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Microwave activated persulfate oxidation of leachate subsequent to optimized chemical coagulation

Gamze Varank, Bihter Uykan, Emine Can-Güven, Senem Yazici Guvenc*

Department of Environmental Engineering, Yıldız Technical University, Davutpasa Campus, Esenler, Istanbul 34220, Turkey, Tel. +90 212 3835383; Fax: +90 212 3835358; email: syazici@yildiz.edu.tr/senem.yazici87@gmail.com (S.Y. Guvenc), Tel. +90 212 3835377; Fax: +90 212 3835358; email: gvarank@yildiz.edu.tr (G. Varank), Tel. +90 212 3835377; Fax: +90 12 3835358; email: bihteruykan95@gmail.com (B. Uykan), Tel. +90 212 3835428; Fax: +90 212 3835358; email: ecguven@yildiz.edu.tr (E. Can-Güven)

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ABSTRACT

In this study, a chemical coagulation process in which alum and poly aluminum chloride (PAC) were used as coagulants were applied to the leachate and the process operating conditions were optimized with the response surface method and Box–Behnken design. Operating parameters of the chemical coagulation process were coagulant dose, initial pH, and reaction time while COD and UV_{254} removal were model responses. The COD removal obtained statistically under the optimum conditions determined by the model was 58.1% and 54.2% for alum and PAC, respectively. The experimental COD removal efficiencies were 56.9% and 50.8% for alum and PAC, respectively. Based on the results of the coagulation process, alum was selected as the coagulant. As a second step, persulfate oxidation activated by the microwave method was applied to the leachate. The effect of initial pH, microwave power, reaction time, and PS dose on COD and UV_{254} removal by persulfate oxidation was determined using the conventional optimization method. The COD and UV_{254} removal obtained in 3 min reaction time under the conditions of microwave power 450 W, pH 5, and 5 g/L persulfate dose was 51.7% and 55.4%, respectively. As a result of the combined coagulation and oxidation process, a total of 79.2% COD removal and 92.1% UV_{254} removal from leachate was provided.

Keywords: Leachate; Chemical coagulation; Microwave activation; Persulfate; Energy consumption

1. Introduction

The leachate is composed of the rainwater flowing along the waste body stored in the storage areas, the water formed from the biochemical processes occurring in the tank body, and the water released through the compaction of the water content of the stored waste [1]. Leachate contains high amounts of organic matter, ammonia nitrogen, heavy metals, chlorinated organic matter, and inorganic salts. If the leachate is not collected and stored properly and is not treated sufficiently, it mixes into the soil, infiltrates the lower layers of the soil, surface water, groundwater, and causes serious environmental problems. Leachate is a complex and variable structured wastewater and very difficult to treat. Thus, it is inevitable to apply pre-treatment, post-treatment, or combined treatment methods in the treatment of leachate [1].

The coagulation process, which is one of the physicochemical methods widely used in industrial wastewater treatment, is successful in leachate treatment. In the coagulation process, the hydrolyzed coagulant species contact with the pollutants in the water in the rapid mixing step and form destabilized particles. As a result of the destabilized particles colliding with each other, larger particles or flocs

* Corresponding author.

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are formed, then the flocs are removed through sedimentation, flotation, or rapid filtration mechanisms [2]. Chemical coagulants such as aluminum sulfate (alum), ferrous sulfate, ferric chloride, and ferric chloro-sulfate or vegetable salts called biocoagulants are used in the coagulation [3]. Recently, polymerized forms of metal coagulants such as poly aluminum chloride (PAC) have been used in wastewater treatment. While such products provide higher efficiency in particulate or organic matter removal compared to conventional coagulants, they also consume lower alkalinity and create less sludge [4]. The main parameters affecting the efficiency in the coagulation process are pH and coagulant dose, and if the purpose is to remove organic load or color, organic substances do not mineralize with this process alone [5].

Treatment processes can be considered into two groups as destructive and non-destructive based on the treatment mechanism. Coagulation, adsorption, membrane processes can be given as examples of non-destructive processes whose main mechanism is separation. In these processes, the crushers in wastewater are transferred from the liquid phase to the solid phase and the solid phase obtained is called sludge. Destructive processes are advanced treatment processes. Resistant organic pollutants can be removed with free radicals that occur in advanced treatment processes [3,6,7]. The application of advanced oxidation processes integrated with the coagulation process provides an advantage in terms of the removal of resistant organic matter contained in the leachate.

Advanced oxidation processes are the general name of oxidation methods that are used to remove contaminants present in the water and are principally based on the production of hydroxyl and sulfate radicals [8]. Commonly used oxidants in advanced oxidation processes are persulfate (PS), peroxymonosulfate, and peroxide. Persulfates and peroxides are strong oxidants with standard oxidation-reduction potential and shows limited performance in resistant organic matter removal. Therefore, oxidants are activated by various methods, and reactive oxygen species are formed [9–11]. However, when an activator is used, sulfate and hydroxyl radicals are formed. The oxidation–reduction potential of free radicals (sulfate and hydroxyl radicals) that occur due to the activation of oxidants is higher and can oxidize most resistant organic materials. While hydroxyl radicals are not selective and react rapidly with all organic pollutants, sulfate radicals are highly selective [11]. The microwave (MW) method is one of the activation methods used to increase the oxidation potential of oxidants and to provide effective resistant organic matter removal. In the literature, there are studies on different treatment processes applied in combination with coagulation–flocculation in leachate treatment [1,3,6,12,13]. Since the leachate contains high amounts of suspended/colloidal and dissolved substances, the processes involving both separation and destruction mechanisms give effective results in the leachate treatment. The high amount of suspended and colloidal substances in the leachate reduce the performance of advanced oxidation processes, increase energy and oxidant consumption, and are indirectly uneconomical. For this reason, applying the separation process as pre-treatment before destructive processes reduces the organic load by providing the removal of suspended and colloidal matter and increases the total removal efficiency [6,14].

In this study, coagulation was applied as a pre-treatment process in leachate treatment, followed by microwave persulfate oxidation, which is a destructive process, for organic load reduction. Coagulation process operating parameters were optimized by using the response surface method and Box–Behnken design (BBD), and the optimum conditions where maximum removals were achieved were determined. Two different oxidants (alum, PAC) were used as an alternative in the coagulation process. At the second stage, persulfate oxidation was applied to the leachate, which was coagulated by adding alum under the optimized operating conditions. In persulfate oxidation activated by microwave method, the optimum conditions of the operating parameters where maximum removal efficiencies were obtained by applying the classical optimization method.

2. Materials and methods

2.1. Characterization of leachate and analytical methods

The leachate samples used in the study were obtained from the Odayeri Sanitary Landfill Leachate Treatment Plant, Istanbul, Turkey. Wastewater samples were preserved at +4°C to prevent biological activity. Characterization of wastewater before and after treatment was carried out using the methods recommended by APHA [15]. The pH and conductivity of the samples were measured by the WTW Multi 9620 IDS device. The UV_{254} value was measured to determine the relative concentrations of aromatic compounds in the samples. UV_{254} value is the absorbance value obtained at 254 nm wavelength measured by the WTW 6600 UV-VIS Photolab Spectrophotometer. The pH and conductivity of the leachate sample were 8.9 and 37.4 mS/cm, respectively. Concentrations of COD, TSS, NH_3–N and UV_{254} were 13,059, 1,110, 3,186, and 2,860 mg/L, respectively. Eq. (1) and (2) were used to determine the process efficiencies.

$$R_{\mathrm{COD}}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$R_{\mathrm{UV_{254}}}(\%) = \frac{\mathrm{Abs}_0 - \mathrm{Abs}_t}{\mathrm{Abs}_0} \times 100 \tag{2}$$

where R_{COD} is the COD removal efficiency, C_0 is the initial COD concentration (mg/L) and C_t is the COD concentration after treatment (mg/L). R_{UV254} is the UV_{254} removal efficiency, Abs_0 is the initial absorbance value, and Abs_t is the final absorbance value.

2.2. Optimization of coagulation processes with Alum and PAC

To create the experimental design matrix of the coagulation process, preliminary studies were carried out for 30 min using pH values of 3, 8.09 (raw pH value of the wastewater), and 11 along with the coagulant (alum and PAC) doses of 0.1 and 10 g/L (Table 1). Preliminary studies and optimization studies were carried out following the same experimental flow. 100 mL of leachate was used in coagulation studies. The pH value of the leachate was adjusted with 6 N NaOH and 6 N H_2SO_4 before experiments. 100 mL of

Table 1
Results of the preliminary studies

pH	Reaction time (min)	Coagulant dose	% COD removal by alum coagulation	% COD removal by PAC coagulation
3	30	1 g/L	26.8	25.7
8.09	30	1 g/L	45.4	36.2
11	30	1 g/L	28.2	27.2
8.09	30	0.1 g/L	17.6	14.3
8.09	30	5 g/L	58.8	50.5
8.09	30	10 g/L	64.4	55.8

leachate samples were put into 250 mL beakers and placed into the Jar-test apparatus. A predetermined amount of coagulant was added and the first stirring was made at 200 rpm for 2 min, then the slow mixing was performed at 45 rpm for the times specified in the experimental design matrix. After the reaction time was completed, the mixing process was terminated and the beakers from the Jar-test were taken and it kept for 30 min for the precipitation process. The amount of sludge accumulated at the bottom at the end of 30 min was recorded. Approximately 50 mL of wastewater samples collected on the surface were taken and centrifuged at 40,000 rpm for 4 min, then the supernatant was diluted in the required amount, and COD and UV_{254} analyzes were performed.

2.3. Experimental design matrix

The coagulation process was modeled using the BBD, one of the response surface method designs. Among all response surface methods, when the Box–Behnken experimental design is applied, the number of experiments required is less [16,17]. The response surface method allows designing experiments, modeling data, evaluating the parameters that affect the process, and determining the optimum conditions for the responses [18]. The BBD allows the interactive effects of the parameters to be determined and the level of effect to be measured [19]. Eq. (3) shows the relationship between responses and process parameters.

$$M = f\left(x_1, x_2, \ldots, x_k\right) \pm \delta \tag{3}$$

where M is the system response, x_1, x_2, … x_k are the variables, f is the response function, and δ is the statistical error.

To optimize the coagulation process, the response surface regression analysis was applied and the quadratic equation model was used. The quadratic equation model is shown in Eq. (4).

$$M = \omega_0 + \sum_{i=1}^{k} \omega_i x_i + \sum_{i=1}^{k} \omega_{ii} x_i^2 + \sum\sum_{i<j} \omega_{ij} x_i x_j + \delta_r \tag{4}$$

In this equation, M is the response, x_i is the coded levels of variables, ω_0 is the model constant, ω_{ii} (i = 1, 2, … k) and ω_{ij} (i = 1, 2, … k; j = 1, 2, … k) are interactive coefficients, k is the number of factors or parameters, and δ_r is the statistical error.

Coagulant dose, initial pH, and reaction time, which are the operating parameters of the coagulation process were selected as independent variables while COD and UV_{254} removal efficiencies were the model responses. Process independent variables and levels are given in Table 2.

2.4. Experimental procedure of microwave/persulfate process

Microwave activated persulfate oxidation (MW/PS) was studied with 100 mL of pre-coagulated leachate sample. 100 mL sample was taken in a 250 mL graduated flask and studies were carried out at different initial pH values to determine the effect of pH. After determining the optimum initial pH value, optimum MW power, persulfate dose, and reaction time values were determined respectively. The amount of oxidant determined by preliminary studies was dosed and the flask was placed in a domestic microwave device and the process was started. In the studies conducted against time, the oxidation time was selected based on the studies in the literature [20,21]. At the end of the period, samples taken from the microwave were first put into ice water to end the reaction. Then, COD and UV_{254} analyzes were conducted.

2.5. Energy consumption

One of the most important parameters when choosing the most suitable technology in wastewater treatment is the cost of the process [22]. The operation cost of the MW/PS process mainly arises from electricity consumption for MW irradiation. The energy costs consumed in the microwave process were calculated using Eq. (5) [23].

$$\mathrm{EC}\left(\mathrm{kWh/m^3}\right) = \frac{P \times \mathrm{time} \times 10^3}{\mathrm{volume} \times 60 \times \log\left(\frac{C_i}{C_f}\right)} \tag{5}$$

Table 2
Coded and actual values of experimental design matrix variables

Factors	Original factor	–1	0	+1
Coagulant dose, g/L	X_1	1	3	5
pH	X_2	6	8	10
Reaction time, min	X_3	15	30	45

In Eq. (5), EC is the energy consumption (kWh/m^3), P is the MW power (kW), C_i is the initial COD concentration, C_f is the final COD concentration.

3. Results and discussion

3.1. Coagulation of leachate with Alum and PAC

The BBD provides the development of mathematical equations in which each $Y = f(x)$ response is calculated by summing one constant, three first-order effects (A, B, C), three quadratic effects (A^2, B^2, C^2), and three interactive (AB, AC, BC) effects. The conformity of the experimental data to the polynomial model representing the COD and UV_{254} removal efficiencies (%) as a function of coagulant dose, initial pH, and reaction time were analyzed using the Design Expert 11.0.1.0 software and the model equations are given below.

Equations for alum:

$$\text{COD removal},\% = 46.27 + 1.78A + 7.47B + 1.35C + 0.7750AB + 0.1250AC + 0.5250BC - 7.47A^2 + 2.38B^2 + 3.23C^2 \quad (6)$$

$$UV_{254}\ \text{removal},\% = 37.30 + 15.57A + 18.08B + 2.62C + 2.42AB - 0.2750AC + 2.94BC + 13.52A^2 - 7.19B^2 + 4.45C^2 \quad (7)$$

Equations for PAC:

$$\text{COD removal},\% = 39.78 + 2.65A + 7.28B + 2.75C + 0.1422AB - 0.3389AC + 0.3041BC - 1.45A^2 - 1.23B^2 + 7.36C^2 \quad (8)$$

$$UV_{254}\ \text{removal},\% = 39.37 + 7.46A + 12.50B + 5.44C + 0.9608AB - 2.34AC + 2.68BC + 4.83A^2 - 10.38B^2 + 8.22C^2 \quad (9)$$

Experimental sets were carried out under different operating conditions determined by the model where the removal of COD and UV_{254} from leachate was investigated by the coagulation process in which alum and PAC were used as coagulants. The experimental design matrix consisting of 15 experimental sets and the pollutant removal efficiencies obtained as a result of the experimental study and estimated using the model are given in Table 3. It is clear from Table 3 that model estimates and experimental results are close to each other.

The results of quadratic response surface models are given in the form of Variance analysis for coagulation with alum and PAC in Tables 4 and 5, respectively. The significance level of both models and their suitability to experimental data were tested with ANOVA. The ANOVA results break down the total variation into two subcomponents: model-related variation and experimental error-related variation. By comparing these two variations, it is revealed whether the model is significant or not [24,25]. The F-value is used for this comparison. If the model's ability to predict experimental results is high, the F-value should be high and the corresponding p-value should be low. F-values are 5.59 and 22.56 for COD and UV_{254} removal in coagulation with alum, respectively while they are 5.78 and 33.10 for COD and UV_{254} removal in coagulation with PAC, respectively. The larger the F-value and the smaller p-value, the more significant the relevant coefficient [26]. Variables with p-values below 0.05 are expressed as significant, and variables with p-values below 0.0001 are expressed as highly significant for the process. Besides, if the lack of fit value is not significant, the model is interpreted as having high predictability. In both models, F-values were found to be high, p-values were less than 0.05, and lack of fit values was higher than 0.05 for both responses. Based on these data, both models can be interpreted as suitable to explain the experimental data.

On the COD removal efficiency in coagulation with alum, the coagulant dose among the linear parameters, and the pH among the quadratic parameters are significant, and the interactive parameters are not significant. The linear and quadratic parameters of pH and coagulant dose have a significant effect on UV_{254} removal efficiency. In coagulation with PAC, while the linear parameter of the coagulant dose and the quadratic parameter of the reaction time has a significant effect on the COD removal efficiency, all of the linear and quadratic parameters have a significant effect on the UV_{254} removal efficiency. Quadratic equations were revised by removing insignificant terms in Eqs. (10–13):

Equations for alum:

$$\text{COD removal},\% = 46.27 + 7.47B - 7.47A^2 \quad (10)$$

$$UV_{254}\ \text{removal},\% = 37.30 + 15.57A + 18.08B + 13.52A^2 - 7.19B^2 \quad (11)$$

Equations for PAC:

$$\text{COD removal},\% = 39.78 + 7.28B + 7.36C^2 \quad (12)$$

$$UV_{254}\ \text{removal},\% = 39.37 + 7.46A + 12.50B + 5.44C + 4.83A^2 - 10.38B^2 + 8.22C^2 \quad (13)$$

The accuracy of the model estimation is generally evaluated by the coefficient of determination (R^2). It is desired that the R^2-value of a model with good prediction ability should be close to one. However, the model estimation ability cannot be evaluated with the R^2-value alone since the R^2-value increases as the number of terms in the model increases, regardless of statistical significance. The R^2-value should be compared to the adjusted R^2-value reflecting the number of factors in the experiment [27]. Adjusted R^2-value decreases as the number of non-significant variables increases. The large difference between R^2 and adjusted R^2-values indicates that the model contains non-meaningful terms. The difference between estimated and actual values is expressed as the difference in terms and the difference values play an important role in the evaluation of model compatibility. The adjusted R^2-value increases as the number of independent variables that have a significant effect on the dependent variable increases and

Table 3
BBD matrix with experimental and predictive data obtained after coagulation

Run	Factor			Alum, %				PAC, %			
	A	*B*	*C*	Exp.COD	Pred.COD	Exp.UV_{254}	Pred.UV_{254}	Exp.COD	Pred.COD	Exp.UV_{254}	Pred.UV_{254}
1	6	1	30	29.4	32.7	16.6	12.4	24.8	27.3	16.7	14.8
2	10	1	30	32.7	34.7	40.9	38.7	29.9	32.3	30.0	27.8
3	6	5	30	48.1	46.1	41.5	43.7	43.9	41.6	35.6	37.9
4	10	5	30	54.5	51.2	75.5	79.7	49.6	47.2	52.8	54.7
5	6	3	15	40.9	39.0	37.6	36.8	39.1	39.9	38.1	37.2
6	10	3	15	42.9	42.3	71.3	68.5	44.9	45.9	57.4	56.7
7	6	3	45	40.9	41.5	39.8	42.6	47.1	46.1	52.1	52.7
8	10	3	45	43.4	45.3	72.4	73.2	51.6	50.7	62.0	62.9
9	8	1	15	45.0	43.6	11.8	16.8	38.9	35.6	19.1	21.9
10	8	5	15	53.6	57.5	48.5	47.1	49.3	50.7	42.8	41.6
11	8	1	45	49.1	45.2	14.8	16.2	43.1	41.7	26.2	27.5
12	8	5	45	59.8	61.2	63.2	58.2	52.3	55.6	60.6	57.8
13	8	3	30	45.4	46.3	38.7	37.3	42.8	39.8	37.3	39.4
14	8	3	30	48.2	46.3	39.8	37.3	39.9	39.8	39.5	39.4
15	8	3	30	45.2	46.3	33.4	37.3	36.5	39.8	41.2	39.4

the adjusted R^2-value decreases as the non-significant variables are added to the model. Besides, as the number of independent variables increases, the value of R^2 increases whether it is significant or not. Therefore, as the number of non-significant variables increases, the difference between the R^2-value and the adjusted R^2-value increases [28]. It can be seen from Tables 3 and 4 that the difference between R^2 and adjusted R^2-values obtained for all responses is low. The coefficient of variance (CV) is used to express the repeatability of the model. If the CV is below 10%, it means that the model is reproducible [28,29]. An adequate precision (AP) value is required to have a value above 4 for model suitability [29]. Both models have CV values below 10% and AP values above 4 for both responses (Tables 4–5).

Three-dimensional (3D) response surface graphs drawn as a function of two factors are used to understand the individual and interactive effects of the two factors desired to be monitored by keeping all other factors constant at certain values. 3D response surface graphs are based on model equations. Since the regression model has three independent variables, one variable is kept constant in the center, and the change in the response is determined by monitoring the other two variables within the specified range. Nonlinear 3D response surfaces indicate a significant interaction between each independent variable and the removal efficiency [30]. To better understand and interpret the obtained results, regression models were visualized as three-dimensional response surface graphs and 3-D graphs expressing COD and UV_{254} removal efficiencies are given in Figs. 1 and 2.

Although the coagulation process of the leachate is a highly variable application, the coagulant dose and pH are the most important parameters affecting the process efficiency [31,32]. In the coagulation process with alum, the removal efficiency increases as the pH increases in the range of pH 6–8, and removal efficiency in the range of 8–10 slightly decreases (Fig. 1). It is from Fig. 1 that seen that the maximum removal efficiency is obtained around pH 9. The obtained results are similar to those of Cheng et al. [32]. Fig. 1 shows that as the coagulant dose, which is another important parameter, increases, the removal efficiency increases in the coagulation process with alum. Besides, removal efficiencies in the process conducted with alum increase in direct proportion to the reaction time (Fig. 1). In the coagulation process with PAC, removal efficiencies do not change significantly with increasing pH (Fig. 2). When the coagulation dose is considered, it is seen that the removal efficiency increases as the dose increases. However, the effect of the coagulant dose is not as effective as in the alum process. To achieve maximum removal efficiencies the required coagulant dose is lower in PAC process than that of alum process similar to other studies [4,31]. Besides, the increase in reaction time also increases removal efficiencies in the coagulation process conducted with PAC (Fig. 2).

The graphs showing the compatibility of experimental values for both coagulants and the estimated values given by the regression equations obtained by the model are given in Fig. 3. The graphs were drawn using the values obtained with the help of the model versus the values obtained experimentally and they give the first-order line for both answers. R^2-values of the graphs obtained for COD and UV_{254} removal from leachate by the alum coagulation process were determined as 90.96% and 97.60%, respectively. R^2-values of the graphs obtained for COD and UV_{254} removal from leachate by the PAC coagulation process were determined as 91.24% and 98.35%, respectively. High R^2-values indicate that the experimental data are in agreement with the model results. It was observed that the estimated values obtained by the models are very close to the experimental values, thus the validity of the equations has been proved.

The adequacy of the models is evaluated with residual values in addition to the correlation coefficient. Residual value can be defined as the difference between estimated

Table 4
ANOVA results of coagulation process using alum

Source	Sum of squares	df	Mean Square	*F*-value	*P*-value	Remark
Model (COD)	777.04	9	86.34	5.59	0.0363	S
A-pH	25.21	1	25.21	1.63	0.2574	NS
B-Alum dose, g/L	447.01	1	447.01	28.95	0.0030	S
C-Reaction time, min	14.58	1	14.58	0.9444	0.3758	NS
AB	2.40	1	2.40	0.1556	0.7095	NS
AC	0.0625	1	0.0625	0.0040	0.9517	NS
BC	1.10	1	1.10	0.0714	0.8000	NS
A^2	206.08	1	206.08	13.35	0.0147	S
B^2	20.90	1	20.90	1.35	0.2971	NS
C^2	38.50	1	38.50	2.49	0.1751	NS
Residual	77.19	5	15.44			
Lack of fit	71.56	3	23.85	8.48	0.1073	NS
Pure error	5.63	2	2.81			
Cor. total	854.23	14				
R^2	0.9096					
Adjusted R^2	0.7470					
C.V. %	8.68					
A.P.	8.89					

Source	Sum of squares	df	Mean Square	*F*-value	*P*-value	Remark
Model (UV_{254})	5,655.80	9	628.42	22.56	0.0016	S
A-pH	1,939.71	1	1,939.71	69.64	0.0004	S
B-Alum dose, g/L	2,616.54	1	2,616.54	93.94	0.0002	S
C-Reaction time, min	54.86	1	54.86	1.97	0.2194	NS
AB	23.38	1	23.38	0.8393	0.4016	NS
AC	0.3025	1	0.3025	0.0109	0.9211	NS
BC	34.52	1	34.52	1.24	0.3163	NS
A^2	675.17	1	675.17	24.24	0.0044	S
B^2	190.88	1	190.88	6.85	0.0472	S
C^2	73.20	1	73.20	2.63	0.1659	NS
Residual	139.27	5	27.85			
Lack of fit	115.85	3	38.62	3.30	0.2413	NS
Pure error	23.42	2	11.71			
Cor. total	5,795.07	14				
R^2	0.9760					
Adjusted R^2	0.9327					
C.V. %	12.26					
A.P.	15.62					

values and experimentally obtained values. Residuals are a variation of the elements that cannot be explained by the model and are desired to conform to the normal distribution. Normal probability plots are the graphical method used to evaluate the normality of residuals. In Fig. 3, normal distribution graphs are given for two processes where alum and PAC are used as coagulants. As can be seen from Fig. 3, the residual values are randomly distributed in the lower and upper part of the normal distribution line and they are seen as points very close to the line.

To determine the optimum operating conditions that give the maximum COD removal, numerical optimization has been applied based on the response surface model, and the values obtained are given in Table 6. Optimum conditions for achieving maximum COD removal in alum coagulation are initial pH-value 9.70, coagulant dose 4.99 g/L, and reaction time as 45 min. Optimum conditions where maximum COD removal was achieved in coagulation with PAC were determined as pH-value 9.99, coagulant dose 4.10 g/L, and reaction time 44.8 min. In the coagulation process in which alum was added as a coagulant, the COD and UV_{254} removal efficiencies estimated by the model under optimum conditions were 58.1% and 83.2%, respectively. Experimental studies were carried out under optimum conditions to

Table 5
ANOVA results of coagulation process using PAC

Source	Sum of squares	df	Mean Square	*F*-value	*P*-value	Remark
Model (COD)	766.72	9	85.19	5.78	0.0338	S
A-pH	56.28	1	56.28	3.82	0.1080	NS
B-PAC dose, g/L	423.91	1	423.91	28.78	0.0030	S
C-Reaction time, min	60.50	1	60.50	4.11	0.0985	NS
AB	0.0809	1	0.0809	0.0055	0.9438	NS
AC	0.4594	1	0.4594	0.0312	0.8668	NS
BC	0.3700	1	0.3700	0.0251	0.8803	NS
A^2	7.73	1	7.73	0.5245	0.5014	NS
B^2	5.61	1	5.61	0.3807	0.5642	NS
C^2	199.87	1	199.87	13.57	0.0142	S
Residual	73.65	5	14.73			
Lack of fit	53.36	3	17.79	1.75	0.3832	NS
Pure error	20.29	2	10.14			
Cor. total	840.37	14				
R^2	0.9124					
Adjusted R^2	0.7546					
C.V. %	9.08					
A.P.	9.0368					
Source	Sum of squares	df	Mean square	*F*-value	*P*-value	Remark
Model (UV_{254})	2,779.74	9	308.86	33.10	0.0006	S
A-pH	445.44	1	445.44	47.73	0.0010	S
B-PAC dose, g/L	1,250.68	1	1,250.68	134.02	<0.0001	HS
C-Reaction time, min	237.05	1	237.05	25.40	0.0040	S
AB	3.69	1	3.69	0.3956	0.5570	NS
AC	21.94	1	21.94	2.35	0.1858	NS
BC	28.67	1	28.67	3.07	0.1400	NS
A^2	86.00	1	86.00	9.22	0.0289	S
B^2	397.74	1	397.74	42.62	0.0013	S
C^2	249.32	1	249.32	26.72	0.0036	S
Residual	46.66	5	9.33			
Lack of fit	39.03	3	13.01	3.41	0.2351	NS
Pure error	7.63	2	3.82			
Cor. total	2,826.40	14				
R^2	0.9835					
Adjusted R^2	0.9538					
C.V. %	7.49					
A.P.	19.3098					

verify the model fit, and COD and UV_{254} removal efficiencies were obtained as 56.9% and 82.2%, respectively. In the coagulation process where PAC is added as a coagulant, the estimated removal efficiencies were 54.1% and 68.4% for COD and UV_{254}, respectively, while the removal efficiencies obtained in validation experiments were 50.8% and 61.0% for COD and UV_{254}, respectively. These results show that estimated and actual removal efficiencies are close to each other.

When the experimental results of the coagulation process performed using two different coagulants were evaluated, it was determined that the removal efficiencies were very close to each other, however, the yields were slightly higher in the process using the alum process. The leachate was subjected to the coagulation process in which alum was used as a coagulant under optimum conditions, and the second stage of the study was initiated.

3.2. MW-activated PS oxidation of pre-coagulated leachate

Recently, the microwave method is widely used in wastewater treatment due to its rapid and selective heating mechanism. Hot zones occur around the materials especially organic matter that absorbs microwaves [33,34].

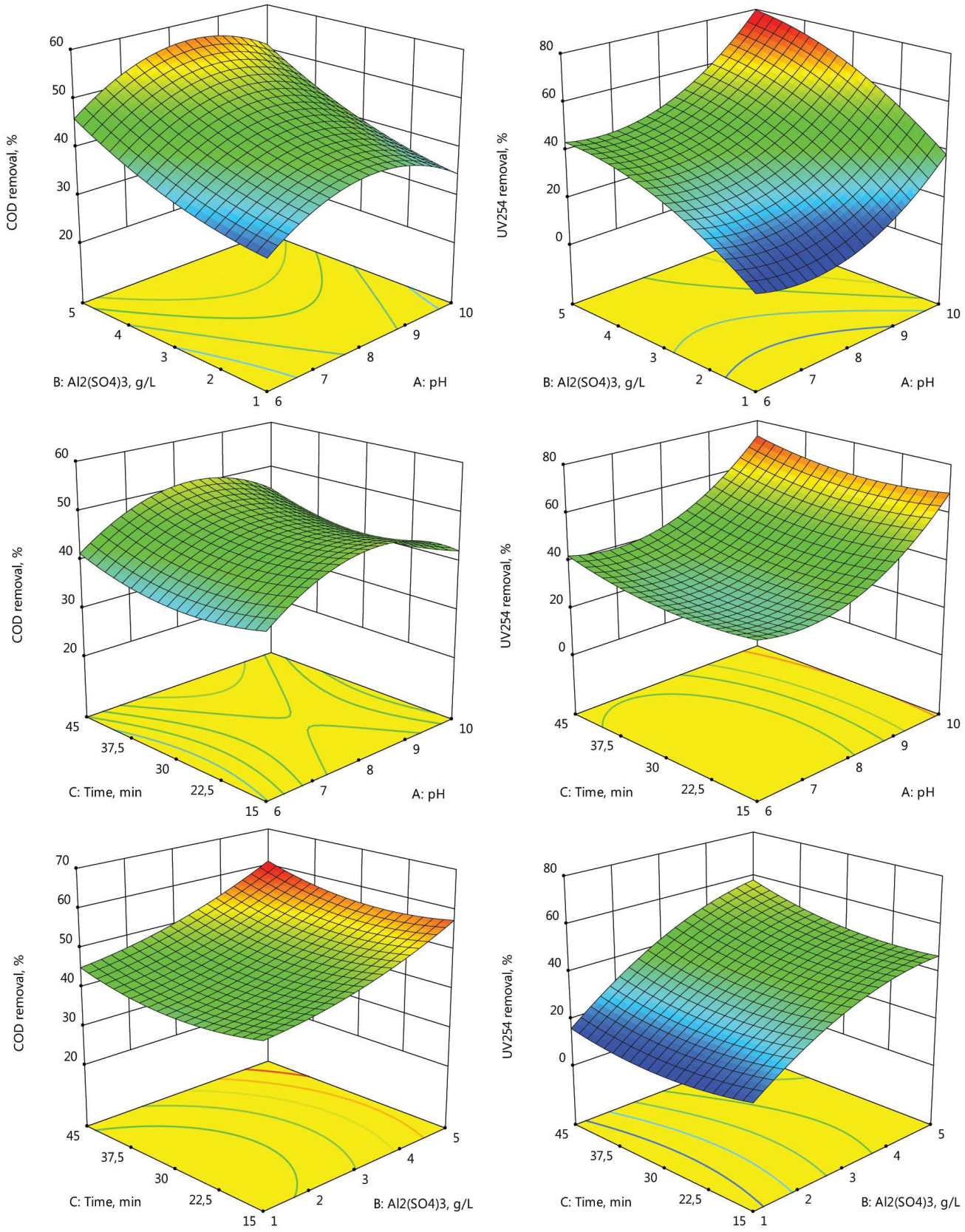

Fig. 1. 3-D plots showing the effects of alum dose, pH, and time for alum process.

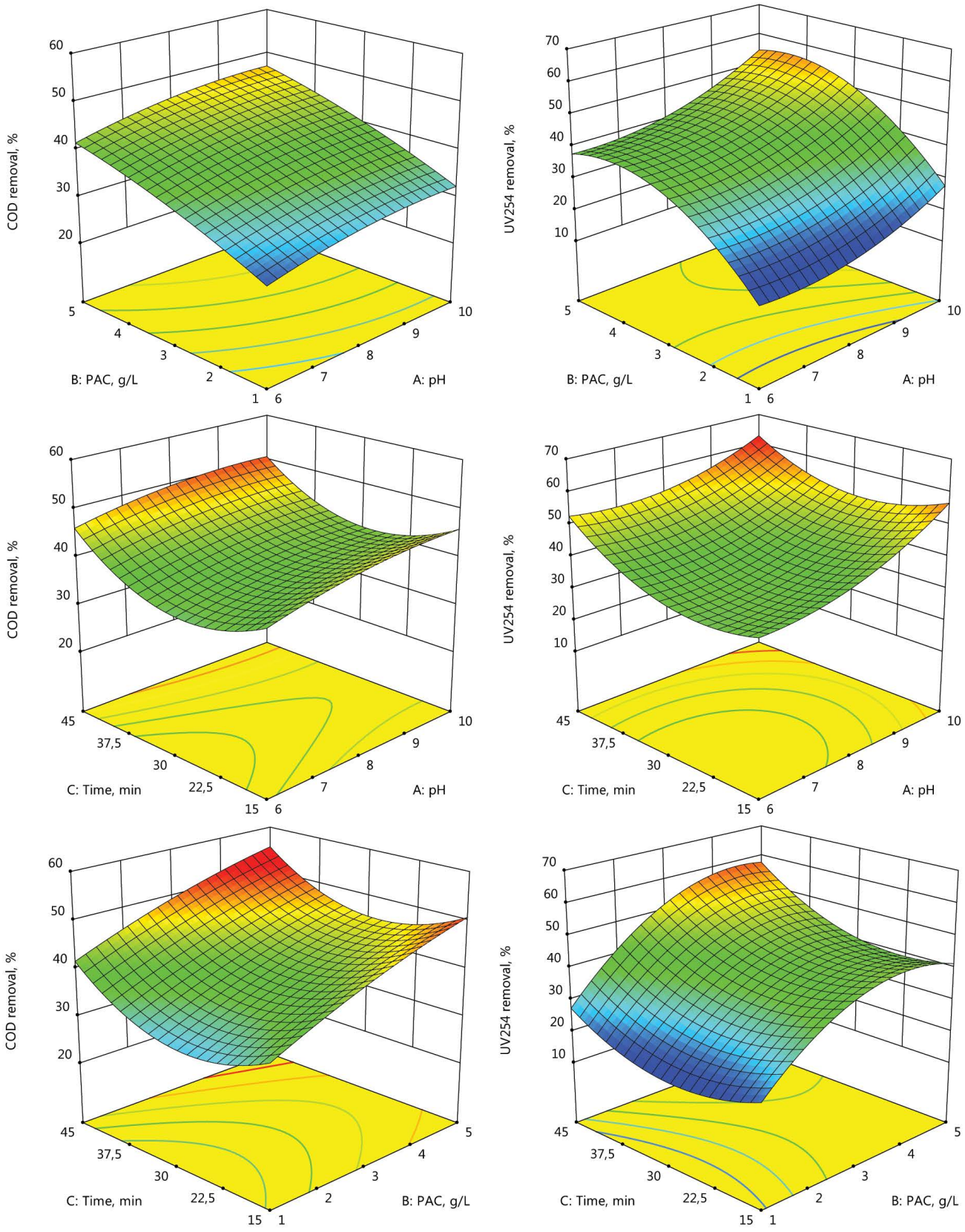

Fig. 2. 3-D plots showing the effects of PAC dose, pH, and time for PAC process.

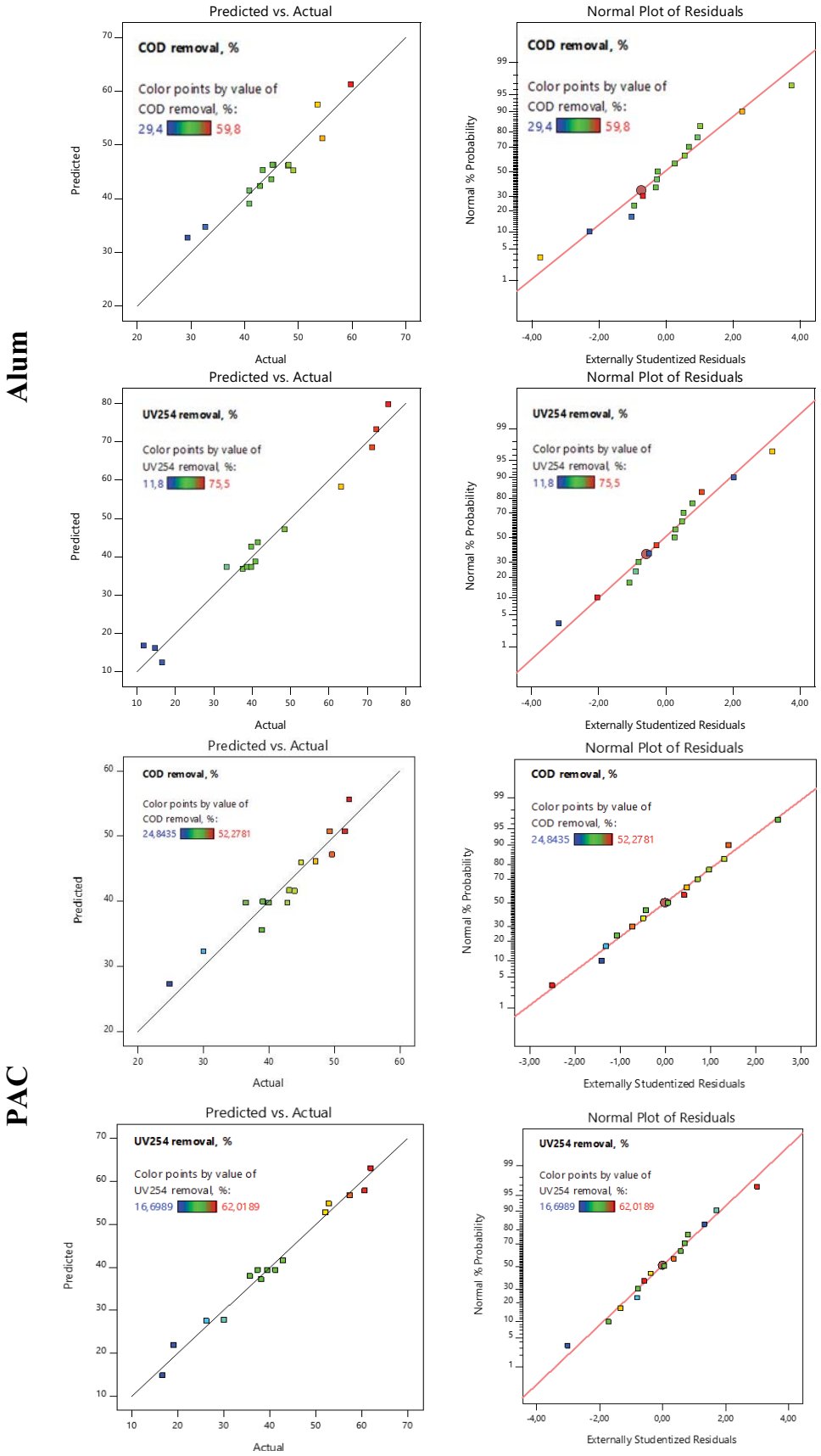

Fig. 3. Normal probability plots and predicted versus actual values plotting.

Table 6
Optimum results of alum and PAC coagulation processes

Parameters	Alum		PAC	
	COD	UV_{254}	COD	UV_{254}
Coagulant dose, g/L	4.99		4.10	
pH	9.70		9.99	
Reaction time, min	45.0		44.8	
Predicted removal efficiency, %	58.1	83.2	54.1	68.4
Experimental removal efficiency, %	56.9	82.2	50.8	61.0

Although microwave energy is not high (0.4–40 J/mol at the frequency of 1–100 GHz), it is used in applications based on thermal or non-thermal effects that increase reaction rate [33,34]. Free radicals are successfully obtained by combining microwave with other oxidation technologies [35]. Persulfate is effectively used as an oxidant in combined systems. Oxidation of organic matter by microwave-persulfate (MW/PS) mechanism is given in Eqs. (14–16). As microwaves reduce the activation energy of the reaction in combined systems, sulfate radicals are generated, and organic matter is oxidized. Moreover, hydroxyl radicals formed by microwave irradiation help the oxidation process.

$$S_2O_8^{2-} + \text{MW heat} \rightarrow 2SO_4^{\bullet -} \quad \left(E_a = 33.5 \text{ kcal/mol}\right) \tag{14}$$

$$SO_4^{\bullet -} + H_2O \rightarrow OH^{\bullet} + HSO_4^- \tag{15}$$

$$SO_4^{\bullet -} + \text{organics} \rightarrow \left(\text{radical formation}\right) \rightarrow CO_2 + H_2O + SO_4^{2-} \tag{16}$$

The activation energy of 140.2 kJ/mol is required for sulfate radical generation from persulfate [36]. In literature, it is reported that microwave irradiation increases the decomposition rate of persulfate by reducing activation energy, and thereby removal rate of organic matter increases [37–39]. Removal efficiencies obtained by the combined process were higher than those obtained by a single process were. COD and UV_{254} removal efficiencies were determined as 5.2% and 7.4%, respectively by the microwave process solely whereas COD and UV_{254} removal efficiencies were 7.2%, and 9.6%, respectively by persulfate oxidation. COD and UV_{254} removal efficiencies were 26.2% and 32.9%, respectively by the MW/PS combined process under the conditions of pH value of 3, PS dose of 3 g/L, MW power of 450 W and reaction time of 1.5 min. Organic contaminants existing in leachate are resistant contaminants having high thermal and chemical stability [40]. Since the MW energy is not sufficient to break chemical bonds of resistant organic compounds, removal efficiencies were found to be low. In the PS process, the adequate amount of sulfate radical is not generated without an activator and removal efficiencies were be found lower than that of the combined process.

To determine the effect of initial pH on removal of COD and UV_{254} from leachate, experiments were conducted at different pH values at the operational conditions of MW power 450 W, PS dose 3 g/L, and reaction time 1.5 min. Previous studies in the literature indicated that pH is effective on reactive oxygen species and the highest removal efficiencies were obtained at acidic conditions [41]. High concentrations of H^+ ions at low pH values reduce PS hydrolysis thereby PS amount activated by microwave irradiation increases. More reactive oxygen species form and removal efficiencies increase [Eqs. (17–19)].

$$H_2O + S_2O_8^{2-} \rightarrow 2HSO_4^- + 1/2O_2 \tag{17}$$

$$HSO_4^- \rightarrow SO_4^{2-} + H^+ \tag{18}$$

$$H_2O_2 \leftrightarrow H^+ + HO_2^- \tag{19}$$

In MW/PS process, sulfate radicals are dominant. At high pH values, sulfate radicals react with hydroxyl ions forming hydroxyl radicals. The rate of hydroxyl radicals in the total amount of radicals is higher in alkali conditions. Since the redox potential of hydroxyl radicals is low at alkali conditions, reaction rate and removal efficiencies are lower at alkali conditions. It can be seen from Fig. 4 that removal efficiencies were found to be higher at acidic conditions than alkali conditions. The highest COD and UV_{254} removal efficiencies were obtained at the pH value of 5.

In Fig. 4 the effect of MW power on contaminant removal is given. The MW power has a significant effect on COD and UV_{254} removal. COD removal efficiency increased from 11.1% to 38.3% and UV_{254} removal efficiency increased from 18.2% to 45.0% as MW power increased from 150 W to 750 W. The electronic vibration and the temperature of the system increase rapidly as MW power increases. Thereby, a higher amount of radical generation is observed by activation and a higher amount of organic matter is removed. Removal efficiencies increase as MW power increase from 150 W to 450 W while there is no significant difference was observed when MW power increases from 450 W to 750 W. Although removal rates were found to be a little higher at MW 600 W optimum MW power was determined as 450 W considering energy consumption and cost of the process.

To determine optimum PS dose, experimental studies were carried out at pH value of 5 and MW power of 450 W and PS doses in the range of 1–9 g/L. It can be seen from Fig. 4 that as PS dose increased to 5 g/L, COD and UV_{254} removal efficiencies increased, however, at higher doses removal efficiencies decreased. A higher amount of sulfate radicals is generated by microwave activation of higher doses of persulfate. However, the scavenging effect of sulfate radicals causes a decrease in removal rates [42]. The optimum PS dose was determined to be 5 g/L.

As optimum process conditions were determined as pH 5, PS dose 5 g/L, and MW power 450 W, finally the effect of reaction time on contaminant removal was evaluated. Removal rates increased while reaction time increased (Fig. 4). This can be attributed to the increase in temperature depending on the increase in reaction time. As the temperature increases, a higher amount of sulfate radicals were generated by activation of higher concentrations of persulfate by MW. Considering the cost of the process and energy consumption, the optimum reaction time was determined to be 3 min. At optimum conditions, COD and UV_{254}

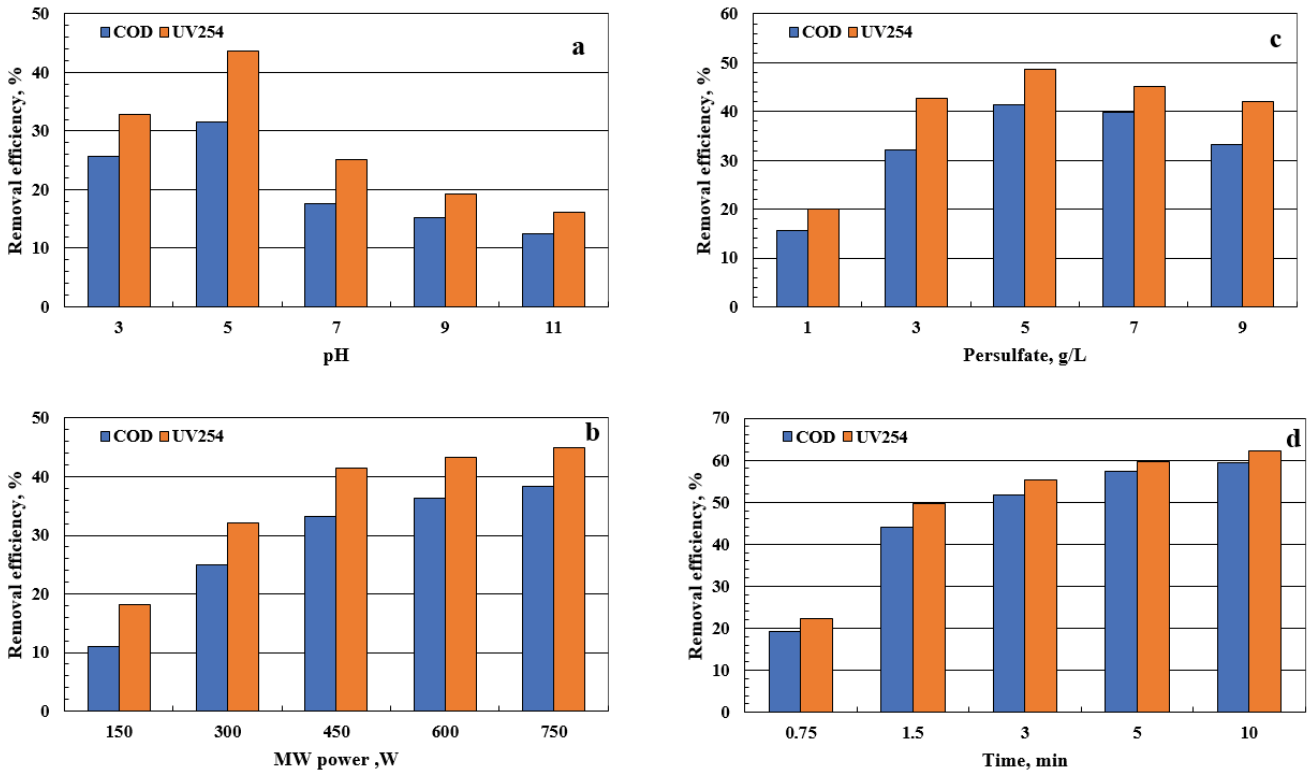

Fig. 4. MW/PS process (a) MW power = 450 W, PS dose = 3 g/L, and reaction time = 1.5 min, (b) pH = 5, PS dose = 3 g/L, and reaction time = 1.5 min, (c) pH = 5, MW power = 450 W, and reaction time = 1.5 min, (d) pH = 5, PS dose = 5 g/L, and MW power = 450 W.

removal efficiencies were obtained as 51.7% and 55.4%, respectively.

Performance of combined coagualtion-PS oxidation process is given in Table 7. Overall 79.2% COD and 92.1% UV_{254} removal efficiencies were obtained by application of combined process. It can be concluded that combined Alum coagulation-PS oxidation process is an effective alternative method for resistent organic mater removal from landfill leachate.

3.3. Energy consumption

The cost of the MW/PS process depends on the electrical energy consumption and the added oxidant dose. The graph regarding the electrical energy consumption, which is a function of the reaction time, is given in Fig. 4d. The amount of power consumed for unit volume of leachate treatment increases depending on the reaction time and COD removal efficiency. This means more energy consumption and operating cost. The electrical energy consumption varied in the range of 447.0–1915.8 kWh/m^3 in the different reaction time values. Chen et al. [43] applied microwave activated persulfate and peroxide oxidation for COD, $UV_{254,}$ and color number removal from mature leachate, and energy consumption of both processes was calculated at the end of the 16 min reaction time. As a result of the study, the energy consumption of microwave activated persulfate and peroxide oxidation processes was 1788.03 kWh/m^3 and 2139.45 kWh/m^3, respectively [43]. Tripathy and Kumar [20] investigated the performance of microwave activated single persulfate and peroxide process along with a binary process in which peroxide and persulfate were used together to remove COD from dinitrodiazophenol wastewater. Energy consumption of microwave activated persulfate oxidation was 1730.7 kWh/m^3 at the end of 10 min reaction time. In the study conducted by Wang et al. [20] microwave activated single persulfate and peroxide oxidation processes and the binary process using peroxide and persulfate together were applied in dinitrodiazophenol wastewater treatment and the energy consumption of the applied processes was calculated. Energy consumption of microwave activated persulfate and microwave activated peroxide processes was found to be much higher than the energy consumption of the binary process. Binary process energy consumption was determined as 1897.17 kWh/m^3 at the end of the 16-min reaction time [20]. In this study, the energy consumption value calculated after 3 min of reaction time in COD removal from leachate is 712 kWh/m^3 and this value is consistent with the values obtained in the studies in the literature.

4. Conclusion

In this study, a two-step treatment process was applied to remove COD and UV_{254} from leachate. In the first step, the leachate was subjected to the coagulation process in which alum and PAC were added as coagulants. The advanced oxidation step was started by selecting alum as a coagulant, which provides higher removal efficiency. In the second step, an advanced oxidation process in which persulfate

Table 7
Performances of alum coagulation and MW/PS oxidation processes

Parameter	Raw Leachate	Alum Coagulation	MW/PS oxidation	Combined process
COD, mg/L	13,059	5,629	2,719	2,719
COD removal, %	–	56.9	51.7	79.2
UV_{254}, mg/L	2,860	510	227.5	227.5
UV_{254} removal, %	–	82.2	55.4	92.1

was activated by microwave method was applied for leachate treatment. In the coagulation process, COD and UV_{254} removal efficiencies were evaluated as a function of the initial pH value, coagulant dose, and reaction time. Using the response surface method and BBD, the effects of independent variables (initial pH, coagulant dose, and reaction time) on the responses (COD and UV_{254} removal) and their interactions with each other were determined, and the operating conditions were optimized to achieve maximum pollutant removal efficiency. Under the optimum conditions determined by the model, the statistically obtained COD removal efficiency was 58.1%, and the experimental COD removal efficiency was 56.9%. In persulfate oxidation, the COD and UV_{254} removal efficiencies obtained under optimum conditions (microwave power 450 W, pH 5, persulfate dose 5 g/L, and 3 minutes reaction time) determined using the classical optimization method were 51.7% and 55.4%, respectively. The results of the study showed that with the destructive process applied after a separation process, it is possible to effectively treat the leachate with high resistant organic matter content.

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