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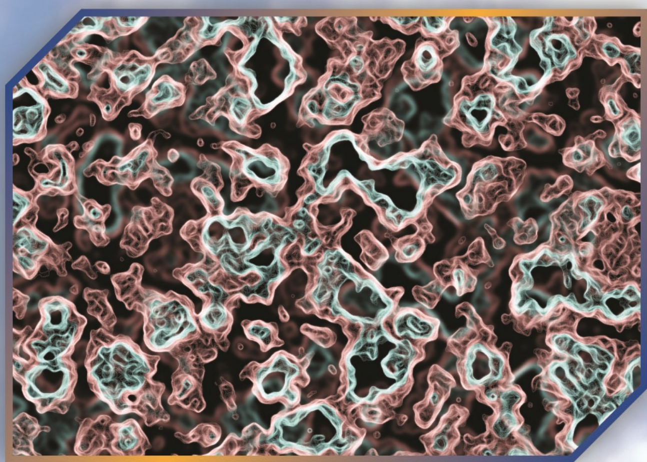

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RESEARCH ARTICLE

The oxidation study of N,N-diethyl-meta-toluamide in dual frequency ultrasonic reactor

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ABSTRACT

With the increasing concern of emerging contaminants (ECs), advanced oxidation processes (AOPs) have been widely investigated to fulfill the drinking water quality because of the potential adverse health effects of ECs. Accordingly, N,N-diethyl-meta-toluamide (DEET) is selected as a model compound belonging ECs to monitor its ultrasonic oxidation which is one of the most popular AOPs in a dual frequency ultrasonic reactor (DFUR) using low-frequency probe (20 KHz) and high-frequency transducer (640 KHz) type sources. DFUR was calorimetrically optimized in terms of power densities of both ultrasonic sources in order to provide the highest sonochemical yield with efficient energy output. Pseudo-first order kinetic equation was applied to results by measuring the concentration decreasing during the oxidation reactions. The pseudo-first-order rate constants, k, increased from $7.8x10^{-3}$ min^{-1} (640 kHz, R^2=0.930) to $13.5x10^{-3}$ min^{-1} (DFUR, R^2=0.990), by contrast, the rate constant was only $0.7x10^{-3}$ min-1 (R^2=0.281) for 20 kHz low-frequency ultrasonic source. DEET oxidation was evaluated with the presence of different gas saturation (Ar, Air, O_2, and N_2); addition of hydrogen peroxide (PO), persulfate (PS) and monoperoxysulfate (MPS) and PO concentration effect (molar ratio of DEET:PO; 1:1, 1:2, 1:5, 1:10 and 1:20). The DEET oxidation rate was calculated as 35.8 $x10^{-3}$ min^{-1} (R^2=0.994) in the presence of Argon gas saturation, while it was 13.5 $x10^{-3}$ min^{-1} (R^2=0.990) when no gas bubbling. Therefore, the main degradation pathway was predicted as pyrolysis taking place inside the cavitation bubble where DEET molecules can reach. On the other side, a lower degradation rate in the presence of PO, PS, and MPS than that of no additives has indicated that the bulk phase degradation pathway for some part of DEET molecules are still occurred.

Keywords: DEET, dual frequency ultrasound, emerging contaminants (ECs)

1. INTRODUCTION

N,N-diehtyl-meta-toluamide, commercially called DEET, is widely used as an active ingredient in many repellant products used for insects such as mosquitoes and ticks. It is estimated that thirty percent of US population use DEET to be protected from some illness like West Nile and Zika viruses, malaria caused by mosquitoes and Lyme disease caused by ticks. Even it is not designed to directly kill the organism, it should be taken into consideration in terms of environmental risk assessment as it is registered a pesticide in EPA. Furthermore, its extensive use for common personal care products in the US (9.2 million lb in 2011) has been turning the attention on its environmental transportation mechanism especially when drinking water is taken into consideration as Emerging Contaminants (ECs) [1, 2]. DEET has been detected in surface waters, the effluent of WW treatment plants, and even in groundwater and drinking water in the last few years. This occurrence indicates that potential recalcitrance of DEET to conventional water treatment techniques [3, 4]. Costanzo et al. [5], have reported that DEET concentrations have been detected in the range of 40-3000 ng L^{-1} all around the world and 8-1500 ng L^{-1} in coastal Australia in contrast to earlier assumptions that it is not a persisting compound in the aquatic environment. In a very recent study, Lesser et al. [6], analyzed a wide range of organic micropollutants including DEET in the Mezquital Valley which uses untreated wastewater for agricultural irrigation. They indicated that even though DEET was found in relatively low concentrations in wastewater, it was detected in the highest frequencies in groundwater due to its complex matrix with other micropollutants such as sulfamethoxazole. They also

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analyzed the DEET concentration in the range of 37 – 2500 ng L^{-1} for raw wastewater consistent with all around, while DEET concentration was found in the groundwater with a concentration range of between <0.4 and 99.9 ng L^{-1} in the same study. DEET had low removal efficiencies and quite recalcitrant to biodegradation with its concentration range of 1.4-6232 ng L^{-1} in the urban surface water and its degradation half-life of 29 days [7]. Also, the National groundwater monitoring program in England and Wales detected DEET more than 10 times in the level of 6500 ng L^{-1} in 2011 in groundwaters [8]. Some other publications have reported that DEET can also accumulate in sediments with discharged wastewater into surface water [9].

Despite DEET is generally depicted as safe for external use if followed its labeling recommendation, some researchers reported potential health risks even a few deaths when exposed in high concentration through extensive skin absorption or inhalation [10-12]. Furthermore, the long-term exposure of DEET and some other pesticides produced mood and cognitive changes in animal experiments that had consistency with neuro-inflammatory changes in hippocampal brain areas experienced by GW veterans [13, 14]. Even, some neurotoxicity signs and genotoxic effects were reported to be received by DEET in a few pieces of research [15]. Although, the environmental risk assessment results of DEET indicate that is unlikely to produce an adverse biological effect in aquatic systems [16]. Campos et al. [17], studied the chronic effect of DEET on some test organisms that DEET inhibited development rates leading to population-level effects at the higher concentration of DEET than the observed in water sources. In other studies, they have reported that DEET is slightly toxic to freshwater insects in the higher concentrations than observed in water sources, but they advised the further studies to be conducted on the seasonal monitoring of DEET concentration in the aquatic environment due to its widespread occurrence in a great frequency and recalcitrant persistency in the water sources.

The degradation pathway of DEET in conventional wastewater treatment plants (WWTP) has been studied by many researchers. For example, in a WWTP characterized by nitrification and denitrification processes, activated sludge and rotating biological contactors, DEET showed an irregular removal percentage with a 47% average ranging between 1-98% [18]. This is most probably due to the high octanol-water partitioning coefficient, K_{ow}, of DEET (log K_{ow}=2.02) indicating that its tendency towards moderate hydrophobicity and low affinity for sorption according to soil column experiments [6]. In another adsorption study, DEET and some other micropollutants were subjected to treat in pilot-scale drinking water biofilters containing an Anthracite adsorption column. Even this study has shown that DEET removal was more dependent on sorption than biotransformation but its adsorption efficiency was still below 50% operated for 245 days [19]. This result has a consistency with recent adsorption studies that activated carbon (AC) adsorption of DEET was around 40% [20] and granulated activated carbon (GAC) filters adsorption of DEET was less than 30% indicating adsorption fairly suitable method for ECs like DEET [21]. There is also one study on the biotransformation of DEET in microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) pointing out the low-level degradation (below 40%) of DEET by microorganism in their processes [22]. Even they supported their results that DEET removal from wastewater was not higher than 30% after anaerobic treatment [23]. Recently, the elimination of ECs including DEET with the membrane treatment methods have become an increasing interest. However, Huang et al. [24], achieved 82.3% removal percentage of DEET with reverse osmosis (RO) method representing the lowest removal efficiency among other organic micropollutants in the natural water.

Therefore, AOPs has recently drawn increasing attention as an emerging technology for the degradation of micropollutants and DEET since AOPs are the main sources for the production of highly reactive OH radicals (•OH). The high oxidation capacity of •OH (10^8-10^{10} $M^{-1}s^{-1}$) produced by AOPs in situ applications leads to treating a wide range of ECs with their low selectivity providing complete mineralization to CO_2, H_2O, and inorganic ions or acids [25]. Therefore, DEET degradation has been investigated by using several AOPs including mostly ozonation [26]; ozone and biologically activated carbon system [27, 28]; photo-ozonation [29, 30]; photocatalysis [31]; photocatalysis with TiO_2 [3]; Fenton-like reaction [32] and finally electrochemical oxidation [33]. But there have not been enough studies on the ultrasonic oxidation of DEET in the literature so far. Ultrasonic oxidation processes are very effective techniques for the degradation of a wide range of problematic pollutants based on mainly hydroxyl radical (•OH) production. Additionally, the simultaneous US at low and high frequencies can lead to improved degradation yields [34]. The principle of ultrasonic irradiation mechanism for water treatment was explained in our previous studies [25, 35].

The degradation of N,N-diethyl-m-toluamide (DEET) in dual frequency ultrasonic reactor (DFUR) including a 20 kHz low and a 640 kHz high-frequency sources was investigated in this comprehensive study as a pioneer for the literature in terms of ultrasonic DEET degradation. The enhancement effect of using dual or multiple frequencies ultrasonic sources in one reactor is probably due to obtaining a more active volume of cavitation than a single one, enhanced bubble collapse ratios resulting in higher temperature, therefore, increased sonochemical activity [36, 37]. The calorimetric experiments were firstly conducted to optimize the dual-frequency operation conditions for the enhancement of sonochemical yields. Then, DEET degradation was evaluated in terms of several operation modes of DFUR, under different gas saturation (Ar, O_2, N_2), presence of some oxidants (PO, PS and MPS). Finally, DFUR was conducted in the addition of several PO doses which had the highest degradation efficiency for DEET degradation.

2. MATERIALS AND METHODS

2.1. Synthesis of hydrotalcite-like compounds

All chemicals were of analytical grade (99%) except for hydrogen peroxide (30%). DEET (wet basis, 99%) was purchased from Sigma-Aldrich, USA. Millipore filtered water (18 MΩ.cm) was used to dissolve DEET in all cases instead of methanol. Its highest absorbance was shifted in 192 nm instead of 230 nm [38] dissolved in methanol. Fig. 1 depicts the chemical structure of DEET.

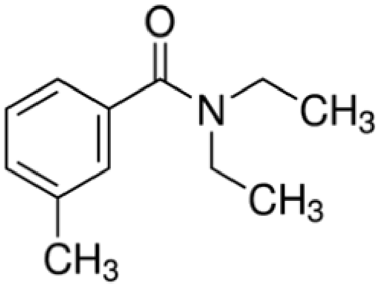

Fig 1. The chemical structure of DEET (MW=191.27 g mol^{-1})

UES Model 15-660 ultrasound generator (640 kHz) with the power range of 100-1000 W, obtained from Ultrasonic energy system company (Panama City, Florida) was used for all experimental procedures as a high-frequency source [39]. The sound wave is transmitted via a transducer which is placed into the wall of a 580 mL glass reaction container immersed into 40-liter water cooling bath and kept at room temperature as 20±2 °C. The reaction volume in the reaction container was 500 mL containing aqueous DEET or only distilled water for the case of calorimetric experiments. Low-frequency ultrasonic horn was purchased by Sonic materials, Inc. (Danbury, Connecticut) (20 kHz) with the power range of 10-100 W. The horn was dipped into reaction solution to conduct dual-frequency as a dual-frequency ultrasonic reactor, DFUR. The illustration of the DFUR was depicted in our previous study [40].

3. RESULTS AND DISCUSSION

3.1. Analysis of DEET

The stock DEET solution was prepared in 2.614 mM concentration and, it was diluted in the desired concentration to develop a calibration curve. Calibration standards of DEET were prepared from 0 to 20 μM concentrations for its UV-Vis absorption. The DEET degradations were observed by UV-Vis absorption at time intervals of 0, 1, 3, 5, 7, 9, 12 and 15 mins on a Cary Eclipse Spectrophotometer from Agilent Techn. with the maximum absorbance wavelength of 192 nm. All DEET solutions were fixed to 20 μM concentration during the experimental procedure. The calibration curve of DEET to accurately monitor the final concentrations is shown in Fig 2.

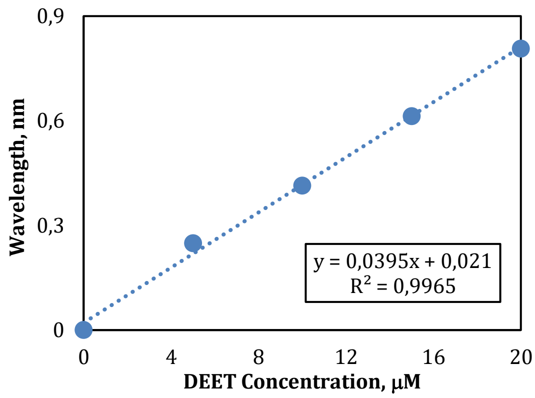

Fig 2. The calibration curve of DEET on its maximum absorbance at 192 nm dissolved in millipore filtered water.

3.2. DEET degradation in DFUR

20 kHz and 640 kHz ultrasonic sources were operated individually to calculate their power densities in each operated power (i.e. 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 W for 640 kHz and 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 W for 20 kHz) according to our previous calorimetric studies [35]. By changing the power output of 20 kHz against the fixed power of 640 kHz at 600 W, the power density of DFUR was measured. The optimum power density dissipated by solution was calculated as 10.1 x 10^{-2} WmL^{-1} for DFUR with the highest synergistic index (0.991) combined frequency of 20 kHz of which power density was 4.1 x 10^{-2} WmL^{-1} and 640 kHz of which power density was 8.1 x 10^{-2} WmL^{-1} at their operating power of 60 W and 600 W, respectively. This method has provided energy savings most of which disappear in the reactor solution as heat energy. The following experiments were performed at these power settings called DFUR.

The DEET degradation and kinetic constants under three operation modes of DFUR were discussed in this section and experimental results were shown in Fig. 3. The ultrasonic degradation of DEET in DFUR was assessed by absorption abatement at 192 nm which is responsible for the aromatic compound of DEET. For this reason, 20 μM DEET solution was sonicated by 20 kHz low frequency, 640 kHz high-frequency ultrasonic sources alone and finally irradiated with dual frequencies simultaneously for 15 mins (Fig 3). It was concluded that the contribution of 20 kHz ultrasonic source to 640 kHz high frequency for the degradation of DEET was increased, but the effect of only 20 kHz low-frequency irradiation was negligible, it could reach 2% after 15 min reaction time. The ultrasonic DEET degradation can be evaluated as low but the combination of both frequencies increased DEET degradation up to 19% while it was only 11% by high-frequency source, 640 kHz. Additionally, the pseudo-first-order degradation of DEET was used to explain the removal rates by Eq. (1):

$$\ln \frac{DEET_t}{DEET_0} = -kt \qquad (1)$$

where DEET concentrations at the time of 0 and t, μM, and k is the pseudo-first-order rate constant, min^{-1} and t is the reaction time, min. The pseudo-first-order rate constants, k, increased from 7.8x10^{-3} min^{-1} (640 kHz, R^2=0.930) to 13.5x10^{-3} min^{-1} (DFUR, R^2=0.990), by contrast, the rate constant was only 0.7x10^{-3} min^{-1} (R^2=0.281) for 20 kHz low-frequency ultrasonic source.

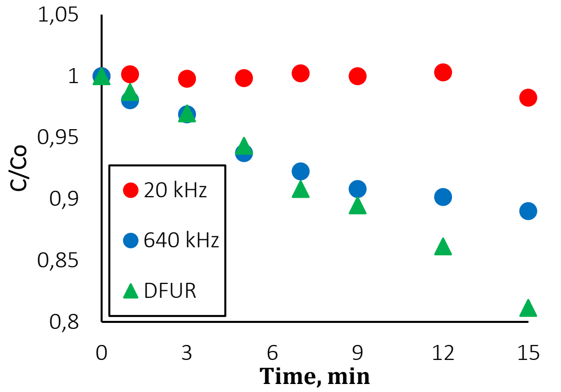

Fig 3. Time-dependent ultrasonic DEET degradation by 20 kHz, 640 kHz and DFUR ([DEET]$_0$= 20 µM)

3.3. DEET degradation in DFUR under different gas saturation

In this experimental setup, the initial DEET solution was individually saturated with Ar, air, O_2, and N_2 before the experiment for 15 min and during ultrasonic irradiation in DFUR for 15 min. The time-dependent DEET concentration under different gas saturation in DFUR was plotted in Fig 4. The presence of dissolved gases in the ultrasonically induced solutions is a crucial parameter since they become a nucleation site for cavitation bubbles and also enhance the final temperature of the collapsing bubble due to their specific heat capacities [41]. Therefore, additional pyrolysis reactions take place inside of a cavitation bubble which is the main degradation reaction for hydrophobic compounds like DEET. As its hydrophobic tendency, DEET is supposed to reach the interior of a cavitation bubble formed during ultrasonic irradiation. Our results were consistent with the idea that pyrolysis played a significant role during DEET degradation due to faster degradation (nearly two-fold) than that of no gas bubbling and the highest rate constant (35.8x10^{-3} min^{-1}) under Ar saturation. After then, the pseudo-first-order degradation constants followed the order of 25.1x10^{-3} min^{-1}, 15.0x10^{-3} min^{-1}, 13.5x10^{-3} min-1, and 5.5x10^{-3} min^{-1} for the O_2, N_2, NA (Not applicated any gas) and air, respectively. Since oxygen provides additional pathways to form •OH, DEET degradation was higher compared to N_2 saturated solution and N2 could be responsible for the consumption of •OH [42, 43]. However, DEET degradation slowed down during the air bubbling to DFUR probably due to the interference of the propagation of ultrasonic waves through the solution [44]. The Pseudo first-order kinetic constants of DEET degradation in the presence of various gas saturation are shown in Table 1 as well.

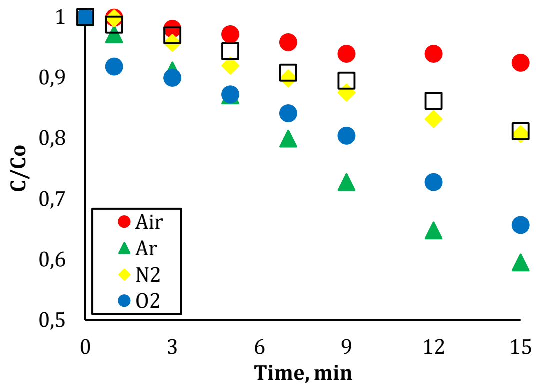

Fig 4. The effect of different gas saturation on the degradation of DEET ([DEET]0= 20 µM, gas flow rate=1 ml min^{-1})

Table 1. Pseudo-first-order kinetic constants of DEET degradation in the presence of various gas saturation

Gas saturation	Ar	O_2	N_2	NA	Air
k, min^{-1}	35.8 x10^{-3} R^2=0.994	25.1x10^{-3} R^2=0.968	15.0x10^{-3} R^2=0.992	13.5x10^{-3} R^2=0.990	5.5x10^{-3} R^2=0.960
Additives	PO	MPS	PS	NA	
k, min^{-1}	10.1x10^{-3} R^2=0.971	7.5x10^{-3} R^2=0.921	6.4x10^{-3} R^2=0.921	13.5x10^{-3} R^2=0.990	

3.4. Effect of PO, PS and MPS on DEET degradation

AOPs in the presence of some oxidants such as PO, PS and MPS which can be activated by ultrasonic, light or heat sources cause to form different radicals such as •OH and $SO_4^{\bullet-}$ and $S_2O_8^{\bullet-}$ [45, 46]. Therefore, DEET degradation was studied by the addition of these three radical sources with the same molar ratio of DEET to enhance the efficiency of DFUR and the results are depicted in Fig. 5. The pseudo-first-order rate constants were kinetically evaluated from Fig. 5 as 10.1x10^{-3} min^{-1} (R^2=0.971), 7.5x10^{-3} min^{-1} (R^2=0.921) and 6.4x10^{-3} min^{-1} (R^2=0.921) for the presence of PO, MPS and PS which was slower (already depicted in Fig 3 as 13.5x10^{-3} min^{-1}) than that of no catalyst addition. The slower degradation rate of DEET under these oxidants can mostly be attributed to hydroxyl radical scavenging effect of PO beyond a critical dose [47] which is continuously produced by recombining of hydroxyl radicals in a cavitational collapse according to following equations (Eq. 2-3) [25]:

$H_2O +))) \rightarrow \bullet H + \bullet OH$ (2)

$2 \bullet OH \rightarrow H_2O_2$ (3)

Additionally, some other researchers indicated that the interaction between hydroxyl ions and sulfate radicals can produce •OH [48] which is associated with DEET degradation in bulk solution. However, it was discussed that DEET degradation mostly took place interior gas phase of a cavitation bubble in the previous section. Although DEET degradation increased in the presence of Ar gas supporting the degradation via pyrolysis, we can draw a conclusion that another degradation pathway is either the bulk solution phase where additional •OH, $SO_4^{\bullet-}$ and $S_2O_8^{\bullet-}$ mostly reside and act as a scavenger. Therefore, a slower degradation rate in the presence of PO, PS, and MPS due to partition of these ions in bulk phase can be supported with the idea of DEET degradation occurring in the bulk phase following pyrolysis.

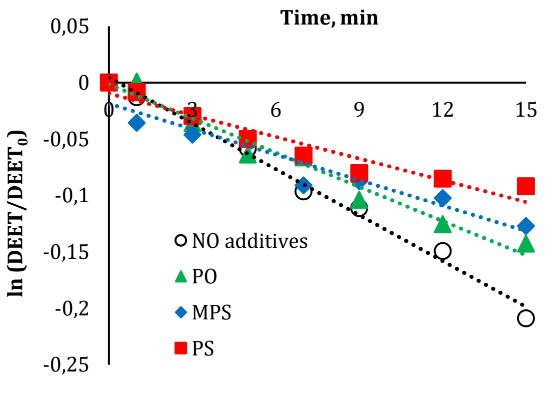

Fig 5. Determinations of pseudo-first-order kinetic plots of DEET degradation with the addition of PO, PS, MPS additives in DFUR ($[DEET]_0$= [PO]=[PS]=[MPS]= 20 μM, 1:1 molar ratio of DEET and additives)

3.5. Effect of PO dose on DEET degradation

In order to efficiency assessment of PO for the degradation of DEET, different DEET:PO molar ratio in the range between 1:1, 1:2, 1:5, 1:10 and 1:20 was subjected to sonicate in DFUR. Although the degradation rate of DEET slowed down in the presence of low dose PO (20 μM), the higher dose of PO was widely examined so as to define the DEET degradation pathway through the bulk phase in ultrasonically induced solution. The application of pseudo-first-order kinetic equation (Eq. 1) is plotted in Fig. 6 by evaluating their rate constant for the degradation of DEET in DFUR. The DEET degradation rate was almost zero in the presence of a higher ratio 1:10 and 1:20, but it slowed down even in a lower ratio of DEET:PO (1:1, 1:2, 1:5, 1:10 were only shown in the Fig 6). The degradation rate constants decreased from 10.1x10^{-3} min^{-1} (R^2=0.971) of which DEET:PO molar ratio 1:1 to 5.7x10^{-3} min^{-1} (R^2=0.896) and 5.7x10^{-3} min-1 (R^2=0.956) which were associated with the molar ratio of 1:2 and 1:5. However, DEET had its highest degradation rate in the absence of PO that provides information about its degradation pathway both through the interior gas phase and gas-liquid interface of a cavitational bubble in DFUR used in this study. Because, 20 kHz and 640 kHz ultrasonic sources form •OH in the reactor that is, over those of •OH act as a scavenger according to Eq. (3). Therefore, there is still DEET degradation occurring via pyrolysis inside of the gas phase of a cavitational bubble but degradation via •OH occurring in the bulk solution phase is inhibited.

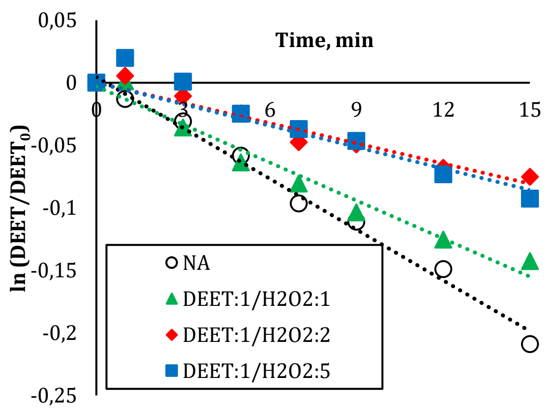

Fig. 6. Determinations of pseudo-first-order kinetic plots of DEET degradation in the presence of different DEET:PO molar ratio of 1:2, 1:5, 1:10 and 1:20 ($[DEET]_0$=20 μM)

4. CONCLUSIONS

DEET considered an emerging water contaminant, quite recalcitrant to biodegradation, was selected as a model compound for the study of a DFUR applying simultaneously 20 kHz as the low-frequency and 640 kHz as the high-frequency ultrasonic source. Considering calorimetric measurements, the optimum power density dissipated to the solution was calculated as 10.1 x 10^{-2} W mL^{-1} for DFUR, while the power densities were 4.1 x 10^{-2} WmL^{-1} for 20 kHz and 8.1 x 10^{-2} WmL^{-1} for 640 kHz US source, individually. The DEET degradation was monitored as a function of treatment time and nicely fit to pseudo-first-order kinetic model. Treatment of DEET was negligible by separate 20 kHz low-frequency US in 15 min reaction period, but the simultaneous operation of 20 kHz low-frequency US and 640 kHz high-frequency US i.e. DFUR provided nearly two times higher degradation efficiency than that of 640 kHz high-frequency US alone. Among other gas saturation (O_2, N_2, and air), Argon enhanced the final temperature of collapsing bubble due to its highest specific heat capacity and pyrolysis played a significant role for DEET degradation by increasing the degradation rate constant nearly three-fold than that of no additional gas bubbling to reaction solution in DFUR.

Slower degradation rate in the presence of PO, PS and MPS additives can be probably attributed to the partition of these ions in bulk phase supporting the idea of some part of DEET degradation occurring in the bulk phase where additional •OH, $SO_4^{\bullet-}$ and $S_2O_8^{\bullet-}$ mostly reside and act as scavenger following pyrolysis. To assess the degradation part of DEET which takes place in the bulk phase, effect of PO concentration on the degradation of DEET was examined and the higher dose of PO even stopped the degradation of DEET in bulk phase indicating the hydroxyl radical scavenging effect of PO beyond a critical dose and small part of

DEET degradation in bulk phase. Finally, this study has proven that combined low and high frequency US, DFUR, provides better cavitational yields for DEET as a hydrophobic compound of which degradation pathway mostly takes place in a cavitational bubble inside and gas-liquid interface.

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RESEARCH ARTICLE

Evaluation of waste management using clustering algorithm in megacity Istanbul

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ABSTRACT

Industrialization and urbanization are increasing with the effect of globalization worldwide. The waste management problems are rising with the rising population rate, industrialization, and economic developments in the cities, which turned into environmental problems that directly affect human health. This study aims to examine waste management performance in the districts located in the city of Istanbul. To ensure that the districts are clustered in terms of the similarities and differences base on waste management. On this occasion, the authorized unit managers of the districts in the same cluster will be able to establish similar management policies and make joint decisions regarding waste management. In addition, the division of districts into clusters according to the determining indicators can provide information about the locations of waste storage centers. Also, these clusters will form the basis for the optimization constraints required to design appropriate logistics networks.

Waste management performance of 39 districts in Istanbul in 2019 was compared by taking into consideration domestic waste, medical waste, population, municipal budget, and mechanical sweeping area. The data were obtained from The Istanbul Metropolitan Municipality (IMM) and Turkey Statistical Institute (TURKSTAT). One of the non-hierarchical clustering methods, the K-means clustering method, was applied using IBM SPSS Modeler data mining software to determine the relations between 39 districts. As a result, the waste management performance of the districts was evaluated according to the statistical data, similarities and differences were revealed by using the determined indicators.

Keywords: Waste management, clustering, K-means, data mining

1. INTRODUCTION

With the rapidly increasing population and the increasing amount of waste, waste management has become an essential field of study. Waste storage areas that do not have the standards required in modern landfill facilities cause serious environmental problems. Therefore, determining these areas and efficiently and collecting waste has great importance. In addition, the urbanization and population that increase in parallel with the increase in industrial activities all over the world cause pressure on the environment. Wastes that accumulate more rapidly with increasing consumption trends have reached threatening environmental and human health due to their quantity and harmful content.

In recent days, the decision-making activities of waste management systems have become more prominent, as recycling of waste has become essential due to the reduced capacity of waste incinerators. The amount of waste per capita in Turkey is always below the average of European countries between 2009 and 2018. However, when the amount of recycled waste per person is examined between the years 2016-2018 (Turkey has registered 3-year data), the average of Turkey is falling far below the average of Europe, as shown in Fig 1 (a-b). The graphs show the need to pay attention to Turkey's waste management and recycling policies

When the studies on waste management are investigated, waste management can be defined as "minimization of domestic, medical, hazardous and non-hazardous waste, separate collection at the source, intermediate storage, determination of transfer centers for waste where necessary, transport of waste, recovery, disposal and operation of disposal

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facilities, maintenance, monitoring and control processes" [1]. The goal of waste management is to ensure less waste generation, to collect waste, to recycle waste and to eliminate it without harming the environment. Completing these steps will be possible with interdisciplinary approaches efficiently.

Waste services in Turkey are carried out by local governments. For this reason, each municipality proceeds in line with its strategies so that policies implemented for waste management is essential in the megacity Istanbul is Turkey's most populous city. When all regions and Istanbul are examined, it is seen that the amount of waste collected in Istanbul is strikingly higher than in other regions, as seen in Fig 2. For this reason, in this study, waste management in Istanbul is analyzed on a district basis; similarities and differences in the waste management of the districts were tried to be found by the clustering analysis method.

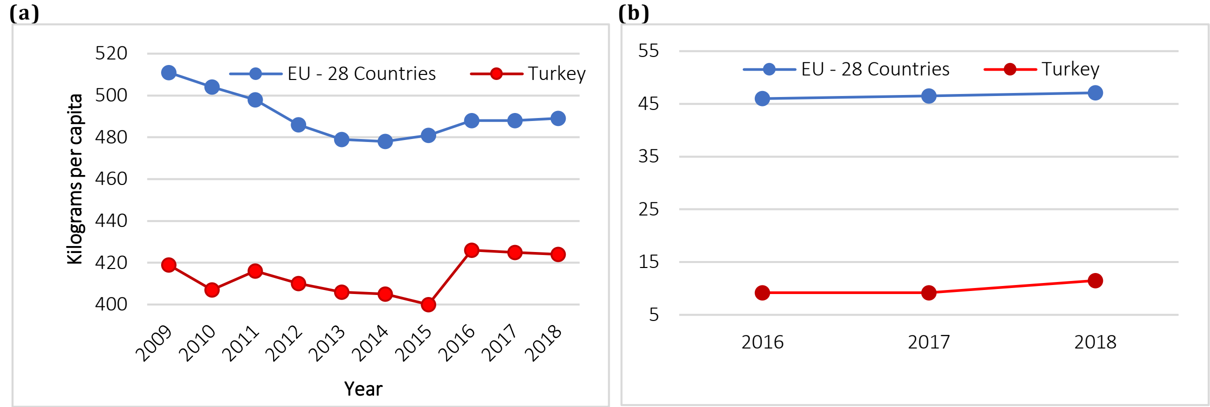

Fig 1. Comparison of waste generation (kilogram per capita; (a) Waste Generation (kilogram per capita), (b) Waste Recycling (kilogram per capita)

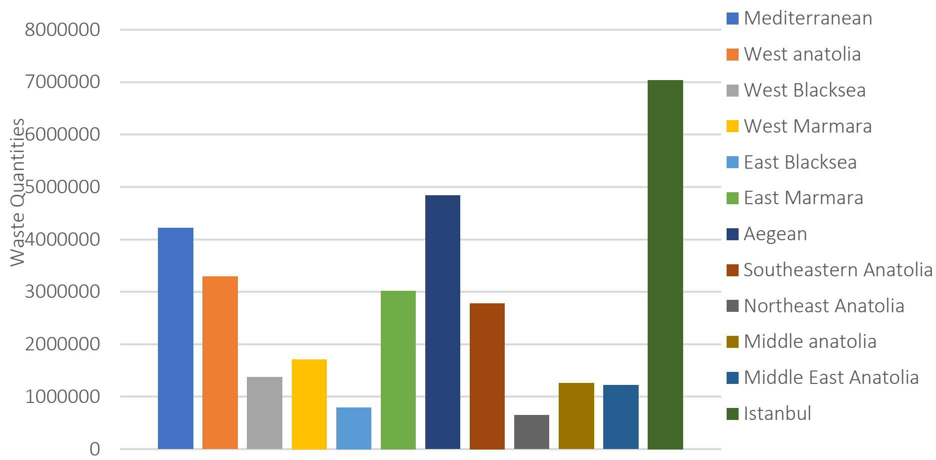

Fig 2. Comparison of waste quantities in Turkey

Domestic waste generated daily in Istanbul with 39 districts is 18,000 tons [2]. Progress in line with 18,000 tons of waste collection and waste management objectives, it is possible with the unification of the districts in a common framework. Thirty-nine districts of Istanbul were clustered using the data mining algorithms, namely the k-means method via five indicators taking into consideration the similarities and differences.

Other applications of the clustering for waste management focus the relationships between the indicators were determined and optimizing waste collection and recycling in previous studies. This study aims to determine the clusters of districts and according to these clusters, waste management policies can be made for differences and similarities for the districts.

There are many studies on waste management in the literature. Management models [3], multi-criteria decision-making methods [4], mathematical models [5,6], and data mining applications [7,8] are some of these studies. Table 1 summarizes the studies which use data mining methods for management cases in the past.

Agovino et al. [1] analyzed the waste management process based on the amount of waste in waste storage areas and they made suggestions to improve waste management activities. Cluster analysis was applied to 103 Italian provinces. As a result of the study, it has been found that the waste disposal rate has a dual structure, and activities that do not directly affect the quality of the institution and the environment are the main factors in the waste management process [1].

Table 1. Previous studies on clustering

Reference	Year	Area	Methods
Agovino et al. [1]	2016	Waste management	Spatial correlation processes and spatial clusters
Sharma et al. [9]	2020	Waste management	K-means clustering
Shi et al. [10]	2014	Environmental risk	K-means clustering
Ecer and Aktas [11]	2019	Healthcare analyzing	K-means clustering
Dorn et al. [12]	2012	Waste disposal facilities	QFD and clustering
Otoo et al. [13]	2014	Waste management	Capacitated clustering
Lin et al. [14]	2011	Food Waste management	K-means clustering
Parfitt et al. [15]	2001	Waste management	Hierarchical clustering
You et al. [16]	2017	Solid Waste management	ANN, ANFIS, SVM, and RF
Niska and Serkkola [17]	2018	Waste management	SOM and K-means clustering
Márquez et al. [18]	2008	Waste management	Clustering, Classification, decision tree
Song et al. [19]	2014	Waste management	Entropy and Spatial Clustering
Caruso and Gattone [20]	2019	Waste management	Unsupervised Classification

Sharma et al. [9] worked on waste management with the K-means method. As a result of their studies, it was expected to facilitate the decision-making process via k-means. For this reason, they made clustering with the solid waste data set, considering the indicators such as land use, financial costs, labor force needs [9].

Otoo et al. [13] have developed an optimization model for logistics and disposal of waste, which is vital for waste management. In this study for the Kumasi region of Ghana, two methods, clustering, and heuristic optimization, were used. In the optimization model, cost and waste transport distances are used as variables. When the results of the study are compared with the existing schedules, the weekly distance decreased by 40% [13].

Lin et al. [14] used questionnaires as a method of gathering data sets. The multivariate factor analysis and clustering were used to analyze the results they obtained from the questionnaires. As a result of clustering and factor analysis applications, a more robust decision-making process was aimed to design. They used SWOT analysis to evaluate the results of the two methods. The optimal waste management system was selected [14].

Parfitt et al. [15] proposed a system for accumulating waste and recycling waste to increase the efficiency of local governments in England and Wales. In this system, which is based on hierarchical cluster analysis, related regions are clustered and compared with the existing system. The cluster analysis results indicated that different waste management practices could be used for regular household waste collection [15].

Niska and Serkkola [17] have developed a system that stores information for waste management using the Self-Organizing Map (SOM) and the k-average algorithm. The results showed the potential of an advanced analytical approach to analyze waste management procedures further. Cluster analysis is recommended for planning and optimizing waste collection and recycling [17].

Márquez et al. [18] proposed a management strategy using data mining methods to manage household waste. In the analysis, household waste data from the settlements in Mexicali were used. K-means cluster analysis was applied with socio-economic indicators, and decision tree application was made with clustered data. As a result of their study, the relationships between the indicators were determined [18].

This study aims to cluster waste management practices in the districts of Istanbul by using the K-means clustering algorithm that is a well-known algorithm among data mining methods. Examining the additive waste management performance in the districts of Istanbul and clustering the districts by considering the similarities and differences for waste management. On this occasion, managers authorized to make decisions on waste management will be able to establish similar management policies and make joint decisions on solid waste management.

The following parts of the study are data collection process, explanations of data mining methods and k-means clustering method, determination of the number of clusters, implementation of k-means clustering via IBM modeler using waste management data for Istanbul, identifying of the cluster for districts of the cluster of districts according to results of k-means clustering methods and results and discussion for the case study.

2. MATERIALS AND METHODS

2.1. Data collection process

The waste management performance of 39 districts of Istanbul in the year 2019 was analyzed according to base on the domestic waste amount, population, municipal budget, medical waste amount and mechanical sweeping area variables. As shown in Table 2, data were collected from different data sources. The data set is presented in Table 3 used for the analysis.

Table 2. Information about the variables

Variables	Unit	Sources
Domestic Waste amount (DW)	Ton	IMM[a][2]
Population (PO)	Capita	TURKSTAT[b][21]
Municipal Budget (MB)	Million TRY	IMM[2]
Medical Waste amount (MW)	Ton	IMM[2]
Mechanical Sweeping area (MS)	Square meter	IMM[2]

[a]The Istanbul Metropolitan Municipality
[b]Turkish Statistical Institute

It is essential to normalize the data to make more meaningful model comparisons in data mining applications [22]. The normalization standardization method was used, and the normalization formula can be seen in Eq. 1.

$$z_i = \frac{x_{i-\bar{x}}}{S_x} \quad (1)$$

where x presents mean and standard deviation of the related variable is shown via S_x in the dataset. The dataset was represented in Table 3 for the clustering analysis.

The statistical significance of the normalized dataset can be seen in Table 4.

2.2. Data mining and clustering

The rapidly growing information pool with the developing technology has made it necessary to work on big data. It is a complicated process to distinguish useful information from big data. For this reason, data mining is processed by automatic or semi-automatic methods in order to analyze large amounts of data and make meaningful results and reaching meaningful results. The most important disciplines of those interested in data mining are Machine learning and artificial intelligence, so developments in these two areas are also significant for data mining. Also, Big data is encountered every day in many areas such as meteorology, complex physics simulations, environmental research, and health services. Therefore, traditional data processing methods cannot respond to Big Data complexity. Especially in many areas, it is necessary to continuously conduct extensive and real-time queries on many unstructured or structured datasets. This demand led to the development of search and sorting technologies to obtain the necessary information from big data [23].

Wu et al. [24] showed that C4.5, k-Means, SVM, Apriori, EM, PageRank, AdaBoost, kNN, Naive Bayes, and CART methods are the top 10 data mining methods [24]. Briefly, clustering is the classification of the observations into groups without supervision. Therefore, the clustering algorithm plays a vital role in a wide variety of real-life applications with its multi-disciplinary application structure.

Clustering algorithms are generally divided into two as hierarchical and non-hierarchical. Two methods are used in hierarchical clustering methods. The first of these methods accept each variable as a cluster initially and continues with iterations that combine the clusters according to their similarities (based on a specified distance measure. For instance, Euclid, Manhattan, Minkowski Distances), so the number of clusters decreases every step. Various visual methods can demonstrate the cluster structure obtained as a result of iterations, such as dendrogram and tree diagrams. The most commonly used algorithms of hierarchical clustering methods in the literature are Single Linkage, Nearest Neighbor, Ward, Centroid, Lance & Williams methods [25]. The most significant disadvantage of hierarchical methods is that it is challenging to decide the proper number of clusters needed to solve the problem.

Clustering is one of the most extensive data analysis techniques applied to gain knowledge about the structure of the data. Although the data in different clusters have different properties and data in the same subgroup have very similar statistical properties, it can also be defined as the task of identifying subgroups in data. In this study, the k-means algorithm, which is accepted as one of the most used clustering algorithms, will be used for clustering 39 districts because of its ease of application and excellent results.

2.3. K-Means Clustering Algorithm

Suppose x = (x_1, x_2, …,x_n) is the dataset of observed values. The clustering method aims to split the dataset into K sub-groups, considering the clustering criterion. There are several clustering methods, and the sum of the squared Euclidean distances between each variable is one of the most commonly used clustering criteria. This criterion is known as cluster error and bases on cluster centers. The cluster error formula represents in Eq. 2.

$$E(m_1, m_2, \ldots, m_M) = \sum_{i=1}^{N} \sum_{k=1}^{M} I(x_i \in C_k) \, \|x_i - m_k\|^2 \quad (2)$$

where if x is true I(X) = 1 and otherwise I(X) = 0.

Where x_i represents each data point, c_k is cluster-k, and the center of the cluster is denoted by m_k. The K-means algorithm determines the most suitable results locally regarding cluster error. In many clustering applications, it is a fast-iterative algorithm that is employed. In addition, it is also a point-based clustering method that initially begins with cluster centers placed at random locations and continues with each step centered by the cluster to minimize cluster error. The primary drawback of the method is that it is sensitive to the starting point since it is based on the initial positions of the cluster centers. Therefore, to obtain the most suitable solutions using the k-means algorithm, several iterations should be done [26].

Table 3. DW, PO, MB, MW and MS values for the 39 districts of Istanbul (2019)

District	Domestic Waste	Population	Municipal Budget	Medical Waste	Mechanical Sweeping
Adalar	16718	15238	41	3	9082500
Arnavutkoy	93010	282488	311	127	87659454
Atasehir	174355	425094	518	947	48441360
Avcilar	155042	448882	325	379	54300948
Bahcelievler	212956	611059	426	1250	29185767
Bagcılar	278547	745125	525,4	1863	656353,9512
Bakirkoy	121614	229239	481	966	102057107
Basaksehir	208181	460259	540	126	68632635
Bayrampasa	124328	274735	301	495	24971001
Besiktas	123926	182649	436	616	84754551
Beykoz	123766	248260	465	282	59293920
Beylikduzu	113246	352412	481	533	59448773
Beyoglu	133928	233323	325	248	142649721
Büyükcekmece	108522	254103	409	146	33305508
Catalca	29868	73718	88	38	18678348
Cekmeköy	97751	264508	270	81	27396912
Esenler	140148	450344	375	320	64918291,5
Esenyurt	356789	954579	900	635	73692424
Eyup	148273	400513	380	109	200202139,5
Fatih	234880	443090	391,8	2562	204703315
Gaziosmanpasa	154480	491962	379	1244	25908042
Gungoren	111236	289441	245	188	14957499
Kadıkoy	209382	482713	670	1502	75382581
Kagithane	156949	448025	370	295	60961389
Kartal	160725	470676	615	1276	96889383
Kucukcekmece	322731	792821	650	1420	88936494
Maltepe	171185	513316	488,4	883	123889441
Pendik	233929	711894	610	1546	141648519
Sancaktepe	142699	436733	466	238	34515090
Sarıyer	164783	347214	421,9	988	67267368
Silivri	86341	193680	254,5	224	8582196
Sultanbeyli	120453	336021	313	286	27600975
Sultangazi	178280	534565	435	361	89081175
Sile	27487	37692	85	13	14128357,5
Sisli	157137	279817	670	2599	116745879
Tuzla	122584	267400	325,6	412	87903284
Umraniye	258042	710280	550	1017	81827844
Uskudar	222645	531825	650	2023	88358349
Zeytinburnu	139747	293574	505	822	103765050

Table 4. The statistical information of normalized data set

	DW	PO	MB	MW	MS
Mean	-1,6E-16	6,83E-17	3,2E-16	2,03E-16	-7,7E-17
Std. Dev.	1	1	1	1	1
Min	-1,97	-1,89	-2,28	-1,08	-1,45
Max	2,80	2,76	2,77	2,71	2,80
Skewness	0,62	0,56	0,06	1,17	0,95
Kurtosis	1,03	0,51	0,85	0,76	1,08

2.4. Determination of k

In order to specify the number of clusters, there are various methods are used in the literature. The most common methods are The Elbow Method and The Silhouette Method. To identify the optimal number of clusters, the Elbow method is the best-known method among them. Within-Cluster-Sum of Squared Errors (WCSS) value is based on the different values that k can take. The number of clusters is specified by selecting the k value where the WCSS begins to decrease. On the WCSS-versus-k chart, this situation is an elbow shape.

The method starts with k = 2, the number of clusters is increased by 1, and each step calculates the amount of error. For a one-unit change for k, the point at which the amount of error is dramatically reduced is determined. The error is recalculated by changing the number of clusters. If the error continues stably or increases in the next change, the value of k with a dramatic decline is determined as the number of clusters [27]. As seen in Fig 3 the Elbow method was applied, and the number of clusters was determined as 5. Calculations for the Elbow method was performed via Python.

Fig 3. Diagram of the Elbow method

As seen in Fig 3, the error of k = 2 is 1.52. The error is 1.22 when the number of clusters is raised to 4. According to the result of the elbow method, the number of clusters was determined as 4. As shown in Table 5, the most considerable value belongs to 4 clusters with 0.4808.

Table 5. The results of Silhouette method

k	2	3	4	5
Silhouette	0.4291	0.4342	**0.4808**	0.4581

3. RESULTS AND DISCUSSION

3.1. Results of K-Means

Thirty-nine districts of Istanbul are clustered by using k-means method for the optimization of waste management activities, considering the variables of DW, PO, MB, MW and MS. All clustering analyses were performed via IBM SPSS Modeler. Since the number of districts owned by each cluster is different, the number of districts included in the clusters as a percentage and map display of clustered districts are given in Fig 4.

The obtained clusters can be seen as a 3-dimensional in Fig 5.

As a result of the analysis, obtained clusters have different statistical properties. Cluster-1 comprises nine districts, cluster-2 has six districts, cluster-3 has four districts and cluster fourth includes 20 districts. The clusters can be seen in Table 6.

The significance levels of clusters by the k-means method are shown in Table 7. Variables with significance levels above 0.90 are significant on the cluster in IBM SPSS Modeler. According to Table 7, it can be concluded that the effects of all variables on four clusters are significant.

3.2. Statistical Evaluation

In determining the path to be followed in waste management, it will be easy to include the relevant variables in the system and separate the problem into sub-problems. Therefore, the variables determined for cluster analysis are essential. The five variables selected for waste management determined in this study are DW, PO, MB, MW, and MS values. The predictor importance values of these variables can be seen in Fig 6.

Table 8 presents descriptive statistics of clusters based on observed data for all variables.

When domestic waste average is analyzed, it is seen that cluster-1 consisting of 9 districts has the least amount. Although cluster - 4 covers 20 districts, the municipal budget does not have the highest average. The cluster with the highest municipal budget is cluster-2, consisting of 6 districts. Considering the amount of medical waste, the cluster with the highest amount of medical waste is cluster-3, covering four districts. The most mechanical sweeping area belongs to cluster-4. Districts in cluster-2 are in cooperation with medical waste management and can apply standard rules. Likewise, counties located in cluster-1 can determine standard policies for domestic waste management. Clustering the districts according to the variables associated with waste management will be useful in the province of Istanbul regarding zero waste, which is also among the goals of sustainable development. Recently, studies on reducing environmental pollution from supply chains have increased in the literature, considering the sustainability goals. Supply chain planning for municipalities will also be more easy than the k-means cluster analysis results made in this study [28].

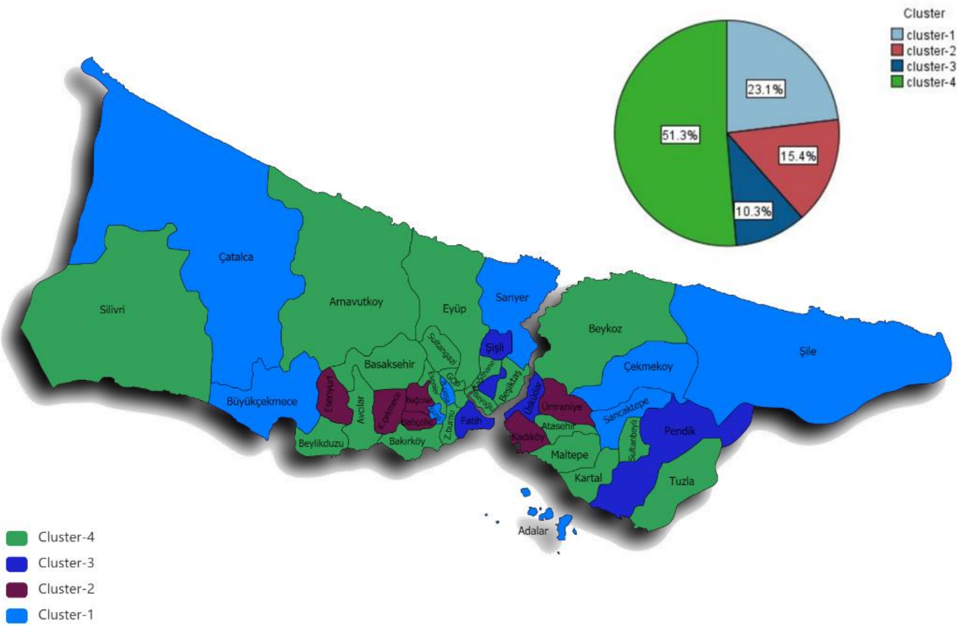

Fig 4. Cluster sizes and map display of clustered districts

Table 6. Clusters and distances from the centers

Cluster-1 (9)		Cluster-2 (6)		Cluster-3 (4)		Cluster-4 (20)	
District	**Distance**	**District**	**Distance**	**District**	**Distance**	**District**	**Distance**
Adalar	0.350	Bahcelievler	0.340	Fatih	0.429	Arnavutkoy	0.287
Bayrampasa	0.222	Bagcılar	0.379	Pendik	0.348	Atasehir	0.266
Büyükcekmece	0.250	Esenyurt	0.547	Sisli	0.353	Avcilar	0.217
Catalca	0.255	Kadıkoy	0.338	Uskudar	0.268	Bakirkoy	0.257
Cekmeköy	0.117	Kucukcekmece	0.234			Basaksehir	0.299
Gungoren	0.142	Umraniye	0.180			Besiktas	0.217
Sancaktepe	0.279					Beykoz	0.222
Sarıyer	0.193					Beylikduzu	0.164
Sile	0.285					Beyoglu	0.373
						Esenler	0.166
						Eyup	0.603
						Gaziosmanpasa	0.410
						Kagithane	0.185
						Kartal	0.372
						Maltepe	0.294
						Sancaktepe	0.279
						Sarıyer	0.193
						Sultangazi	0.210
						Tuzla	0.193
						Zeytinburnu	0.189

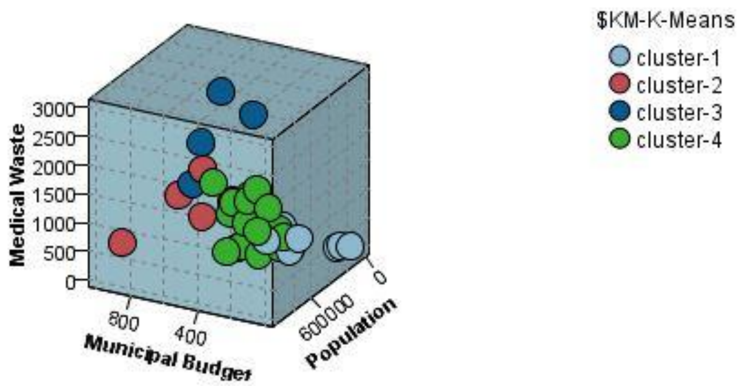

Fig 5. Clusters of districts

Table 7. The normalized mean values of variables for each cluster

Variables	Cluster-1 (9)	Cluster-2 (6)	Cluster-3 (4)	Cluster-4 (20)	Importance
Domestic Waste	-1.081	1.623	0.769	-0.154	★1.0000 Important
Population	-1.013	1.575	0.464	-0.109	★1.0000 Important
Municipal Budget	-1.205	1.130	0.896	0.024	★1.0000 Important
Medical Waste	-0.849	0.782	2.098	-0.272	★1.0000 Important
Mechanical Sweeping	-1.053	-0.251	1.410	0.267	★1.0000 Important

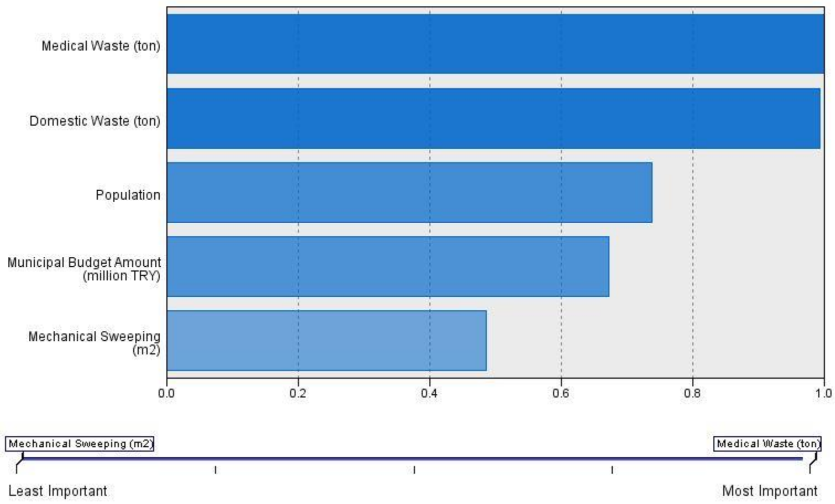

Fig 6. Predictor importance of variables

The k-means clustering is relatively simple to implement to find similarities and differences of the districts that scale to extensive waste data and guarantees convergence. The data mining process allows municipalities to collect useful information they can use in waste management. The data can be analyzed from several different perspectives to provide valuable information that can reduce waste management costs. With this application, the relationships and patterns between variables determined on waste management and data were analyzed. The statistical results found can be used in decision making for administrative activities. The data related to waste management was provided to be "analyzed in detail," and more information was obtained from the waste management data in the archive by using the k-means clustering method. The relationships between external factors such as internal factors and cost factors, personnel skills and demographic characteristics can be examined. For example, using one of the data mining clustering methods for waste management can help identify subgroups with different characteristics in the district of waste management. Variables analyzed by clustering can have a significant impact on internal processes and citizen satisfaction.

Table 8. Statistics of clusters for variables

Cluster	Mean	Standard Deviation	Standard Error
Cluster-1 (9 Districs)			
DW	80300.44	43330.92	14443.64
PO	193237.33	120016.41	40005.47
MB	222.94	123.92	41.31
MW	163.70	158.172	52.724
MS	19855921.83	8840655.49	2946885.163
Cluster-2 (6 Districs)			
DW	273074.5	58992.84	24083.73
PO	716096.2	160709.54	65609.39
MB	620.233	163.27	66.65
MW	1281.12	423.138	172.745
MS	58280243.99	35188980.23	14365841.023
Cluster-3 (4 Districs)			
DW	212147.75	37092.47	18546.23
PO	491656.5	180141.4	90070.7
MB	580.45	128.217	64.108
MW	2182.40	499.42	249.71
MS	137864015.5	49593686.18	24796843.094
Cluster-4 (20 Districts)			
DW	146346.050	26584.57	5944.49
PO	375846.4	107739.83	24091.36
MB	432.14	82.62	18.5
MW	558.8	379.34	84.82
MS	83126956	39769453.6	8892720.19

4. CONCLUSIONS

Due to globalization causes an enormous amount of consumption and that induce to increase the amount of waste by leaps. In terms of environmental resources, waste is one of the main issues that need to be taken before it reaches dangerous levels. In many parts of the world, academic studies are carried out for the solution to environmental problems. Hence, reducing the environmental damage of waste and recycling should be the primary target of all countries. Also, three of the seventeen targets determined for sustainable development are directly related to waste management. Therefore, well-planned waste management decisions will directly contribute to sustainable development. For this reason, waste management data is carefully recorded in European countries. Waste management differentiated according to the structural and geographical features of the country that are carried out by municipalities in Turkey.

In this study, Turkey's most populous city of Istanbul, which has 39 districts, is divided into clusters using Domestic waste, medical waste, population, municipal budget, and Mechanical Sweeping area. The data for the variables were obtained from IMM for 2019. In order to divide the districts into clusters, the k-means clustering method, which is the most familiar explorative data analysis technique in data mining, was used. In the first step, the data is normalized to state the number of clusters. Then, the elbow method and the silhouette method calculations, which are frequently used in the literature, were performed to specify the number of clusters. According to these calculations, the number of clusters was determined as 4. Thirty-nine districts are distributed as cluster-1 involves nine districts, cluster-2 comprises six districts, cluster-3 has four districts, and cluster-4 contains 20 districts. Based on statistics, it was concluded that all variables were significantly affected on all four clusters. As a result, it has been observed that there are significant differences in the clusters of the districts obtained by using domestic waste, medical waste, population, municipal budget and Mechanical Sweeping area variables.

For future research, an extensive database can be used. Other indicators that are important according to the regional conditions can be included in the model as a variable. Different clustering algorithms in the literature such as Mean-Shift Clustering, Gaussian Mixture Model, Agglomerative Hierarchical Clustering would be used to compare the clustering results.

Besides the practical results, this study contributed to the existing literature by creating clusters for districts in Istanbul for waste management in order to develop the necessary policies and to reduce costs and environmental impact in waste management activities. In addition, supportive policies can assist in carrying out waste management activities

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RESEARCH ARTICLE

A statistical analysis of municipal waste treatment types in European countries

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ABSTRACT

In today's world, the municipal waste management is becoming a main concern for every country and city. In environmental problems, how to collect and eliminate the municipal waste is extremely important. Different countries take different approaches towards the elimination of municipal waste and try to create policies. In this study, municipal waste treatment types for European Union (EU) and EU candidate countries is investigated. The data is taken from a report of EUROSTAT about municipal waste treated in European Union (EU) and EU candidate countries for 2012. There are 4 variables which form how municipal waste is treated in these countries. These variables are called as Recycled, Composted, Landfilled and Incinerated. Using correspondence analysis as a main statistical technique with the help of cluster analysis, a classification of the countries according to municipal waste treatment types is created.

Keywords: Correspondence analysis, cluster analysis, EUROSTAT, waste treatment

1. INTRODUCTION

According to a EUROSTAT news release on 26 March 2015, each person in the European Union generated 481 kg of municipal waste in 2013. There is a decreasing trend in the generation of municipal waste per person in EU. Amount of municipal waste generated per person differs significantly among EU member countries. In 2013, the lowest waste generated per person was in Romania and the highest was in Denmark.

Every country uses a different method to eliminate waste generated by households. The most important part of the waste disposal is to use a method which will have the minimum negative impact on the environment. Even though countries try to employ different methods to eliminate municipal waste, these methods can be classified into 4 main groups. These groups are called Recycled, Composted, Landfilled and Incinerated.

Eurostat publishes statistics about the waste treatment of the European countries [1]. In this study, the data set is obtained from Eurostat reports. Specifically, the report used is created for 2012 where most of the data points are finalized. According to Eurostat report, 492 kg of municipal waste was generated per person in 2012 and 480 kg of municipal waste was treated per person. Also, the report states that the municipal waste was treated in different ways and the overall percentages of waste treatment by treatment types are as follows: 34% was landfilled, 24% was incinerated, 27% was recycled and 15% was composted.

There are a few studies related with solid waste management. Henry et al. [2] investigates the municipal solid waste management in developing countries using Kenya as an example. The paper deals with approaches of possible solutions that can be undertaken to improve municipal solid waste services. Sharholy et al. [3] investigates Municipal solid waste management (MSWM) identified as one of the major environmental problems of Indian cities. The study pertaining to MSWM for Indian cities has been carried out to evaluate the current status and identify the major problems. Various adopted treatment technologies for municipal solid waste (MSW) have been critically reviewed, along with their advantages and limitations. Del Mundo et al. [4] analyze the correlation of socio-economic status, environmental awareness, knowledge, and perception with solid

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waste management practices in the coastal barangays of Talisay and Balibago, Calatagan, Batangas Philippines. The study shows that total family monthly income and environmental awareness are negatively correlated with solid waste management practices. However, environmental knowledge and perception are positively correlated with solid waste management practices. Chamizo-Gonzalez et al. [5] studies the waste management problem in Spain. Their paper examines traditional forms of levying charges for Waste-collection-treatment-disposal under the coverage of the Polluter-Pays-Principle in The Organization for Economic Co-operation and Development (OECD) countries and Spanish provincial capitals, finding a prevalence of flat fee systems in Spain. Regarding Madrid specifically, the paper analyses the relationship between its Waste - collection - treatment - disposal charges and some possibly independent variables. Relationships between MSW generated and some potentially-linked variables are identified. Analysis rejected that Madrid waste generation-treatment-disposal charges based on dwelling values had a positive relationship with waste generated (more value of the properties in a district does not imply more waste generated), and reveals/- confirms other significant correlations between some variables; it being remarkable that neither age, gender, nationality nor education were found relevant.

Waste management is also important for companies. Maranan et al. [6] investigates operations and waste management of Slaughterhouses in the province of Laguna. In their study, authors try to provide an overview of environmental and public health concerns in relation to the operations and waste management practices of slaughterhouses in the Laguna Province. Results revealed that only four (36.4%) of the eleven slaughterhouses in the province were accredited with the National Meat Inspection Service (NMIS), which implies that that the majority of the slaughterhouses in Laguna do not comply with the set standards for abattoir operations. Moreover, the non-accredited establishments operate with substandard and outdated facilities and equipment.

Pires et al. [7] studies the solid waste management in European countries. Authors make a review of systems analysis techniques. The authors put their focus on waste management strategies in terms of how systems analysis, a discipline that harmonizes these integrated solid waste management strategies, has been uniquely providing interdisciplinary support for decision making in this area.

Alzamora et al. [8] reviews of municipal waste management charging methods in different countries. Their main focus is on the charges bought by city officials to disseminate the waste. They suggest that public debates should be carried out in order to get a more organized charging systems in the cities.

In this study, using correspondence analysis and cluster analysis, groups of countries are created to form similar countries in terms of their municipal waste treatment types for European Union data set. Some results and comparisons are provided by looking at the similar studies.

2. MATERIALS AND METHODS

2.1. Data collection process

Correspondence analysis (CA) is a method which is used for dimension reduction and visualization of a multivariate data set similar to principal components analysis (PCA) [7]. Both of the mentioned methods are based on singular value decomposition (SVD) providing the dimension reduction property and the lower dimensionality visualization. Therefore, CA and PCA are similar methods while the differences of these two rely on the type of the distance matrices used, the applied data type and weighting of the data. CA is a method mainly applied to contingency tables (cross tabulation of two categorical variable); however, it is not only restricted to contingency tables. It can also be applied to ratio-scaled data, binary data, preferences and fuzzy-coded continuous data [9]. Correspondence analysis has found a place in many areas of social sciences such as: sociology, linguistics, psychology (survey data), in ecological sciences in biology and, in environmental sciences. Reference [10] indicates that ecological data can be represented in nature as abundances or positive amounts like biomasses on a set of species at different sampling sites.

In correspondence analysis, a row (column) point of a data matrix is called row (column) profile. The row (column) profiles are the ratios of the row elements to their row (column) sums. Weights of these profiles are called masses which are the ratio of marginal sum of row or columns. Euclidean distances are employed in PCA method; on the other hand, chi-square distances are the subject of the SVD in CA. Chi square distance between rows i and i' can be given as following in Eq. 1:

$$\chi_{i,i'} = \sum_{j=1} \left(\frac{X_{ij} - X_{i'j}}{c_j} \right)^2 \quad (1)$$

Here c_j is the j.th average column profile. The algorithm for CA application is given as follows: [7]

- Divide the original data table **N** by its grand total $n = \sum_i \sum_j n_{ij} : \mathbf{P} = (1/n)\mathbf{N}$
- Denote by **r** and **c** the marginal sums of **P** (rows and column sums respectively);

r = **P1**, c = $\mathbf{P}^{\mathrm{T}}\mathbf{1}$

- Calculate the matrix of standardized residuals $\frac{p_{ij} - r_i c_j}{\sqrt{r_i c_j}}$ and its SVD:

$$\mathbf{S} = \mathbf{D}_r^{-\frac{1}{2}}(\mathbf{P} - \mathbf{r}\mathbf{c}^{\mathrm{T}})\mathbf{D}_c^{-\frac{1}{2}} = \mathbf{U}\mathbf{D}_\alpha\mathbf{V}^{\mathrm{T}}$$

- Calculate the coordinates:

Principal coordinates of rows: $= \mathbf{D}_r^{-\frac{1}{2}}\mathbf{U}\mathbf{D}_\alpha$, of columns: $\mathbf{G} = \mathbf{D}_c^{-\frac{1}{2}}\mathbf{V}\mathbf{D}_\alpha$

Standard coordinates of rows: $\Phi = \mathbf{D}_r^{-\frac{1}{2}}\mathbf{U}$, of columns $\Gamma = \mathbf{D}_c^{-\frac{1}{2}}\mathbf{V}$

An exploratory graph can be drawn to examine both the columns (variables) and rows (individuals or objects) together. These graphs are called biplots, that is, a generalization of scatterplots, and they have the possibility of containing more than two axes [9].

The variance of the CA analysis is called total inertia and it is indeed related to chi-square statistics. The explained variances for each dimension can be calculated through the ratio of the eigenvalue of the concerned dimension to the sum of the all eigenvalues. A scree plot can be an assistance to choose the number of dimensions containing the maximum variance of the CA solution.

The most preferred visualization of the CA solution is called symmetric map and is described as an approximation to the true biplots. It provides a better use of plotting area because of the property of having the same column and row point inertias along the dimensions [9].

The interpretation of the proposed visualization is that the individuals who have higher variable values than average tend to situate close to the corresponding axis which are the variables of the analysis. In addition, it can be an assistance as a visual clustering of multivariate data sets through this aggregation of the same kind in the same location feature. Contributions to CA solutions can also be calculated and can be shown in the biplots as the lighter shades of a specified color indicate low level contribution while the darker shades indicate high level contribution.

The second statistical analysis, which is used in this study, is the hierarchical cluster analysis. Biplot visualization may only be considered as a visual assistant for hierarchical clustering methods. Clustering is a process for grouping objects or individuals into a cluster by a distance measure. The goal in this process is to achieve the grouping of clusters such that objects in the same clusters have small distances from each other while others have not [12].

Hierarchical clustering can be agglomerative or divisive. Respectively, each object can be thought as a cluster to be merged into more than one or the objects can be thought whole as a cluster to be divided into more than once. It has an iterative algorithm that in each step distance matrix will be upgraded and merging or dividing can be done via a linkage method after the first cluster is formed. A single linkage is based on minimum distance between clusters and objects. A complete linkage is the merging of two clusters that are far apart. Average linkage is the method that uses average distances for merging. In order to show the clusters, a graph called dendrogram can be used. A dendrogram, which resembles a tree with branches, shows the hierarchical relation of the objects subjected to clustering. The algorithm ends when optimum clusters are found. Dendrogram can be cut through at a certain distance or through a cluster number given before the analysis. In most social studies, analysis clusters can be formed according to average linkage rule and the cluster numbers are given before the analysis by an expert view. One major drawback of the analysis is when the number of objects is high, the algorithm takes longer time to find optimum clusters.

In this study, the data is taken from a report of EUROSTAT about municipal waste treated in European Union (EU) and EU candidate countries for 2012. Data includes values for 35 countries and EU averages. There are 4 variables which define how municipal waste is treated in these countries. These variables or municipal waste treatment types are named as Recycled, Composted, Landfilled and Incinerated. The Data set published in 2012 was the most collect set as the article was written, but as the EUROSTAT publishes new data, the authors have an intention to repeat the analysis in order to changing trends in waste treatment types. The values are given as the ratios of each treatment type that adds up to 100%. As noted in the report, data of some countries are estimated values. Furthermore, some values indicate real zeros so the data we will examine is a ratio-scale data. Zeros in the data indicate percentages lower than 0.5%. Municipal waste treated and generated per person was also included in the data for each country. Our initial aim is to visualize the data in lower dimensions and to form clusters of similar countries having similar pattern of waste management. Then, an examination of the differences of clusters by means of treatment type is shown.

3. RESULTS AND DISCUSSION

In order to create the statistical results, R software is used for the calculations [13]. CA is a package of R which is used for correspondence analysis [9]. Using correspondence analysis, a biplot of the data is obtained and shown in Figure 1. In Figure 1., there are five unlabeled countries located close to the landfilled axis in the far-right corner of the graph. These countries are Bosnia and Herzegovina, Former Yug. Rep of Macedonia, Romania, Serbia and Turkey. These countries' common approach towards the municipal waste treatment is mostly to landfill it. Additionally, Former Yug. Rep of Macedonia and Bosnia and Herzegovina have the same profiles. Countries with higher than average incinerated waste are located in the top left of the Figure 1. and these countries are identified as Austria, Belgium, Denmark, Germany, Netherlands, Norway, Sweden and Switzerland. Biplot indicates that Iceland, Ireland and Slovenia are countries of having higher amounts of Recycled municipal waste than others. In the middle and through the middle right of the Figure 1, it can be seen that there are countries with lower landfilled municipal waste when they are compared to the far right located countries like Turkey and Romania. Portugal and Czech Republic is recognized as lower contributor countries to Correspondence Analysis solution of the data set.

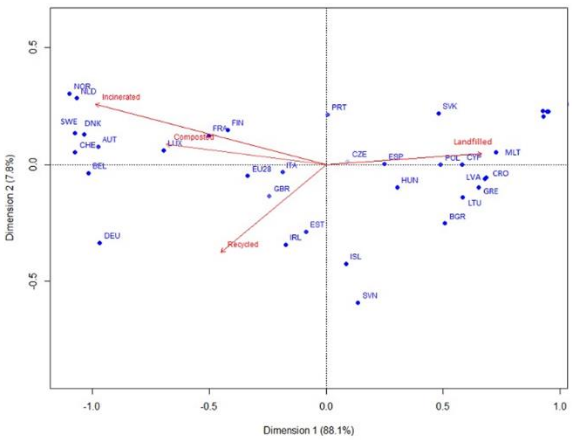

Fig 1. Correspondence analysis biplot of waste management data

The results of hierarchical cluster analysis are given in Table 1. A slight modification is used (0.1%) to represent a value for a treatment type if the value equals absolute zero. Therefore, it was possible to make a comparison of countries that do not apply the specific treatment type with the countries that apply the type in small amounts. This modification of the data does not change the course of CA and clustering because the row sums values are not changed. As a result of hierarchical clustering, countries are clustered into 6 homogenous groups according to municipal waste treatment types. The results obtained from correspondence analysis (Figure 1) are very similar with the results obtained from cluster analysis.

Table 1. Clusters of the countries via hierarchical Cluster analysis

Clusters	Countries
Group 1	Estonia, Ireland, Italy, Slovenia, Great Britain, Iceland
Group 2	Belgium, Denmark, Germany, Netherlands, Austria, Sweden, Norway, Switzerland
Group 3	Bulgaria, Greece, Croatia, Republic of Cyprus, Latvia, Lithuania, Malta, Poland, Slovakia
Group 4	Czech Rep., Spain, Hungary, Portugal
Group 5	France, Luxembourg, Finland
Group 6	Romania, Rep. of Macedonia, Serbia, Turkey, Bosnia and Herzegovina

In order to make a comparison of the clusters, boxplots of clusters are drawn for each municipal waste treatment type and they are given in Figure 2. Looking at the boxplots, it is possible to investigate the similarities and differences of different clusters and treatment types.

Cluster 1 and Cluster 2 have the highest amount of municipal waste that were recycled. Moreover, their median values are alike; however, cluster 2 has got a higher variability than cluster 1. Cluster 2 is formed of leading countries in incinerated municipal waste and Norway is in the first place. A discriminatory feature of Cluster 1 is that it includes the EU28 which is the average of 28 countries in European Union. Hence, it can be considered that the countries in this cluster show the average characteristics of European Union. In close inspection, it can be seen that the countries in cluster 2 have got their municipal waste distributed on only three methods. They have very little amount of landfilled waste. Countries in Cluster 3 have got the second highest amount of landfilled municipal waste. Another property of these countries in this cluster is that they share the second place in incinerated amount of waste with countries in the cluster 6 is the first. Slovakia stands out as an outlier with 10.1% of incinerated amount. Countries of Cluster 5 have got less variability in incinerated amount of municipal waste amongst all other clusters. In addition, they have the least amount of landfilled waste following Cluster 2. Cluster 3 is the third cluster in the ranking of highest amount of landfilled municipal waste.

In Figure 3, combining the information from the cluster analysis and correspondence analysis, a Biplot is produced. From left through the right of the biplot, the grouping of the countries can also be easily recognized in Figure 3.

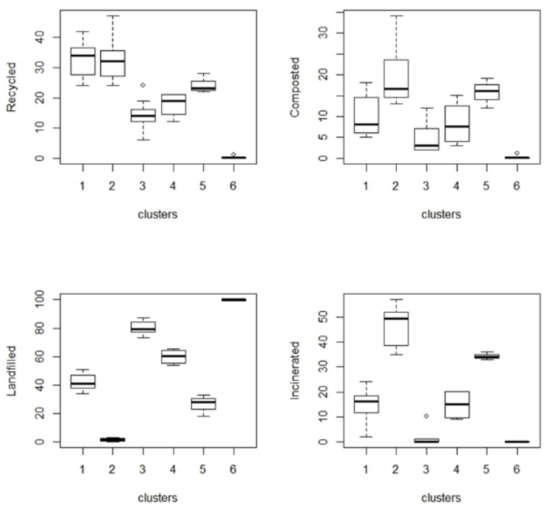

Fig 2. Boxplots of the clusters

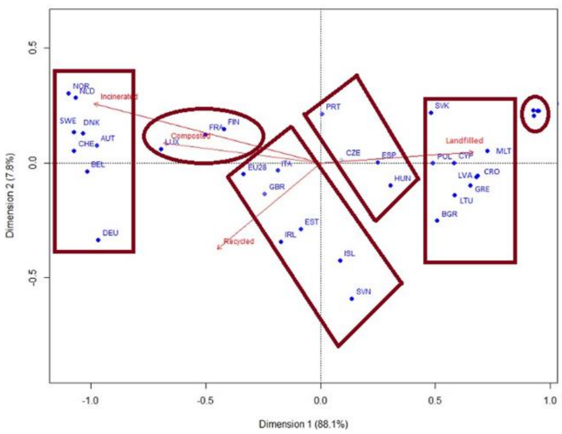

Fig 3. Clustering shown in the CA biplot.

In Figure 4, Clustering dendrogram is given. The relationship of similar countries in terms of treatment type is obvious in clustering dendrogram. As the height of the dendrogram increases, dissimilarity of the objects/countries gets higher.

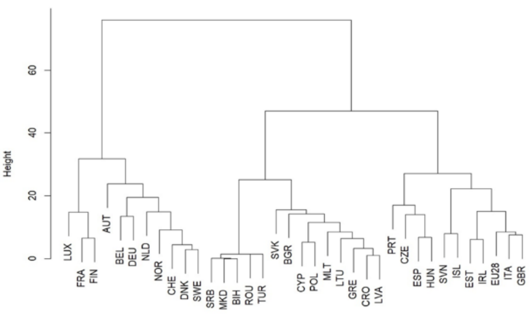

Fig 4. Clustering dendrogram of waste management data

4. CONCLUSIONS

Vujić et al. [14] investigate the relationship between the GDP and municipal solid waste management of 27 European Union countries in the period between 1995 and 2007. In the study, correlation and regression analysis is used to show the relationship. Moreover, they found positive correlation with GDP and incineration, recycling and biological treatments. On the other hand, a negative correlation for landfilling and GDP was found out. Hence, as the ratio of landfilling increases, the GDP decreases dramatically. The study described three phases of economic development for countries with three GDP levels. An initial phase where approximately 100% of the waste is landfilled while in intermediate phase, the majority is still landfilled but recycling and incineration is also improving. Lastly, there is too little or no amount of landfilled waste in some cases and majority is recycled or incinerated in final phase. This can be thought as a clustering into three groups in our case. Our study supports the findings of this study. Cluster 6 coincides with the initial phase countries given. This cluster consists of EU candidate countries like Former Yug. Rep. of Macedonia, Turkey and Serbia and also Romania as a recent EU member and Bosnia and Herzegovina as a potential EU candidate. Additionally, Cluster 2 is similar to final phase countries including EU and EU founder countries with a noticeably higher GDP value compared to others.

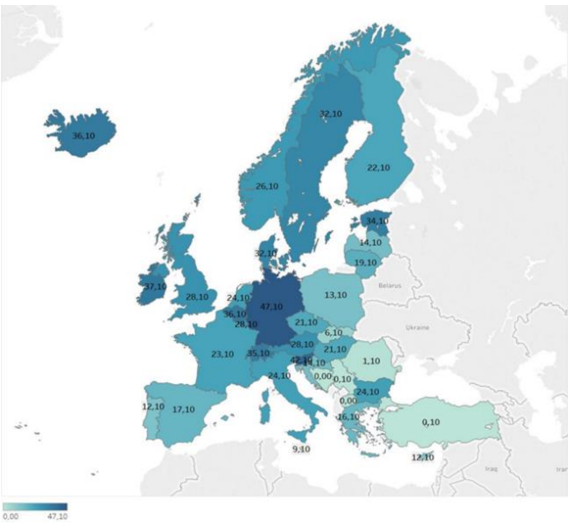

Fig 5. Thematic map of countries for Recycled waste

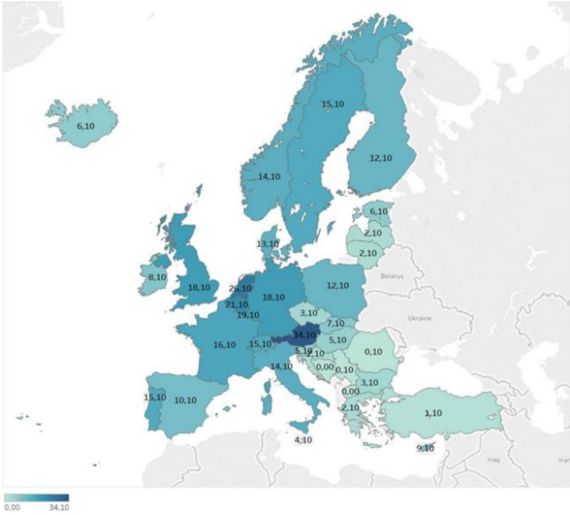

Fig 6. Thematic map of countries for Composted waste

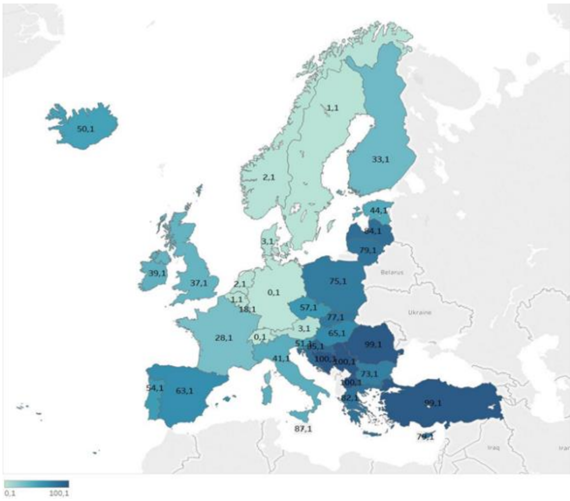

Fig 7. Thematic map of countries for Landfilled waste

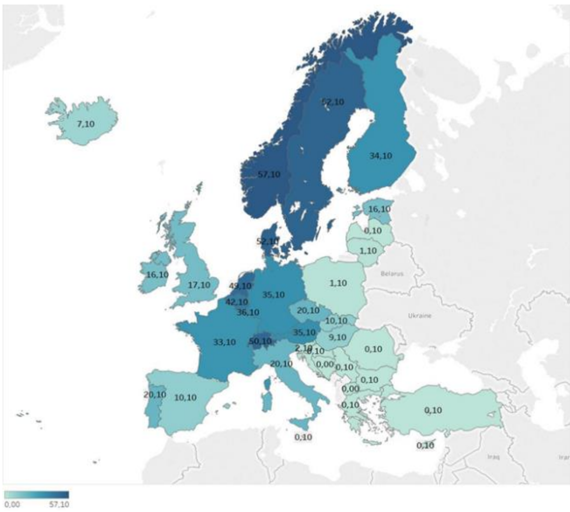

Fig 8. Thematic map of countries for Incinerated waste

Using Tableau software [15], in Figure 5, 6, 7, and 8; the thematic maps of countries in terms of their waste management are shown. By using these maps, we believe that it is not too difficult to see which countries depends on which waste management type more than the others.

In this study, the data set is a very special one where each row representing a country adds up to 100%. The suitable technique to analyze this type of data set is the correspondence analysis. Additionally, the cluster analysis helps us to interpret the results of correspondence analysis. By looking at the clusters and geographical information, each country may create policies towards better municipal waste treatment. We believe that, this study will offer guidance for countries in terms of the positions of the countries for municipal waste treatment. The countries in the same clusters may learn from the other countries in the same cluster and also learn from the countries in different clusters. Looking at the results, it is not too difficult to see which country is inclined towards a specific treatment type. Therefore, the countries' authorities responsible for municipal waste management may decide which direction to go, and once they decide to continue on the direction of the treatment type, they are able to see which countries should be taken as an example to follow.

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RESEARCH ARTICLE

Aluminum accumulation in treatment using submerged membrane electro-bioreactor of young landfill leachate: Statistical analysis

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ABSTRACT

Herein, landfill leachate containing high amount of organic matter, which is quite difficult to treat, was first treated using the new submerged membrane electro-bioreactor (SMEBR) system. Aluminum (Al) electrode was used for the treatment of leachate in the SMEBR and Al accumulation was detected. This study aims to examine Al accumulation in the treatment of leachate with high organic content in the SMEBR system. The Al values obtained were plotted on a graph using MS Excel, and Mann–Whitney U test was used to determine whether there is a statistical difference between the observed Al values. Also, correlations between Al accumulations and conductivity and TOC in SMEBR and SMBR were evaluated. Resultantly, it was found that relationship between Al and conductivity is very weak, correlation between Al and TOC% is a weak-moderate, the Al accumulation in the SEMBR has a linear relationship with time and there is a very strong correlation between the two variables (R^2= 0.7591). Its correlation with time in the SMBR is moderate (R^2= 0.3316). MS Excel 2016 and Minitab 16.0 programs were utilized in the statistical analyses.

Keywords: Aluminum accumulation, landfill leachate, membrane bioreactor, statistical analysis, submerged membrane electro-bioreactor

1. INTRODUCTION

In landfill, leachate production is an inevitable consequence of water leaking through degredation and separation of waste. Depending on factors such as landfill age, precipitation, seasonal weather changes and waste composition, leachate characteristics vary and pollution load is higher than other wastewaters [1-3]. The leachate contains toxic components, recalcinant structures and heavy metals that can damage humans and ecosystems. This hardly treatable wastewater can be effectively treated by electrochemical methods such as biological treatment, chemical precipitation, chemical oxidation, coagulation-flocculation. In addition, leachate can be treated by membrane bioreactors (MBR) which are integrated into biological treatment processes or formed by combination of membrane filtration systems such as ultrafiltration and nanofiltration externally [4]. MBRs are also reported to be effective in the treatment of leachate. In recent years, electrocoagulation (EC), which provides removal of pollutants by the introduction of electric current to metal electrodes, has been used successfully in the treatment of leachate and wastewater of many different characteristics [5-11]. There is no need to add any coagulants or chemicals in the EC process and the cost is quite low compared to conventional systems. Several chemical and physical mechanisms occur during EC. The metal electrode used is dissolved by electrolysis. Coagulant species and hydroxides depending on ambient pH are formed which can coagulate and desatabilize suspended particles or remove contaminants by flotation, adsorb contaminants or assist their precipitation. By EC treatment, a high rate of pollution removal is provided. However, after the EC process is carried out, large amounts of EC sludge are produced [12-13]. Formed sludge contains a high number of hydroxides ($M(OH)_3$) of metal electrodes and also shows dependence on the characteristics of the treated wastewater.

Recently, hybrid system submerged electromembrane bioreactor (SMEBR) has been prominent in

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wastewater treatment. The SMEBR covers the simultaneous operation of the SMBR system and the EC system in a single reactor. The metal electrodes are immersed in the SMBR for EC to occur in the SMBR. Literature studies showed that by applying the electric field to the electrodes, a high rate of waste water treatment can be achieved by both MBR and EC working together [14-17], membrane clogging can be significantly reduced [18-20] and active sludge properties can be improved much more comparing with conventional MBR systems [21-22]. In the SMEBR, metal hydroxide sludge is produced both by biological treatment and by dissolving the metal electrode in EC systems. Accumulation of Al was observed in a study of Bani Melhem and Elektorowicz [23] MBR also allows coagulant to be added to improve activated sludge properties. These coagulants form metal containing precipitated sludge as in EC. It was stated that if the sludge remains in MBR systems for a long time, it can also accumulate in bacteria and inhibit nitrification [23].

In the literature, there is no study about the accumulation of the soluble metal electrode in the SMEBR or coagulant added externally to the MBR in the bioreactor. The aim of this study is to find the daily amount of Al accumulated in the SMEBR system and to determine the amount of Al that can be accumulated by statistical interpretation. For the first time, young leachate was treated with SMEBR and Al was determined by ICP-OES by sampling the waste activated sludge almost every day throughout the operation. The data obtained were modeled by appropriate tests.

2. MATERIALS AND METHODS

2.1. Experimental set up

Two reactors, SMEBR and SMBR, were installed (Fig 1) in Yildiz Technical University Research Labratory. The reactors were made of plexiglass. Both reactors are 19.5 cm in diameter and 63 cm in height. The working volume of the reactors is 5 L. Operation conditions in reactors, hydraulic retention time (HRT) and organic loading rates (OLR) were 5 days and 13.2 kg COD m^{-3} day, respectively. In order to provide filtration, hallow fiber membranes were used. Hallow fiber membranes were obtained from the National Research Center on Membrane Technologies (MEM-TEK). The membrane pore diameter and the effective surface area are 0.4 µm and 0.05 m^2, respectively.

In the SMEBR, cylindrical aluminum (Al) anode and cathode electrodes are placed in the bioreactor. Perforated electrodes were used to ensure homogeneous mixing in the reactor. Perforation ratio of perforated anode and cathode electrodes were 73.3 and 15.6%, respectively and both electrodes were 1 mm thick. The distance between the electrodes was 5.4 cm. The Al electrodes were immersed into activated sludge in the SMEBR approximately 18 cm from the bottom. The electrodes were connected to the Direct Current (DC) power supply and the timer was used to deliver intermittent DC. The current density applied to the SMEBR was determined as 24 mA cm^{-2} [24]. At the earliest stage of SMEBR lasted for 25 days, 180 s electrical field per day during 5 days of HRT was applied to the activated sludge of young leachate [25]. Consequently, the applied daily electrical field was increased since no satisfactory difference was observed between SMEBR and SMBR in terms of treatment performance [25]. An electrical field of 360 s day^{-1} was applied for another 25 days in the same current density with 12-h intervals during 5 days of HRT. Accordingly, the first 25-day period was named as Stage I and the second 25-day period was named as Stage II.

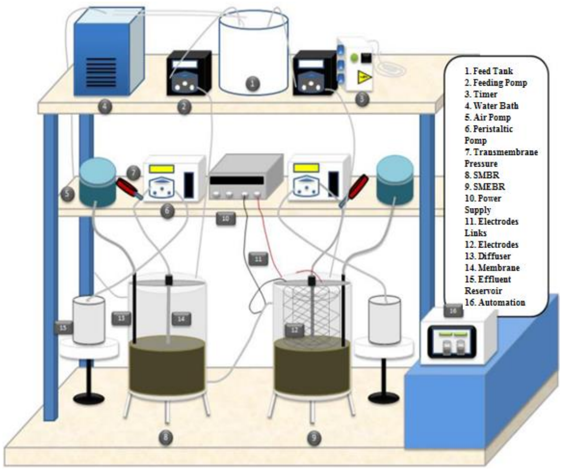


Fig 1. Schematic shown of SMEBR and SMBR [25]

2.2. Analytical procedure

Leachate was obtained from Leachate Treatment Plant in Odayeri Solid Waste Landfill Site located on the European side of Istanbul. The conductivity, TOC and Al values of the young leachate used were between 20.2-28.3 mS cm^{-1}, 17,000-23,000 mg L^{-1} and 2.50-2.58, respectively. Conductivity in SMEBR and SMBR was measured using Termoscientific Orion 5 star. In both reactors, inlet and outlet wastewater samples were taken daily. The TOC concentrations of the reactors were analyzed using the HACH IL 550 TOC-TN instrument. TOC removal efficiencies were calculated using the degredation rate equation: Degradation Rate (%) = $(A_0\text{-}A_1) / A_0\text{x}100$ where A_0 and A_1 represent the initial initial and final percent of the parameter, respectively.

2.3. Statistical analysis and computational procedure

Statistical models were used for modeling the amount of Al accumulated in SMEBR and SMBR mathematically and to find out whether the accumulation amounts in both bioreactors differ from each other. For this purpose, MS Excel 2016 and Minitab Version 16.0 software were used on Windows 10 operating system. In all analyzes, the hypotheses were tested at 95% statistical significance level.

Firstly, univariate linear regression analysis was applied for mathematically modeling the amount of Al accumulation in both bioreactors. The relationship between two variables (Al accumulation and time) was measured by this analysis conducted using MS Excel

2016 Data Analysis module. In this relationship, time (measurement day) is an independent/descriptive variable where Al accumulation is dependent/explained variable. Following the simple linear regression, the relationship between the two variables was also visualized using the Graphing module of MS Excel 2016 (Fig 4 and Fig 5).

Mann-Whitney U test, one of the non-parametric statistical analysis methods, was used to see whether the amounts of Al accumulated in SMEBR and SMBR were significantly different from each other. The main reason for using this analysis method was that it was determined that the data obtained due to the unsufficient sample numbers (N = 25) did not have a normal distribution according to the Shapiro-Wilk W test. Mann-Whitney U test (found by Henry Berthold Mann and Donald Ramson Whitney) is used to determine whether the mean values of the two data are equal. In this test, after obtaining two data sets, $x_i = \{x_1, x_2, \ldots, x_n\}$ and $y_i = \{y_1, y_2, \ldots, y_n\}$, the test statistics ($U_x$, U_y, and U) are is calculated as:

$$U = \min(U_x, U_y) = \begin{cases} U_x = n_x n_y + \frac{n_x(n_x+1)}{2} - R_x \\ U_y = n_x n_y + \frac{n_y(n_y+1)}{2} - R_y \end{cases} \quad (1)$$

In the above equation, nx represents the magnitude of the x data set and ny represents the magnitude of the y data set, and R_x represents the corrected sum of the order data of x data set and R_y represents the corrected sum of the order data of x data set. The test is significant at the determined level of significance, if the observation is as $U \leq U_{critical}$; that is, the Zero Hypothesis (H_0: There is no difference between the order of the two samples) is rejected and the Alternative Hypothesis (H_1: There is a difference between the order of the two samples) is accepted.

In large samples (ie, $n_x > 20$ and $n_y > 20$), the U statistic has an almost Normal distribution, $N(\mu_U, \sigma_U)$, which can be represented as (mean and standard deviation values of μ_U and σ_U, U). In this case, the standardized z statistic ($z_{critical} = \pm 2.58$ at $\alpha = 0.01$ significance level for two-tailed test) can be calculated and interpreted as follows:

$$Z = \frac{U-\mu_u}{\sigma_u} = \frac{U-(n_x n_y)/2}{\sqrt{\frac{n_x n_y (n_x+n_y+1)}{12}}} \rightarrow |z| = \begin{cases} |z| > z_{critical} \rightarrow p < \alpha \rightarrow H_1 \\ |z| < z_{critical} \rightarrow p > \alpha \rightarrow H_0 \end{cases} \quad (2)$$

In addition, Box-Plot graphs of Al values in two bioreactors were plotted to show descriptive statistics (eg minimum, first cartil (Q_1), medyn (Q_2), third cartil (Q_3), maximum) of the obtained data (Fig 7).

3. RESULTS AND DISCUSSION

3.1. Conductivity change

Conductivity is a numerical expression of the ability of an aqueous solution to conduct electricity. The conductivity of the water depends on the total and relative concentrations of ions, their mobility, their valence and the measurement temperature in the water. By measuring the conductivity of the water, the number of ions in the water can be determined approximately. Leachate is a highly conductive wastewater. The active sludge conductivity value of the leachate in SMEBR and SMBR studies was determined to be less than 20 mS.

Fig 1 shows the conductivity values in SEMBR and SMBR. Conductivity in the SMEBR was measured at lower values than the SMBR system. Applying the electric field in the SMEBR reduces conductivity [26]. This reduction is due to charge neutralization. The ionic species consisting of total dissolved solids in the activated sludge coagulated with the positive ions obtained by dissolving the electrodes and the conductivity decreased with the reduction of the ionic species. Conductivity depends on many factors. pH in SMEBR and SMBR was 8.26-9.07, 8.54-9.0 and 8.5-9.00, 8.44-9.00; and the temperature varied between 21-27 °C, 21-27 °C and 21-30 °C, 22-29 °C in Stage I and Stage II, respectively. In Stage II, the amount of Al given to the water was higher than that of Stage I. As a result, the conductivity values in Stage II were lower than those in Stage I (Fig 2). The contribution of the electric current is evident here. Ilhan et al. [27] found similar situation in his study. Wang et al. [28] stated that the conductivity values decreased with the introduction of electrical current into the aqueous medium. Conductivity was affected by both temperature and pH changes, so no stable increase or decrease was recorded. The polarization of the electrodes occurred on days 8, 22 and 46 in the SMEBR, so the current could not be fully transmitted to the activated sludge as 26 mA cm^{-2}. Therefore, conductivity in SEMBR increased in the following days compared to SMBR. In addition, there are high amounts of Ca and Na salts in the leachate, and their accumulation over time can increase the conductivity in the SMEBR.

3.2. TOC change

Electrochemical treatment is carried out together with biological treatment for SMEBR treatment of leachate. When electric current is applied in the SMEBR, Al^{+3} is produced by electrooxidation of the aluminum anode. The electrolytic dissolution of the aluminum anode is first converted to $Al(OH)_3$ at convenient pH levels, Al^{3+} and $Al(OH)_2$ at low pH and finally to polymerized $Al_n(OH)_{3n}$ [29]. Other components such as $Al(OH)^{2+}$ and $Al_2(OH)_2^{4+}$ are formed depending on the pH of the aqueous medium. While water oxidation produces hydrogen and oxygen gas in the anode, hydrogen gas and hydroxide in the cathode are produced by reducing water. In addition, oxidation produces a strong oxidizing hydroxyl radicals and forms of dehydrogenated and hydroxylated species can react with organic pollutants [30-33]. Accordingly, when leachate enters the anode and cathode from the region between the reactor wall and the anode, it is subjected to electrokinetic conditions and organic oxidation occurs. Thus, it contributes to TOC removal.

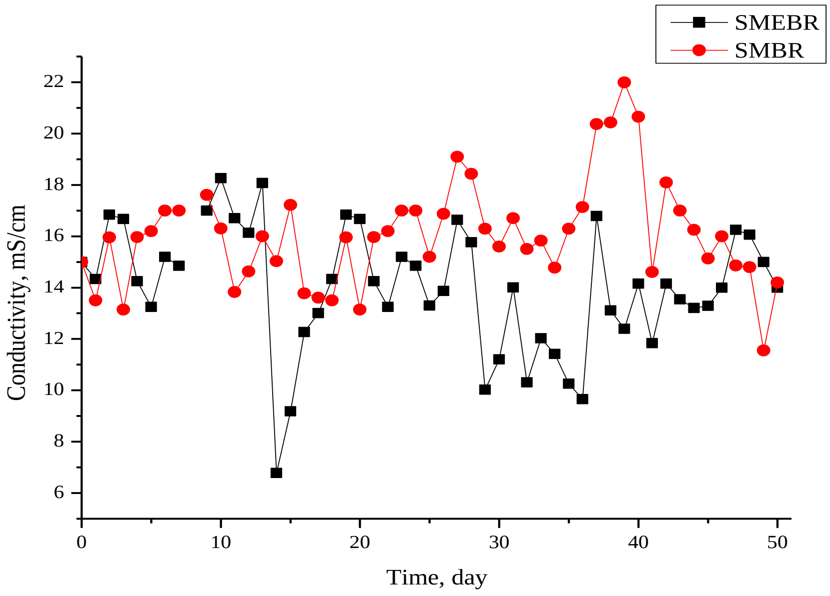


Fig 2. Conductivity change in SMEBR and SMBR

TOC removal efficiency is presented in Fig 3. Average TOC removal in Periot I was 89, 88% for SMEBR and SMBR. In Stage II, TOC removal efficiency in SMEBR was increased 7% with increasing electric current compared to SMBR. Feng et al. [34] found that the application of electric current increases TOC removal. There was a reduction in TOC removal efficiency from 86% to 81% in 20-22nd days of Stage I. This was because the electrical current cannot be transmitted as 24 mA cm^{-2}. Electrodes were taken out of the reactor and checked and it was observed that the electrodes were passivated. Physical washing was performed under the tap water with the help of sponge, but the biofilms on the electrodes could not be removed. The electrodes were then soaked in 1% HCl acid for 1 hour followed by physical washing. Electrical current could not be introduced to the SMEBR for 3 days. In order to obtain more treatment efficiency by SMEBR compared to SMBR in the treatment of young leachate, the applied electric field exposure time has been doubled and the reactors were operated for a further 25 days (Stage II). On day 25, the electrodes were reintroduced into the SMEBR. Passivation in SEMBR on days 31, 32 and 42 in Stage II affected TOC removal.

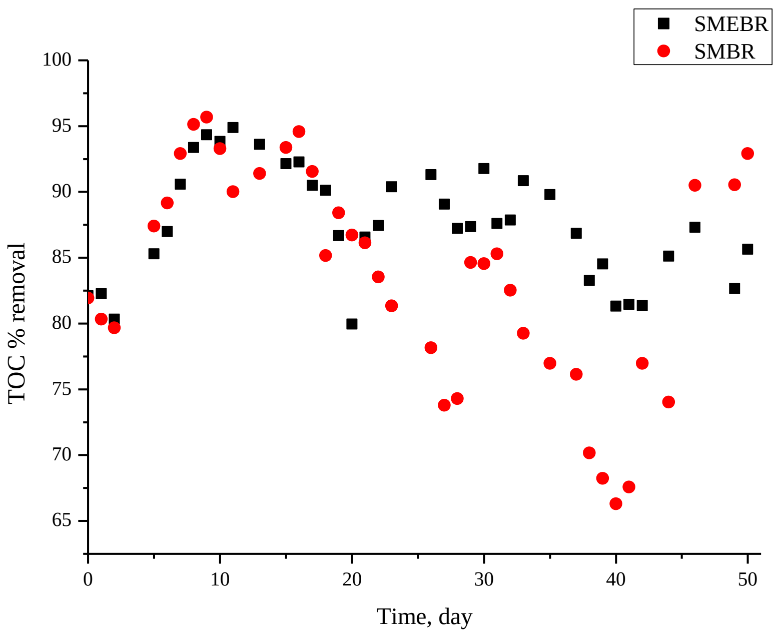


Fig 3. TOC change in SMEBR and SMBR

3.3. Statistical analysis

3.3.1. Modelling of Al accumulation in SMEBR and SMBR

SMEBR is an effective treatment method for wastewater treatment. With the dissolution of metal electrodes in the SMEBR, the pollution removal efficiency is higher than in other treatment processes. However, dissolving electrodes in the SMEBR acummulate in the activated sludge as well. There is uncertainty as to how much electrodes will accumulate during the operation of reactors. This study was conducted to find out how much Al accumulates daily and to estimate how much it can accumulate in longer operations. Firstly, waste activated sludge samples were taken from SMEBR and SMBR and Al values were plotted using MS Excel. These drawings are given in Fig 4. As young leachate is a difficult wastewater, occasional operational problems were observed; sludge samples could not be taken because of sludge loss due to the sludge swelling and overflowing and Al determination could not be conducted.

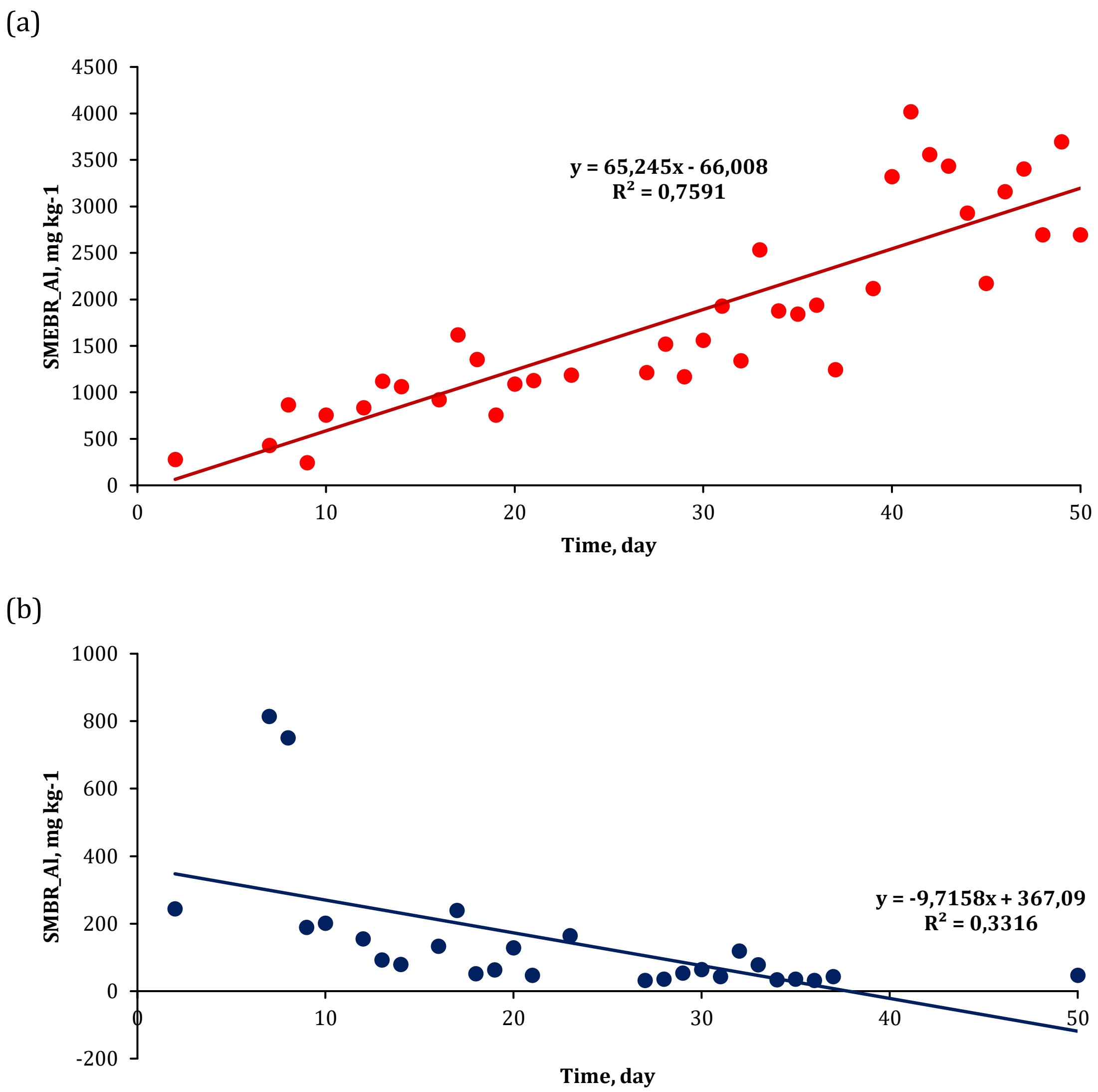


Fig 4. Change of Al over time in waste activated sludge in SMEBR (a) and SMBR (b)

In the SMEBR, coagulant agents Al ions are produced by electrooxidation of the Al electrode in situ in the activated sludge media when the DC electric field is applied to the leachate. Activated sludge pH varied between 8.01-9.02 in SMEBR. It can be said that $Al(OH)_3$ and polymerized $Al(OH)_{3n}$ precipitated in this pH range. The phosphorus value in the leachate is TP=10.2-12.0 mg L^{-1}. SMEBR and SMBR effluent TP values were less than 0.1 mg L^{-1}. Therefore, Al reacts with phosphate ions to form $AlPO_4$ in the reactors and precipitation occurs.

In the SMBR, Al influent in activated sludge is only possible through leachate. Al reactions occurring in the SMEBR also occur in the SMBR. However, Al was found in the waste activated sludge in the range of 0.03-0.82 g kg^{-1} since there was no external Al introduction.

The sludge retention time in SMEBR and SMBR is approximately 15 days. The sludge retention time was checked regularly. Operating problems such as sludge swelling or overflow occurred in the SMBR. The sludge retention time and daily discarded sludge amount could not be kept stable. Therefore, Al increased on days 6, 15, 19, 22 and 31. On days 40 and 50, the amount of Al was less than 0.0 g kg^{-1}. In SMEBR, sludge retention time remained stable compared to SMBR. The SMEBR had less sludge swelling/overflow problems comparing to SMBR. In a study, it was stated that Al accumulation prevents sludge swelling [35]. Al accumulation in the SMEBR turned out as an advantage over SMBR in the treatment of young leachate. Therefore, Al accumulation is related to sludge retention time. In the SMEBR, Al amount increased by accumulation in the reactor since more Al dissolved in Stage II over Stage I and all Al could not be discarded in the daily sludge.

Al accumulation in waste activated sludge was observed in SMEBR and SMBR for 50 days. In order to estimate how much Al will accumulate in SMEBR for more than 50 days operated processes, time-dependent change of Al values is modeled by regression analysis and the following equations are obtained:

Al (SMEBR) = -66.008 + 65.245*(day) (3)

Al(SMBR) = 367.09 – 9.7158*(day) (4)

As can be seen in Fig 4 and the above equations, an increasing Al accumulation occured over time in the SMEBR, whereas the opposite is depicted in the SMBR, which decreased over time. Al accumulation in the SMEBR bioreactor indicated by (3) is statistically significant at 95% significance level. In addition, the R^2 value of simple linear regression is 0.75; there is also a strong correlation between the two variables (R^2 = 0.7591).

On the other hand, the accumulation of Al in the SMBR reactor does not give a linear appearance as in the SMEBR. For this reason, different functional transformations (eg logarithmic, exponential, etc.) have been tried and the most suitable transformation is found to be 1/x. When the change of 1/Al value over time is modeled, the following graph and equation are found:

1/Al (SMBR) = 0.0008 + 0.0006*(day) (5)

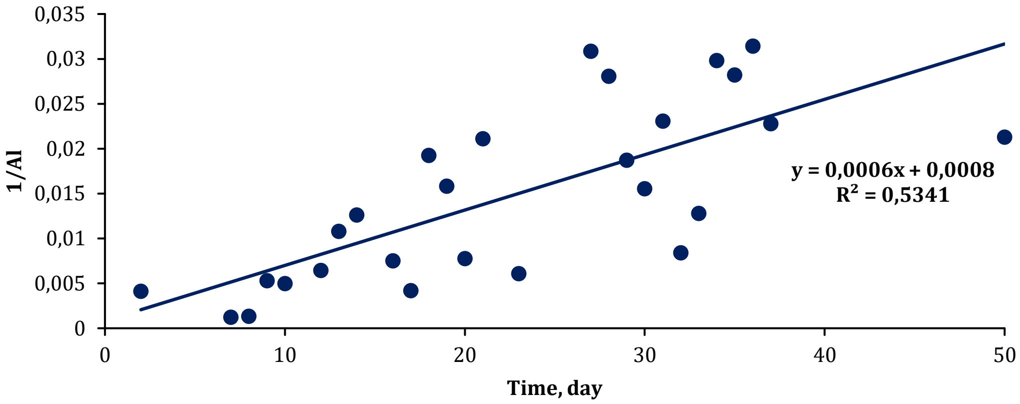


Fig 5. Variation of 1/Al value over time in SMBR

The correlation of 1/Al value over time is moderate (neither strong nor weak) (R^2 = 0.5341) and equation (5) explains Al accumulation in SMBR more accurately than linear equation (4) (R^2 value of linear equation is only 0.3316). Therefore, if it is desired to estimate the accumulation of Al values in SMBR over time, using equation (5) will provide more accurate results. This time, it can be deduced that the accumulation of Al in the SMBR decreases with time since not the Al value but the value of 1/Al will increase in direct proportion over the day variable.

3.3.2. Statistical Comparison of SMBR and SMEBR

Not only were the relation of Al accumulations in SMEBR and SMBR over time measured but also statistical differences were also measured. For this purpose, Al data obtained from both reactors on the same days were used. Since the size of this data set is only 27, the normal distribution assumption would not be appropriate. As a matter of fact, when the Shaphiro-Wilk test was applied, Al (SMBR) values do not have normal distribution ($p < 0.1$) (Fig 6).

Since one of the data sets does not have a normal distribution, it would be more appropriate to perform non-parametric tests. Thus, Mann-Whitney U test was applied to Al values data sets obtained from two reactors using Minitab software. The result is as follows:

	N(sample size)	Median
SMBR	27	78.1
SMEBR	27	1183.3

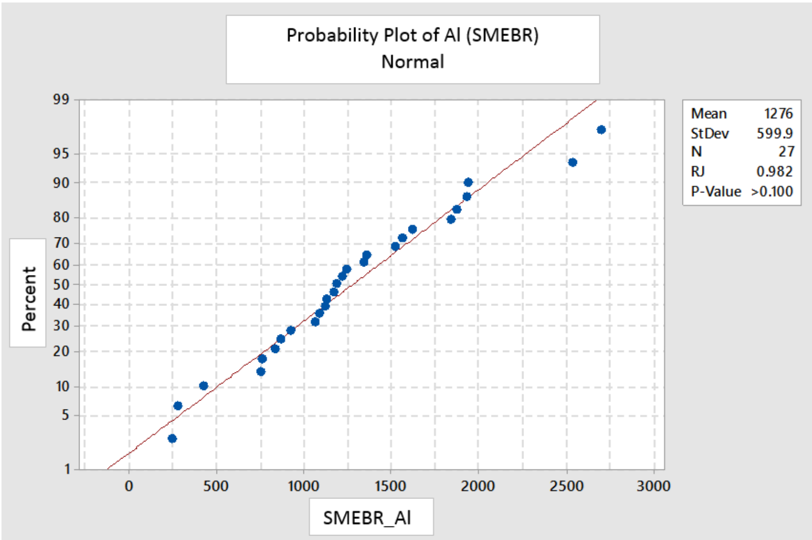
Point estimate for η1 - η2 is -1083.5

95.1 Percent CI for η1 - η2 is (-1285.0,-887.7)

W = 387.0

Test of η1 = η2 vs η1 ≠ η2 is significant at 0.0000

(a)



(b)

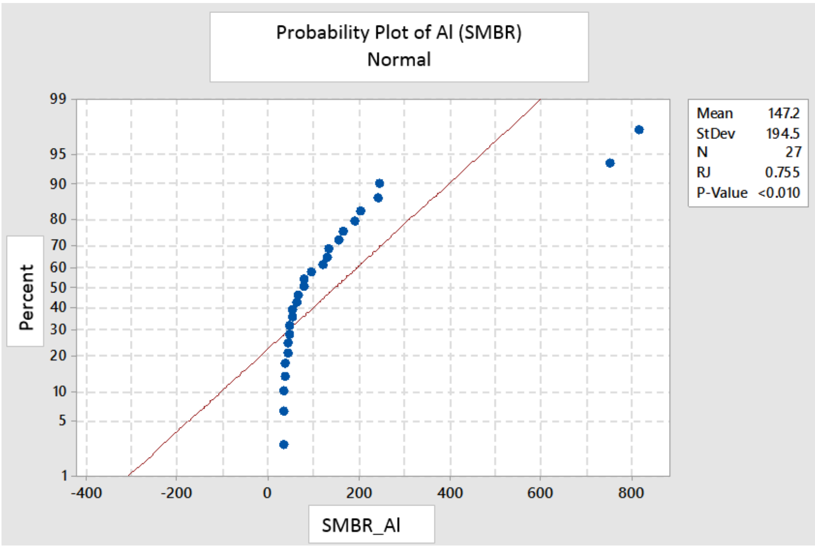


Fig 6. Probability plot representation of SMEBR (a) and SMBR (b) Al values

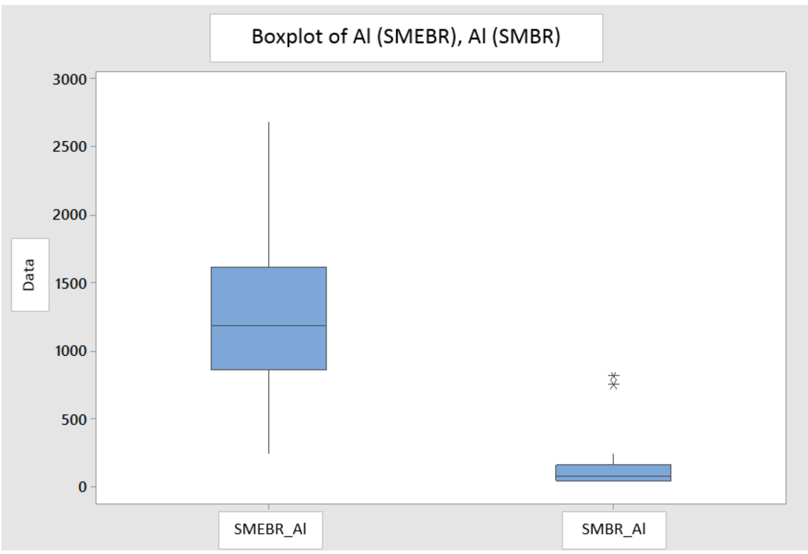


Fig 7. Display of SMEBR and SMBR Al values in Boxplot

In summary, the two data sets are significantly different (99% significance level). Al accumulation rate in SMEBR (median value = 1183.3) is significantly higher than Al deposition rate in SMBR (median value = 78.1). The distribution of data from both reactors is also summarized in the boxplot graph below. As can be seen, both the median and the maximum values of the Al accumulation in the SMBR are much lower than the Al accumulation in the SEMBR.

3.3.3. Relation of Al accumulation with conductivity and TOC values in SMEBR and SMBR

The relationship between accumalated Al amounts in SMEBR and SMBR, and conductivity and TOC% values was examined. The relationship between the data from the SMEBR reactor is as in the following Table 1.

As is known, the correlation coefficient r is between -1 and 1. It can be said that if the value of r approaches -1, there is a stronger negative correlation, and if it approaches +1, there is a stronger positive correlation between the two variables. At values close to 0, the correlation between the two variables is also small. In this case, a negative but very poor relationship between Al accumulation and conductivity is observed according to Table 1. There is also a negative, moderate relationship between Al and TOC; it is neither too strong nor weak.

Table 1. Correlation coefficients between Al accumulation and other parameters in SMEBR

Parameter	Al
Conductivity	-0.17712
TOC%	-0.54366

There is also a negative, moderate relationship between Al and TOC; it is neither too strong nor weak.

According to the data obtained from SMBR reactor, the correlation coefficients between these variables are as follows (Table 2):

Table 2. Correlation coefficients between Al accumulation and other parameters in SMBR

Parameter	Al
Conductivity	0.148134
TOC%	0.375518

According to Table 2, there is a positive correlation between Al and other variables. However, the relationship between Al and conductivity is very weak. There is a weak-moderate correlation between Al and TOC%. It can be said that Al accumulation negatively affects the variables, even though it has a weak correlation with these variables. Because it is stated that Al accumulation in biological systems affects nitrification bacteria. With this effect, conductivity can lead to a decrease in TOC% values.

3.4. Impact of Al Accumulation on SMEBR and Environment

Electrocoagulation, chemical coagulation or the addition of appropriate coagulant to any point of the treatment process are the processes performed to improve the quality of treated water. However, metal-containing sludges are formed in these processes. Also, for the SMEBR, the amount of Al increases day by day with the electric current applied to the activated sludge. Bani Melhem and Maria [23] stated that nitrification bacteria were affected by the accumulation of Fe electrode used in SMEBR system. Al coagulants added to the activated sludge system to improve sludge properties have been observed to affect nitrified bacteria [23, 36]. In the treatment of young leachate by SMEBR, Al accumulated in the reactor had no significant effect on nitrification. On the contrary, it reduced sludge swelling/foaming in the SMEBR. No studies have been found in the literature on the assessment of Al accumulated in waste SMEBR sludge. However, in one study, aluminum sulfate was added to MBR. Al sludge was removed from MBR by adsorption [37]. In addition, studies were carried out for the elimination of metal-containing sludges obtained from drinking water treatment, electrocoagulation/coagulation wastewater treatment and coagulant added treatment processes. Okuda et al. [38] used sludge with metal content in plant growing in their study. For this purpose, Al amount was reduced by applying extraction pre-treatment on Al sludge.

Many scientists produced adsorbents by reusing metal sludges [39-41]. They used them again in wastewater treatment and removal of heavy metals (Hg, Pb, As, Cr, Cu) [40, 42, 43]. Recycling of sludge reduces the cost of coagulant metals used in wastewater treatment plants [39]. Al is also a very common metal in the crust. Therefore, it is not possible to adjust the limits in the soil. Al-containing sludge has also been used as soil conditioner or fertilizer [44], [45]. The most important parameter in these applications is soil pH. Depending on the pH of the soil, Al may cause toxic effects on the soil. This negatively affects plant growth [46-48].

As a result, the waste sludge obtained from the SMEBR can be easily applied to the soil by controlling the soil pH and can be used as an adsorbent. It is therefore that the Al-containing sludge to be obtained in the SMEBR will not pose a problem in the treatment of leachate.

4. CONCLUSIONS

In this article, the Al accumulation in treatment of leachate with high organic content by SMEBR was evaluated by statistical studies such as regression analysis and Mann Whitney U test. Mathematical modeling has been performed to estimate how much Al accumulation will occur if the SMEBR is operated for more than 50 days. Al accumulation had no significant effect on the SMEBR. Therefore, the use of the SMEBR system in leachate treatment is advantageous over SMBR. This superiority of SMEBR over SMBR has not been discussed in the literature before, and our study makes an important contribution in this respect.

ACKNOWLEDGMENTS

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RESEARCH ARTICLE

Effects of nitrogen recycling by human urine fertilization on butterfly pea (*Clitoria ternatea*) plant in green wall system on AIT campus

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ABSTRACT

The use of wastewater (urine) as a fertilizer was shown to potentially reduce the campus wastewater load and contribute to saving in expensive wastewater treatment, while dealing with it as valuable resource. If one assumed that this wastewater fertilizer (arguably, one of the best agriculturally acknowledged fertilizers), was applied at odor appropriate and physiologically sustainable rates (Nitrogen Loading Rate (NLR) of up to 0.73 g N m^{-2} $week^{-1}$ equivalent to 104.28 mL urine m^{-2} $week^{-1}$ applied for 16 weeks) and considered total available area for potential green walls, it could be stated that the entire urine stream generated daily on campus (varying from 2.2 to 4.5 m^3) could be accommodated on campus green walls as a valuable resource with significant benefits. In the studies on monitored plant physiological parameters under various conditions, it was observed that urine fertilizer positively affected to the food production, inflorescences and health of butterfly pea (C*litoria ternatea*) plant as well as could say that it was the most suitable plant for green wall. Further integration of urban wastewater management and agriculture (urban food production) into this scenario can make it even more attractive and economically sustainable.

Keywords: Fertilizer, fertigation, human urine, nitrogen loading rate, wastewater

1. INTRODUCTION

Urine is a liquid item, yellowish color that's emitted by the kidneys from the human body. Depends on the amount of liquid, a person drinks, the range of urine produced per day by person. More often, for a mature person, the ranges from 0.8 L to 1.5 L per day and around half range for children [1-2]. Less than 0.5 % of entire household wastewater constitute by urine but it contains basic nutrients N, P and K which are essential for plant growth. Flush less urinals or urine diversion toilets or no mixing toilets are very effective to gather raw urine for use it as a fertilizer in agriculture [3-4]. On the other word, stored urine which has been gathered a partly and hygienised, is a concentrated source of nutrients too that could apply as a liquid fertilizer in green wall and could be a good substation with the commercial chemical fertilizers [5]. Expand the time of storage is the only, cheapest and common way to treat urine with the point of pathogen kill and nutrients restoration [6]. Pathogen removal is accomplished by a composition of the ascending of pH and ammonium concentrations, temperature and time. Relevant on the chance for cross-impurity and the crop species to be fertilize, the perfect storage time at temperatures of 4 to 20 °C differ between one to six months for large-scale systems [7]. The capacity for changing these nutrients has limitations. It would be recognized that biological efficiencies are continuously less than 100%. Typical N uptake capacities of most agronomic crops range from 30 to 70%, due to many factors [8]. First, it is impossible for a plant to drain the entire inorganic N from the soil solution. As the nitrate and ammonium concentrations reduce in solution, the range of N uptake also reduces, in a connection similar to substrate-enzyme reactions [9]. Second, little N concentrations in the soil are needed to run the N influx into crop roots. In addition, some N vaporize (volatilization or leaching) from the root level are obvious during the season [10]. As a result, not all of the N accumulated will be available for consumption of plant. Finally, perhaps most significantly that to earn major or average yields, N must be stored at high levels [11].

A 2:1, 3:1 to 4:1 ratio mean mix of water and urine is an effective ratio of dilution for urban agriculture which

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also avoid odor [12]. Urine should not be deploying on leaves, the roots, stems or other parts of the plants to cause foliar burning [13]. A proper distance of plants should be observed, and make a hole on the soil then urine spread and applied on the hole. In the rainy season, urine application can also be done directly into holes nearby plants, then the rain will dilute it naturally [14].

2. MATERIALS AND METHODS

Wastewater (urine) will be used for fertigation of plants for 16 weeks. Different rates of nitrogen (N) fertigation will apply to the plant. The initial loading rate will be 0.036 g N m^{-2} $week^{-1}$ with dilution of 4L of water and the value of (N) will increase by 2 times every week. The nitrogen loading rate through conservative (low-rate) fertigation with wastewater fertilizer (urine) applied based on (g) of nitrogen m^2 $week^{-1}$ and mL of urine m^2 $week^{-1}$ while the composition of nitrogen per 1 liter urine is 7 g [15]. The values are given in Table 1.

Table 1. Nitrogen loading rate application on green wall in 16 weeks

Conservative (low-rate) fertigation with wastewater fertilizer (urine)		
Time (weeks)	**g N m^{-2} $week^{-1}$**	**mL urine m^{-2} $week^{-1}$**
1	0.036	5.10
2	0.080	11.40
3	0.120	17.10
4	0.170	24.30
5	0.210	30.00
6	0.250	35.70
7	0.300	42.80
8	0.340	48.50
9	0.380	54.30
10	0.420	60.00
11	0.470	67.10
12	0.510	72.80
13	0.550	78.57
14	0.620	88.57
15	0.680	97.14
16	0.730	104.28

Table 2. Analytical methods for urine analysis

Parameter	**Analytical Methods**
pH	pH meter
NH_3-N (mg L^{-1})	Titrimetric method
TP (mg L^{-1})	Persulfate digestion method
TN (mg L^{-1})	Kjeldahl Method

The different parameters to be analyzed include pH, amount of ammonium nitrogen (NH_3-N) and amount of total phosphorous (TP) in different method as given in Table 2. Since nitrogen and phosphorous are important plant macronutrients, the effect of their availability on the plant will be compared. The plants will be irrigated with different sources of water namely wastewater from canal and tap water. The plants irrigated with canal water and tap water will also undergo urine fertigation [16-17].

The experimental set up will be as follows: 4 blocks of passage each containing the same type of plants will be considered.

- The plants in the first treatment will be irrigated with canal water.
- The plants in the second treatment will be fertigated with wastewater (ww) fertilizer urine dilute with different urine and water ratio.

Urine fertigation is classified into four stages consisting of urine generation point (source), collection, storage, dilution and finally using as fertilizer [18-19] as given in Fig 1.

Fig 1. Schematic diagram of fertigation process

3. RESULTS AND DISCUSSION

3.1. *Determination of the nutrients concentration present in wastewater (WW) fertilizer (urine)*

The concentration of total nitrogen (TN), total phosphorous (TP), and ammoniumia (NH_3) has been analyzed in fresh (first weeks) and stored (3-4 months) urine [20]. The average TN, NH_3, and TP concentration of fresh urine was 9,625 mg L^{-1}, 4,424 mg L^{-1}, 1,165 mg L^{-1}, respectively. The average TN, NH_3, TP concentration of stored urine was 9,625 mg L^{-1}, 5,166 mg L^{-1}, 964 mg L^{-1}, respectively, as given in Table 3.

Table 3. Chemical composition of fresh urine and stored urine on lab analyzation

Parameter	**Fresh urine**	**Stored urine**	**Number of sample**
pH	7.1	8.7	10
Total nitrogen (TN, mg L^{-1})	8,894	10,360	10
Ammonium/ammonia (NH^{4+}/NH_3, mg L^{-1})	4,424	5,166	10
Total phosphorous (TP, mg L^{-1})	992	964	10

3.2. *Plant species used in green wall construction*

In total 60 butterfly pea (*Clitoria ternatea*) plants are grown in 2 blocks of passage and has shown its performances on the effects of human urine in percentage of plant coverage, food production, inflorescence and health of butterfly pea (*Clitoria ternatea*).

3.3. Integration of wastewater fertilizer (urine) recycling into green walls

Urine fertilization was collected manually and stored for minimum of 3 months before use. The plant species fertigated with urine fertilizer with respect to their Nitrogen Loading Rate (NLR) measured in g N m^{-2} $week^{-1}$ over a period of 16 weeks as shown in Table 1. The experiment was carried out with wastewater (ww) fertilizer with different N application rates (0.036–0.73 g N m^{-2} $week^{-1}$) [21]. The quantity and quality of experimental plants and control plants were analyzed with the effect of wastewater (ww) fertilizer [22].

The NLR for the conservative fertigation carried out on the plant species located in the passage green wall. The initial loading rate was 0.036 g N m^{-2} $week^{-1}$ and this value was increased by 2 times every 2 weeks as shown in Fig 2.

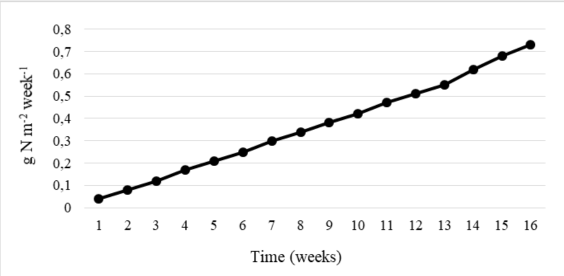

Fig 2. Progressive increase in fertigation rate (nitrogen loading rate, g N m^{-2} $week^{-1}$) for all the butterfly pea (*Clitoria ternatea*) plants over the period of 16 weeks on the green wall

3.4. Growth rate of butterfly pea (Clitoria ternatea) with and without application of wastewater (WW) fertilizer

The wall area covered by butterfly pea (*Clitoria ternatea*) grown in block 1 and 2 and the area of each block is 15 m^2 while the block wide is 6m and its height is 2.5m. The area covered by plant before and after growing was calculated using the Canopeo Software. Canopeo Software used for finding the green wall percentage coverage of control and experiment blocks before and after fertigation. Then, through the percentage coverage of green wall and growth rate of plants we can also calculate and find the area of coverage by (m^2) as follow:

Initial fertigated (experiment) block characteristics

- Area of block = 2.5m x 6m = 15m^2
- Initial percentage coverage = 24.42%
- Area covered by plants = 0.2442 x 15m^2 = 3.66m^2

Ultimate fertigated (experiment) block characteristics

- Area of block = 2.5m x 6m = 15m^2
- Percentage coverage = 59.09%
- Area covered by plants = 0.5909 x 15m^2 = 8.86m^2

Initial unfertigated (control) block characteristics

- Area of block = 2.5m x 6m = 15m^2
- Initial percentage coverage = 20.41%
- Area covered by plants = 0.2041 x 15m^2 = 3.1m^2

Ultimate unfertigated (control) block characteristics

- Area of block = 2.5m x 6m = 15m^2
- Ultimate percentage coverage = 43.33%
- Area covered by plants = 0.4333 x 15m^2 = 6.49m^2

Fig 3. Actual initial image of fertigated (experiment) section of butterfly pea (*Clitoria ternatea*)

Fig 4. Actual image of fertigated (experiment) section of butterfly pea (*Clitoria ternatea*)

Fig 5. Binary image showing percentage coverage of fertigated (experiment) section of butterfly pea (*Clitoria ternatea*) using Canopeo Software

The first block of plants was irrigated with canal water from the canal. The second block was fertigated with wastewater (ww) fertilizer (urine) also irrigated with canal water once a week [23]. The growth rate in the experimental block was higher than the control block as a result of the added wastewater (ww) fertilizer (urine) as shown in Fig 3. The initial growth of fertigated (experimental) plants in block 1 is 3.66 m^2. However, the ultimate growth of fertigated (experimental) plants in block 1 is 8.86m^2 and the initial growth of unfertigated (control) plants in block 2 is 3.5 m^2. However, the ultimate growth of unfertigated (control) plants in block 2 is 6.49m^2 as shown in Fig 3. After 16 weeks the wall area covered by the fertigated and unfertigated section were 8.86m^2 and 6.49m^2, respectively. On an average the wall area covered by the fertigated section was 26% higher than that covered by the unfertigated section (Fig. 9).

Fig 6. Actual initial image of unfertigated (control) section of butterfly pea (*Clitoria ternatea*)

Fig 7. Actual image of unfertigated (control) section of butterfly pea (*Clitoria ternatea*)

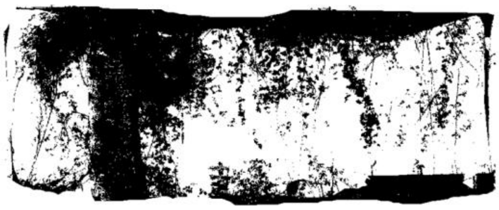

Fig 8. Binary image showing percentage coverage of unfertigated (control) section of butterfly pea (*Clitoria ternatea*) using canopeo software

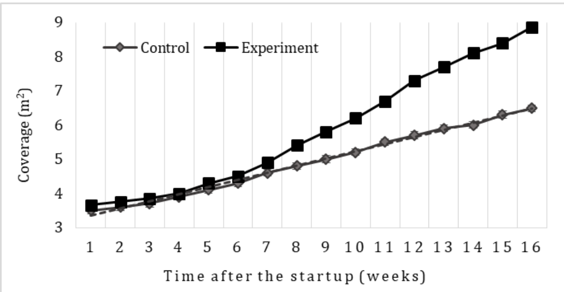

Fig 9. Comparison of wall area coverage of fertigated (experiment) and unfertigated (control) section of butterfly pea (*Clitoria ternatea*) growing at the passage green wall

3.5. Food production

The fruits were planted on the two blocks at the east side of the green wall. The total number of experimented and control plants of butterfly pea (*Clitoria ternatea*) was 50. The experimented plants were fertigated by wastewater (ww) fertilizer (urine) which they were very bright and impressive during the 16 week observation while the control plants were irrigated by canal water which the plant were not in a good health of producing food. The experimented plants block which was fertigated by wastewater (ww) fertilizer, plants were produced 0.95 kg of peas per 50 plants. However, in the control plants block, plants were produced 0.58 kg peas per 50 plants. The value given in Fig 10.

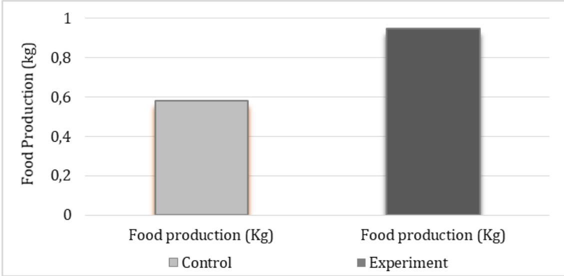

Fig 10. Comparison of food production of (experiment) and (control) of butterfly pea (*Clitoria ternatea*) plants on the green wall

3.6. Inflorescence

Butterfly pea (*Clitoria ternatea*) flowers are sometimes not much clearly seen. However, if this plant irrigates and fertigate properly it will produce flowers very dense and visible. Butterfly pea (*Clitoria ternatea*) flowers were consist of 0.0002 m^2 while the flowers biomass for each flower regarding to laboratory result was 0.039 g m^{-2}. Number of flowers in the entire experimented plant sections at passage green walls was 300 which is equivalent of 11.7 g m^{-2} biomass of flowers per 50 plants. However, the number of flowers in control plants was 55 which is equivalent of 6.4g biomass of flowers per 50 plants as shown in Fig 11.

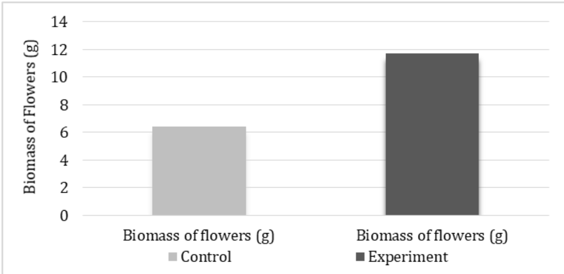

Fig 11. Comparison of biomass of flowers of (experiment) and (control) of butterfly pea (Clitoria ternatea) plants on the green wall

4. CONCLUSIONS

According to results of small scale experiment and conservative (low-rate) fertigation with wastewater (ww) fertilizer of the green wall, it was possible to recycle the amount of 100,500 mg of urea, 2,512.5 mg of ammonia (NH_3), 5,025 mg of phosphorous (P) and 35,175 mg of nitrogen (N) from total 5.025 liters of wastewater (ww) fertilizer (urine) per 16 experimental weeks which had the contribution of 0.05 m^3 in total 56,000 m^3 wastewater of AIT campus in the 16 weeks period [24]. Irrigated water and wastewater fertilizer (urine) could easily go through the poorly pervious soil and plants root easily took up fertilizer nutrients. A conceptual design for combining urine fertigation and water irrigation was developed and based on different fertigation rates, the optimal start-up wastewater fertigation rate was suggested as 100 ml m^{-2} $week^{-1}$ which corresponds to NLR of 0.73 g N m^{-2} $week^{-1}$. The optimum irrigation rate was found to be 4 L $plant^{-1}$ per day. As a result of this experimental design quantify of plants benefits like food production and inflorescence were studied. The results shown that a domestic green wall was able to produce considerable harvest from butterfly pea (*Clitoria ternatea*) plant (up to 0.95 kg pea per month per section), flowering and plant biomass increased and this all testified for efficiency of wastewater (ww) fertilizer application. Moreover, a higher inflorescence rate was observed in the section fertigated with wastewater. Thus, it can be said that the waste nutrients are utilized to produce flowers and fruits in butterfly pea (*Clitoria ternatea*). Urine fertigation was shown to increase the growth rate of butterfly pea (*Clitoria ternatea*) with regard to the studies carried out to monitor plant physiological parameters under various conditions.

Using conservative low level of human urine on plants as fertilizer can be a good idea in real life. It does not produce odor meanwhile it is rich of nitrogen and phosphorous which help the growth and physiological performance of plants. Moreover, this is very low cost system for small scale practices that everyone can collect urine from separate urinal and store it in tanks or containers at 4 to 20°C for two to 6 months out of sunlight and proper hygiene behavior should be observed while storing the urine until fertigating plants. However, this system can be used for large scale but it needs some cost from the first stage of collecting until the end of application to the plants.

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RESEARCH ARTICLE

Ultrasound assisted extraction for the recovery of phenolic compounds from waste hazelnut shell

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ABSTRACT

Hazelnut shell is the primary byproduct of hazelnut industry which has the potential source of antioxidants, and phenolics with interest of pharmaceutical, food, and cosmetic industries. The main goal of this study is to determine effects of extraction method, extraction time, solvent type, solid to liquid ratio, and particle size on extraction yield, antioxidant capacity, and total phenolic content of waste hazelnut shell. The highest extraction yield was found as 15.4% by using methanol as solvent, in combined extraction for 16 h total extraction time. As for the best antioxidant capacity, 0.0508 mg TE mL^{-1} was observed by using methanol as a solvent in ultrasonic extraction, whereas the highest phenolic content was found as 0.188 mg GAE mL^{-1} by Soxhlet extraction with acetone for 8 h. After extraction of hazelnut shell waste, major components were found as oleic and palmitic acids for all solvent types according to GC-MS results.

Keywords: Biomass, hazelnut shell, polyphenols, byproducts, extraction

1. INTRODUCTION

In every year, a vast amount of plant is being produced and their wastes have been disposed of to nature rather than using them [1]. Utilization of these waste biomass has great potential due to not only their abundancy, and zero carbon emission [2] but also for their valuable ingredients.

Hazelnuts are one of the most dominant nut crops in the world [3] that includes many salutary chemicals like fatty acids, amino acids, vitamins, minerals, phenolics, and antioxidants [4]. Hazelnut shell is the major byproduct of hazelnut that consist of 36.02% cellulose, 12.66% hemicellulose, 40.14% lignin, and 7.86% extractives [5].

In Turkey, each year 1 million tons of hazelnut waste have been produced and burned for heating [6]. Researchers have proposed new alternative ways to valorize hazelnut shell waste rather than burning such as production of sugars [5, 7], platform chemicals [8], bio-oil [9], antioxidants, and phenolics [10].

Antioxidants and phenolics are bioactive components coming from plants and have good effects on human health like antiradical activities, antimutagenic, anticarcinogenic, and antiproliferative potential. Presently, many antioxidants have being used to put the oxidation process off in food systems, synthetically. However, application of synthetic antioxidants in food products are strictly regulated considering health hazards [11].

Extraction is an important process in isolation of phenolics and antioxidants from plant matrix. Traditional methods like maceration, boiling, soaking, and soxhlet extraction are most commonly used extraction methods due to low cost, easy to operate, and high extraction yields. Moreover, Soxhlet extraction is well known extraction method since it shows great performance for recovering phenolics and antioxidants compared with other traditional methods [12].

Ultrasonic extraction is another attractive extraction method that decreases extraction time and solvent consumption [13]. Additionally, cavitation promotes

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solid solubility, diffusivity of the solvent, and transportation of the solutes [14-16].

In literature, antioxidant capacity and phenolic content have been reported about hazelnut kernel, green leafy cover, and brown skin in many studies [3, 4, 17, 18]. For example, antioxidant capacity and phenolics from hazelnut by-products (shells and defatted skins) have been reported by using solvent maceration at room temperature with extraction yield of 30% and 502 mg g^{-1} GAE phenolic content in ethanol/water (80/20 v/v) mixture [3]. Another study has reported the effect of ultrasound-assisted extraction on antioxidants and phenolic compounds from hazelnut shells using acetone as solvent and determined optimum the extraction conditions using response surface methodology (RSM) [4]. The highest phenolic content (12 mg g^{-1} GAE) was obtained in acetone as a solvent for 12 h extraction time.

The main goal of this study is to valorize waste hazelnut shell by extracting phenolic compounds from it by different extraction methods (soxhlet extraction, ultrasonic extraction and combined extraction). For this purpose, effects of extraction time, extracting solvents and solid to liquid ratio on extraction yield, antioxidant capacity, phenolic content were investigated.

2. MATERIALS AND METHODS

2.1. Feedstock and chemicals

Hazelnut shell waste provided form Ordu, Turkey, was used as a feedstock without separating husks and shells. Hazelnut shell waste was dried at 60 °C and grounded into 1 mm particle size for extraction processes by using blade-knife laboratory grinder. ACS grade ethanol, acetone, methanol and hexane were purchased from Merck. To determine total phenolic content and antioxidant capacity, sodium carbonate (99.5%), potassium persulfate (99.9%), gallic acid (97.5%), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (97%) and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonicacid (ABTS+) were purchased from Sigma-Aldrich. Folin-Ciocalteu reagent was purchased from Merck.

2.2. Experimental setup and procedure

In this study, soxhlet, ultrasonic and combined (including soxhlet and ultrasonic extraction) extractions were used as extraction methods. Soxhlet extraction setup includes 500 mL solvent flask, 250 mL thimble flask, condenser, and heating mantle (Wisd, DH.WHM 12295). An ultrasonic bath (WUC-D06H, WiseClean) with 40 kHz maximum frequency was used in ultrasonic extraction part. The combined extraction was formed by two steps: extraction of waste was done first by soxhlet extraction and then the remaining waste was subjected to ultrasonic extraction. In this combined method, after 8h of soxhlet extraction, solid residue was dried in vacuum oven at 50 °C for overnight to remove remaining solvent. After drying, solid residue was reextracted by ultrasonic extraction. At the end, solid residue was dried under the same conditions to calculate the extraction yield by using Eq. (1). Extracted oil and solvents were separated with a rotary evaporator under specific pressure and temperature according to nature of solvents. Experiments were carried out with different extracting solvents (ethanol, methanol, n-hexane, acetone) for 2 to 8 h. Initial solid to liquid ratio (4, 8 and 12 g in 250 ml) was another extraction parameter.

$$\text{Extraction yield (\%)} = \frac{\text{Mass of initial hazelnut shell} - \text{mass of final hazelnutsehell}}{\text{Mass of initial hazelnut shell}} \times 100 \quad (1)$$

2.3. Analytical methods

2.3.1. Total phenolic content

The total phenolic content in liquid product was determined by Folin-Ciocalteu's method: Folin Ciocalteu reagent was diluted 10-fold with deionized water and 7.5% (75 g L^{-1}) of Na_2CO_3 was prepared with distilled water. 0.5 mL of extracted liquid product, 0.5 mL of Folin Ciocalteu solution, and 1 mL of Na_2CO_3 were mixed and then volume adjusted to 10 mL with deionized water. After this step, mixture was kept in dark room for 45 mins at room temperature. Then, the absorbance was measured at 725 nm by using distilled water as a blank. The phenolic content of liquid product was designated as milligrams of Gallic Acid Equivalents (GAE) per milliliter of liquid product.

2.3.2. Total antioxidant capacity

Total antioxidant capacity of liquid product solution was evaluated by using ABTS method: ABTS radical solution was prepared by using 14 mM ABTS solution and 4.9 mM potassium persulfate solution with volume ratio of 1:1. This solution was kept in dark room for 16 h. Then, $ABTS^+$ solution was diluted with ethanol (1:50 v/v%). After dilution, 1 mL of liquid product was mixed with 4 mL of ABTS+ solution and kept in the dark at room temperature for 5 min. The absorbance was measured at 734 nm with water was used as a blank. The antioxidant capacity of liquid product was expressed as milligrams of Trolox Equivalents (TE) per milliliter of liquid product.

2.3.3. FTIR analysis

Functional groups in solid residue were examined in the wave number range of 4000- 650 cm^{-1} by using Fourier Transform Infrared Spectrometry that equipped with attenuated total reflectance (ATR-FTIR) (Perkin Elmer-Spectra Two, USA).

2.3.4. GC-MS analysis

GC-MS (Agilent 6890 N/5973 N Network) was used for the analysis of hazelnut shell waste decomposition products. Stabilwax®-DA (Crossbond® Carbowax® polyethylene glycol, 30-meter-long, 0.32 mm inner diameter, 1 µm particle size) column was used. Injection volume was 1.0 µL and helium was used as a carrier gas. GC-MS analysis was conducted in SCAN mode with the following method; initial oven temperature set as 40 °C and then, first heating (8 °C min^{-1}) to 140 °C kept for 5 minutes, second heating (10 °C min^{-1}) to 220 °C and kept for 10 minutes. Total run time of method is 35 minutes. GC-MS chromatograms were analyzed by using MSD ChemStation E.0202.1431 software and the area of specified chromatogram peaks were calculated accordingly. Moreover, product distributions were given as the ratio of peak area of governing species at given reaction to its maximum area obtained throughout the extraction process (Eq. (2)). Analyzed products were identified by using National Institute of Standard (NIST) MS search and compounds are tabulated in Table 1 in 'Results and Discusion' section.

$$Relative\ peak\ area = \frac{peak\ area\ of\ species\ i\ at\ specified\ extraction}{Total\ peak\ area\ of\ all\ extracted\ species} \quad (2)$$

3. RESULTS AND DISCUSSION

In this study, effect of different solvent type, extraction time, extraction method and solid/liquid ratio were examined to determine extraction yield, total phenolic content, and antioxidant capacity of hazelnut shell waste.

3.1. Effect of solvent type

The extraction was carried out with different solvents (ethanol, methanol, n-hexane, acetone) to clarify the effects of solvent type on extraction yield, phenolic content and antioxidant capacity and the results were shown in Fig 1a-c. The total phenolic content (Fig 1-a) was found as 0.006, 0.02, 0.0185 and 0.0191 mg GAE mg mL^{-1} for hexane, ethanol, methanol, and acetone extraction, respectively. It can be inferred that ethanol was the best solvent in terms of phenolic content which are compatible with previous studies in literature. Shahidi et al. reported phenolic content of hazelnut kernel and by-products as 214 .1 mg CE per gram of hazelnut skin in ethanol/water mixture (80:20 v/v) medium [19].

Total antioxidant capacity results were represented in Fig 1-b. The highest antioxidant capacity was found in hexane extracts as 0.055 mg TE mL^{-1}. On the other hand, the lowest value was obtained in methanol extracts as 0.049 mg TE mL^{-1}. Polarity of the solvents dominates the antioxidant capacity. Hexane is nonpolar solvent while ethanol, methanol and acetone are polar. In other words, difference in solvent polarity, dispersibility, and penetrability may affect the antioxidant capacity due to selective different extracts from the hazelnut shell [20].

Extraction yield (Fig 1-c) is another important response in extraction process. The lowest extraction yield in Fig 1-c was found in hexane as 6.94%, while the best extraction yield was obtained as 10.55% and 10.1% in methanol and ethanol, respectively. As well known, ethanol and methanol are polar protic solvents and they donate hydrogen to the medium [21]. Since they gave the best results, it is possible to say that hazelnut shell waste includes more polar extractives. In another words, polar protic solvents provide higher extraction yield thanks to -OH bonds and probable hydrogen donation to extraction medium [9].

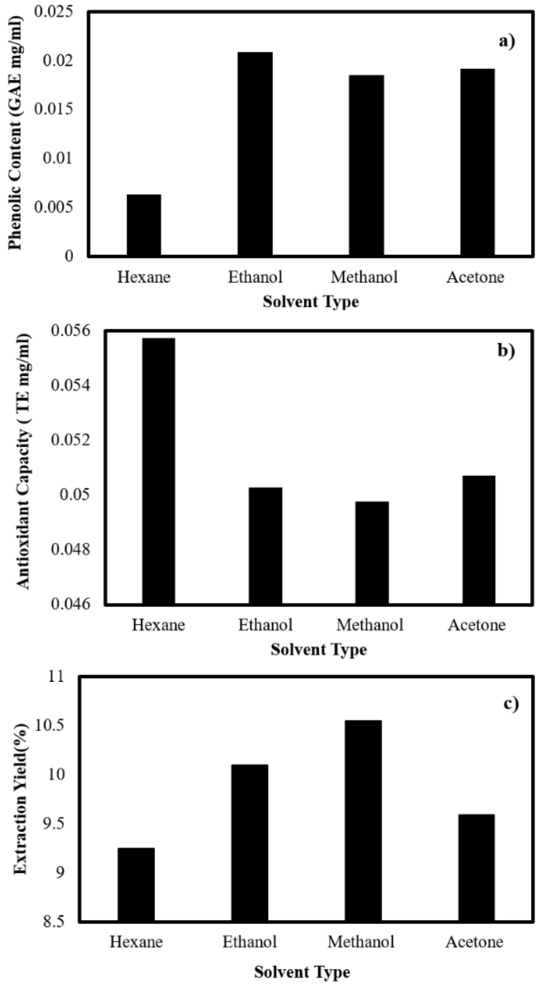

Fig 1. Effect of solvent type on a) phenolic content, b) antioxidant capacity, c) extraction yield in soxhlet extraction for 8 h

3.2. Effect of extraction method

In this work, three extraction methods (soxhlet, ultrasonic and combined) were carried out for the valorization of waste hazelnut shell and results are given in Fig 2. The highest extraction yield was obtained in combined extraction for each solvent and the maximum extraction was recorded as 15.40% with methanol.

If individual extraction methods are compared, it is possible to say that extraction yield was higher in ultrasonic extraction resulting from high diffusion rates of solvent and increment of the cavitation [22]. Furthermore, combined (soxhlet and ultrasonic) extraction gave better results compared with soxhlet extraction. This was caused from erosion, breakdown of cell, and rupturing the surface because of the generated shear forces by the ultrasound cavitation [23].

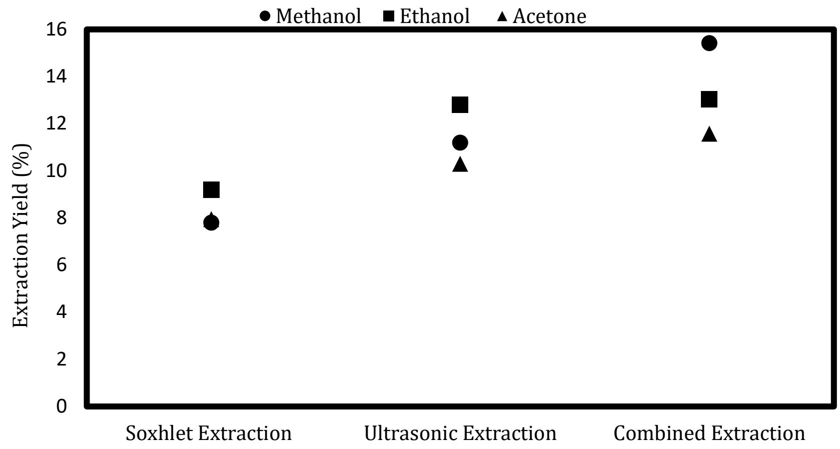

Fig. 2. Effect of extraction methods on extraction yield (Soxhlet extraction: 8 h, Ultrasonic extraction: 8 h and combined extraction: 8 h Soxhlet and 8 h ultrasonic extraction

3.3. Effect of extraction time

Extraction time is another parameter in the extraction process due to imperative in reduction of energy and cost. In soxhlet extraction, extraction time was varied from 2, 3, and 8h for each solvent. Fig 3 indicates the effect of extraction time on extraction yield.

The highest extraction yield was found as 10.55% in methanol for 3 h. In the extraction by using ethanol as solvent, the yield for 2 h was 9.7%, while it was 10% for 8 h extraction, respectively. In methanol extraction, extraction yields were very close to each other from 2 to 8 h (10.55%). The results indicate that there is no significant difference in extraction yields after 3 h due to Fick's second law of diffusion [12, 15]. Final equilibrium will be reached between hazelnut shell and extraction solvent at certain time of extraction. Besides, extraction yields tend to decrease after 3 h due to the fact that over-exposure of hazelnut shell to localize heating. This over exposure may cause the degradation of extractives in the extraction medium [24, 25].

Antioxidant capacity was also investigated with different extraction times. Results were given in Fig 4. There is no significant difference in antioxidant capacity with time (except in hexane). Hexane is a nonpolar solvent and dissolves nonpolar extractives from the extraction medium, whereas other solvents are polar and extracts the polar extractives. In hexane extraction, there was an increment from 2 to 3 h and dramatic decrement from 3 h to 8 h. This dramatic difference means that extractives would be decomposed after a certain time due to exposure of excess heating [26]. The difference between antioxidant activities of polar solvents and nonpolar solvent might be concluded as follows; extractives coming from ethanol, methanol, and acetone are more stable compared with extractives coming from hexane.

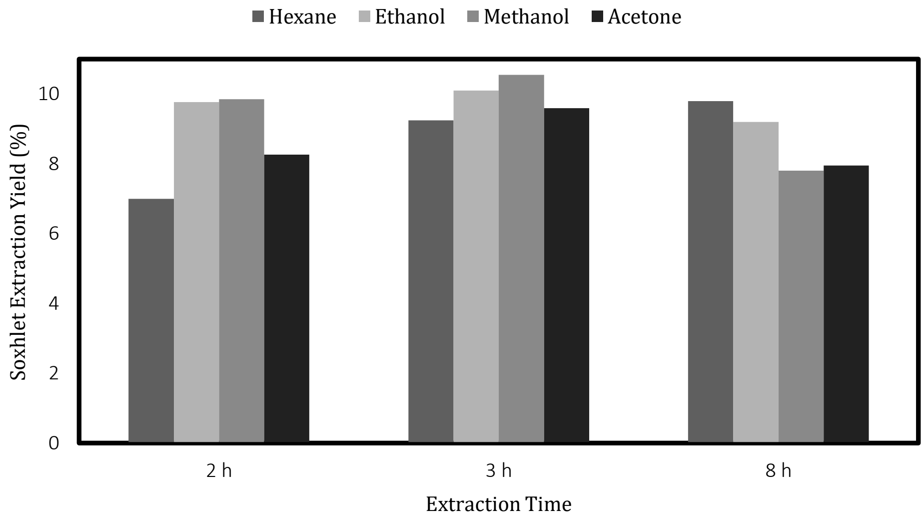

Fig 3. Effect of extraction time on extraction yield

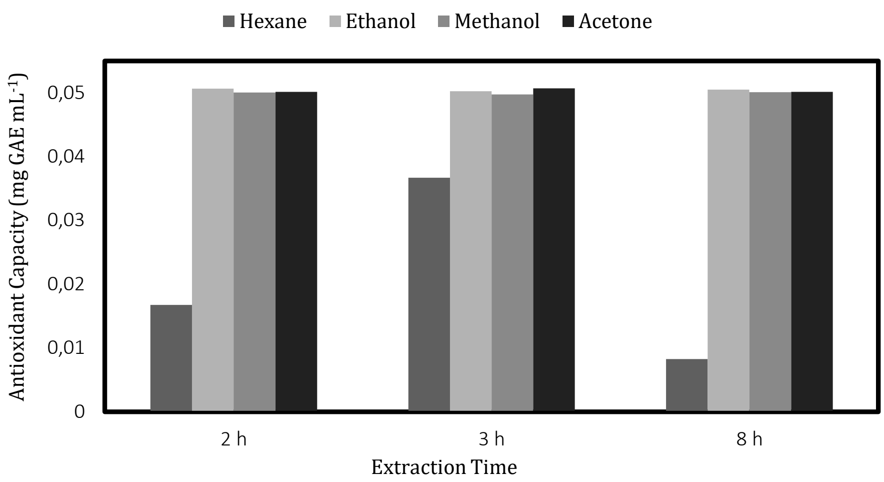

Fig 4. Effect of time on antioxidant capacity

3.4. Effect of solid/liquid ratio

The solid/liquid ratio is another parameter that affects extraction yield, total phenolic content, and antioxidant capacity. In this study, three different solid/liquid ratios (g mL^{-1}) as 4/250, 8/250, and 12/250 were investigated. Fig 5 shows how solid/liquid ratio effects extraction yield with methanol, ethanol, and acetone as extracting solvents. The extraction yield decreased with increasing solid/liquid ratio with each individual solvent. The highest extraction yield was found as 10.55% with 4/250 g mL^{-1} solid/liquid ratio in methanol extraction, whereas the lowest one was found as 7.62% with 12/250 g mL^{-1} in acetone extraction. These results, which are compatible with literature, may arised from the fact that high amount of solid causes mass transfer limitations in the extraction experiments [26, 27]. Mohammadpour et. al. conducted a study about extraction of Moringa peregrina with hexane [26]. Increasing solid to liquid ratio resulted in a decrease in the extraction yield due to the mass transfer limitation. Also, Jadhav et al. reported increasing vanilla beans amount caused an attenuation of vanillin concentration.

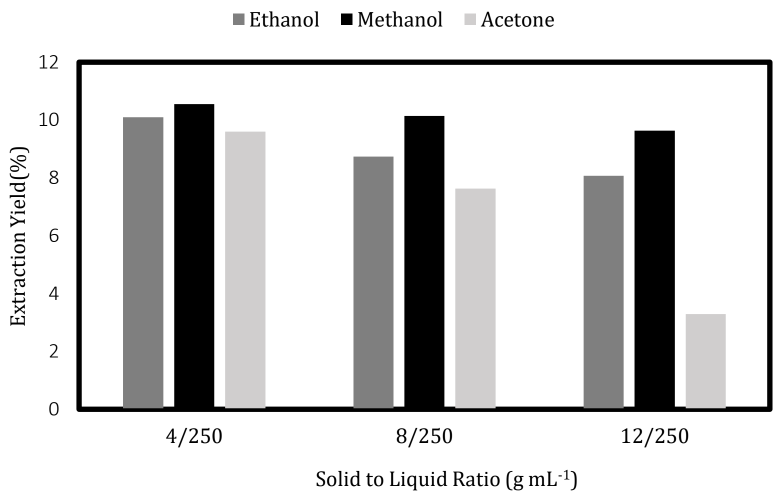

Fig 5. Effect of solid to liquid ratio on extraction yield with different solvents

Antioxidant capacity results with different solid to liquid ratios were given in the Fig 6 for different solvents. Antioxidant capacity first increased from 4/250 solid liquid ratio to 8/250, then decreased for 12/250 solid to liquid ratio when ethanol was used as solvent. On the other hand, there was gradual decrement in antioxidant capacity with acetone extraction, whereas slight increment in antioxidant capacity was observed when ethanol was used as solvent. The highest antioxidant capacity was found as 0.0507 TE mg mL^{-1} with 8/250 g mL^{-1} solid to liquid ratio in methanol and the lowest one was 0.0497 TE mg mL^{-1} with 4/250 g mL^{-1} solid to liquid ratio. Since hexane extraction efficiency is very low, it has been removed from the system.

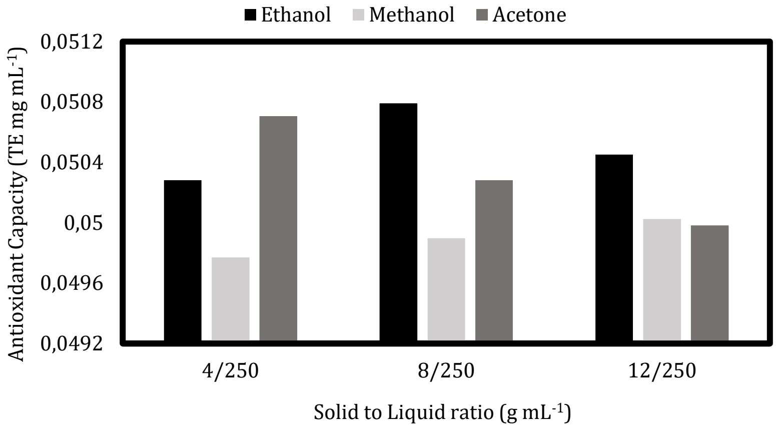

Fig 6. Effect of solid to liquid ratio on Antioxidant capacity

There were 21 major components identified by GC-MS analysis after extraction of hazelnut shell waste with various solvents. These major components were tabulated in Table 1. On this table, numbers under the given solvent type refers to the relative peak areas of components calculated from GC-MS analysis (see Eqn 2 in Materials and Methods).

Distribution of extraction components was related with the polarity [28], dielectric constant, donation of hydrogen [5, 9] to the extraction medium, and viscosity at boiling point. All solvents extracted oleic acid and palmic acid from the hazelnut shell since they have both polar and nonpolar sites. Hexane is the most powerful solvent for extracting oleic acid with 75.52% extraction yield and methanol comes next with an extraction yield of 75.6% extraction yield.

Hydrophobic part dissolves in nonpolar hexane and hydrophilic -COOH part dissolves in polar methanol. Although both ethanol and methanol are polar protic solvents, which gives hydrogen to the medium, methanol dissolves -COOH part of the oleic acid more than ethanol due to the large dielectric constant of methanol. Product distribution of methanol and ethanol were similar except 1-pentadecene,1-nonadecene. This may be caused from boiling point difference and degradation pathway of components. Methyl propyl ketone is the only ketone extracted with all solvent types and acetone mainly extracts the methyl propyl and oleic acid from the hazelnut shell. Moreover, chloroform is the only solvent that extracts the Stigmasterol, 22,23-dihydro- also called as beta sitosterol. Similar results were found in literature about extraction of beta-sitosterol from plants [29]. Gamma sitosterol were detected in polar solvents such as ethanol, methanol, acetone. In literature, there is a reported extraction and isolation of gamma-sitosterol from Asteracae by using methanol [30].

Hazelnut shell waste and products after the extraction process were investigated with FT-IR. Analysis results were shown in Fig. 7. Peaks at the 1229,1609, 3337 cm-1 represent aliphatic C=C stretching, C-C and O-H bonds, respectively. These bonds are typical lignin structure. In addition to that, peaks at 1028, 1371 and 2981 cm-1 belong to cellulose and hemicellulose structures [5, 31]. 1028 cm-1 represents C-O stretching of alcohols, while 1371 cm^{-1} shows C-O stretching of carboxylic acids. Moreover, 2981 cm^{-1} belongs to C-O stretching esters and aliphatic C-H stretching [32]. Hazelnut shell residues were also examined by using FT-IR to determine where extractives come from mostly and also how the levels of lignin, cellulose and hemicellulose decreases due to the type of solvent.

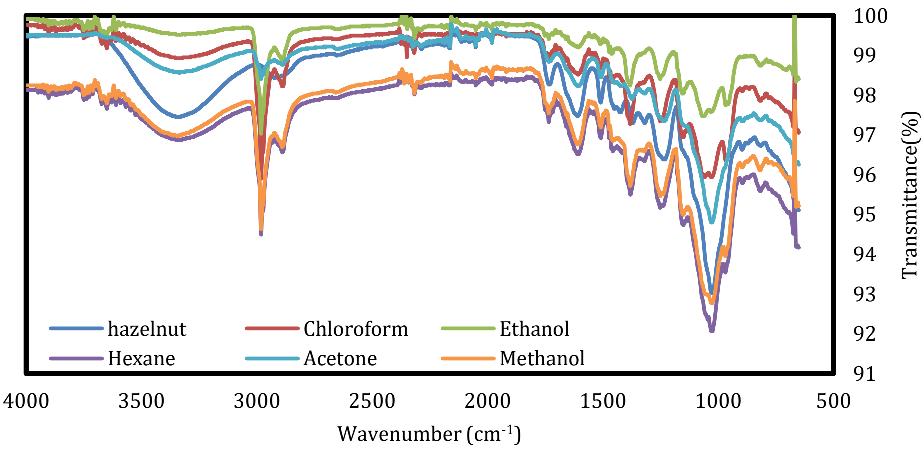

Fig 7. FT-IR spectra of hazelnut shell due to solvent type

Table 1. Major components for different solvents in extraction

Retention Time (min)	Identified Components	Relative Peak Areas of Components with Different Solvents				
		Hexane	Chloroform	Ethanol	Methanol	Acetone
4.26	methyl propyl ketone	-	-	-	-	35.43
10.7	1-Dodecene (alpha-olefin)	-	-	3.23	1.03	4.52
14.14	1-Pentadecene	-	-	4.08	-	-
14.16	1-Tetradecene	-	-	-	-	4.01
14.44	Vanillin	-	2.8		-	-
17.22	1-Hexadecene (palmitic acid)	-	-	2.71	0.98	-
17.24	9-Octadecene					2.76
19.99	1-Nonadecene	-	-	1.49	-	-
22.29	n-Hexadecanoic acid-palmitic acid	6.81	10.99	5.68	5.51	5.01
24.43	9-Octadecenoic acid, oleic acid	75.52	52.49	59.93	75.6	35.03
24.55	stearic acid	-	-	-	-	3.2
24.55	Ethyl Oleate	-	-	4.05	-	-
24.64	Octadecanoic acid-oleic acid	7.8	7.45	3.67	-	-
27.1	Hexanedioic acid, bis(2-ethylhexyl) ester	3.6	-	-	-	-
27.41	Oleic acid, 3-hydroxypropyl ester	5.12	-	-	-	-
27.79	9-Octadecenal	-	-	6.29	-	3.38
27.81	9-Octadecenal (Olealdehyde)	-	-	-	8.7	-
28.9	Sitosterol	-	-	8.87	8.54	5.01
28.97	Stigmasterol, 22,23-dihydro-	-	22.49	-	-	-
29.89	Heptacosane	-	3.78	-	-	-

In Fig 7, the highest lignin extraction of hazelnut shell was achieved by using hexane as a solvent, since all typical lignin peak intensities (1229,1609, 3337 cm^{-1}) decreased with hexane extraction. On the other hand, ethanol was the most destructive agent for the O-H bonds of lignin as a consequence of disappearance of O-H peak (3334 cm^{-1}). However, other typical lignin bonds (1229 and 1609 cm^{-1}) did not disappear when ethanol was used as a solvent. Therefore, it may be said that ethanol had the lowest extraction potential in terms of lignin-based extractives. The intensity of C-O stretching esters and aliphatic C-H was mostly decreased in hexane rather than other solvents. In other words, hexane extracts more cellulose and hemicellulose-based extractives. It can be validated by checking C-O stretching alcohols at 1028 cm^{-1} and carboxylic acid bonds at 1371 cm^{-1}. Lignin, cellulose and hemicellulose-based extractives were observed in the order of hexane> methanol> acetone> chloroform > ethanol [31, 32].

Extraction yield were statistically analyzed via Analysis of Variance (ANOVA) by considering interaction of solvent type (hexane, acetone, ethanol and methanol), extraction time (2-18 h) and solid to liquid ratio (4-8-12 g 250 mL^{-1}). Response surface methodology (RSM) was used to optimize process parameters in a way of maximizing extraction of phenolic compounds from waste hazelnut shell with a significance level as 95% ($p \leq 0.05$).

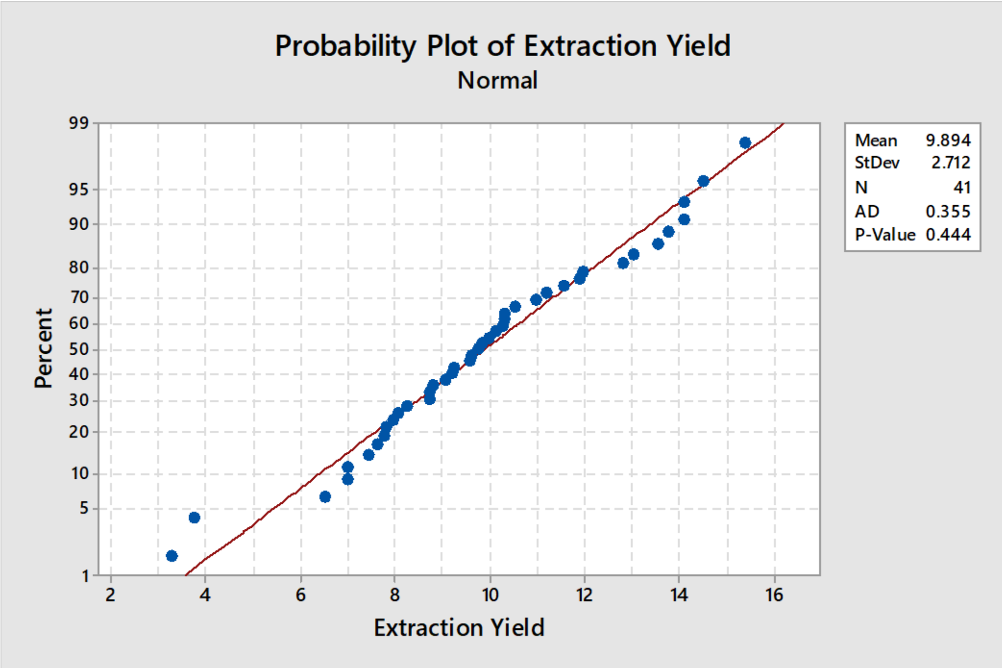

Fig 8. Normality plot of extraction yield

Normality plot of the extraction yield is shown in Fig 8 and it was checked by Anderson-darling test. As a result of ANOVA, extraction yield data was distributed normally.

Histograms and residual plots from RSM showed the linear distributed data (Fig. S1 and Fig. S2). The results were tabulated in Table S1 and Table S2. According to the results, extraction and solvent type were the only statistically significant terms since their p-values were smaller than 0.05. R^2 and adjusted R^2 values were 84% and 71%, respectively. Furthermore, solvent type was the only parameter that affected the total antioxidant capacity with a p-value of 0.013.

4. CONCLUSION

Hazelnut shell waste represent a rich and inexpensive source of natural and effective phenolic antioxidants. This study investigated the effects of different factors, such as extraction method, extraction time, solid-to-solvent ratio, solvent type, and particle size on the antioxidant capacity and recoveries of extract, and total phenolic compound from hazelnut shell waste. Response surface methodology was successful to develop an adequate model which describes total phenolic compounds and antioxidant capacity values of hazelnut shell extracts obtained by Soxhlet extraction, ultrasonic extraction and combination of them. Statistical analysis results showed that solvent type ($p<0.05$) was demonstrated to be the most significant parameter, affecting the extraction yield and antioxidant capacity of extracts obtained from hazelnut shell waste. Compared with Soxhlet extraction, the extraction yields improved significantly with the application of both ultrasonic (14.12%) and combined extraction (15.40%) by using methanol as solvent. On the other hand, extraction time did not show significant effect on extraction yield, antioxidant capacity, and phenolic content. GC-MS analysis results showed that major phenolic compounds obtained from hazelnut shell waste extraction were oleic acid and palmitic acid for all solvent types. In conclusion, these results indicated that selective extraction from natural sources, by an appropriate solvent, is important for obtaining fractions with high antioxidant activity and the development and utilization of hazelnut shell waste. Ultrasonic extraction and combination of it with Soxhlet extraction have been presented to be efficient methods for the extraction of phenolic compounds from hazelnut shell compared to the Soxhlet extraction.

ACKNOWLEDGMENT

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SUPPLEMENTARY DATA

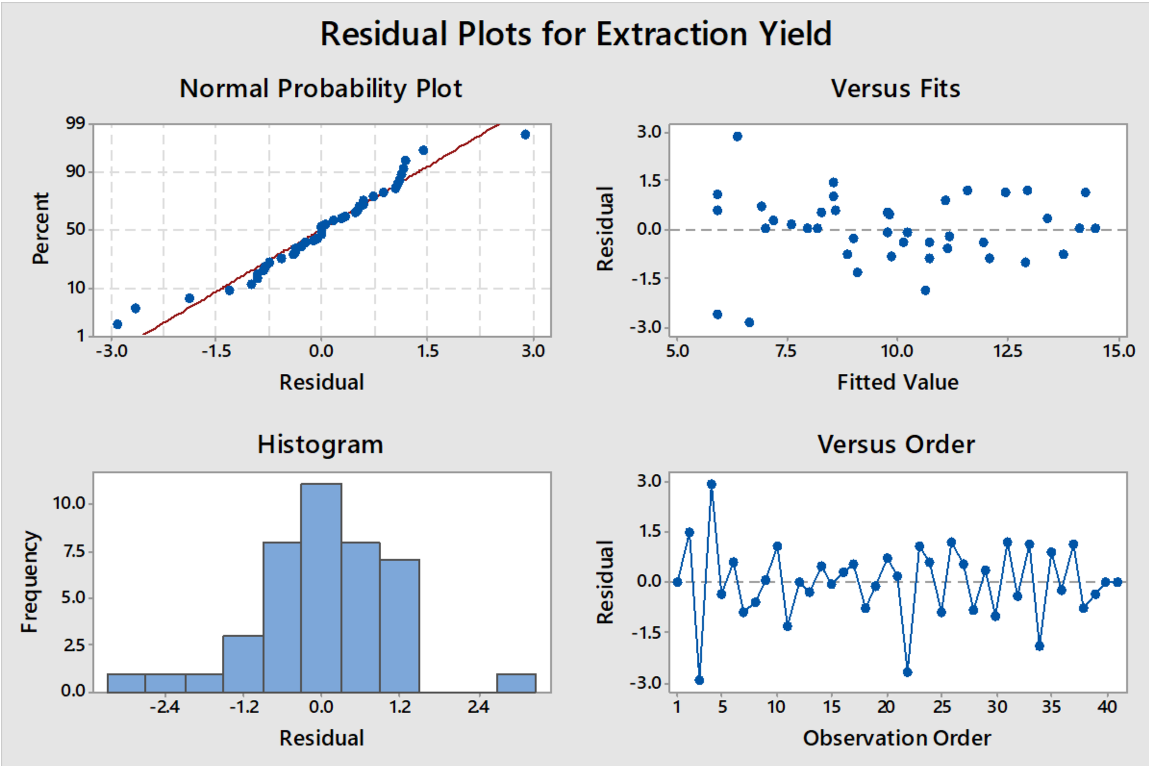

Fig S1. Residual plot for Extraction yield

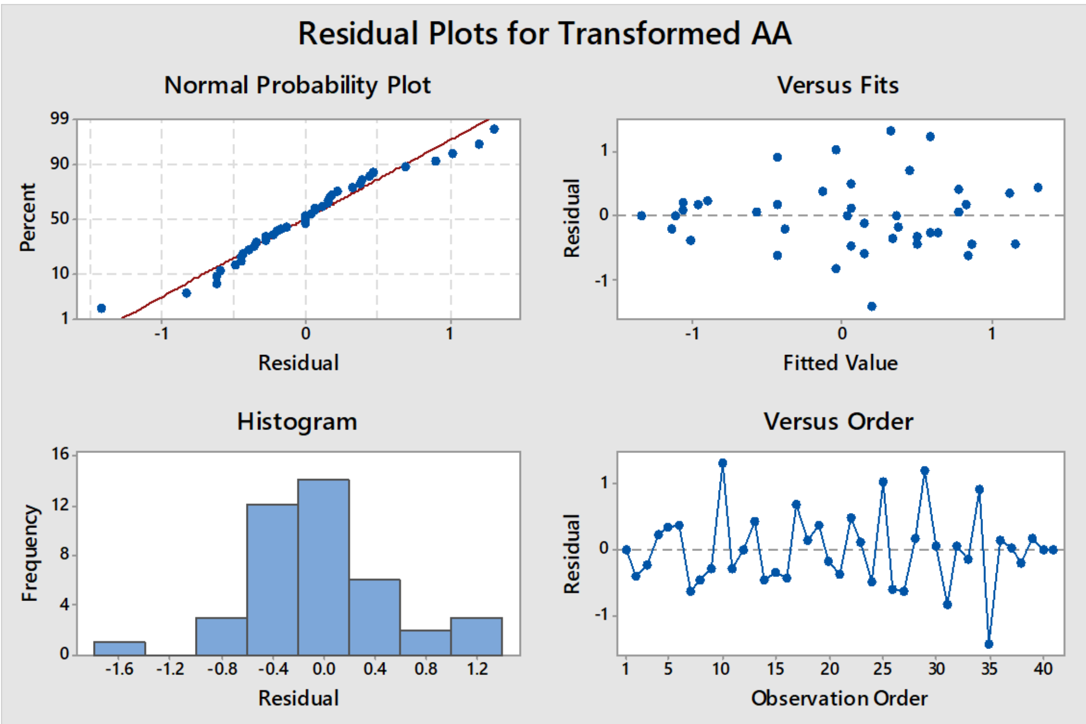

Fig. S2. Residual plot of Antioxidant Capacity after Johnson Transformation

Table S1. ANOVA Results of Extraction Yield

Analysis of Variance							
Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	18	246.839	83.93%	246.839	13.7133	6.38	0.000
Linear	12	240.21	81.68%	140.742	11.7285	5.46	0.000
Time	1	82.119	27.92%	4.231	4.2313	1.97	0.174
Solid to liquid ratio	1	7.336	2.49%	0	0	0	0.997
Extraction Type	2	73.631	25.04%	46.566	23.2829	10.84	0.001
Solvent	7	60.278	20.50%	46.798	6.6855	3.11	0.019
Square	2	2.991	1.02%	2.663	1.3317	0.62	0.547
Time*Time	1	1.93	0.66%	2.412	2.4124	1.12	0.301
Solid to liquid ratio*Solid to liquid ratio	1	1.061	0.36%	0.022	0.0217	0.01	0.921
2-Way Interaction	4	3.638	1.24%	3.638	0.9094	0.42	0.79
Time*Solid to liquid ratio	1	0.349	0.12%	0.009	0.0091	0	0.949
Solid to liquid ratio*Extraction Type	2	2.983	1.01%	2.983	1.4915	0.69	0.51
Error	22	47.256	16.07%	47.256	2.148		
Lack-of-Fit	20	39.096	13.29%	39.096	1.9548	0.48	0.85
Pure Error	2	8.16	2.77%	8.16	4.08		
Total	40	294.096	100.00%				

Table S2. ANOVA Results of Antioxidant Capacity

Analysis of Variance							
Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	18	20.5173	63.11%	20.5173	1.13985	2.09	0.051
Linear	12	18.4085	56.62%	18.5642	1.54702	2.84	0.016
Time	1	2.0565	6.33%	0.3593	0.35931	0.66	0.426
Solid to liquid ratio	1	0.6313	1.94%	0.1288	0.12877	0.24	0.632
Extraction Type	2	1.7182	5.28%	1.1199	0.55997	1.03	0.375
Solvent	7	13.8604	42.63%	13.0446	1.86352	3.42	0.013
Square	2	0.7721	2.37%	0.8266	0.41332	0.76	0.48
Time*Time	1	0.755	2.32%	0.7952	0.79521	1.46	0.24
Solid to liquid ratio*Solid to liquid ratio	1	0.0171	0.05%	0.0005	0.00053	0	0.975
2-Way Interaction	4	1.3367	4.11%	1.3367	0.33417	0.61	0.658
Time*Solid to liquid ratio	1	0.0369	0.11%	0.0425	0.04251	0.08	0.783
Solid to liquid ratio*Extraction Type	2	0.2624	0.81%	0.2624	0.13118	0.24	0.788
Error	22	11.9945	36.89%	11.9945	0.5452		
Lack-of-Fit	20	11.5179	35.43%	11.5179	0.57589	2.42	0.333
Pure Error	2	0.4766	1.47%	0.4766	0.23831		
Total	40	32.5118	100.00%				

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BOOK REVIEW

Resilient water services and systems: The foundation of well-being

by Petri Juuti, Harri Mattila, Riikka Rajala, Klaas Schwartz, Chad Staddon, (Eds.), 2019
ISBN 978-952-6697-26-0

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Resilience is replacing sustainability as the buzzword for developing better solutions to our current environmental issues. But resilience is a multifaceted concept which cannot be reduced to single dimensions as it is usually done in engineering or ecology. This book, edited and written by professionals of different backgrounds but with expertise on Water and Sanitation Systems (WSS), seeks precisely to offer a renewed and much more ambitious conceptualization o resilience able to confront the enormous challenges faced by WSS in the world today, especially the sheer injustice of billions of humans without safe and reliable water and sanitation. As professor Tapio Katko states in the preface, if the problem is not the resource or the technology but lies in faulty and unjust governance and institutions, then the concept of resilience needs to expand its horizons and move from the relatively well known and safe world of technology and management to the much more difficult and uncertain social and political arenas.

The book is structured in 15 chapters. Five chapters are conceptual and the remaining ten are case studies ranging from continents (Latin America and the Caribbean) to large and small countries (the United States and several, mostly Northern and Central European countries), to regions (the province of Zhejiang in central China) and to cities, including Tampere in Finland (compared to Carletonville in South Africa) Riga in Latvia, Tucson, in the arid North American South West, and Cape Town in South Africa. Examples from almost all geographical scales allow to develop a rich and variegated view of resilience that is not singular or uniform but multiple and heterogeneous striving to adapt to the very different contexts of WSS found in the world today.

In order to explore in full resilience as applied to WSS in all the case studies, the editors have taken the intelligent option of avoiding a too tight structure allowing authors of the chapters to develop specific views of resilience implicitly under the key concept of historical path dependency. The overall framework is resilience as the editor's state clearly in the first chapter. However, the concept is never uniform and monolithic but diverse and malleable. The road map provided to authors emphasizes a few basic keywords, namely history, integration, management challenges, and futures. Above them, concept of path dependence or how past decisions influence specific notions of resilience (see for example Figure 2.1) acts as a common thread throughout the chapters. Path dependence is responsible for the dominant view in WSS of resilience as a technical and managerial problem. The picture emerging from most case studies, however, situates resilience in the realm of institutions and politics away from single expertise and requiring interactions between professionals and different stakeholders. Some of the empirical chapters include their own views of resilience so the reader is able to learn about the different meaning of the concept according to different political cultures, for example between the Scandinavian view, more centered on technical risk management (see for example the chapter on Sweden) and the Anglo-American view, more attentive to financial and operational issues (Chapter on the UK). Contrasting these different approaches is for me one of the great assets of the book since international comparisons always leave rich details for a comprehensive view on this subject.

The first two case studies include the USA and the Latin America and Caribbean Region with separate and yet converging challenges regarding resilience. In the first case the problem of mature systems reaching obsolescence is a cause of concern since aging WSS infrastructures are a major threat for the resilience of these systems. Perhaps a mention could have been made to the increasing and dramatic problem of water poverty in many American cities. Since no other sources of funding appear unavailable, the cost of

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infrastructure renovation will be passed on to consumers making inevitable rises in price with dire effects on vulnerable households. In his comprehensive view on WSS in Latin America and the Caribbean, Esteban Castro insists that the greatest challenges for resilient WSS in this region are socioeconomic, political and institutional, above all the tremendous inequities regarding access to safe and reliable water services. More importantly (p. 63), essential public services cannot be separated from the democratization of social and political life. On chapter 6, Heino et al take a definitive step towards the full incorporation of social sciences to resilience studies arguing that infrastructures are sociotechnical constructs and not simple physical artifacts. Resilience, they argue, has to do with individuals and organizations and their ability to engage in collaborative action (p. 70). Resilience must cross discipline boundaries and integrate many sources of knowledge which is fundamental to cope with unexpected, chaotic, and sometimes malevolent actions such as terrorist attacks.

The chapters on cities show a fascinating bundle of challenges for resilient WSS, from the most dramatic (Cape Town) to the innovative (Tucson) and to the unforeseen a few decades ago (Riga and Tampere). Undoubtedly, the Cape Town water crisis has become an example of WSS pushed to their limits. The chapter by Templehof tells vividly and with much detail how one the wealthiest and best managed African Cities went into a near collapse between 2015 and 2018 because of extreme water scarcity. In this case resilience (including the creation of a Resilience Committee by municipal authorities) was built at the same time than the crisis unfolded and lately emerged as an international benchmark for innovation in water management. However, as the quote by two key water managers on p. 141 reflects, it remains to be seen whether the crisis will have any effect on future episodes of water stress. At the other extreme, some cities such as Riga and Tampere must deal with oversized water infrastructure either because of population decline (Riga) or because of unmet projections of water consumption (Tampere). Here being resilient implies an entirely new challenge: whether experts and stakeholders are prepared to downsize capacities promoting a new generation of infrastructural works away from the common and firmly established philosophy of growing and expanding. Tucson's approach to resilience takes on the classical paradigm of risk reduction by diversifying sources of supply but including in the process a strong compromising in diversifying decision making as well and making citizens active in their water futures. This is not just a rosy path as negative tradeoffs appear in many of the options explores to secure water for the city but it combines nicely a traditional version of resilience thinking in WSS, that of diversification of water portfolios, with public involvement in the process.

Finally, some case studies develop new and interesting concepts to build up resilience in WSS. For example, the concept of "One Water" (in the chapter devoted to the USA) which attempts to break down siloed flows (potable water, wastewater, stormwater, and reclaimed water). The separation of flows is another example of the relevance of the concept of path dependency in water approached historically. Likewise, the "Five Water Governance" of the Zhejiang province, one of the most problematic in China in terms of water pollution, envisages a hand in which wastewater treatment is the thumb and subject to the highest priority, and flood control, drainage, water supply and water conservation are the four fingers, different but highly integrated. The Dutch case study also proves that changes in resilience thinking and practice are also needed in what is probably one of the most robust WSS in the world. For Dutch water utility Vitens, resilience, a "magic concept" according to authors, starts by assuming that "things can go wrong and will go wrong". Hence the futility of being obsessed with zero risk. On the contrary, risks and potential failures become admissible and to a certain extent may be even welcome as long as performance levels are sustained. Vitens follows what is one fundamental shift in risk management; that is, going from "fail -safe to "safe to fail". This is not easily accepted and hence the controversies between the utility and its stakeholders but has been proposed as the main component of the Long-Term Vision (up to mid-21st century) of the company.

In the last chapter, lesson learned from the case studies are summarized and relevant points for a renewed approach to resilience in WSS exposed (p. 234). Words unfortunately still little heard in resilience debates such as multi-dimensional, multi-disciplinary, bottom up, local knowledge, and education appear as keywords for the renewed perspective on resilience developed in the book. One cannot avoid thinking of resilience as a version of the famous expression by Lampedusa "If we want things to stay as they are, things will have to change". This book, however, indeed sees resilience in a different light. Resilience of WSS is fundamental for human well being and, as the book argues through and through. The many experiences, strategies, proposals, compiled and presented in this book through the case studies will hopefully contribute to make WSS suited to human well being in many parts of the world.