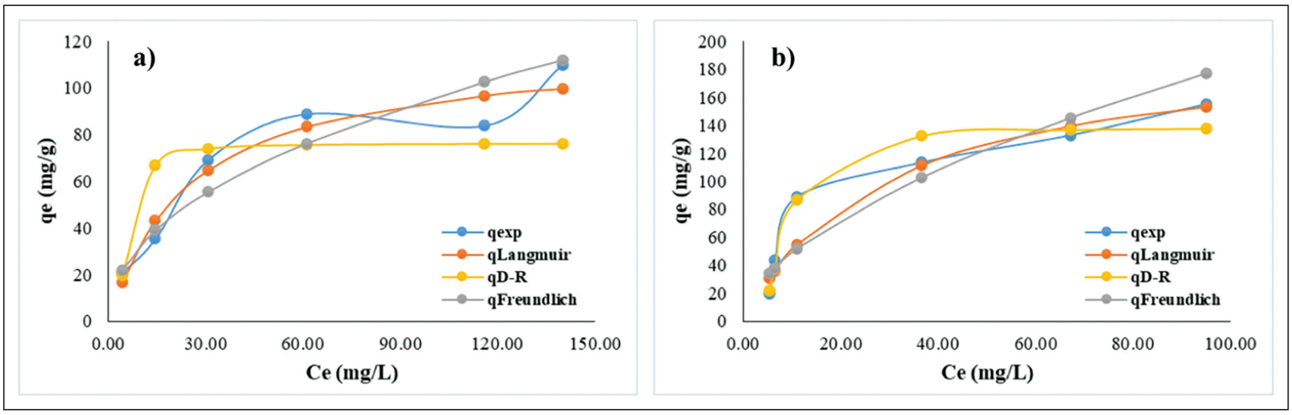

Figure 15. Comparison of adsorption capacities found from experimental and isotherm models for **(a)** GO and **(b)** rGO.

Table 3. Comparison of the maximum adsorption capacity of Pb(II) with various graphene-based adsorbents

Carbon-based adsorbent	Synthesis method	Isotherm model	Q_{max} (mg/g)	Reference
GO	Tour's	Langmuir	117.6	This work
rGO	Green Reduction by L-Ascorbic Acid	Dubinin–Radushkevich	138.5	This work
Graphene nanosheet	Vacuum-promoted low- temperature exfoliation	Langmuir	22.42	[49]
Graphene aerogel	Modified Hummer's	-	80.0	[50]
Polydopamine coated GO	Modified Hummer's	Langmuir	53.6	[51]
GO– Chitosan	Modified Hummer's	Freundlich	90.0	[52]
rGO-Mn3O4NC	Modified Hummer's chemical reduction followed by hydrothermal treatment	-	105.39	[53]
SiO_2/graphene	Hummer's	Langmuir	113.6	[54]

In this study shows higher Pb(II) capacities than other reported values for Pb(II) removal as mentioned in Table 3. These results suggests that graphene-based materials synthesized by environmentally friendly methods show great potential to remove Pb(II) ions in water pollution control applications.

The thermodynamic parameters that are ΔH^0, ΔS^0, and ΔG^0 for Pb(II) on GO and rGO were calculated from the temperature dependent adsorption isotherms. The related equations are shown from the following equations.

$$\Delta G^0 = -\ln K_L \quad (14)$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (15)$$

where ΔH^0 is the standard enthalpy change, ΔS^0 is the standard entropy change and ΔG^0 is the standard free energy change R is the ideal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin. The K_L is the thermodynamic equilibrium constant.

In this study, the experiments were carried out at 298, 308 and 313 K with a solution concentration of 50 mg/L of Pb(II) for GO and 100 mg/L for rGO. Linear plots of $\ln K_L$ vs 1/T for Pb(II) adsorption on prepared GO and rGO are shown in Figure 16. ΔH and ΔS were calculated from the slopes and intercepts of the plot of ln K_L vs 1/T by using eq 15.

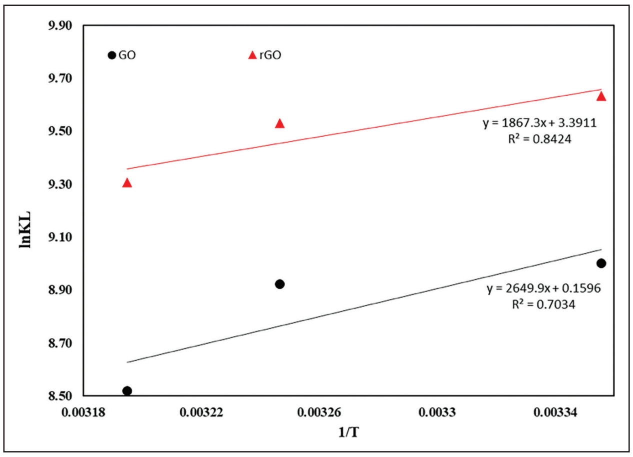

Figure 16. Thermodynamic studies for adsorption of Pb(II) by the GO and rGO materials.

The negative values of ΔG^0 for both materials show that the adsorption processes are spontaneous. The negative value of ΔH^0 infers the exothermic behavior of the adsorption. The positive value ΔS^0 indicate the increasing

Table 4. Thermodynamic Parameters for the Adsorption of Pb(II) on graphene oxide and reduced graphene oxide

Material	T (K)	ΔG (kJ mol⁻¹)	ΔH°/kJ mol⁻¹	ΔS°/J mol⁻¹ K⁻¹
rGO	298	-23.866	-15.525	28.194
	308	-24.400		
	313	-24.217		
GO	298	-22.299	-22.031	1.327
	308	-22.850		
	313	-22.165		

randomness at the solid/solution interface during the adsorption process. Related values of thermodynamic parameters were listed in Table 4.

In order to have an idea about the adsorption mechanism, the enthalpy and the size of the free energy change are used. Generally, the magnitude of ΔH° is less than 20 kJ/mol for absolute physical adsorption, while this value is in the range of 80–200 kJ/mol for chemical adsorption [55].

In general, the absolute magnitude of the change in Gibbs free energy for physisorption is between -20 and 0 kJ/mol, and chemisorption is in the range of -80 to -400 kJ/mol [56]. The results found for rGO and GO are in the range from -24.217 to -23.866 and -22.165 to -22.850 kJ/mol, respectively. These values are in the between physisorption and chemisorption [57]. It can be evaluated that physical adsorption was improved by a chemical effect. In addition, since ΔG° values are between 20 and 80 kJ/mol, adsorption type can be explained as ion exchange. Presumably the ion-exchange has a range from -20 to -80 kJ/mol [58, 59]. It can be concluded that the adsorption process is carried out with the control of several mechanisms together.

CONCLUSION

In the current study, GO was synthesized from graphite powder by Tour's method, which is a green method among the others and did not generate toxic gases during synthesis, and then non-toxic reducing agent L-ascorbic acid was used to obtain reduced graphene oxide. Both materials were characterized and compared by various methods. XRD results showed that the oxidation of graphite has given highly oxidized GO with a 10.37 Å interlayer space and decreased to 3.53 Å after the reduction of rGO by L-ascorbic acid. In addition, ATR-FT-IR analysis revealed that oxygen-containing functional groups present in GO were disappeared or decreased in intensity when converted to rGO. Wrinkled morphology was shown via SEM images and EDS analyses confirmed following reduction of GO to rGO; ratio of carbon content to oxygen content increases from 0.87 to 3.31. The intensity ratio D band to G band of rGO was higher than GO due to the removal of oxygen moieties and restoration of sp^2 carbon networks during the reduction which is confirmed by Raman spectroscopy. Pb(II) removal experiments by GO and rGO were done and investigated the effect of parameters such as solution pH, contact time, initial Pb(II) concentration and temperature. Obtained results from fitting the experimental data Langmuir model showed a suitable correlation (R^2=0.949) and the maximum adsorbing capacity of GO was found to be 117.6 mg/g while Dubinin-Radushkevich model offered a proper correlation (R^2=0.971) and the maximum adsorbing capacity of rGO was calculated to be 138.5 mg/g. In addition, thermodynamic parameters showed that the adsorption of Pb(II) ions is spontaneous and exothermic in nature.

Due to their high toxicity, the removal of Pb(II) ions from aqueous solution is vital for the remedy of environmental pollution. Considering the characterization and adsorption results of green synthesized GO and rGO, it is clearly understood that they are promising and environmentally friendly alternative adsorbent materials and have high adsorption capacity for Pb(II) ions. The outcomes of present investigation hint that both GO and rGO have the potential of being effective adsorbents of removal of heavy metal ions from large volumes of aqueous solutions in the pollutant cleanup.

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.

ETHICS

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

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Research Article

Investigation of the potential of greenhouse post-harvest wastes for bioenergy production and utilization for heating and carbon dioxide application

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ABSTRACT

In this study, raw biomass feedstock characterization of greenhouse post-harvest residues of tomato, pepper, and eggplant has been investigated using the wastes of stem and leaves as a source of energy gained from palletization. The characterization was compared to both sawdust and the relevant ISO and EU pellet standards. The proximate and ultimate analyses results of all the tested feedstock materials have proven to be successful candidates for pelletizing and combustion process. The bulk density of tomato, pepper, and eggplant pellets were found to be 568 kg/m^3, 575 kg/m^3, 589 kg/m^3, respectively, and the higher heating values of these produces were found to be 17.25 MJ/kg, 17.45 MJ/kg, and 17.80 MJ/kg, respectively. Based on the results, it is possible to generate 10 tons of waste per hectare capable of producing almost 50 MWh of heating energy. Furthermore, this waste could generate more than 6.5 tons of CO_2 per hectare. The study results suggest that the heating energy potential and the amount of CO_2 emitted could be used in greenhouses to support photosynthesis during low temperature and low solar radiation periods.

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INTRODUCTION

In recent years, the replacement of fossil fuels with environmentally friendly alternative fuels has been intensively studied. There are several reasons to replace fossil fuels with renewable energy resources: increasing oil prices, efforts to reduce carbon dioxide (CO_2) emissions to mitigate global warming, need for sustainable waste management, and collectively adopting a circular economy perspective for all production activities. In this context, biomass could offer clean, renewable energy resource in solid, liquid, and gaseous fuels by valorizing various biomass wastes, including crop harvest residues [1–3].

Limited land resources and agricultural input material pose a risk for increasing food shortages and are currently critical factors that hinder the agriculture sector from achieving global food security goals [4]. In this regard, greenhouse production systems have brought pivotal technologies enabling the implementation of highly productive agricultural systems. On the other hand, intensive farming generates an immense amount of harvest residue that needs sustainable management, every year [5]. It is estimated that the greenhouse vegetable production generates 253,000 tons of harvest residue in Türkiye, annually and most of this residue is either landfilled or incinerated without beneficial use [6].

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One approach to utilizing these wastes could be applied to produce pellet biofuel for space heating in greenhouses, as greenhouse production systems demand heat and CO_2, especially in soilless cultures.

In greenhouse production, producer needs more energy for heating during the cold season, as well as excess CO_2 to support photosynthesis. The countries that experience the four seasons usually need heating for most of the year. For example, the annual greenhouse energy demand in Northern European countries (e.g., Netherlands, Germany, Poland) reaches 3,600 megajoule per square meter (MJ/m^2) [7], while it remains in the range of 220–320 MJ/m^2 in the Mediterranean region. Similarly, the average heat consumption of the Mediterranean region has been estimated to be 200 kilowatt-hour per hectare per hour (kWh/ha.hr), while 500 kWh/ha.hr in Netherlands [8]. Moreover, the average demand of greenhouses for CO_2 has been estimated to be 2,628 t ha−1, annually [8].

For this purpose, greenhouses must be equipped with gas installations metering CO_2 in a pure form or obtaining it by combusting liquefied petroleum gas. In soilless cultures, the enrichment of greenhouses with external CO_2 is generally necessary during cold and low solar radiation. Pellet fuel production from crop harvest residue and combustion thereof could provide a solution for the sustainable management of greenhouse wastes and satisfy the need for energy and CO_2 [7].

Biomass fuel is considered carbon-neutral, locally available, processes modern fuels, and lead to increased employment. A key advantage of harvesting residue products is that their manufacturing processes are fundamentally based on organic waste valorization, aligning with the circular economy concept [9, 10]. Depending on the nature of the feedstock, a diversity of techniques can be used, such as thermal conversion, anaerobic digestion, and solid-state fermentation. Fabricating densified pellets is justified as a simple and well-known technology and can be easily adaptable to the greenhouse that uses solid fuel for heating purposes.

The greenhouse vegetable production industry is one of the agriculture sectors that generate large amounts of post-harvest residue, a potential feedstock for pellet fuel preparation. Tomato, pepper, and eggplant represent the majority of the vegetable crops grown through greenhouse production, worldwide [11]. The cover-crop industry generates wastes of various plants during both the harvesting of crops and post-harvest, and thus, extensively contribute to environmental pollution.

The low density of these biomass resources is a significant limitation for efficient handling, transportation, and possible valorization methods. Pelletizing these biomasses by applying pressure can increase the bulk density by 4 to 5 times [12]. The densified biomass provides a definite size and shapes with higher individual pellet and bulk densities. This, in turn, helps improve the handling and transportation, thereby enabling the possible valorization of the biomass through direct combustion for greenhouse heating. In addition, as densified biomass has a lower moisture content, it could also be stored for longer times with the minimum loss of quality.

Sustainable management of greenhouse residues was subject of many studies in recent decades. Several disposal alternatives such as composting, anaerobic digestion for biogas production, and torrefaction to improve energetic properties have been suggested. There are a few studies in the literature investigating the use of greenhouse harvest residues as pellet fuel materials for the potential of their sustainable and effective use. Due to the increasing demand for alternative fuel sources in recent years, pellet production facilities experienced the supply shortages of raw materials. For this reason, both research institutions and industrial organizations have turned to search for alternative raw materials that can replace wood pellets.

The use of agricultural residues as raw materials for pellets is regarded as one of the alternative solutions to increase the security of raw material supply given the increasing demand triggered by the growth in the pellet industry worldwide, increasing investment in renewable energy, and continuing raw material supply risk [10]. In addition, valorizing greenhouse post-harvest residues as pellet fuel has the potential to contribute to the establishment of small- and medium-sized agro-energy chains [6].

To that end, this study aims to pelletize post-harvest residues of greenhouse vegetables, i.e. tomato, pepper, and eggplant stalks, which are not currently used as biofuel, and determine the pellet fuel characteristics compared to the well-known sawdust pellet. The obtained pellets were evaluated for compliance with the relevant standards compiled by International Standards Organization (ISO) such as ISO 9831:2005 and ISO 18122:2016, and European Union (EU) EN ISO 18847:2016 [13, 14] pellet physical properties of sawdust.

MATERIALS AND METHODS

The post-harvest residues from tomato, pepper, and eggplant crops, which were cultivated in and harvested from a greenhouse in Sakarya, Türkiye, have been investigated in this study. The stalks of tomato, pepper, and eggplant were collected from the greenhouse after the harvest seasons were completed. These crop residues were then dried in the greenhouse for seven days. The vegetable crops were grown, with the density of 3.0 plants per m^2 from April 2020 to November 2020. The air-dried residue samples, with 9–11% moisture content, were ground to the particle size less than 4 mm sieve hole diameters using an industrial scale grinder. Afterwards, biomass pellets were manufactured using an industrial scale pellet mill currently used at biomass

Table 1. Proximate and ultimate analyses of the raw material samples

Parameter	Tomato stalks	Pepper stalks	Eggplant stalks	Sawdust
Proximate analysis				
Volatile matter (%)	62.39	63.88	66.90	67.44
Ash (%)	17.73	16.86	11.82	8.26
Moisture (%)	10.23	9.78	11.12	13.05
Fixed carbon (%)	9.65	9.48	10.16	11.25
Ultimate analysis				
C (%)	38.86	38.25	40.29	47.64
H (%)	5.34	5.77	6.83	6.03
N (%)	0.94	1.14	0.52	0.05
S (%)	0.21	0.42	0.09	0.02
O (%)	54.65	54.42	52.27	46.26

combustion plant for biomass pelleting. Pellet mill parameters were set at a pellet diameter of 10 mm. Samples were continuously fed into a pellet mill through a rotating die-hole press. Approximately 100 kg of samples at equilibrium moisture content were compressed for each experimental trial with a predefined procedure.

Proximate and Elemental Analyses

The dried and ground biomass samples were subjected to physical and chemical analyses to determine the basic chemical parameters, energy potential, and elemental composition. The contents of moisture content, volatile matter, fixed carbon, and ash were measured as proximate analysis parameters. The moisture content was determined on a wet weight basis after drying at the constant weight at 100 °C in a drying cabinet. The volatile matter and ash content were determined by the mass change at 900 °C in a capped crucible and at 550 °C in an open crucible, respectively. The fixed carbon content was estimated by subtracting the mass of the moisture content, volatile matter, and ash from the total mass.

The analyses results provided the percent weights of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) contents of the biomass samples. C, H, and O are the most important components of biomass. C and H are exothermically oxidized to CO_2 and H_2O and contribute positively to the biomass higher heating value (HHV). On the contrary, O contributes negatively to the calorific value. N and S generate gaseous NOx and SO_2 emissions during the combustion of biomass, hence are not desired nor required in biomass fuel. According to the test method, the elemental analysis was carried out using a Leco CHNS-932 elemental analyzer, which enables the simultaneous determination of the C, H, N, and S contents of the raw material samples. O was determined by difference as in Eq. 1.

$$O=100-(C+H+N+S) \quad (1)$$

The calorific value of the samples was determined by using a bomb calorimeter IKA, type C 200 manufactured in Germany. The obtained results represented the HHV (MJ/kg), while lower heating value (LHV) (MJ/kg) was estimated based on the moisture and hydrogen contents of the samples using the following Eq. 2.

$$LHV=HHV-24.42\times(Mc+8.94\times H) \quad (2)$$

In Eq. 2, the coefficient of water in the sample at 25°C (MJ/kg) was assumed to be 24.42; Mc denotes the moisture content in the sample; the coefficient of the hydrogen to water conversion was assumed to be 8.94; and H denotes the hydrogen content in sample (%).

Particle and Bulk Densities

The densities of pellets were determined by measuring the dimensions and weights of the pellet samples. The calculated density is represented by the average of 10 measurements. The bulk density of pellets was determined by filling a known volume container and taking the ratio of measured mass of sample in the container to the volume of the container.

RESULTS AND DISCUSSION

Proximate and Ultimate Analyses

The results of the proximate and ultimate analyses on the harvest residues of raw greenhouse crops and those of the sawdust are given in Table 1. As expected, the volatile matter, ash and fixed carbon contents of the harvest residues of tomato, pepper and eggplant were significantly different from and were lower compared to those of sawdust. In general, a low level of moisture content is required for biomass palletization, as higher levels of Mc cause serious complications during the pressure application and in the final quality of pellet products. The equilibrium Mc is desired to be around 10% for both densification process and pellet storing, handling, and combustion applications. The

Table 2. Pellet quality parameters of tomatoes, pepper, and eggplant, and comparison with sawdust pellet, ISO and EU pellet quality criteria

Parameter	Tomato stalks	Pepper stalks	Eggplant stalks	Sawdust	ISO	EU
Diameter (mm)	10	10	10	10	6–8±1	6–8±1
Length (mm)	14–30	13–32	13–31	13–35	3.15≤ L ≤40	3.15≤ L ≤40
Moisture (%)	11.50	10.20	10.39	12.97	≤10	≤10
Ash (%)	17.64	15.85	12.82	18.90	≤5.0	≤3.0
Bulk density (kg/m^3)	568	575	589	693	≥600	≥600
LHV (MJ/kg)	15.87	16.04	16.16	16.08	≥16.5	16.3–19.0
HHV (MJ/kg)	17.25	17.45	17.80	18.30	–	–
Powder (%)	4.4	3.75	3.60	2.1	≤7.0	≤7.0
Pellet unit density (kg/m^3)	993	1008	985	1080	–	–

high feedstock moisture content (i.e., Mc > 15%) means an unsuccessful densification process. The Mc of the investigated samples was in the range of 9.78% for pepper stalks to 11.12% for eggplant stalks and was lower than those of sawdust (Table 1), which represents a satisfactory Mc range.

Ash content is another parameter determining the fuel quality of the pellets. The ash content was in the range of 11.82% for eggplant stalks to 17.73% for tomato stalks, which were in alignment with the range reported in the literature [5]. Low level of ash content is required for pellet fuel due to the negative impact of high ash content on combustion efficiency, low burning rate, and HHV [3]. The relevant ISO and EU standards respectively set an ash content of 5% and 3% for wood pellets. Based on these standards, the post-harvest residues of tomato, pepper, and eggplant could have potentially initiate incineration and cause ash related problems in a burner.

The proximate analysis results were also confirmed by the elemental analysis data. Elemental composition differs depending on investigated plant parts. In general, biomass samples indicate a carbon content of 45–50%. The elemental analysis results show that the carbon contents in the analyzed samples were 38.25% for pepper stalks, and 40.29% for eggplant stalks. The H contents were measured as 5.34% for tomato stalks and 6.83% for eggplant stalks. The increase in C and H improves the fuel properties of biomass feedstock. Based on their C and H contents, the eggplant stalks indicated better biomass characteristics compared to the pepper and tomato stalks. The analyses results are also in alignment with the study by [15], who observed similar elemental composition for eggplant residues. Biomass N content also varies depending on plant parts; higher content in leaves (2.56%–4.00%) than in stems (0.15%–0.28%) [16]. High content of N and S generally are not desired nor required in biomass fuel due to the possibility of formation of gaseous emissions and possible ash related problems in a burner during combustion. However, the data presented in Table 1 may be average, yet satisfactory levels of quality of N and S within their roles in biomass and solid biofuel burning.

Overall, the evaluation of the proximate and ultimate analyses proved a satisfactory level of all investigated parameters, demonstrating the potential of tomato, pepper and eggplant post-harvest residues for producing biomass pellet fuel by direct combustion processes.

Pellet Characterization

After the proximate and elemental evaluations of the dry biomass samples, a commercial size pelletizing technology has been used for pellet production. The pellet characterization of the produced pellet samples from the post-harvest residues of tomato, pepper, and eggplant is presented in Table 2, comparing the results parameters to those of the sawdust and ISO and EU wood pellet standards. All three feedstock samples were successfully pelletized, and durable pellets were obtained, which indicated the feedstock's suitability for the densification process.

Bulk and individual pellet density are essential for densified pellets for handling, storage, and transportation, and a higher level is more desired. The obtained bulk density values were around the recommended values by the relevant ISO and EU standards, which suggest a density of >600 kg/m^3. However, the measurement values were observed to be all below the mandatory standard, though the obtained results were within the reported values for straw pellets [2]. Previously published research proved the bulk density of pellets from greenhouse melon harvest waste to be higher than 667 kg/m^3 [12]. Found the maximum bulk density of 350 kg/m^3 for tomato waste pellets [17]. The pellet bulk density parameter is related to the particle size distribution, applied pressure, characteristics of raw feedstock, moisture content, diameter, and pellets size. The smaller bulk density could be attributable to the applied pellet diameter of the present study. However, the ISO and EU standards indicate the mandatory values of 6 to 8 mm in diameter. On the other hand, the pellet unit density results proved the reported density for pepper residue [6], eggplant stalks [15], and tomato residue [5]. Notably, the samples showed a satisfactory bulk and pellet unit density (Table 2).

The moisture content of pellet samples varies between 10.2 and 11.5 for pepper and tomato, respectively. These values are close to the ones obtained for the raw materials, indicating the equilibrium moisture contents of specific materials. Low moisture content is very important to ensure good combustion [12], handling, storage, and transportation [3].

The three types of harvest residue pellets showed similar calorific values (i.e., HHV) to sawdust and lower boundary values compared to the ISO and EU standards. The proximate and ultimate analyses results contribute to the understanding of the calorific values of biomass pellet. The positive and negative contributor parameters might balance the calorific value of the tested materials. In fact, the HHV increases with an increasing C and H ratio. On the other hand, oxygen, moisture, and ash contents negatively correlate with HHV. The C content of the fuel is the primary resource of the heat generated during combustion. This result clearly indicates that the HHV of pelleted biomass can be potentially used for greenhouse heating.

An application that could help improve the referred parameters such as moisture content, ash content, and bulk density in accordance with the referred ISO and EU standards could be to dry sawdust and add more of it into the residues of other crops, e.g. pellets made out of pepper and sawdust.

Energy Potential

Most greenhouses are built at locations where climate conditions are more suited to year-round vegetable production based on either one or two crops production annually [11]. [18] reported an estimation of 1.3 kg/m^2 post-harvest residue for tomatoes in Italy. Similarly, [19] estimated 0.9 kg/m^2 of post-harvest residue for tomatoes on a dry weight basis. On the other hand, [11] estimated an average of 1.6 kg/individual plant harvest residue for tomatoes in fresh weight. Combining the above values and the average number of plants per square meter, which is in the range of 1.5 and 3.0, vegetable crop residues in a greenhouse are estimated to exceed 1.0 kg/m^2 on a dry weight basis, annually. This amount of waste can sustainably produce 17.50 MJ/m^2 of heating energy. Based on the information given in the introduction section, the average heat consumption in the greenhouse of the Mediterranean region is estimated at 200 kWh/ha.hr [8].

Greenhouse energy demand is determined by different factors such as local climate, temperature, and solar radiation. According to the long-term meteorological data on Sakarya, Türkiye, the annual temperature ranges from 2 to 30 °C, and the solar radiation has been estimated to be 1340 kWh/m^2. Based on the solar radiation intake of different world regions, the heating energy necessary to maintain an adequate temperature in a greenhouse Sakarya, the case city, has been assumed to be 300 kWhth (in the range of values specific to the conditions in the Mediterranean region and the conditions in the Netherlands) and corresponding to an annual demand of 3,066 MWhth per hectare (8,760 hours).

Assuming the average heating value of 4.86 kWh per kilogram of waste, 10 tons of waste residue per hectare can annually produce approximately 48,600 kWh of heating energy. Accordingly, this obtained heating energy can supply about 1.85% of the energy needed in an average greenhouse under the climatic conditions in Sakarya.

Moreover, the average greenhouse CO_2 demand is estimated to be almost 2,650 t/ha [15]. The carbon content of the tomato plant, including stem and leaves, has been reported to be as 18% [14]. Hence, the annual tomato waste would give approximately 1,800 kg C and 6,600 kg CO_2 per hectare. The excess CO_2, which is to enough to supply only about 0.4% of the annual CO_2 demand of an average greenhouse, could be fed into the greenhouse to support photosynthesis during low temperature and low photosynthetically active radiation (PAR).

CONCLUSION

This study focused on characterizing the greenhouse vegetable post-harvest residues of tomato, pepper, and eggplant for pellet production. Proximate and ultimate analyses of the investigated plant species were satisfactory for pellet fuel production. HHV values were 17.25 MJ/kg, 17.45 MJ/kg, and 17.80 MJ/kg for tomatoes, pepper, and eggplant harvest waste pellets, respectively, and comparable to the calorific value of sawdust pellet (18.30 MJ/kg). The moisture (10.20–11.50%) and ash (12.82–17.64%) contents were evaluated in investigating the harvest residues' suitability for energy generation by direct combustion. Thus, the investigated pellet input material proved its suitability as a promising feedstock for pellet biofuel production. According to the average heating value and dry plant harvest residue, it is possible to obtain 10 tons of wastes per hectare capable of producing 48,600 kWh of heating energy and 6,607 kg of CO_2 to be supplied to the greenhouse for photosynthesis. For an effective waste management strategy to ensure environmentally friendly treatment and utilization of such significant amounts of energy for greenhouse heating, the assumed pelleting technology proved its advantage and efficiency within the clean energy generation and CO_2 utilization. Future research on this line will focus more on both comparative and prospective life cycle assessment of different palletization technologies.

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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.

ETHICS

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

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Research Article

Optimizing the amount of concrete for the construction of wastewater stabilization ponds: A case study of Ayvadere, Trabzon, Türkiye

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ABSTRACT

Natural systems are a cost-effective way to clean wastewater from small communities. This paper aims to use an optimization technique to minimize the volume of concrete needed to construct a facultative pond provided within a series of three ponds. A nonlinear constrained optimization model was written and then solved using one of the Add-Ins of MS office. The add-in used was Excel Solver, and the algorithm was generalized reduced gradient (GRG). Before applying the optimization model, wastewater stabilization ponds (WSPs) were designed using various configurations and arrangements. The best possible configuration that gave minimum area and hydraulic detention time was selected for the study area. Afterward, the optimization model was applied that further reduced the area by 11.46%, hydraulic detention time by 11.47%, and concrete volume by 6.94% compared to the traditional approach. In both methods, effluents satisfy the Turkish class-B standards for irrigation. It is recommended that a small-scale application of the model be made to compare the results before applying it on a large scale.

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INTRODUCTION

Wastewater treatment helps improve aquatic ecosystems' health and reduces contamination of natural water bodies. Treating wastewater minimizes the pollution of water bodies and improves the health of aquatic ecosystems. Natural methods for wastewater treatment, such as wastewater stabilization ponds (WSPs) and constructed wetlands, are promising techniques for treating wastewater in decentralized communities [1].

Natural wastewater treatment systems, like (WSPs), have many advantages over traditional methods, such as similar treatment performance. The use of renewable energy helps to reduce operating costs. Minimal involvement of mechanical parts helps in long-term operation without needing repair and maintenance. Due to their primary reliance on nature, there is no need to employ qualified personnel for construction, operation, and maintenance, hence decreasing the overall cost. The wastewater treatment based on natural processes may also provide indirect benefits,

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such as making that part of the land look better, making a home for wildlife, or giving people a chance for recreational and educational activities. Also, their effluent can be used to irrigate various crops. The problem with natural systems is that they need a large area which increases their construction cost [2]. So, there is a need to explore ways to reduce the overall cost of natural wastewater treatment systems. This study sought to reduce the cost of building a facultative pond provided within a series of three ponds.

When it comes to the construction of wastewater treatment plants, wide-ranging materials, like concrete, steel, gravel, sand, soil, and other similar materials are used to build wastewater treatment plants (WWTPs) [3, 4]. Additionally, wastewater treatment is based on several processes that require chemicals, electricity, and air. There are also byproducts of treatment, such as sludge, carbon dioxide (CO_2), and methane (CH_4) [5]. WSPs have several types, such as aerobic, anaerobic, facultative, and maturation ponds. They have different flow conditions: complete mix, dispersed, and plug flow [6]. As WSPs are based on natural systems for wastewater treatment, minimizing the overall area required to construct the treatment plant is necessary. This area reduction will help reduce the needed concrete volume for WSPs [2].

According to Goodarzi et al. [7], baffle walls (BWs) in pond systems improve flow conditions, eliminate dead spots, and enhance pollution removal efficiency. So far, there have been studies about stabilization pond systems, including different numbers and lengths of BWs. Li et al. [8] have discussed the effect of various lengths, numbers, and spacing between BWs. He has also discussed the works of multiple authors who worked on the effect of BWs. Goodarzi et al. [7] discussed that the BWs increase the efficiency of the hydraulic system in WSPs. Their addition helps the piston flow and, therefore, increases the efficiency of wastewater treatment. This research also examines how BWs reduce the acreage and concrete needed to build a facultative pond. One of the Add-Ins for MS excel is used to ensure the facultative pond is built in the best way possible. The system uses the generalized reduced gradient algorithm (GRG) to run the analysis [9]. The program inspects and adjusts variables until constraints are met [10].

This research optimized the concrete volume needed to build a facultative pond provided between anaerobic and maturation ponds. Following were the goals of this study: (a) Design of WSPs with the traditional method, including various numbers and lengths of baffles, to select the best configuration for the study area. (b) Optimize the design using the GRG algorithm. Three decision variables were optimized: hydraulic detention time, number, and length of baffles. (c) Design facultative ponds by applying the results of an optimization model. (d) Compare the results and determine the reduction in the volume of concrete. The design of WSPs involves the meteorological parameters of the pond area, which is in the Ayvadere village of Arakli city in Trabzon province of Türkiye.

MATERIALS AND METHODS

Acronyms and Abbreviations

MPN, Most probable number; LPCD, Liter per capita per day; N_{BW}, Number of baffle walls; L_{BW}, Length of baffle walls; BWs, Baffle walls; WSPs, Wastewater Stabilization Ponds; APs, Anaerobic Ponds; FP, Facultative Pond; MP, Maturation Pond; D_T, Detention time; O_L, Organic load; Q_i, Inflow of the wastewater stabilization ponds (m^3/d); Q_e, Outflow from the wastewater stabilization ponds (m^3/d); $(BOD_5)_i$, Concentration of 5 days influent biochemical oxygen demand (mg/l); $(BOD_5)_e$, Concentration of 5 days effluent biochemical oxygen demand (mg/l); T_{avg}, Region's coldest average monthly air temperature (°C); V_p, Pond volume (m^3); d_p, Pond depth (m); t; Thickness of concrete slab and walls; A_p, Area of the pond (m^2); Kt, Overall decay constant (d^{-1}); K_b, Bacterial decay constant (d^{-1}); K_f, BOD_5 decay constant at the average temperature of the coldest month in the region (d^{-1}); N, Population (Number of persons); N_i (MPN/100 mL), Influent Fecal coliform; N_f/N_o (MPN/100 mL), Effluent fecal coliform; N_e (MPN/100 mL), Effluent fecal coliform; X, Ratio between length and width; W_{avg}, Average width of the pond (m); L_{avg}, Average length of the pond (m); L_{top}, Length from top of the pond (m); W_{top}, Width from top of the pond (m); A_{top}, Area from top of the pond (m^2); A_f, Area of the facultative pond (m^2); d_f, Dispersion factor; a, Dimensionless constant; λ_v, Volumetric load ($g/m^3/d$); λ_s, Surface loading (kg/ha.d).

Marais method was followed for the design of anaerobic ponds. The facultative and maturation ponds were designed based on the Yanez method for the dispersed flow. Martinez et al. [11] have summarized the design steps of these ponds. The design of WSPs involved in this manuscript followed the same steps. There were three configurations analyzed in this study: (i). Configuration 1: Anaerobic, facultative, and maturation ponds. (ii). Configuration 2: Facultative and maturation ponds. (iii). Only facultative pond. The changes made to the design calculations based on meteorological conditions of the study area are mentioned below.

Anaerobic Pond

a. Volumetric $\left(\frac{g.\ BOD_5}{m^3.d}\right) = \lambda_v = 100$ (1)

b. BOD_5 removal (%) = 40 (2)

Facultative and Maturation Ponds

c. The maximum surface loading rate of biochemical oxygen demand (BOD_5) is calculated using the equation below.

$$\lambda s\left(\frac{kg}{ha.d}\right) = 350 \times \left(1.107 - 0.002 \times T_{avg}\right)^{T_{avg}-25} \quad (3)$$

The equation incorporates safety factors to give a design equation for FPs that can be used globally [12].

d. The coefficient of bacterial reduction was also different. First, $(K_b)_{20}$ was calculated based on the depth of FPs and MPs. Then $(K_b)_{T_{avg}}$ was calculated based on the last ten years' average temperature during the coldest month of the study area.

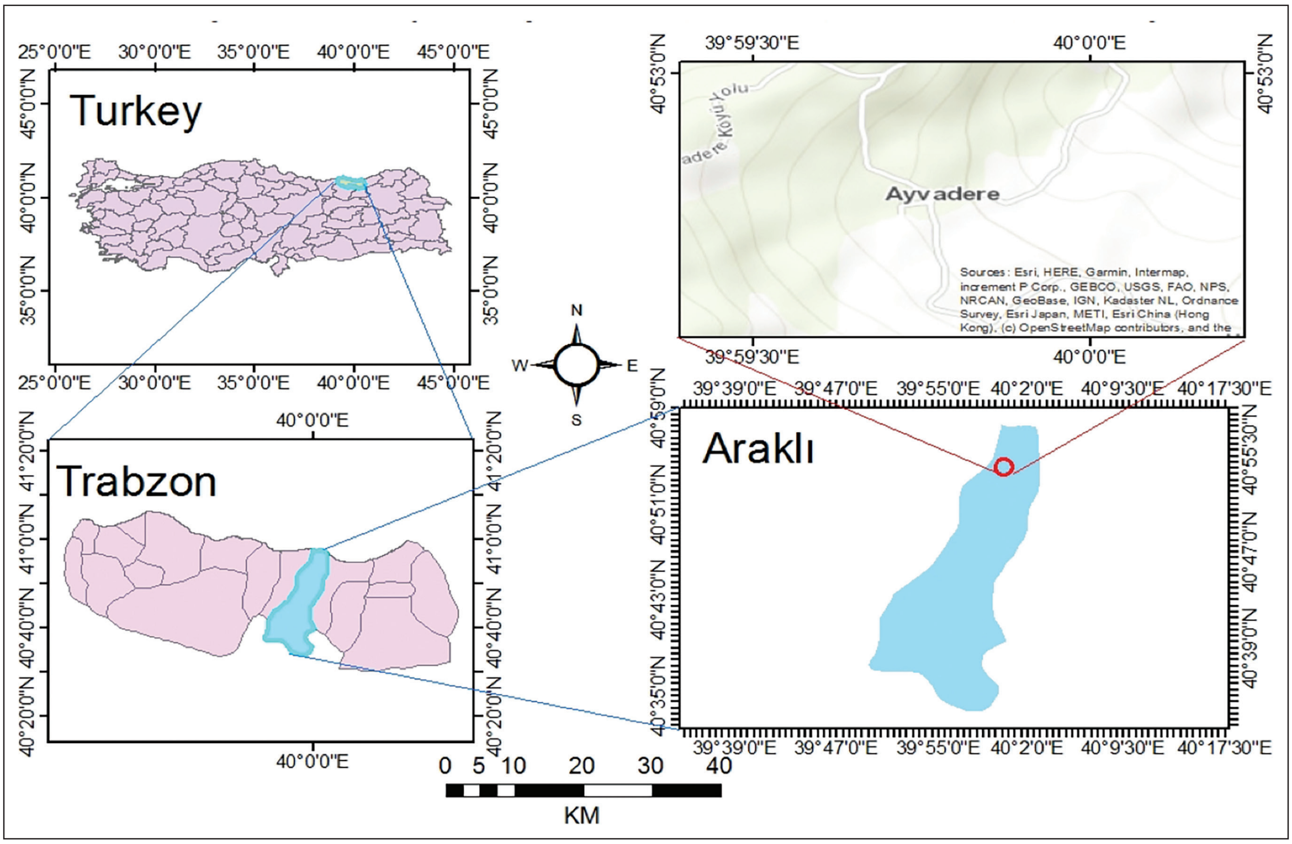


Figure 1. Study area map of Ayvadere, Araklı, Trabzon, Türkiye.

$$(k_b)_{T_{avg}} = (k_b)_{20} \times \theta^{\,T_{avg}-25} \tag{4}$$

Where: $(k_b)_{20}$= 0.542 x $H^{-1.259}$, and the value of θ was taken constant; Marais 1974 used 1.19. However, Yanez 1993 mentioned that the value is overestimated and must be taken as 1.07 [13].

Note: To meet the Turkish design standards for WSPs, manual adjustment was made to the hydraulic detention time of facultative ponds, as it is done in the design procedure of the maturation ponds.

Optimization Model

The Excel solver performed the concrete volume optimization for the facultative pond, which employed a GRG algorithm. As the objective function, the volume (V_{conc}) is written in terms of concrete required for the slab, parameter walls, and BWs of the facultative pond. The mathematical relationships explored for the design optimization are listed below. The hypothesis is to maintain the mathematical link between detention time, length, and the number of BWs in the model. The design and or decision variables represent the hydraulic detention time (D_T), number (N_{BW}), and length of BWs (L_{BW}). The dimensions of the base slab, parameter walls, and BWs are written in terms of these variables in equations 12 and 13. The equation 13 was used as the objective function in this optimization model.

Minimize concrete volume for the facultative pond =V=

Concrete volume for the base slab $((L\times W)\times t)+$

Concrete volume for the parameter walls $((2\times L\times d_p+2\times W\times d_p)\times t)+$

Concrete volume for BWs (%age length of the BWs×((L× Number of BWs × d_p)×t) (5)

The walls and floor slab thicknesses were considered equal (t=15 cm). For simplification, t was taken as common, and the equation was modified as given below.

$$Min. V = \left[(L\times W) + (2\times L\times d_p + 2\times W\times d_p) + \left(\left(\frac{L_{BW}}{L}\times 100\right)\times N_{BW}\times d_p\right)\right]\times t \tag{6}$$

Following are the steps that were taken to represent the dimensions in terms of design variables.

Average hydraulic detention time:

$$D_T = \frac{V_p}{Q_i} \tag{7}$$

$$V_p = A_p \times d_p \tag{8}$$

If the length-to-width ratio is 3, then the length and width of the facultative pond can be calculated as mentioned below.

$$L = 3\times B \tag{9}$$

Depth of the parameter walls and BWs was equivalent and represented as: (d_p)=1.5 m.

Table 1. Design calculations using traditional methodology

Pond	N	LPCD	T_{avg} °C	$(BOD_5)_i$	N_i	d_p
Anaerobic	1200	179	8.9	200	10000000	4
Facultative			8.9	120	5717492	1.5
Maturation			8.9	19	11104	1
Q_i	O_L	% Removal of BOD_5	λ_v	λ_s	V_p (m^3)	A_p (m^2)
214.80	42.96	40	100		429.60	107
214.18	25.70	87.49		88	10494.68	6996
173.60		67.99			3472	3472
DT	$(BOD_5)_e$	$(BOD_5)_e$ corrected by evaporation	Qe	BW Length (% × L)	X	d_f
2.00	120	120	214.18			
49.00	15	19	173.60	0.5	38	0.0261
20	5	5	153.46	0.5	19	0.0524
71.00						
a	K_t	K_f	N_e	N_e corrected by evaporation	BWs	L-W ratio
	0.3771		5700912	5717492		2
1.34	0.1534	0.14271	9000	11104	4	3
1.44	0.2558	0.14271	162	183	4	
W_{avg}	L_{avg}	W_{top}	L_{top}			A_{top}
7.33	14.66	7.33	14.66			107
48.29	144.88	48.29	144.88			6996
48.29	71.89	48.29	71.89			3472
The total area of WSPs with traditional methodology (m^2)			10576			
Concrete volume for the facultative pond with traditional methodology (m^3)						1201.59

$$B = \sqrt{\frac{D_T \times Q_i}{3 \times d_p}} \tag{10}$$

$$L = 3 \times \sqrt{\frac{D_T \times Q_i}{3 \times d_p}} \tag{11}$$

The equation 6 was modified as given below by substituting the length (L) and width of the pond.

$$\text{Min. } V = \left[\left(3 \times \sqrt{\frac{D_T \times Q_i}{3 \times d_p}} \times \sqrt{\frac{D_T \times Q_i}{3 \times d_p}}\right) + \left(\left(2 \times \sqrt{\frac{D_T \times Q_i}{3 \times d_p}}\right) + 3 \times \left(2 \times \sqrt{\frac{D_T \times Q_i}{3 \times d_p}}\right)\right) \times d_p + 3 \times d_p \times N_{BW} \times L_{BW} \times \sqrt{\frac{D_T \times Q_i}{3 \times d_p}}\right] \times t \tag{12}$$

By following the square root multiplication rules and multiplying the other terms involved, equation 12 can be further simplified as below:

$$\text{Min. } V = \left[\left(3 \times \frac{D_T \times Q_i}{3 \times d_p}\right) + \left(8 \times \sqrt{\frac{D_T \times Q_i}{3 \times d_p}}\right) \times d_p + 3 \times d_p \times N_{BW} \times L_{BW} \times \sqrt{\frac{D_T \times Q_i}{3 \times d_p}}\right] \times t \tag{13}$$

It is essential here to notice and keep in mind that the design flow is not a decision variable. Instead, it is used to design the pond based on the project's population. The design and optimization constraints are given below.

$BOD_5 \leq 30$ mg/l,

Fecal coliform ≤ 200 MPN/100mL,

$N_{BW} \leq 10$,

N_{BW} = Integer,

$30 \leq D_T \leq 50$ days,

$0.5 \leq L_{BW} \leq 0.9$,

N_{BW}, D_T, and $d_f > 0$.

Application of the Model

Ayvadere is a neighborhood in Arakli, Trabzon, Türkiye (Fig. 1). A facultative pond was designed for this neighborhood provided in configuration 1. The number of residents in the study area was calculated by considering 20 years design period were, 950; the rate of water supply taken was, 179 (LPCD), wastewater generation rate was considered 80% of the water supplied; design flow in m^3/day (Q_i)=214.8 [14]. The average temperature of the study area's coldest month calculated from the last ten years' meteorological data was 8.9 °C. The evaporation rate was also calculated from the last ten years' metrological data, which was 5.8 mm/day. The influent BOD_5 concentration was 200 mg/L, and the concentration of fecal coliforms was 10^7 MPN/100 mL. These are the typical values for wastewater generated from a domestic source [15].

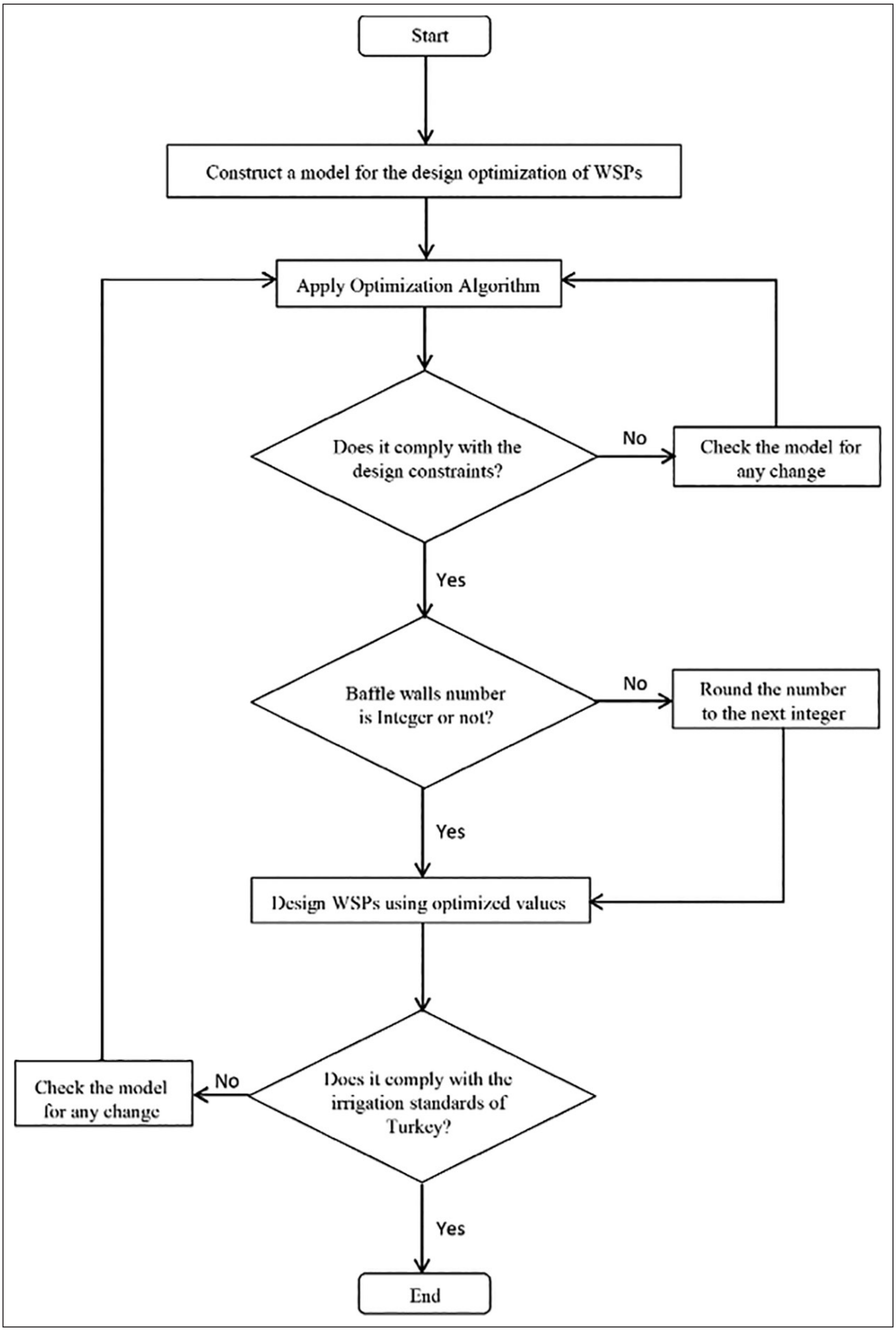


Figure 2. Flowchart of the optimization model.

Table 2. Design calculations using optimization results of the optimization model

Pond	N	LPCD	T_{avg} °C	$(BOD_5)_i$	N_i	d_p
Anaerobic	1200	179	8.9	200	10000000	4
Facultative			8.9	430	5717492	1.5
Maturation			8.9	6194	13185	1
Q_i	O_L	% Removal of BOD_5	λ_v	λ_s	Vp (m^3)	Ap (m^2)
214.80	42.96	40	100		429.60	107
2.00	25.70	86.09		88	9290.90	6194
43.38		68.83			3565	3565
D_T	$(BOD_5)_e$	$(BOD_5)_e$ corrected by evaporation	Q_e	BW Length (% × L)	X	d_f
2.00	120	120	214.18			
43.38	17	20	178.25	0.5	96	0.0103
20	5	6	157.57	0.5	22	0.0452
65.38						
a	K_t	K_f	N_e	N_e corrected by evaporation	BWs	L-W ratio
	0.3771		5700912	5717492		2
1.13	0.1534	0.14271	10973	13185	7	3
1.39	0.2558	0.14271	177	200	4	
W_{avg}	L_{avg}	W_{top}	L_{top}			A_{top}
7.33	14.66	7.33	14.66			107
45.44	136.32	45.44	136.32			6194
45.44	78.46	45.44	78.46			3565
The total area of WSPs with traditional methodology (m^2)			9866			
Concrete volume for the facultative pond with optimization model (m^3)						1118.23

The class-B Irrigation Standards of Türkiye were considered to determine the suitability of the effluents. According to the standards, effluent BOD_5 must be less than 30 mg/L, whereas fecal coliforms concentration must be less than 200 MPN/100 mL. As mentioned above in the design constraints, the maximum number of BWs for the design of the facultative pond was 10, and their length varied between 50 to 90 percent of the total calculated length of the pond. Moreover, it was ensured in the optimization model that N_{BW}, D_T, and d_f are greater than zero, and the BWs are integer. The maximum and minimum D_T in the Turkish design standards for a facultative pond ranged between 30–50 days [16]. Figure 2 shows the flowchart for the functioning of the optimization model.

RESULTS AND DISCUSSION

Results

Appendix B summarizes the results of 60 analyses performed to select the best configuration for the study area. Generally, it is observed that adding BWs reduces the design area and D_T needed. Moreover, it is also observed that an increase in the length of the BWs also decreases the total area and D_T of FP. The effluents of configurations 1 and 2 comply with Turkish irrigation water pollution regulations [16]. Configuration 3 had the lowest area; however effluents did not meet BOD_5 and fecal coliform standards in this investigation. It confirms that the WSPs effluent cannot be utilized for unrestricted irrigation until MPs are provided [13]. Compared with configuration 2, configuration 1 needs less area for constructing WSPs. Due to this reason, configuration 1 is selected to apply the optimization model.

Table 1 shows the design calculation of configuration 1 using traditional methodology. Moreover, it shows the overall area to be occupied i.e., 10576 m^2, and the concrete volume (1201.59 m^3) needed to construct the WSPs for Ayvadere village. Figure 3 shows the solver parameters window that includes the objective function cell set to minimization. Furthermore, it also shows the variable cells and the constraints applied to them. The algorithm that the solver follows can also be seen in Figure 3. The results window of the solver, shown in Figure 4, depicts that all constraints have been met. Figure 5 shows the report from the solver with the initial and end values. In addition, it illustrates the restrictions' satisfaction with values and the gap between them.

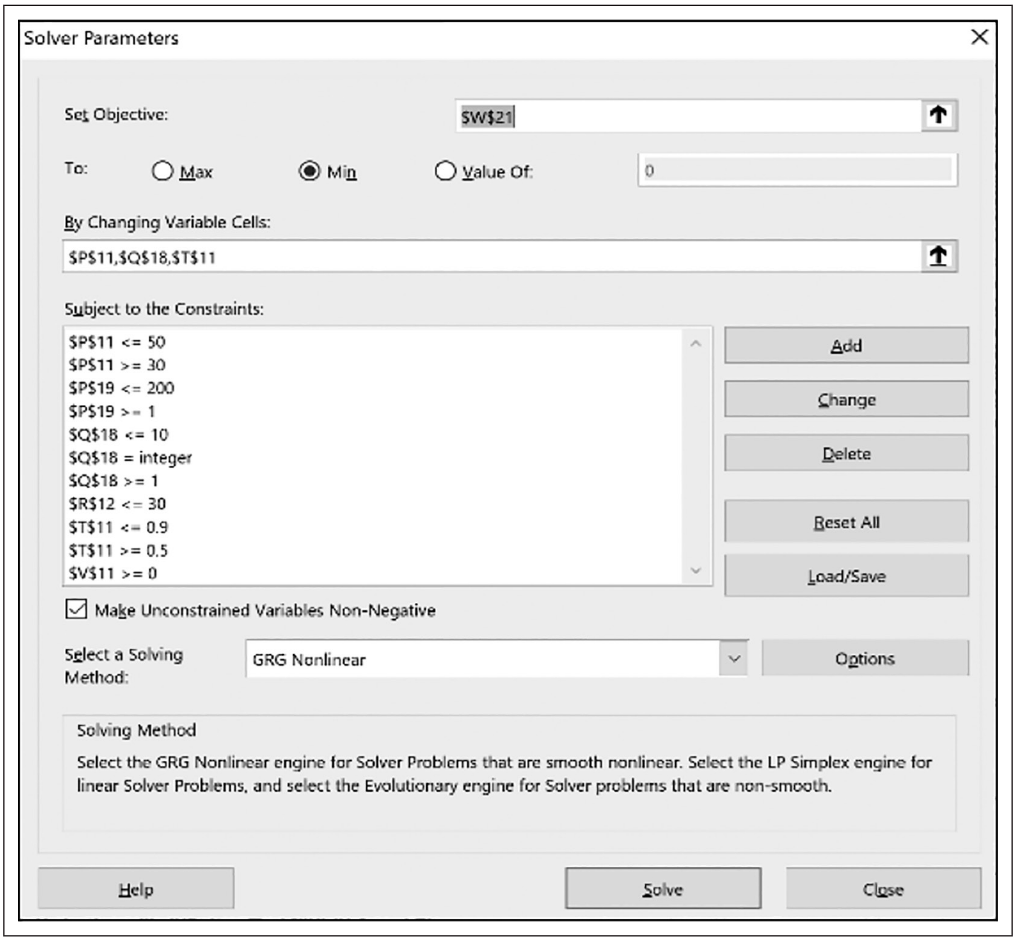


Figure 3. Optimization model application to the design of a facultative pond with Excel Solver.

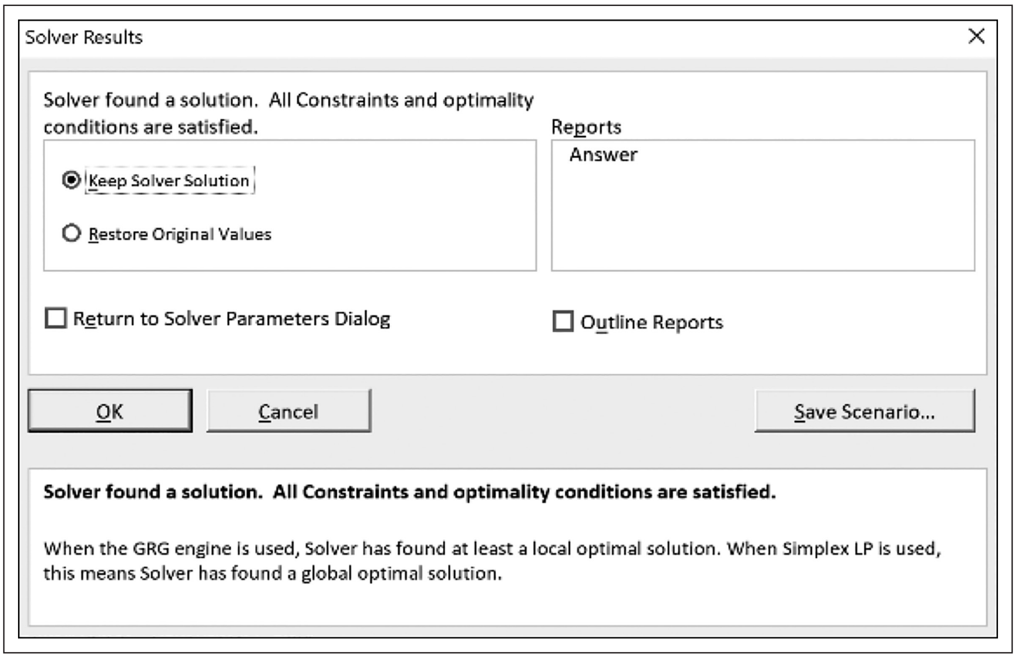


Figure 4. Excel Solver results dialogue box.

Microsoft Excel 16.0 Answer Report
Worksheet: [GRG Excel Solver.xlsx]Sheet1
Report Created: 6/28/2022 10:17:54 AM
Result: Solver found a solution. All Constraints and optimality conditions are satisfied.
Solver Engine
Solver Options

Objective Cell (Min)

Cell	Name	Original Value	Final Value
W21	Concrete volume with mathematical modeling Atop	1201.588574	1118.227495

Variable Cells

Cell	Name	Original Value	Final Value	Integer
P11	DT	49.00	43.38	Contin
Q18	BWs	4	7	Integer
T11	BW Length (% × L)	0.5	0.5	Contin

Constraints

Cell	Name	Cell Value	Formula	Status	Slack
P19	Ne corrected by evaporation	200	P19<=200	Binding	0
P19	Ne corrected by evaporation	200	P19>=1	Not Binding	199
R12	(BOD5)e corrected by evaporation	6	R12<=30	Not Binding	24.11502268
V11	d	0.0103	V11>=0	Not Binding	0.0103
P11	DT	43.38	P11<=50	Not Binding	6.62046112
P11	DT	43.38	P11>=30	Not Binding	13.38
Q18	BWs	7	Q18<=10	Binding	0
Q18	BWs	7	Q18>=1	Not Binding	6
T11	BW Length (% × L)	0.5	T11<=0.9	Not Binding	0.4
T11	BW Length (% × L)	0.5	T11>=0.5	Binding	0
Q18=Integer					

Figure 5. Optimization report using Excel solver.

Table 3. Comparison of the results achieved with both approaches

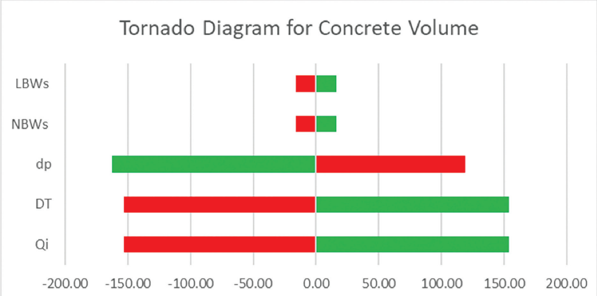
Component	Traditional methodology	Optimization model	Reduction	%
D^T	49	43.38	5.62	11.47
N_{BW}	4	7	–	–
Area (m^2)	6996	6194	802	11.46
Concrete (m^3)	1201.59	1118.23	83.36	6.94

Table 2 shows the calculation of the design using the optimization model results. The area and concrete volume needed for WSPs are 9866 m^2 and 1118.23 m^3, respectively. Moreover, it shows how the results of the solver analysis system changed the values of the d_f, the dimensionless constant, from 0.0261 to 0.0103 the pond's width reduced (from 48.29 m to 45.44 m), and length reduced (from 144.88 m to 136.32 m), the concentration of BOD_5 in the effluent increased (from 5 mg/l to 6 mg/l). In the same way, the three variables, N_{BW} & L_{BW} and D_T, were optimized.

DISCUSSION

It is important to note that the optimization model found the three decision variables or the best variables that meet the constraints. Even though the parameters proposed for the right side of the constraints (D_T and N_{BW}) were higher than what the system solver produced, this is necessary. It is proposed because the solver system needs the upper limits to work. Therefore, it is wise to suggest much higher limits so that the system can find the best one, but they should still be localized within the range that the constraints consider. The system figured out that the best length for the BWs is 50% of the length of the pond. The result is consistent with Li et al. [8]. The author has also discussed other favorable measurements of BWs that can be provided in ponds.

Table 3 shows the original values and those found by the optimization model. The optimized D_T is 5.62 days less than that achieved with the traditional methodology; this reduction in percentage is 11.47%. According to the method, the dimensions of the pond depend on D_T and the influent concentration of the pollutants. Additionally, Table 3 shows that an area reduction of 802 square meters, or 11.46 percent, was achieved. Table 3 also presents that the concrete volume calculated with optimized values is 83.36-meter cube, or 6.94% percent less than that achieved with the traditional approach. As it has already been mentioned in the problem statement, the main problem with pond systems is that they need much land. The percentage reduction



	Qi	DT	dp	NBWs	LBWs
-15%	154.12	154.12	-162.50	16.10	16.10
15%+	-153.05	-153.05	118.94	-16.10	-16.10

Figure 6. Sensitivity analysis for the total volume of concrete.

achieved through the optimization model is considerable.

The only higher value solver system found out is 7 BWs instead of the four that would have been chosen by the traditional design method. The higher number of baffles makes it easier to get rid of the fecal coliforms [17]. Philip et al. [18] listed several authors and their work on the impacts of baffles; all say that adding baffles to a pond improves hydraulic flow and makes it easier to get rid of pollutants. This paper's results agree with the second thing the authors said. Philip et al. [18] listed in their research that all of the authors did research on stabilization ponds with different number of BWs. They all came to the same conclusion: ponds with a larger number of BWs are more hydraulically efficient and better at treating wastewater biologically. The current study also backs up what the authors on the list have said.

Regarding getting rid of BOD_5 (Tables 1 and 2), the two analyses gave effluents that are below the class-B official Turkish standards for irrigation: 30 mg/L [16]. The removal efficiency of BOD_5, from facultative ponds, during the coldest month in the study area, was found to be 87.49 and 86.09 with traditional methodology and optimization model results, respectively. The removal efficiency is slightly higher than that of Gulsen et al. [19]. As it can be seen when the optimization model is used, the removal efficiency of BOD_5 is less, and there is more organic matter in the effluent, but it is still less than what is required by the standards.

Sensitivity Analysis

According to Anderson et al. [20], a tornado diagram can be used for sensitivity analysis. The research mentions that sensitivity analysis can be done by changing the values of the primary variables. The tornado diagram employs bars to describe sensitivity. The widest bar shows the most sensitive parameter on which the constraints rely. Figure 6 presents the sensitivity analysis for the volume of concrete. From the same figure it can be observed that two parameters, Q_i and D_T, are most sensitive and have an equivalent effect on the volume of concrete. The following sensitive parameter is the depth of the pond. It is interpreted that the volume of concrete is more when the depth of the pond is decreased, and it is less with an increase in depth. The number and length of the BWs are the least sensitive and have an equivalent effect on the objective function.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Optimization of the volume of concrete needed for the facultative pond provided within the series of three ponds was done. Even though this optimization model is used in this case study, it can be applied in other situations by changing inputs like temperature, BOD_5, fecal coliforms, evaporation, and depth of the pond. There were several ways to meet the Turkish design standards for the detention time of WSPs: addition of more BWs to the maturation pond, manual adjustment of detention time in the design of facultative pond, increased BOD_5 load, and decreased fecal coliforms load. From these three viable options available, two have been tried within the scope of this research (Appendix A).

Recommendations

It is suggested that this study be done on a small scale first so that the optimization results of the facultative pond can be validated. Moreover, variation in the number of baffle walls be studied for maturation ponds.

Appendix A Supplementary Data

The design calculations to select the best configuration for the Ayvadere village are available from the corresponding author on reasonable request.

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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.

ETHICS

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

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Appendix B. Summary of the results with various configurations and arrangements

Sr. No.	Configuration	BW in FPs	Baffle wall Length									
			0.5		0.6		0.7		0.8		0.9	
			D_T (d)	Total area (m^2)	D_T (d)	Total area (m^2)	D_T (d)	Total area (m^2)	D_T (d)	Total area (m^2)	D_T (d)	Total area (m^2)
1	1	0	58.57	8622	58.12	8547	57.78	8490	57.53	8448	57.33	8415
2	2	0	70.49	9942	69.79	9830	69.30	9752	68.90	9688	68.58	9637
3	1	2	56.18	8223	55.50	8110	55.00	8027	54.63	7965	54.31	7912
4	2	2	65.67	9172	64.55	8993	63.70	8857	63.02	8749	62.48	8662
5	1	4	55.07	8038	54.52	7947	54.13	7882	53.82	7830	53.57	7788
6	3	4	33.92	4063	33.92	4063	33.92	4063	33.92	4063	33.92	4063
7	1	6	54.65	7968	54.17	7888	53.80	7827	53.55	7785	53.32	7747
8	2	6	62.00	8586	61.27	8469	60.74	8384	60.32	8317	60.00	8266
9	1	8	54.45	7935	54.00	7860	53.67	7805	53.42	7763	53.21	7728
10	2	8	61.49	8504	60.82	8397	60.36	8324	59.99	8265	59.70	8218
11	1	10	54.35	7918	53.92	7847	53.60	7793	53.35	7752	53.15	7718
12	3	10	33.92	4063	33.92	4063	33.92	4063	33.92	4063	33.92	4063