Pre-coagulated landfill leachate treatment by Electro-oxidation using MMO/Ti, Pt/Ti, and graphite anodes

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ABSTRACT

In this study, sequential coagulation and electro-oxidation (EO) processes were applied to landfill leachate, which is highly contaminated and complex wastewater. Since the pollutant content of the leachate was too high, the coagulation process (poly aluminum chloride (PAC) as a coagulant) was applied as a pre-treatment to reduce the cost of the EO process. The Box-Behnken design of response surface methodology was used. The color number (CN) removal efficiency estimated by the model under optimum operating conditions was 80.1%, while it was 77.6% in the experimental studies performed under optimum conditions to verify the model conformity. Multi-metal oxide doped Ti (MMO/Ti), Pt doped Ti (Pt/Ti), and graphite were used as anode and stainless steel was used as cathode in the EO process. In the EO process in which Pt/Ti anode was used, chemical oxygen demand (COD), UV_{254} , and CN removal efficiencies were 52.8, 68.1, and 85.6%, respectively under the conditions of applied current 1.25 A and the pH 5. The CN value decreased to 4.2 after the coagulation process and it was 0.6 at the effluent of the EO process.

Keywords: Box-Behnken Design, Coagulation, Color number, Electro-oxidation, Leachate, PAC

1. Introduction

Leachate generated as a result of the storage of solid wastes in landfills can contain paint-based pollutants, pharmaceuticals, personal care products, toxic metals, volatile organic compounds, and pesticides similar to industrial wastewaters. Recent studies show that these pollutants, some of which are classified as emerging contaminants, cause significant micropollutant pollution in wastewater [1, 2]. The controlled and/or uncontrolled discharge of these highly polluted and toxic wastewater results in groundwater, surface water, and subsurface soil contaminants becoming a threat both for human beings and aquatic life [3].

Leachate, one of these highly contaminated and toxic wastewater, contains refractory organic matters, humic and fulvic matters, metallic ions, anions, toxic metals, halogenated and phenolic compounds, xenobiotic organics, and trace elements [4, 5]. Leachate is one of the most difficult wastewaters to treat due to its complex structure and variable content. For this reason, various pretreatment methods and combined treatment methods are applied. Conventional leach-

ate treatment methods are divided into three: (a) Conveying leachate to the domestic wastewater treatment plant where combined treatment methods are applied (b) Applying biological treatment processes (aerobic or anaerobic) (c) Applying chemical and physical methods including coagulation/flocculation, adsorption, sedimentation/flotation, chemical precipitation, and chemical oxidation [6].

The characteristics of the leachate vary due to the age of the landfill site. Leachate is categorized as young leachate if the landfill age is lower than two years and as mature leachate if the landfill age is higher than five years [7]. The organic content of leachate dramatically declines over time and the organic fraction of the mature leachate gradually becomes refractory. Thus, the resistant organic matter content increases as the age of the landfill site increases. Resistant organic matter removal is hard with conventional treatment methods. Therefore, combined or integrated systems are applied to the treatment of middle-aged or mature leachate [8, 9]. Based on the mechanism, treatment processes are classified as destructive and non-destructive treatment processes. The phase

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of the pollutants changes in non-destructive treatment processes whereas pollutants decompose and turn into final products in destructive treatment processes. Due to its complex and variable structure, combined processes in which both separation and destruction mechanisms take place together, give effective results in leachate treatment. The application of non-destructive processes as pretreatment, whose main mechanism is separation, increases the total removal efficiency by providing the removal of high amounts of suspended and colloidal substances and decreasing the organic load, while at the same time decreasing the cost [10, 11]. Coagulation-flocculation, adsorption, membrane processes, and advanced oxidation processes can be given as examples of destructive or non-destructive processes that can be applied for leachate treatment.

Among the advanced oxidation processes, the electro-oxidation (EO) process is an effective process that can be applied at standard conditions. Recently, applications of advanced EO processes have drawn attention especially in the removal of resistant organic compounds [11-13]. The EO processes are based on in situ electro-generation of hydroxyl radicals, which is a strong oxidant that does not show selective behavior. It does not create secondary contamination, as it does not require any flocculants or oxidant addition [14]. EO occurs through two mechanisms; direct oxidation in the anode plate and indirect oxidation driven by the production of oxidants based on electrolyte ion anodization [15]. The EO mechanism follows two different paths. In electrochemical transformation, partial oxidation of organic compounds occurs, more biodegradable reaction turns into by-products, the new form into which the compounds are transformed requires additional treatment processes, especially biological treatment. In EO, complete mineralization of organic matters to carbon dioxide, water, and other inorganic species takes place, and there is no need for further treatment. Although the EO process has technical advantages of easy operation, automation system possibility, and versatility, EO alone causes high-energy consumption. Thus, it is more feasible to apply it after chemical or biological processes [16].

The nature of the anode material used in the EO process has a strong effect on the selectivity and efficiency of the EO process [17]. Because the degradation pathway of organic matter largely depends on the performance of the anode material. The EO process has been applied by many researchers for the treatment of complex wastewater such as leachate using various anode materials and promising results have been obtained [17-22]. These studies used various anode materials including Ti-TiO₂-RuO₂-IrO₂, Ti/RuO₂-IrO₂, Ti/IrO₂-RuO₂, Ti/PbO₂, graphite, and boron-doped diamond (BDD) [23]. Studies were usually carried out in raw leachate, and BDD anode was often used in biologically treated leachate. When the BDD anode is used, the formed hydroxyl radicals allow a higher amount of organic matter to be fully mineralized by the non-selective oxidation process [22]. Biologically treated leachate is difficult to treat due to its very low biodegradability and high amount of resistant organic matter. Therefore, the preferred electrode for biologically treated leachate is the BDD electrode, despite its high cost. In the review prepared by Bashir et al. [23], the anode-cathode combinations used in studies on pollutant removal from leachate by the EO process, pollutant concentrations of wastewaters, operating conditions, and the obtained removal efficiencies were reported. It is seen from the review that Al or Fe electrodes are used in the

treatment of wastewater containing high chemical oxygen demand (COD) concentrations. The reason for this is the cost that will arise for the treatment of wastewater with high COD content with the EO process. The cost of Al and Fe materials is lower than other electrodes. The EO process that occurs with metal oxide anode is based on the electrochemical conversion principle in which the existing chlorine partially decomposes the organic matter [24]. Bashir et al. [25] applied an EO process to the leachate using graphite anode and 68% COD removal was achieved. After the EO process was performed using Pt/Ti anode in leachate treatment, Aloui et al. [26] and Ramprasad [27] achieved approximately 60% COD removal [28].

Gou et al. [29] categorized the research studies based on the anode materials used and COD concentrations of leachate. They concluded that higher COD removal efficiencies were obtained by BDD and PbO₂ anode materials as compared with that obtained by the use of Ti, Ru, Sn, Ir oxide-based anode materials [29]. Moreover, the researchers who studied with lower COD concentrations achieved higher COD removals. In the literature, there are combined process applications as well as stand-alone EO processes in leachate treatment. The other component of the combined processes in which EO is applied as pre or post-treatment can be biological, physical, or chemical applications [13, 30-32]. In the study conducted by Gilvapas et al. [30], the coagulation process was applied before the EO process using BDD anode, and 93.5% COD removal efficiency was obtained. Oliveira et al. [13] applied EO to the raw leachate following the coagulation process. In the sequential process, Al₂(SO₄)₃ was used as the coagulant and the BDD electrode was used and over 90% COD removal was achieved in the process output [13]. Chiang et al. [31] applied coagulation and adsorption processes separately before the EO process since the EO process alone requires a high cost in leachate treatment. In the study, the coagulant was FeCl₃, the adsorbent was granular activated carbon, and the electrode was PbO₂/Ti. It was determined that the removal efficiency increases and the cost decreases after pretreatment with coagulation or adsorption processes [31]. Salek [32] applied ozone oxidation, Fenton, and precipitation with lime as pretreatment before the EO process and used titanium anode coated with multi-metal oxide electrodes in the EO process. As a result of pretreatment with ozonation and Fenton processes, COD removal efficiencies of 52% and 51% were obtained, respectively; however, ammonia concentration increased when the EO process was applied after precipitation with lime [32].

Considering previous studies in the literature, it is seen that the anode materials used in this study are different and the leachate COD concentration is quite high. Besides, the coagulant used in the coagulation process applied as pretreatment is different from the coagulants used in previous studies. Conventional chemical coagulation involves the addition of chemicals like aluminum sulfate or ferric chloride as a coagulant. However, in this study, PAC was used as the coagulant due to its lower cost, easy accessibility, and less sludge formation [33]. In addition, considering the combined process applications, no study was found in which the operating conditions of the coagulation process were optimized with the application of the response surface methodology. To sum up, this study is novel in terms of the high COD concentration of the leachate used, the electrodes used, the coagulant, the modeling

of the coagulation process, and evaluating them all together.

In this study, coagulation was applied as a pretreatment in leachate treatment, followed by the EO process, which is a destructive process for organic matter decomposition. The main objective of the study was to obtain maximum removal efficiencies with the lowest operational cost. Therefore, sequential separation and destruction processes were applied. Operating parameters of the coagulation process were optimized by using the Box-Behnken design (BBD) of response surface methodology (RSM), and optimum conditions were determined where maximum color number removal was achieved. BBD was selected to achieve maximum removal efficiencies by conducting a minimum number of experiments. In the EO process, the most efficient anode type and optimum conditions were determined.

2. Materials and Methods

2.1. The Leachate and Characterization

The leachate used in the study was obtained from the Odayeri Sanitary Landfill Leachate Treatment Plant, Istanbul, Turkey. The samples were stored in a refrigerator in the dark at +4°C. The characterization of the leachate and the methods used in the study are given in Table 1.

Table 1. Characteristics of Raw Landfill Leachate

Parameter	Raw Leachate	Method
pH	8.09	SM 4500 H ⁺ -B
Conductivity, mS/cm	37.4	SM 2510 B
TSS, mg/L	1,110	SM 2540-D
Chloride, mg/L	3,450	SM 4500-Cl ⁻ B
UV ₂₅₄ , mg/L	2,860	[14]
COD, mg/L	13,059	SM 5220-C
CN	18.6	[15]

2.2. Chemicals and Analytical Methods

Analytical grade H₂SO₄ and NaOH purchased from Merck (Germany) were used in this study. Wastewater characterization was carried out with the standard methods given by APHA [34]. SM 5220-C method was used for COD measurement and the SM 2540-D method was used for TSS measurement. WTW Multi 9620 IDS device was used to measure the conductivity and pH of the samples. UV₂₅₄ and color number (CN) were measured using WTW Photolab 6600 UV-Vis device according to the method given by Chen et al. [35]. The UV₂₅₄ parameter, which is the absorbance value obtained at 254 nm wavelength, was used to determine the relative concentrations of aromatic compounds. The color number parameter, which represents dissolved organic matter in terms of the characteristic functional groups, was used to determine the color of the sample. The samples were filtered through 0.45 µm before color number analysis. The equation used to determine the color number is given below [36].

$$CN = \frac{(A_{436})^2 + (A_{525})^2 + (A_{620})^2}{A_{436} + A_{525} + A_{620}} \quad (1)$$

In this equation, A₄₃₆, A₅₂₅, and A₆₂₀ are the absorbance values obtained at the wavelengths of 436, 525, and 620 nm, respectively.

2.3. Coagulation Process

During the coagulation studies, 100 mL leachate samples were placed in 250 mL beakers, the pH was adjusted using 6 N NaOH and 6 N H₂SO₄, and the samples were placed in the Jar-test apparatus. A predetermined amount of PAC was added and the rapid mixing was made at 200 rpm for 2 min. Then, slow mixing was performed at 45 rpm for the times specified in the experimental design matrix. After the reaction time was completed, the beakers were taken from the Jar-test apparatus and kept for 30 min for precipitation. Approximately 50 mL of wastewater samples were taken from the surface and centrifuged at 4,000 rpm for 4 min. Then, CN analyzes were performed from the supernatant.

2.4. Experimental Design Matrix of the Coagulation Process

In the study, the Box-Behnken design method (BBD), one of the sub-design models of RSM, was used to determine the combined effects of the variables on CN removal efficiencies, which is the system's response. The number of experiments was minimized using a quadratic polynomial model to describe the linear and quadratic interactions in the BBD design [37, 38]. The variables of the coagulation process given in Table 2 were arranged so that the levels (low, medium, high) of three independent variables (initial pH, reaction time, and coagulant dose) are -1, 0, and +1. The dependent variable (response) was chosen as CN removal efficiency. The quadratic equation, which is a function of the independent variables, is given as in Eq. (2) [39].

$$R = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

In Eq. (2), R is the predicted response, β₀ is the intercept parameter, β_i, β_{ii}, and β_{ij} are the effects of linear, quadratic, and interactions, respectively, X_i and X_j are independent variables, and ε is the statistical error.

Fifteen experimental sets were conducted to optimize the interactions of the selected variables. The model was statistically analyzed by evaluating the analysis of variance (ANOVA) using the Design Expert 11.0.1.0 software. To visualize the individual or interactive effect levels of the independent variables, three-dimensional response surface graphs were drawn. Optimum process conditions for maximum CN removal were determined by the BBD. The results obtained with the model were validated with batch experimental studies. The BBD matrix used in the experimental studies and experimental and model prediction results are given in Table S1.

Table 2. Independent Process Variables and Their Levels

Factors	Original Factor	-1	0	1
Initial pH	A	1	3	5
PAC dose (g/L)	B	6	8	10
Reaction time (min)	C	15	30	45

2.5. Electro-oxidation Studies

The EO experiments were conducted in a rectangular prism-shaped Plexiglas reactor with the dimensions of H:9 cm, W:6 cm, and L:5 cm (Fig. S1). A magnetic stirrer is used for the homogeneous mixing of the wastewater during the oxidation process. MMO/Ti, Pt/Ti, and graphite electrodes were used as anodes, while stainless steel electrode was used as cathode. The distance between the electrodes was 3.5 cm and the size of the electrodes was H:12 cm, W:4 cm, and L:0.2 cm. In each set of the experiments, 150 mL pre-coagulated leachate was used, and no electrolyte solution was added since the leachate had a high conductivity value. COD, UV₂₅₄, and CN analyzes were carried out by taking samples from the reactor at different time intervals.

2.6. Kinetic Studies

First-order kinetic models (Eq. (3)-(5)) were used to analyze the leachate decomposition characteristics [40].

$$\ln \frac{(COD)_t}{(COD)_i} = -kt \quad (3)$$

$$\ln \frac{(UV_{254})_t}{(UV_{254})_i} = -kt \quad (4)$$

$$\ln \frac{(CN)_t}{(CN)_i} = -kt \quad (5)$$

Where, (COD)_t, (UV₂₅₄)_t, and (CN)_t represent the COD concentration, UV₂₅₄, and CN value at the reaction time of *t*, respectively. (COD)_i, (UV₂₅₄)_i and (CN)_i are the initial COD concentration, UV₂₅₄, and CN value, respectively. *k* (1/min) is the pseudo-first-order rate constant and *t* (min) is the reaction time.

2.7. Specific Energy Consumption

The cost and removal efficiency are two important components for process and electrode selection or determination of optimum conditions. Calculation of the specific energy consumption for a kg of organic matter removed is of great importance in the cost evaluation. In this study, the specific energy consumption and anode efficiencies were calculated using Eq. (6) and (7) [40].

$$SEC(kWh/kg \text{ removed COD}) = \frac{U \times i \times t}{10^3 \times V \times (COD_0 - COD_t)} \quad (6)$$

$$\eta (g \text{ COD/Ahm}^2) = \frac{(COD_0 - COD_t) \times V}{i \times t \times S_{anode}} \quad (7)$$

In these equations, COD₀ and COD_t are the chemical oxygen demand at the influent and effluent of the process (kg/L), respectively, *U* is the applied voltage, *i* is the applied current (A), *t* is the treatment time (h) and *V* is the volume of the wastewater.

3. Results and Discussion

3.1. Optimization and Statistical Analysis of Coagulation Process

The BBD of RSM was used for the optimization and design of the coagulation process. The data were graphically analyzed to describe the interactions between process variables and response, which was obtained by analysis of variance [41]. The ANOVA results are given in Table 3.

The quality of the polynomial fitting model was evaluated by the coefficient of determination (*R*²) and the Fisher's *F*-test was used to assess the statistical significance of the model. *F*-value and *p*-value were used to evaluate the terms of the model. An *F*-value of 21.97 and a *p*-value of 0.0017 indicate the significance

Table 3. The results of ANOVA Analysis in the Removal of CN by Coagulation

Source	Sum of Squares	df	Mean Square	F-value	P-value	Remark
Model	2291.66	9	254.63	21.97	0.0017	S
A-pH	334.11	1	334.11	28.83	0.0030	S
B-PAC dose, g/L	1202.95	1	1202.95	103.79	0.0002	S
C-Time, min	283.22	1	283.22	24.44	0.0043	S
AB	0.5625	1	0.5625	0.0485	0.8344	NS
AC	1.96	1	1.96	0.1691	0.6979	NS
BC	12.96	1	12.96	1.12	0.3387	NS
A ²	159.01	1	159.01	13.72	0.0139	S
B ²	8.45	1	8.45	0.7288	0.4323	NS
C ²	328.86	1	328.86	28.37	0.0031	S
Residual	57.95	5	11.59			
Lack of Fit	51.21	3	17.07	5.07	0.1693	NS
Pure Error	6.74	2	3.37			
Cor Total	2349.62	14				
<i>R</i> ²	0.9753					
<i>Adjusted R</i> ²	0.9309					
<i>C.V.</i> %	6.53					
<i>Adeq Precision</i>	15.10

Fig. 1. Quadratic model 3D, normal, predict and Pareto graphs for CN removal by coagulation.

of the model. The R^2 value of 0.9753 shows that at least 97.53% of the variation in experimentally obtained CN removal efficiencies can be explained by the model. Adj R^2 was found to be in good agreement with R^2 . For obtaining a well-fitting equation, the lack of fit should be insignificant. The lack of fit p-value was determined as 0.17. The lack of fit value higher than 0.05 is interpreted as not significant. In addition, the lack of fit F-value of 5.07 implied that the lack of fit was not significant relative to the pure error. The coefficient of variation (CV) value, which is the measure of the reproducibility of the model, is the ratio of the standard deviation to the mean value, and this value is required to be less than 10% for the model to be reproducible [42]. Low CV values indicate the closeness of the experimental and the predicted data [43]. Another parameter used to evaluate model adequacy is adequate precision (AP). The AP value is desired to be above 4 [44] and the AP value obtained for CN removal by coagulation in this study meets this criterion. This suggests that adequate signals might be utilized to explore the design space and predict reactions [45-47]. Besides, the low amount of standard deviation suggests that the acquired data points were as near to the predicted values as possible. It can be seen from the ANOVA results that the linear parameters of pH, coagulant dose, and reaction time and the interactive parameters of pH and reaction time have a significant effect on the coagu-

lation process. To improve the model, non-significant parameters were removed from the equation. The regression equation obtained by subtracting non-significant parameters is given below.

$$CN\ removal = +42.80 + 6.46A + 12.26B + 5.95C - 0.3750AB + 0.70AC + 1.80BC - 6.56A^2 + 1.51B^2 + 9.44C^2 \quad (8)$$

In Fig. 1, the Pareto graph, actual-predicted graph, normal probability plot, and 3-D response surface graph are given. The Pareto chart and p values of ANOVA give information relative to the effects of factors on the process. Higher values in the Pareto chart and smaller magnitude of p values indicate the higher significance of the corresponding coefficient [48]. It can be seen from Fig. 1 that the parameter with the highest effect is the linear parameter of the coagulant dose, and it can be said that all linear parameters along with the pH and reaction time from the interactive parameters are effective in removing the CN by PAC coagulation. Pareto results and ANOVA results are consistent.

The actual vs predicted graph in Fig. 1 indicates the conformity of experimental values and the estimated values provided by the regression equations. The graphs including experimentally obtained values against predicted values by the model give a first-degree line for the process. The R^2 value of the graph was determined

as 97.53. High R^2 indicates that the experimental data are consistent with the results of the model. It was observed from the graph that the estimated values obtained by the model are very close to the experimental values, and thus the validity of the equation was proven. As it can be understood from the values calculated by estimated equations, it was determined that the model's statistical significance is very close to the experimental values. Normal probability plots are the graphical method used to evaluate the normality of residuals. The normal distribution graph in Fig. 1 shows that the distribution of residuals was irregular and close to the line.

The response surface curves are drawn to understand the interaction of the variables and to determine the optimum level of the variables for maximum response [48]. It can be seen from Fig. 1 that CN removal efficiency increases as the coagulant dose increases and the process is less effective at neutral pH values. Removal efficiency also increases over time. Optimum conditions were determined by applying numerical optimization to reach the maximum removal efficiencies. At values higher or lower than the optimum points, contaminant removal efficiency reduces. In this study, optimum operating conditions determined to reach maximum CN removal efficiency in the coagulation process were pH 9.99, coagulant dose 4.10 g/L, and reaction time 44.8 minutes. The removal efficiency of CN estimated by the model under optimum conditions was 80.1%. In experimental studies performed under optimum conditions to verify the model fit, CN removal efficiency was 77.6%. Estimated and actual removal yields were close to each other. Under optimum conditions, the CN of the leachate was reduced to 4.2 after the coagulation process with PAC. The results of the statistical analysis indicate that the quadratic model constructed for the CN removal is adequate.

3.2. Electro-oxidation Process

EO process performance and degradation efficiency of organic matter largely depend on the anode material. The anode material has a significant effect on the partial oxidation, selective oxidation, and also complete mineralization of the organic pollutant depending on the electrogeneration of hydroxyl radicals. Anodes can be categorized into two groups; active anodes (graphite, carbon plate, IrO_2 , Pt, RuO_2 , etc.) with low oxygen release overpotential and inactive anodes (BDD, PbO_2 , SnO_2 , etc.) with high oxygen release overpotential [28, 29]. Active anodes have high electrocatalytic activity providing faster degradation of organic matter at low potential and tend to direct the reactions towards partial oxidation whereas inactive anodes have high oxygen evolution overpotential favoring complete mineralization of organic matter [49]. The inactive anode is called an inert electrode. Inactive electrodes also have low adsorption properties and don't provide any catalytic active sites for the adsorption of reactants and/or products from the aqueous medium. Inactive anodes also have the advantage of a lower probability of electrode fouling during the direct electron transfer process [49, 50]. As active metal anodes are used in the EO process, higher metal oxides are formed during indirect oxidation, and they will be partially oxidized. Besides, inactive metal anodes cause organic compounds to form hydroxyl radicals by physically adsorbed oxygen, and electrochemical combustion thereafter these radicals will provide complete mineralization of organic pollutants [19, 50].

Fig. 2. Effect of anode materials on COD, UV₂₅₄, and CN removal for 1.25 A by EO process.

Both active and inactive anodes undergo side reactions of oxygen escape during the reaction resulting reduction of the oxidation rate.

In the present study, the removal of COD, UV₂₅₄, and CN from pre-coagulated landfill leachate was investigated using MMO/Ti, Pt/Ti, and graphite anodes. When the anode materials were evaluated based on the pollutant removal efficiency, the efficiency of the anodes was ranked as Pt/Ti > graphite > MMO/Ti (Fig. 2). Under the applied current of 1.25 A with the Pt/Ti, graphite, and MMO/Ti anodes the COD removal efficiencies were 36.3, 31.2, and 24.4%, respectively. The UV₂₅₄ removal efficiencies were 53.1,

48.7, and 38.1%, respectively whereas CN removal efficiencies were 73.6, 67.7, and 56.7%, respectively. The removal efficiencies of UV₂₅₄ and CN were higher than that of COD (Fig. 2). The reason for this is easily separation of chromophoric groups of organic pollutants in the leachate by the EO process. As a result, EO provides an effective color removal from pre-coagulated landfill leachate. The anode materials used in the study are described as the active anode. When the anode materials are compared among themselves in terms of the removal efficiency they provide in the EO process, the difference in efficiency can be explained by the conductivity value of the material. When sorting is done depending on the voltage occurring at the same current values during the process, the sequence is Pt/Ti > graphite > MMO/Ti. The average voltage values of the MMO/Ti, Pt/Ti, graphite anodes during 180 min of reaction time under the optimum current value of 1.25 A were 6.59, 7.57, and 6.54 V, respectively.

One of the important parameters affecting EO is the applied current. At low applied current values, the anode potential is below the electrode potential required for the partial oxidation reaction [17]. Nonetheless, if the applied current remains above the limit of the EO, the current efficiency decreases dramatically since the reaction efficiency is mostly regulated by the mass transfer process [17, 51]. The applied current values in this study were 0.75, 1.25, and 1.75 A. In Fig. 3, COD, UV₂₅₄, and CN removal efficiencies based on the EO process reaction time at different applied current values are given. The figures show that the obtained COD, UV₂₅₄, and CN removal efficiencies vary depending on the used anode type and the applied current. As the applied current increased, the removal efficiency increased in the EO process, where three different anodes were used. This is because both direct and indirect oxidation efficiency is increased. The increase in the applied current increases the hydroxyl radical generation, so the organic matter decomposition efficiency also increases. At the same time, the increase in the applied current supports the formation of active chlorine species, and the organic matter removal efficiency increases [40]. In the study conducted by Moraes and Bertazzoli [52], it was determined that the color removal efficiencies were strongly affected by the applied current. The literature studies stated that increasing applied current enhances hydroxyl radical formation on the anode surface and leads to an increase in the removal efficiency due to the formation of chlorine/hypochlorite [17, 18, 25, 26, 52, 53].

In the literature studies, it has been reported that the effect of applied current on pollutant removal efficiencies is dependent on the leachate chloride concentration. If the chloride concentration in the leachate is low, the COD removal efficiency will be low since the concentration of chloride species to be formed will also be low [54]. Chloride concentrations higher than 3,000 mg/L are needed for the occurrence of indirect oxidation in wastewater [55]. For this reason, chloride should be added to wastewater with chloride concentrations lower than 3,000 mg/L for effective EO. In this study, the chloride concentration of the leachate was 3,450 mg/L and chloride was not added since it was sufficient for effective indirect oxidation. On the other hand, higher chloride concentration does not mean a better decomposition. Another powerful oxidant, hypochlorite, is formed in wastewater containing chloride. The existing chloride in wastewater is transformed into strong oxidants

such as chlorine/hypochlorite at the anode with the electrochemical process. As a result of the chloride oxidation electrochemically in the leachate, chlorine, hypochlorous acid, or hypochlorite formation occurs in gas form. The removal of organic matter obtained with the oxidants produced in this way is called indirect oxidation.

The reactions that occur in the anode are as follows.

The cathodic reactions are as follows.

The pH is an effective parameter on direct and indirect oxidation mechanisms of the EO process. Since the concentration of carbonate and bicarbonate ions (effective hydroxyl radical scavengers) decrease in acidic pH values, the oxidation reaction rate increases [56]. The pH also has a significant effect on oxygen evolution reaction, which is a side reaction. Acidic pH values are more suitable for reducing undesired oxygen evolution reactions. Among the active chlorine species formed during electrolysis, aqueous chlorine is the dominant species at pH < 3.3. At higher pH values, (pH < 7.5) chlorine is transformed to hypochlorite ion (OCl⁻) and hypochlorous acid (HOCl) (pH > 7.5). The distribution of hypochlorous acid and hypochlorite in the solution is highly dependent on the pH value of the solution [28, 56]. At high pH values, chlorine turns into chlorate (ClO₃⁻) ion, which has low oxidation potential (Eq. (12)-(14)) [28, 56]. Chlorine available at pH values lower than 4 is in the form of free chlorine (Cl₂), and free chlorine reduces its oxidation effect through passing from liquid phase to gas phase [15, 17].

Under strongly acidic and alkaline conditions, HOCl formation is negatively affected [57]. Various studies have been conducted in the literature to investigate the pH effect on leachate treatment by the EO process. Zhou et al. [58] evaluated the effect of acidic, neutral, and alkaline conditions in leachate treatment and reported that the maximum COD removal was reached at pH 5.16 with a high HOCl concentration. Turro et al. [20] and Mussa et al. [59] obtained the highest removal efficiency when the pH was 3. Anglada et al. [56] reported that acidic pH values are effective in COD and color removal; however, not in ammonium removal. Although acidic pH values are favorable for organic matter removal from leachate, pH should not go below 3.3 since gaseous chlorine may form [28].

Fig. 3. Effect of applied current on COD, UV_{254} , and CN removal by EO process.

In this study, the effect of anode material and applied current on pollutant removal efficiency was performed at the pH value of 9, which is the value in the effluent of the coagulation process. To evaluate the effect of initial pH on COD, UV_{254} , and CN removal, studies were carried out at pH 3, 5, 7, 9, and 11. The change in COD, UV_{254} , and CN removal efficiencies depending on the pH values is given in Fig. 4. Although removal efficiencies for pH 3 and 5 are very close to each other, the highest removal efficiencies were obtained at pH 3. After 180 minutes of reaction time, the removal efficiency of COD, UV_{254} , and CN at pH 3 was 55.7, 70, and 89%, respectively while they were 52.8, 68.1, and 85.6% at pH 5.

The reaction rate constants were from the results of the analyzes performed on samples taken at certain time intervals during 180 min reaction time (Fig. 4). In this study, the suitability of the experimental data to the pseudo-first-order and pseudo-second-order kinetic model was tested and the pseudo-first-order kinetic model was found to represent the COD, UV_{254} , and CN removal from leachate in a better way with higher R^2 values [60]. According to the reaction rate constants for COD, UV_{254} , and CN removal, the reaction rates decrease as the pH increases, especially at neutral and basic pH values. The rate constants of COD, UV_{254} , and CN at pH 3 were 0.0028, 0.0091, and 0.045 1/min, respectively, whereas they were 0.0027, 0.0089, and 0.0049 1/min, respectively at pH 5. Both the pollutant removal efficiencies and the reaction rate constants at pH 3 and pH 5 are very close to each other. Therefore, the optimum pH was selected as 5 since pH values below 3.3

will cause the formation of gaseous chlorine in the EO process [28].

As can be seen from Eq. (15), one of the most important parameters in the SEC calculation of the EO processes is the voltage value. The reason for the different voltage values between the processes is both the applied electric current and the type of anode material. Therefore, voltage variations were recorded for all three anode types over 180 min and used in the SEC calculation. The SEC calculated for the MMO/TiO₂, Pt/Ti, and graphite anodes were 90, 98.8, and 91.6 kWh/m³, respectively at 0.75 A; 164.7, 189.2 and 163.5, respectively at 1.25 A; 291.5, 320.6, and 320.6, respectively at 1.75 A. While it is difficult to select an anode as the specific energy consumption values for m³ of wastewater are very close to each other, specific energy consumption values for kg removed COD make anode selection easier.

Calculated SEC values based on applied current are given in Fig. 5. As seen in Fig. 5, the SEC value increased as the applied current increased from 0.75 A to 1.75 A for all anode types. On the contrary, the anode efficiency decreased as the applied current increased for all anode types. For Pt/Ti anode, the COD removal efficiency was 29.0% at 0.25 A applied current, while the COD removal efficiency was 40.7% for 1.75 A. Since the SEC values were calculated against the removed COD, the SEC for 1.75 A was much higher since the COD removal efficiencies did not increase at the same rate compared to the increase in the applied current. Therefore, 1.25 A was chosen as the optimum applied current value instead of the high applied current value. The SEC of 81.2 kWh/kg COD was obtained for the selected optimum applied current

Fig. 4. Effect of pH on COD, UV₂₅₄, and CN removal by EO process Pt/Ti 1.25A.

Fig. 5. SEC values for MMO/Ti, Pt/Ti, and graphite anodes in the EO process.

of 1.25 A using Pt/Ti electrode. The anode efficiencies decreased from 58.0 to 34.9 g COD/Ahm² for Pt/Ti anode, from 40.5 to 25.8 g COD/Ahm² for MMO/Ti anode, from 24.2 to 15.7 g COD/Ahm² for graphite anode. As the reaction time and applied current increase, the anode efficiency decreases. The decrease in anode efficiency is due to the resistant organic and inorganic substances present in the leachate.

4. Future Research Perspectives

The sequential treatment method reported in this study can be adopted effectively for the treatment of any kind of complex industrial wastewater effluents. Future research perspectives should be directed towards the application of this approach with composite enhancement technologies (ozone, ultrasound, magnetic field, and UV enhancement). Studying the optimum Cl⁻ concentration, different anode-cathode combinations, or alternative pretreatment processes (adsorption by new nanocomposite materials) and combination of electrochemical technologies with other advanced oxidation processes will provide new ideas to further explore how to achieve low cost, low energy consumption, and high-efficiency treatment of landfill leachate.

5. Conclusions

Since raw leachate is a highly contaminated, complex wastewater including a significant portion of recalcitrant contaminants, the application of the sole EO process would not be cost-effective for leachate treatment. Therefore a physicochemical process was applied before the EO process to decrease the contaminant load of the leachate. Combined coagulation-EO processes were investigated to remove COD, UV₂₅₄, and CN from landfill leachate. The operational conditions of the coagulation process in which PAC was used as the coagulant were optimized by the BBD of RSM and 79.6% CN removal was obtained at optimized conditions. After the reduction of the load of the leachate by coagulation, the EO process was applied to remove the resistant organic substances in the leachate. The effect of different anode materials on the performance of the EO process was evaluated and the highest removal efficiencies were obtained in the evaluated using Pt/Ti anode. Specific energy consumptions were calculated for each anode, and the optimum applied current was chosen as 1.25 A considering both pollutant removal efficiencies and SEC. The optimum pH was determined as 5. Under optimum conditions of the EO process, COD, UV₂₅₄, and CN removal efficiencies were 52.8, 68.1, and 85.6%, respectively. Total COD, UV₂₅₄, and CN removal efficiencies of the combined process were 76.7, 87.5, and 96.7%, respectively. The results of the study show that it is possible to obtain effective leachate treatment with the combined coagulation-EO process.

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Conflict-of-Interest

The authors declare that they have no conflict of interest.

Author Contributions

S.Y.G (Associate Professor) performed the investigation and data collection and revised the manuscript. A.D. (Professor) performed conceptualization and supervision. Y.D. (Undergraduate student) conducted the analyses. G.V. (Associate Professor) and E.C.G. (Ph.D.) wrote the first draft and revised the manuscript.

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