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Final treatment of young, middle-aged, and stabilized leachates by Fenton process: optimization by response surface methodology

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ABSTRACT

In this study, Fenton's oxidation process was applied after electrodialysis (ED) with bipolar membrane system for the final treatment of the ED-treated young, middle-aged, and stabilized leachates. Response surface methodology (RSM) was applied to evaluate and optimize physical and oxidative performances of Fenton process on treatability of leachate. The interactive effects of four operating variables: H_2O_2/COD rate, H_2O_2/Fe^{2+} rate, initial pH, and reaction time were evaluated by RSM. Three dependent parameters such as COD, TOC, and color removal were measured as responses. The Fenton process was found to be successful to treat all ED-treated young, middle-aged, and stabilized landfill leachate. In terms of COD and TOC removals, the efficiency of Fenton's oxidation increased with increasing leachate age while color removal was found to be higher than 89% in all treated leachate samples. Fenton oxidation treatment enhanced the biodegradability of landfill leachates by 400, 100, and 44% for old, middle-aged, and young leachate, respectively. According to analysis of variances results, three proposed models could be used to navigate the design space with high regression coefficient R^2 varied from 0.86 to 0.99 for three types of leachates. The results of optimized parameters and laboratory studies imply that experimental study data agreed well with the model prediction data.

Keywords: Landfill leachates; Electrodialysis with bipolar membrane; Fenton oxidation; Response surface methodology; Optimization

1. Introduction

Landfills are widely used as a method of solid waste disposal. Landfill leachate, which is high-strength wastewater, is produced by physicochemical and biological decomposition of solid wastes and the percolation of rainwater through the solid waste layer [1]. The implementation of the most suitable technique for the treatment of leachate is directly governed by the characteristics of the leachate. Leachates from different landfills vary considerably in their chemical compositions due to factors such as the type of solid wastes deposited, hydrogeology of the landfill site, specific climate conditions, moisture routing through the landfill, landfill age as well as design and operation of the landfill [2]. Various physical, chemical, and

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biological treatment methods are used to remove organic (biodegradable and non-biodegradable carbon, humic acids, and fulvic acids) and inorganic (heavy metals, sodium, calcium, sulfate, ammonia, and high concentration of toxics) pollutants in the landfill leachates [3].

To reduce the negative impacts of discharged leachate on the environment, several techniques have been used, including aerobic and anaerobic biological treatment [4–7], chemical and electrochemical oxidation processes [8,9], chemical precipitation [10], adsorption using various adsorbents [11,12], ion exchange [13,14], reverse osmosis [15], coagulation–flocculation [2,16], and membrane processes [17]. Biological treatment processes are effective for young or freshly produced leachate, but they might be ineffective for middle-aged and stabilized leachates. In contrast, physical–chemical methods, which are not favored for young leachate treatment, are recommended for the detoxification of older leachate [2]. Electrodialysis with bipolar membranes (EDBM) has become a technology of growing importance and a highly competitive alternative, especially for the recovery purpose and treatment of the landfill leachate containing complex pollutants [18–22].

Recently, growing interests have been focused on Fenton treatment of landfill leachate as a post-treatment step commonly [23–25]. As one of the advanced oxidation processes (AOPs), Fenton process can achieve two alternative goals exploiting the strong oxidation potential of hydroxyl radicals ($^{\bullet}OH$): first is the reduction of the chemical oxygen demand (COD) content of wastewater up to the desired maximum allowable concentration value through the mineralization of recalcitrant pollutants; the second is the enhancement of the biodegradability of treated effluents to make their subsequent biological treatment possible [26–28]. In the Fenton process, iron and hydrogen peroxide are two major chemicals that determine operating cost and treatment efficiency [24,29]. During the Fenton reaction, hydrogen peroxide is catalyzed by ferrous ions to produce $^{\bullet}OH$ for degradation of refractory organic matters in the landfill leachate [30]. The success of this process is affected by several parameters, such as chemical dosages, strength of the leachate, and reaction pH [24]. A treatment system containing Fenton process may consist of following stages: pH adjustment, oxidation reaction, neutralization, coagulation, and settlement [26]. Considering results of the above-mentioned studies on the post-treatability of the landfill leachate, in the experimental part of this study, the Fenton's oxidation process is conducted as an effective alternative to improve biodegradability of the EDBM effluent, as well as to remove residual COD, TOC, and color from the EDBM treated landfill leachate.

The Fenton process for the treatment of landfill leachate must be optimized in terms of cost and overall performance. However, many parameters, such as chemical dosages, strength of the leachate, and pH may influence the performance of the Fenton process. In order to better design the process, major factors that can affect the performance and the economy of the Fenton process must be thoroughly investigated and the optimal conditions are established. Generally, there are two approaches available for process optimization: one factor- at-a-time screening and two-level factorial design [31].

The traditional one-factor-at-a-time approach has been widely used in process optimization. Experimental factors are varied one at a time, with the remaining factors being held at constant. This method estimates the effects of a single variable on a particular process while keeping all other variables at a fixed condition. However, for such a technique to have general relevance, it is necessary to assume that the effect exhibited by the variable in question would remain unchanged in the presence of other variables. Certainly, there remains high degree of uncertainty regarding this assumption. Alternatively, other approach such as factorial design may have better reliability. For example, technique such as two-level factorial design can be used to overcome the problem of intervariable interaction [32]. There are a few advantages in two-level factorial design over the one-factor-at-a-time method [31,32]. Response surface methodology (RSM) is multivariate technique which mathematically fits the experimental domain studied in the theoretical design through a response function [33]. Thus, it is proposed to solve above-mentioned problems of other techniques [24,34–36]. RSM application to the treatment of landfill leachate was few. The main types of RSM designs include three-level factorial design, central composite design (CCD), Box–Behnken design, and D-optimal design [34,35,37,38]. In the water treatment field, the application of RSM to optimize the Fenton process for the leachate treatment was reported in many studies [1,29,30,39–42]. Nevertheless, in the area of post-treatment of young, middle-aged, and stabilized leachate, few studies were reported on the application of RSM to optimize the operating conditions of Fenton process using hydrogen peroxide and ferric sulfate with respect to the simultaneous removal of COD, TOC, and color.

Considering the above-mentioned studies, the main objectives of the study were aimed (i) to apply the Fenton's oxidation process to improve biodegradability of the EDBM effluent, as well as to remove refractory organics from the electrodialysis (ED)-treated leachates, (ii) to investigate the effects of variables on the performance of Fenton process, and (iii) to use RSM to design Fenton's process for a cost effective treatment of ED-treated leachates [43].

2. Materials and methods

2.1. Characterization of site and leachates

Daily, 2000 m^3/day of landfill leachate is produced for each day at the Odayeri Sanitary Landfill site which has been in operation since 1995 in Istanbul. Leachate is collected in equalization tanks and it is processed by biological treatment units (MBR) and NF membrane systems. Cross-flow ultrafiltration (UF) membranes are used as external MBR. MBR system is operated with anoxic and aerobic process to remove carbon and nitrogen [44].

Leachate samples (young, middle-aged, and stabilized) were taken with polyethylene bottles from the predetermined points of Odayeri Sanitary Landfill. Collected samples were stored in the refrigerator at 4˚C before the experimental studies. Characteristics of raw landfill leachates and EDBM treated leachates are given in Table 1.

It is commonly known that organics in the landfill leachate are characterized by their biodegradability as a measure of BOD_5/COD ratio. As seen in Table 1, BOD_5/COD ratios were 0.676, 0.51, and 0.124, respectively, for young, middle-aged, and stabilized leachates. The present BOD_5/COD ratio obtained for the young leachate was found to be similar or slightly higher than those reported by other researchers [45–47]. For the stabilized leachate, BOD_5/COD ratio accounted for 0.124 indicating a significant amount of biologically inert material. The BOD_5/COD ratio at the level of 0.1 was found to be lower than those reported for leachates from some aged landfill sites [48,49].

TOC/COD ranges of young, middle-aged, and stabilized were 0.33, 0.24, and 0.81, respectively, indicating that the COD contribution of non-carbon reduction substances increased over time in the leachate. The decrease of TOC in leachate might result from anaerobic degradation during the landfill stabilization process [50]. Ammonia nitrogen of young, middle-aged, and stabilized leachate were determined as 2,295, 2,910, and 3,865 mg/L, respectively. The higher concentration of ammonia nitrogen in the stabilized leachate may be attributed to the hydrolysis and fermentation of the nitrogenous fractions of biodegradable substrates [51]. Based on the experimental ranges given in Table 1, the present characteristics indicated that collected samples showed typical characteristics of raw landfill leachates [29].

2.2. Experimental setup and operation

The young, middle-aged, and stabilized leachates were first pretreated by using UF membrane and five-stage ion exchanger. Each ion exchanger used in the pretreatment process had a working volume of 535 mL and a density of 0.7 kg/L. The UF membrane was used to remove larger molecular weight components of leachates that may tend to foul EDBM membranes. Moreover, with the decrease of cationic species such as calcium and magnesium, EDBM process could be operated for longer time without any fouling problem in the membranes. The ED cell used in this study was the PCCell ED 64-4 Cell unit (PCCell Gmbh, Germany). Characteristics of EDBM treated landfill leachates are presented in Table 1.

Table 1
Characteristics of raw and EDBM treated leachates used in the experimental study

	Raw leachates			EDBM-treated leachates		
Parameter	Young	Middle-aged	Stabilized	Young	Middle-aged	Stabilized
COD (mg/L)	17,760 ± 55	14,400 ± 55	3,550 ± 25	6,400 ± 5	5,100 ± 20	2,500 ± 60
TOC (mg/L)	5,895 ± 50	3,530 ± 15	2,880 ± 5	1815 ± 5	1,660 ± 10	920 ± 5
BOD_5 (mg/L)	12,000 ± 500	7,350 ± 750	440 ± 40	3,000 ± 200	1,600 ± 400	165 ± 35
BOD_5/COD ratio	0.676	0.510	0.124	0.469	0.314	0.066
TKN (mg/L)	2,580 ± 10	3,110 ± 15	3,980 ± 20	275 ± 15	370 ± 5	285 ± 30
NH_3-N (mg/L)	2,295 ± 15	2,910 ± 15	3,865 ± 15	170 ± 2	215 ± 5	130 ± 15
TP (mg/L)	20 ± 2	24 ± 5	23 ± 3	6.9 ± 1	4.7 ± 1.5	9.1 ± 1
PO_4-P (mg/L)	9.80 ± 1,5	4.10 ± 2.5	4.90 ± 1.5	1.6 ± 1	1.3 ± 1	1.6 ± 1
pH (20˚C)	8.07 ± 0.05	8.05 ± 0.03	8.44 ± 0.09	5.73 ± 0.07	7.12 ± 0.05	7.52 ± 0.08
E.C. (μS/cm) (20 ˚C)	31,100 ± 70	39,800 ± 50	38,700 ± 20	2,295 ± 55	2,550 ± 15	2,150 ± 5

Following the pretreatment steps, EDBM treated leachate samples were transferred into the Fenton's oxidation unit used as the post-treatment process to improve the quality of the final discharge. In the Fenton's oxidation process, a stock solution of 10 g/L of Fe^{2+} was prepared by dissolving $FeSO_4 \cdot 7H_2O$ (Merck, Germany) in distilled water. In addition to iron sulfate reagent, 30% H_2O_2 solution having a density of 1.11 kg/L (Merck, Germany) was used in the oxidation process. In each oxidation test, 200 mL of EDBM treated leachate sample was collected from the EDBM effluent. In the first step of Fenton's oxidation process, the pH of the EDBM effluent leachate was adjusted to desired value by the addition of 6 N H_2SO_4 and 6 N NaOH. During the whole oxidation process, the pH of samples was also set at desired value by adding these reagents (6 N H_2SO_4 and 6 N NaOH) gradually in addition to preadjustment of the pH. The $FeSO_4 \cdot 7H_2O$ and H_2O_2 solutions were then added to the effluent sample and conducted for 5 min of rapid mixing at 200 rpm using a Jar Test Equipment (Velp Scientifica, JLT6). In each experimental run, the effluent sample was then gently stirred at 20 rpm for reaction times specified between 30 and 150 min [52].

Preliminary tests demonstrated that when the pH of samples from flocculation process was increased, the quantity of flocs diminished and settling process was failed. For this reason, additional experiments were performed to explore the optimal pH value to be considered in the settling process. Based on the additional physicochemical analyses, the optimal pH was found as 4.0 for the best precipitation (Fig. 1). Therefore, in order to prevent interferences in analytical measurements, the pH of sample was increased up to about 4.0 by adding 6 N NaOH gradually to precipitate residual Fe^{2+} ions. After the pH adjustment, the sample was transferred to a graduated settling column

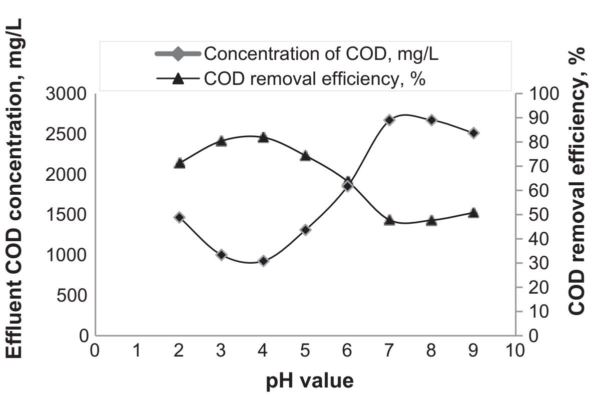

Fig. 1. The results of the experiment for the determination of the pH value for precipitation.

for 60 min of quiescent settling. About 100 mL of supernatant sample was then collected for COD, TOC, and color analyses after the settling process. Finally, to eliminate the effect of residual on COD measurement, the pH of supernatant samples was adjusted to 10 and mixed at 70˚C for 10 min to remove residual H_2O_2 rapidly [40]. Residual H_2O_2 in the treated samples was followed as described in the literatüre [50,53]. According to the method, a sample is acidified with sulfuric acid and titrated with a standardized potassium permanganate solution. H_2O_2 measurements were conducted until all H_2O_2 were consumed in the supernatant samples [53,54].

2.3. Experimental design and analysis

In this study, the CCD was used to create experiment sets, and RSM was applied to optimize the four independent operating variables: H_2O_2/COD rate, H_2O_2/Fe^{2+} rate, pH, and reaction time. Statgraphic Centurion IVI.I was used for the statistical design of experiments and data analysis.

The level of the independent variables are listed in Table 2 and the coded values of the factors together with three dependent responses (COD, TOC and color removal efficiency) for CCD are presented in Table 3.

The results were completely analyzed by analysis of variance (ANOVA) in the Statgraphic Centurion IVI.I. Model terms were evaluated by the *p*-value (probability) with 95% confidence level. The quality of the fit polynomial model was expressed by the coefficient of determination R^2 and Adj R^2, and its statistical significance was checked by the Fisher's *F*-test in the same program. Three-dimensional (3D) plots with the respective contour plots were obtained from the results of the experiments. From these, the effects of interaction between the two factors on responses were studied.

2.4. Analytical methods

The pH of leachate samples were measured by a pH meter (WTW series pH 720) and a pH probe (WTW, pH-Electrode Sentix 41). Color of wastewater samples were measured with a Hach Lange spectrophotometer (model: DR 5000). Electrical conductivity was measured by using a multimeter instrument (Hach Lange HQ 40D). TOC was measured by using Hach Lange IL 550 TOC/TN analyzer. All other experimental analyses were performed by the procedures described in the standard methods [55]: 5220 C (closed reflux-titrimetric method for COD), 5210 B (five-day BOD test for BOD_5), 4500-NH_3 C (titrimetric

Table 2
Experimental levels of independent variables

Factor	Factor level				
	Lowest −2	Low −1	Center 0	High +1	Highest +2
H_2O_2/COD rate (X_1)	0.2	0.4	0.6	0.8	1.0
H_2O_2/Fe^{+2} rate (X_2)	5	10	15	20	25
pH (X_3)	2.0	2.5	3.0	3.5	4.0
Reaction time (X_4)	30	60	90	120	150

Table 3
CCD for the study of four experimental variables for Fenton process and obtained results

	Independent variables				Responses (removal efficiency %) for young leachate samples				Responses (removal efficiency %) for middle-aged leachate samples				Responses (removal efficiency %) for stabilized leachate samples			
	X_1	X_2	X_3	X_4	COD	TOC	NH_3-N	Color	COD	TOC	NH_3-N	Color	COD	TOC	NH_3-N	Color
1	+1	+1	+1	+1	39	18	40	90	82	77	32	97	37	38	54	79
2	+1	−1	+1	+1	52	35	45	97	86	81	31	96	73	70	57	98
3	−1	+1	+1	+1	35	12	52	80	64	60	31	83	7	6	59	21
4	−1	−1	+1	+1	47	28	52	92	74	71	34	88	36	38	58	73
5	+1	+1	+1	−1	45	30	50	95	82	76	30	97	33	41	50	82
6	+1	−1	+1	−1	51	34	49	95	85	82	27	93	73	69	57	98
7	−1	+1	+1	−1	35	15	53	83	62	58	30	74	7	6	57	21
8	−1	−1	+1	−1	47	32	55	90	76	72	33	92	38	39	59	74
9	+1	+1	−1	+1	46	27	44	87	83	74	28	97	43	43	52	83
10	+1	−1	−1	+1	54	37	47	94	80	70	19	85	73	66	48	95
11	−1	+1	−1	+1	36	11	45	84	70	62	27	92	15	20	59	43
12	−1	−1	−1	+1	45	26	50	88	73	64	29	89	40	42	48	75
13	+1	+1	−1	−1	47	28	53	92	83	73	29	96	37	44	44	83
14	+1	−1	−1	−1	54	37	55	94	80	71	26	90	73	67	44	97
15	−1	+1	−1	−1	37	14	51	83	73	62	34	95	15	23	53	46
16	−1	−1	−1	−1	45	28	52	88	77	69	37	91	37	42	50	77
17	0	0	+2	0	47	28	52	94	63	72	37	92	20	12	57	37
18	0	0	−2	0	44	22	51	90	70	70	34	92	43	43	44	85
19	0	0	0	+2	42	23	42	94	82	74	28	96	40	41	52	85
20	0	0	0	−2	45	28	53	95	83	75	30	95	37	39	44	82
21	+2	0	0	0	47	32	49	90	87	78	27	94	64	61	47	97
22	−2	0	0	0	29	8	55	74	59	56	34	77	2	1	55	14
23	0	+2	0	0	36	14	48	86	75	68	30	94	15	16	57	47
24	0	−2	0	0	54	38	53	97	85	77	27	89	79	75	57	95
25	0	0	0	0	45	25	49	94	80	76	29	96	46	46	36	88
26	0	0	0	0	43	24	50	95	81	71	30	93	46	45	35	86
27	0	0	0	0	45	26	49	94	80	72	30	93	48	45	35	86
28	0	0	0	0	45	25	49	94	80	72	31	93	46	44	35	86
29	0	0	0	0	45	26	49	94	79	69	30	91	46	44	36	87
30	0	0	0	0	45	26	50	95	79	72	30	93	46	45	35	86

method for NH_3), 4500-Norg B (macro-Kjeldahl method for total Kjeldahl nitrogen), 4500-P D (stannous chloride method for orthophosphate), 4500-P (sulfuric acid–nitric acid digestion method for total phosphorus), and 2540 D (for total suspended solids).

3. Results and discussion

3.1. Statistical analysis

ANOVA was used to for graphical analysis of the data to find the interaction between the process variables and the responses. The main indicators demonstrating the significance and adequacy of the used model are: the model *F*-value (Fisher variation ratio), probability value (ProbNF), and adequate precision. *F*-test was used to check the statistical significance of the fit polynomial model while model terms were estimated based on probability (*p*-value) with 95% confidence level [3,56].

The relationship between the four variables (H_2O_2/COD rate, H_2O_2/Fe^{2+} rate, pH, and time) and the three important process responses (COD, TOC, and color removal efficiency) for the Fenton process was analyzed using RSM. Significant model terms are desired to obtain a good fit in a particular model. The CCD shown in Table 3 allowed the development of mathematical equations where predicted results (Y) were assessed as a function of H_2O_2/COD rate (X_1), H_2O_2/Fe^{2+} rate (X_2), pH (X_3), and reaction time (X_4) and calculated. The results obtained were then analyzed by ANOVA to assess the "goodness of fit." Equations from the first ANOVA analysis were modified by eliminating the terms found statistically insignificant. Table 4 illustrates the reduced quadratic models in terms of coded factors and also shows other statistical parameters. Data given in this table demonstrates that all the models were significant at the 5% confidence level since p values were less than 0.05.

The R^2 coefficient gives the proportion of the total variation in the response predicted by the model, indicating ratio of sum of squares due to regression to total sum of squares. A high R^2 value, close to 1, is desirable and a reasonable agreement with adjusted R^2 is necessary [55,56]. A high R^2 coefficient ensures a satisfactory adjustment of the quadratic model to the experimental data. The value of the coefficient of correlation (R^2) also suggests that the model is significant with R^2 greater than 0.86. The statistical significance of the model was confirmed by the determination coefficients of the model (R^2 values were determined to be 0.86, 0.96, and 0.90, respectively for COD, TOC, and color removal for young leachate, 0.87, 0.92, and 0.97 for middle-aged leachate and 0.99, 0.97, and 0.96 for stabilized leachate). Joglekar and May suggested that R^2 should be at least 0.80 for a good fit of a model [56].

Diagnostic plots such as the predicted vs. actual values (Fig. 2) help us judge the model satisfactoriness. The predicted vs. actual values plots of parameters removal are presented in Fig. 2 for young, middle-aged, and stabilized leachate, respectively. These plots indicate an adequate agreement between real data and the ones obtained from the models. This illustrated that the prediction of experimental data is quite satisfactory.

3.2. Process analysis

Referring to the Fenton process, it is well known that higher hydrogen peroxide to substrate ratios result in more extensive substrate degradation, while higher concentrations of iron ions yield faster rates. However, in order to maximize the effectiveness of the process, it is preliminarily necessary to determine the optimal operational H_2O_2/Fe^{2+} mass ratio. According to previous studies, all the experiments were carried out fixing a reaction time of 2 h and an initial pH of 3.0 [57]. The contribution of coagulation has not been well recognized, but relative importance of oxidation and coagulation depends primarily on the Fe^{2+}/H_2O_2 ratio. Chemical coagulation predominates at higher ratios, whereas chemical oxidation is dominant at lower Fe^{2+}/H_2O_2 ratio [28].

In the process, Fe^{2+} ions set as $Fe(OH)_2$ ($Ksp = 1.8 \times 10^{-15}$) and the color of the sludge is green [58]. In this case, the color of the sludge was green. Fe^{2+} is oxidized to Fe^{3+}, and the ions set as $Fe(OH)_3$ ($Ksp = 6.0 \times 10^{-38}$) and the color of the settled sludge is brown [58]. In this case, the color of the settled sludge was brown. Due the fact that solubility product of both $Fe(OH)_2$ and $Fe(OH)_3$ are very low in supernatant solutions, total Fe is lower than measurable concentrations. Thus in this study, total Fe was not determined in the supernatant of the Fenton experiments.

Table 3 and Figs. 3–5 show the performance of Fenton's oxidation under various conditions to remove COD, TOC, and color from pretreated young, middle-aged, and stabilized leachate.

The overall COD removal efficiency experiencing strong reductions as initial pH was set out of the interval, which was in accord with the optimal pH value reported for Fenton treatment of landfill leachate range between 2.0 and 4.5. A pH below optimal can inhibit oxidation reaction because at extremely low pH values, the $[Fe(H_2O)]^{2+}$ formed reacts relatively slowly with H_2O_2, less $^{\bullet}OH$ radical production resulting in the reduction of COD removal [23].

As illustrated in Figs. 3–5, the 3D surface plots for young, middle-aged, and stabilized leachate are approximately symmetrical in shape with circular contours, respectively. Because it was similar to the 3D graphics for COD and TOC, graphics for TOC was omitted here. All response plots show clear peaks, which indicate that the optimum conditions for maximum values of the responses are determined by dose and initial pH inside the design boundary. Analysis of the results show that removal percentage increased with hydrogen peroxide and Fe^{2+}. This is due to the oxidation and reduction reactions.

Table 4
ANOVA results for the four responses for young, middle-aged, and stabilized leachate

			Degree of freedom	Sum of square	Mean square	F	Significance F
Young leachate	COD	Regression	14	975.4915	69.67797	7.640393	0.000172
		Residues	15	136.7953	9.119684		
		Total	29	1112.287			
		$R^2 = 0.877014$, Adj. $R^2 = 0.762228$, Standard error = 3.019881					
	TOC	Regression	14	1960.022	140.0016	13.98831	3.82E-06
		Residues	15	150.1271	10.00847		
		Total	29	2110.149			
		$R^2 = 0.928855$, Adj. $R^2 = 0.862453$, Standard error = 3.163617					
	Color	Regression	14	840.1114	60.00796	43.67043	1.41E-09
		Residues	15	20.61165	1.37411		
		Total	29	860.7231			
		$R^2 = 0.976053$, Adj. $R^2 = 0.953703$, Standard error = 1.172224					
Middle-aged leachate	COD	Regression	14	1883.709	134.5507	6.591151	0.000407
		Residues	15	306.2075	20.41384		
		Total	29	2189.917			
		$R^2 = 0.860174$, Adj. $R^2 = 0.72967$, Standard error = 4.518167					
	TOC	Regression	14	1124.338	80.30985	26.35639	5.08E-08
		Residues	15	45.7061	3.047073		
		Total	29	1170.044			
		$R^2 = 0.960936$, Adj. $R^2 = 0.924477$, Standard error = 1.745587					
	Color	Regression	14	773.6393	55.25995	10.05329	3.21E-05
		Residues	15	82.45052	5.496701		
		Total	29	856.0898			
		$R^2 = 0.903689$, Adj. $R^2 = 0.8138$, Standard error = 2.344504					
Stabilized (old) leachate	COD	Regression	14	12453.05	889.5037	101.5762	2.98E-12
		Residues	15	131.3552	8.757012		
		Total	29	12584.41			
		$R^2 = 0.989562$, Adj. $R^2 = 0.97982$, Standard error = 2.959225					
	TOC	Regression	14	10594.52	756.7513	36.61099	4.97E-09
		Residues	15	310.0509	20.67006		
		Total	29	10904.57			
		$R^2 = 0.971567$, Adj. $R^2 = 0.945029$, Standard error = 4.546433					
	Color	Regression	14	17,085	1220.357	28.42994	2.99E-08
		Residues	15	643.8763	42.92509		
		Total	29	17728.88			
		$R^2 = 0.963682$, Adj. $R^2 = 0.929785$, Standard error = 6.551724					

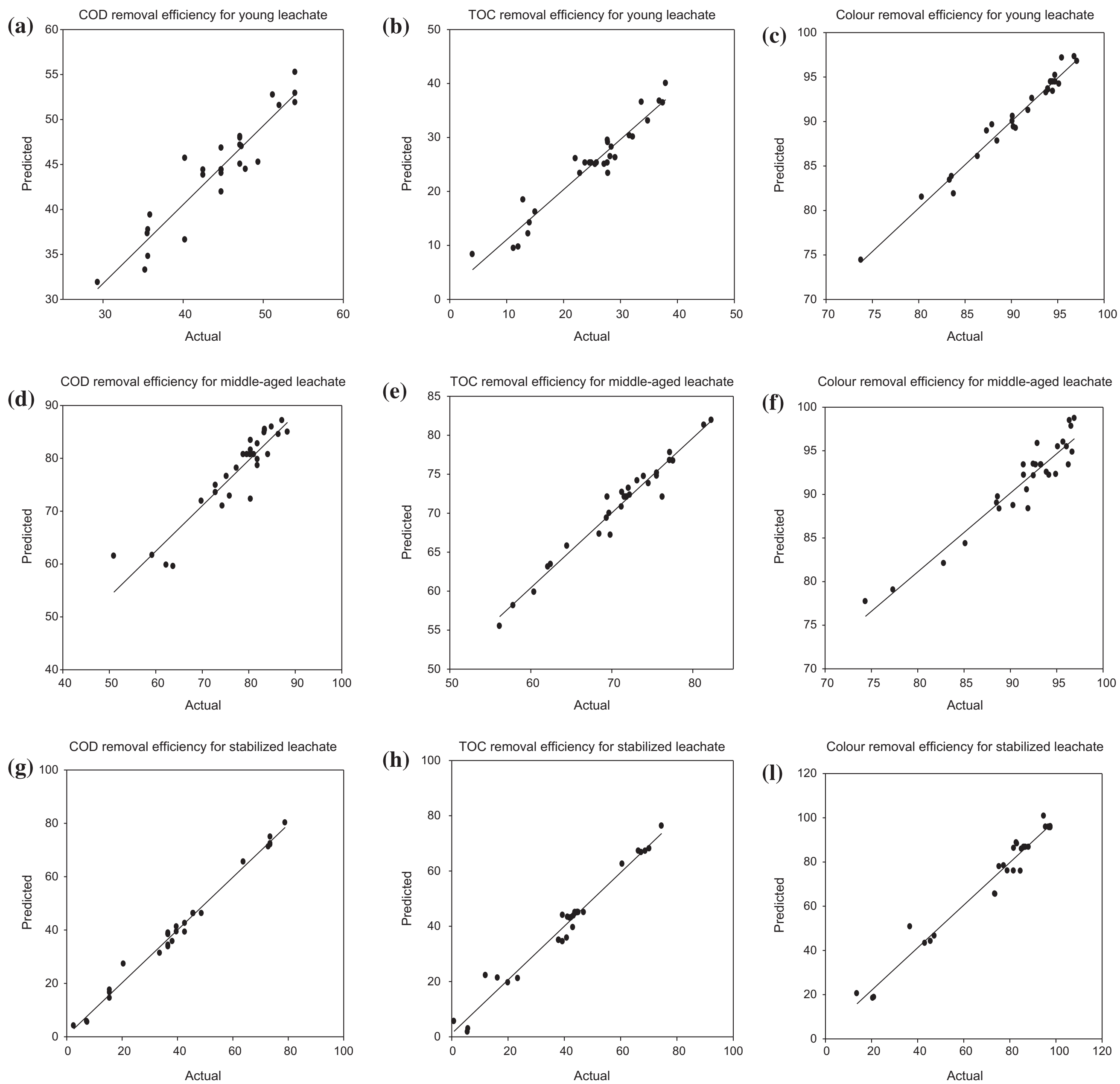

Fig. 2. Predicted vs. actual values plot for (a) COD, (b) TOC, (C) color removal for young leachate, (d) COD, (e) TOC, (f) color removal for middle-aged leachate, (g) COD, (h) TOC, and (l) color removal for stabilized leachate.

In Figs. 3–5, the 3D response surface and contour plots were introduced as a function of H_2O_2/COD ratio, H_2O_2/Fe^{2+} ratio, pH, and reaction time, while the two independent variables were kept constant. The effects of operational variables i.e. H_2O_2/COD ratio and H_2O_2/Fe^{2+} ratio on COD removal efficiency at pH and reaction time of 3 and 90 min are illustrated in Fig. 3(a) for young leachate. The maximum observed removal of COD was 54% and minimum observed removal of COD was 29.3% (Table 3). As shown in Fig. 3(a) and (d), the influence of H_2O_2/COD ratio, H_2O_2/Fe^{2+} ratio, and pH on COD removal efficiency was more significant than with reaction time, which had limited effects on COD removal for young leachate. Response surface plots in Fig. 3(a) and (d) indicate optimal points to be at about H_2O_2/COD ratio 1, H_2O_2/Fe^{2+} ratio 5.08, pH 2, and reaction time 141.5 min for young pretreated leachate. Likewise, Fig. 4(a) and (d) demonstrates that the optimum removal occurred at around H_2O_2/COD ratio 1,

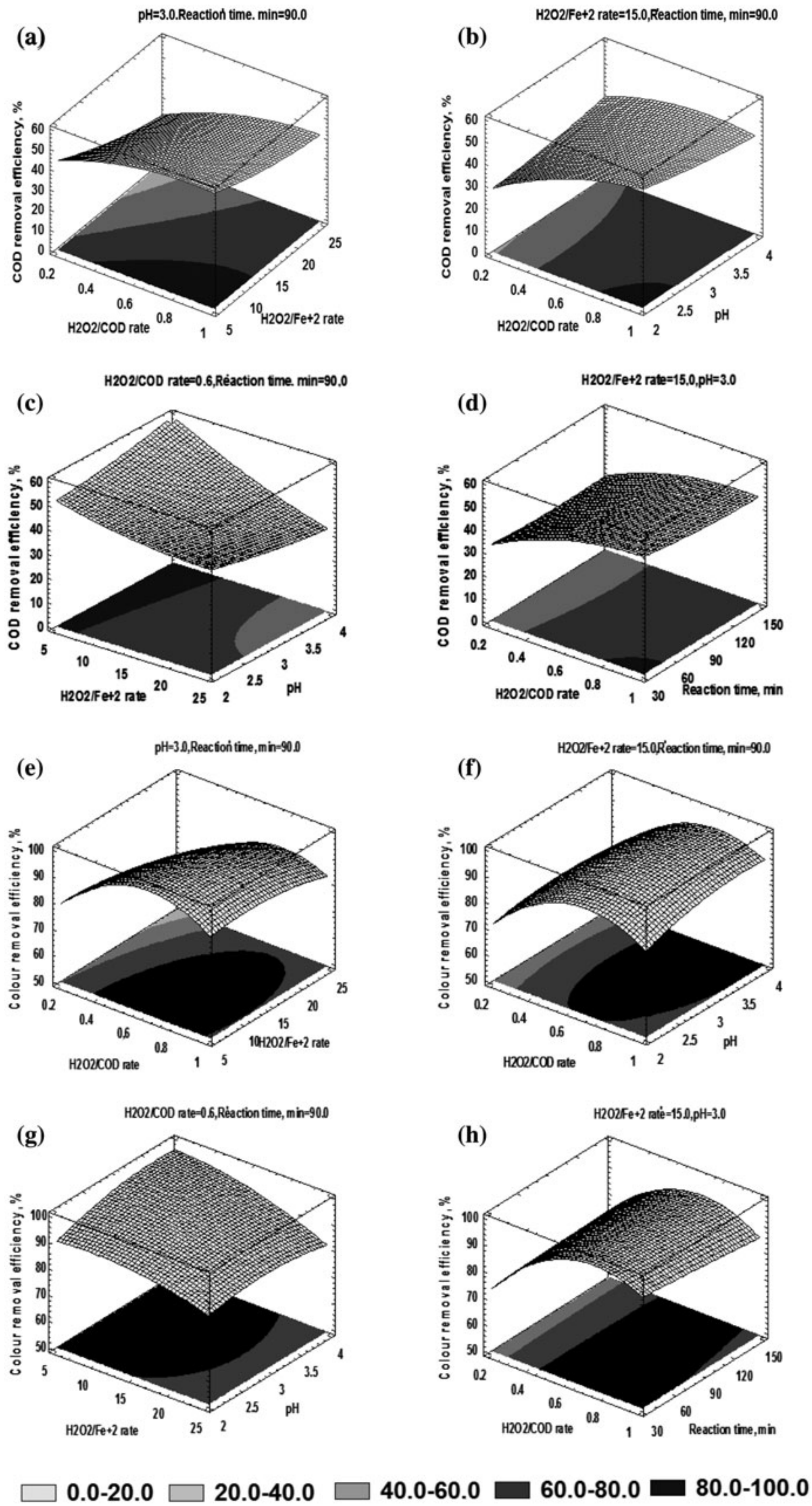

Fig. 3. Response surface graphs for young leachate; (a,b,c, and d) effect of H_2O_2/COD-H_2O_2/Fe^{2+}, H_2O_2/COD-pH, H_2O_2/Fe^{+2} –pH, and H_2O_2/COD reaction time for COD removal, (e,f,g, and h) effect of H_2O_2/COD-H_2O_2/Fe^{2+}, H_2O_2/COD-pH,H_2O_2/Fe^{+2}—pH, and H_2O_2/COD-reaction time for color removal.

H_2O_2/Fe^{2+} ratio 5, pH 3.24, and reaction time 82 min for stabilized leachate. Fig. 5(a) and (d) demonstrates that the optimal removal occurred at around H_2O_2/COD ratio 1, H_2O_2/Fe^{2+} ratio 27.7, pH 2.7, and reaction time 30 min for middle-aged pretreated leachate. In middle-aged leachate post-treatment by Fenton oxidation, COD, TOC, and color removal efficiency were achieved between 59–87%, 56–82%, and 74–97%, respectively. As seen in Table 3, the old leachate treatment by Fenton oxidation, COD, TOC, and color removal efficiency were obtained between 2–79%, 1–74%, and 14–98%, respectively.

3.3. Process optimization

In this study, the primary purpose of the optimization is to confirm the optimal values of independent variables for young, middle-aged, and stabilized landfill leachates treatment with Fenton process from the models obtained by experimental data. Optimization process was carried out to determine the optimum value of COD removal efficiency. According to the optimization step, the desired goal for each operational condition (H_2O_2/COD ratio, H_2O_2/Fe^{2+} ratio, pH, and reaction time) was chosen "within the range" while the response (COD, TOC, and color removal efficiency) was defined as "maximum" to achieve highest performance. The program combines the individual desirabilities into a single number, and then searches to maximize this function. Accordingly, the optimum working conditions and respective percent removal efficiencies were established, and the results are presented in Table 5.

As shown in Table 5, the 62.1, 91.9, and 100% COD removals were predicted according to the model under optimized operational conditions for young, middle-aged, and stabilized leachate, respectively. 54.3, 80.2, and 99.4% COD removals were obtained from the laboratory experiments, which agree well with the predicted response value. As shown in Table 5, the removal efficiencies (TOC and color) for all response parameters obtained from the experiments and as estimated by models were in close agreement. According to the results obtained, middle-aged and stabilized leachate discharge limits have achieved the deep sea discharge criteria based on Istanbul Water and Sewer Authority (ISKI) Sewage Discharge Regulation (COD < 600 mg/L) [59]. On the other hand, the results obtained for young leachate, discharge limits have been achieved for complete water treatment systems (<4,000 mg/L) based on same regulation. Water Pollution Control Regulation's standard discharge limits, which is direct to a receiving water body, were not achieved (24 h composite sample COD < 120 mg/L) [60].

Overall process performance (ion exchanger, UF process, EDBM process, and Fenton Process) were 83% COD and 82.7% TOC removal efficiency for young leachate sample. For middle-aged leachates, results were 97.7% COD and 94.7% TOC overall removal efficiency. COD and TOC overall removal efficiency for stabilized leachate were 95.8 and 97.3%.

Hermosilla et al. reported that conventional Fenton process was able to achieve slightly over an 80% COD removal from a young leachate, while for old and middle-aged leachates was close to a 70% [1]. Under the optimal operation conditions (initial pH = 3, 2000 mg/L Fe^{2+}, 5,000 mg/L H_2O_2), 55.9% of the initial COD and 89.4% color were removed by Yilmaz et al. [61]. Kim and Huh reported decolorization efficiency as high as 92% in Fenton treatment of a mature leachate [62].

Once assessed the optimal H_2O_2/Fe^{2+} mole ratio (i.e. 5), the maximum achievable COD removal (i.e. 54% for pretreated young leachate) and the absolute amounts of H_2O_2 and Fe^{2+} necessary to achieve this maximum removal, experiments were carried out to evaluate leachate's biodegradability enhancement, in terms of BOD_5/COD ratio increase, achieved during the Fenton's treatment. To achieve an exploitable biodegradability improvement (BOD_5/COD > 0.337), it is sufficient to treat the leachate with amounts of optimum conditions for pretreated young, middle-aged, and stabilized leachate, respectively.

In consequence of the final treatment with Fenton oxidation, BOD_5/COD ratio increased to 0.554 from 0.275 for middle-aged leachate, increased to 0.679 from 0.470 for young leachate, and increased to 0.337 from 0.066 for stabilized leachate. Kim et al. [63] reported that BOD_5/COD ratio of the stabilized landfill leachate could be improved from 0.11 to 0.45 by using coagulation and Fenton's oxidation processes. In another work, Kim and Huh [62] performed Fenton's oxidation to enhance the biological treatability of landfill leachate. Results showed that the ratio of BOD_{20}/COD increased after the oxidation process and Fenton process could be an effective alternative prior to the biological process. In a similar study, Lopez et al. [64] investigated the pretreatability of mature landfill leachate and improvement of its overall biodegradability by using the Fenton's oxidation process.

4. Conclusions

In this study, Fenton process was applied as an effective method to treat the EDBM treated leachates

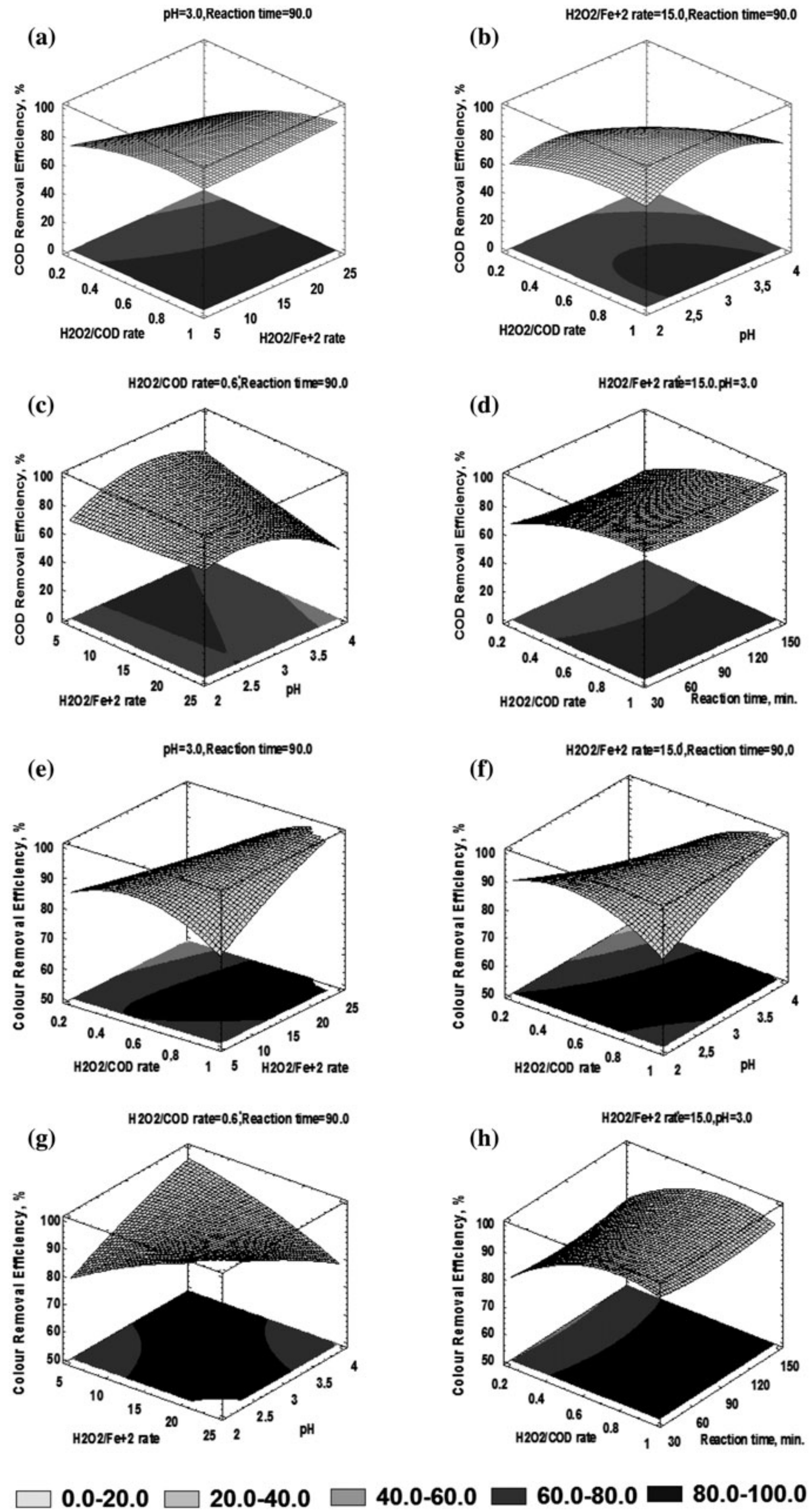

Fig. 4. Response surface graphs for middle-aged leachate; (a,b,c, and d) effect of H_2O_2/COD-H_2O_2/Fe^{2+}, H_2O_2/COD-pH, H_2O_2/Fe^{+2}–pH, and H_2O_2/COD-reaction time for COD removal, (e,f,g, and h) effect of H_2O_2/COD-H_2O_2/Fe^{2+}, H_2O_2/COD-pH,H_2O_2/Fe^{+2}—pH, and H_2O_2/COD-reaction time for color removal.

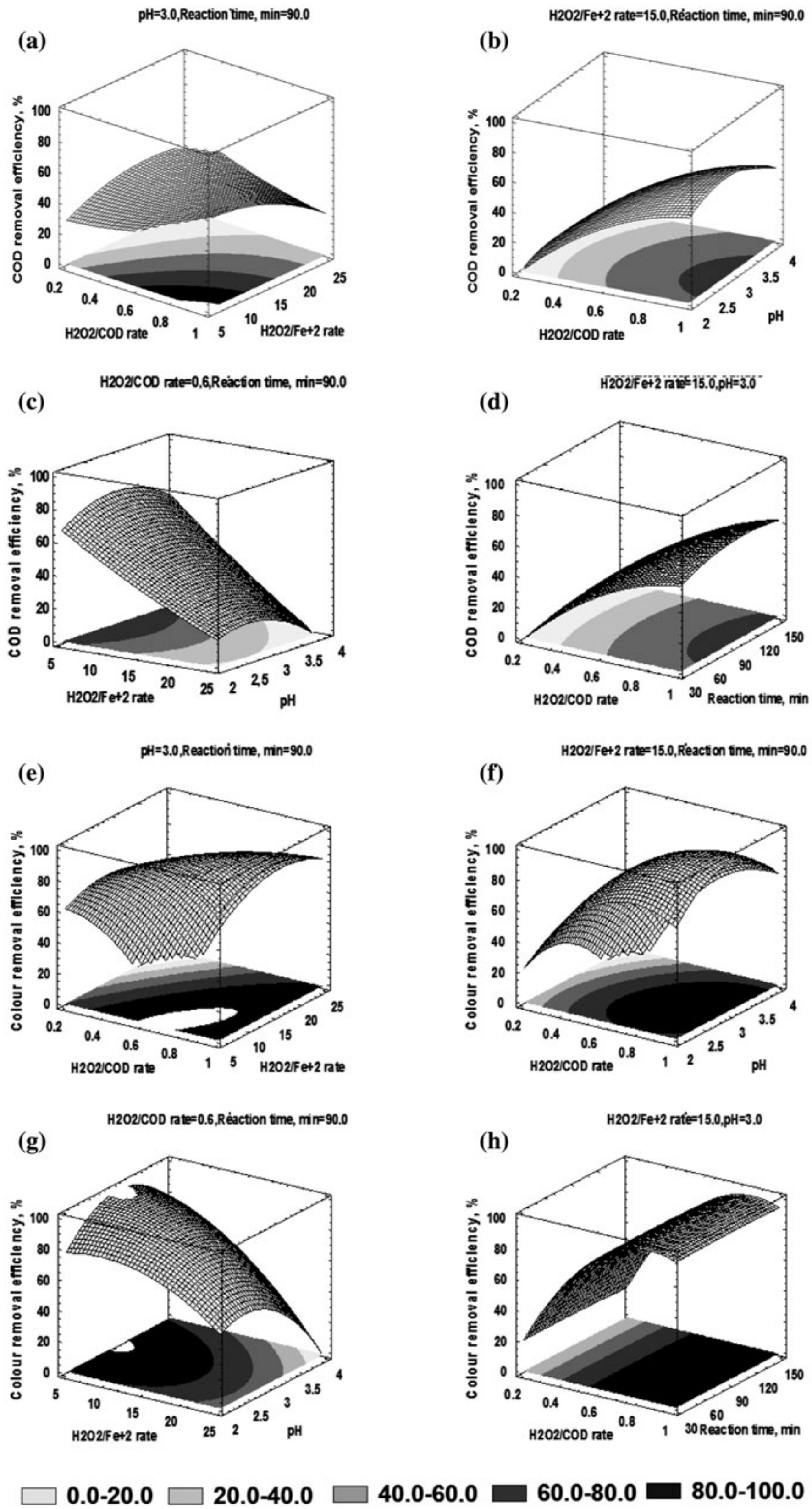

Fig. 5. Response surface graphs for stabilized leachate; (a,b,c, and d) effect of H_2O_2/COD-H_2O_2/Fe^{2+}, H_2O_2/COD-pH, H_2O_2/Fe^{+2} –pH, and H_2O_2/COD-reaction time for COD removal, (e,f,g, and h) effect of H_2O_2/COD-H_2O_2/Fe^{2+}, H_2O_2/COD-pH,H_2O_2/Fe^{+2}—pH, and H_2O_2/COD-reaction time for Color removal.

Table 5
Verification experiments at optimum conditions for COD, TOC, and color Removal for young, middle-aged, and stabilized leachate

	Conditions	Responses removal (%)
Young leachate	COD optimization ($x_1 = 1$; $x_2 = 5.08$; $x_3 = 2$; $x_4 = 141.5$)	
	Model prediction results	62.1
	Laboratory results	54.3
	Error	7.76
	Standard deviation	±5.51543
	TOC optimization ($x_1 = 0.65$; $x_2 = 5$; $x_3 = 4$; $x_4 = 30$)	
	Model prediction results	47.9
	Laboratory results	43.8
	Error	4.1
	Standard deviation	±2.89914
	Color optimization ($x_1 = 0.66$; $x_2 = 5$; $x_3 = 3.68$; $x_4 = 150$)	
	Model prediction results	100.0
	Laboratory results	98.1
	Error	1.9
	Standard deviation	±1.34350
Middle-aged leachate	COD optimization ($x_1 = 1$; $x_2 = 24$; $x_3 = 2.71$; $x_4 = 30$)	
	Model prediction results	91.9
	Laboratory results	80.3
	Error	11.6
	Standard deviation	±8.20244
	TOC optimization ($x_1 = 0{,}75$; $x_2 = 5$; $x_3 = 3{,}99$; $x_4 = 30$)	
	Model prediction results	92.4
	Laboratory results	88.7
	Error	3.7
	Standard deviation	±2.61629
	Color optimization ($x_1 = 0.99$; $x_2 = 22.6$; $x_3 = 3.93$; $x_4 = 147.7$)	
	Model prediction results	100.00
	Laboratory results	89.5
	Error	10.5
	Standard deviation	±7.42462
Stabilized leachate	COD optimization ($x_1 = 1$; $x_2 = 5$; $x_3 = 3.24$; $x_4 = 81.97$)	
	Model prediction results	100.0
	Laboratory results	99.4
	Error	0.6
	Standard deviation	±0.42426
	TOC optimization ($x_1 = 1$; $x_2 = 5$; $x_3 = 3{,}21$; $x_4 = 89{,}45$)	
	Model prediction results	95.1
	Laboratory results	91.6
	Error	3.5
	Standard deviation	±2.47487
	Color optimization ($x_1 = 0.73$; $x_2 = 7.84$; $x_3 = 3$; $x_4 = 103$)	
	Model prediction results	100.0
	Laboratory results	95.4
	Error	4.6
	Standard deviation	±3.25269

under different conditions and the RSM was applied to optimize Fenton process. The results demonstrated that RSM was an effective method for the modeling of experimental parameters in the Fenton treatment of all landfill leachates.

Based on the results of the study, the following conclusions may be obtained;

- Fenton process could be assessed as a possible technique for reduction of COD, TOC, and color in the treatment of EDBM treated leachates. The treatment efficiency was found to be function of the H_2O_2/COD rate, H_2O_2/Fe^{2+} rate, and initial pH. The dosages of H_2O_2 and Fe^{2+} were the most significant factors for the increment contribution of oxidation and coagulation removal efficiency. After Fenton's oxidation, COD, TOC, and color removal efficiencies were found to be 29–54%, 8–38%, and 74–97% in young leachate and 59–87%, 56–82%, and 74–97% in the middle-aged leachate, and 2–79%, 1–74%, and 14–98% in the stabilized leachate, respectively.

- Fenton treatment enhanced the biodegradability of all EDBM treated leachates, and BOD_5/COD ratio increased from 0.470 to 0.679 in the young leachate, from 0.275 to 0.554 in the middle-aged leachate, and from 0.066 to 0.337 in the stabilized leachate.
- According to ANOVA results, RSM could be used to navigate the design space with high regression coefficient R^2 varied from 0.86 to 0.99 for three types of leachates.
- Although has high removal efficiencies, Fenton process generated an important quantity of iron sludge, which will require further disposal, when performed under optimal COD removal conditions. The disadvantage of this process is the high content of iron sludge.

By applying RSM, the optimum region for the reactor operation was located. Experimental findings were in close agreement with the model prediction. From the present study, it is evident that the use of statistical optimization approach, RSM, has helped to identify the most significant operating factors and optimum levels with minimum effort and time.

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