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Optimization of landfill leachate oxidation at extreme conditions and determination of micropollutants removal

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ABSTRACT

The advanced oxidation of macro- and micro-organic pollutants from the landfill leachate using the Fenton reaction was investigated. Central composite design with response surface methodology was applied to evaluate the interaction and relationship between operating variables (i.e., pH, reaction time, ferrous iron and H_2O_2 dosages) and to develop the optimum operating condition. Based on statistical analysis, quadratic models for the two responses (chemical oxygen demand [COD] and aromatic content [UV_{254}]) proved to be significant with very low probability values (<0.001). The obtained optimum conditions were 1,755 mg/L Fe^{2+} and 26,422 mg/L H_2O_2 concentration, pH 3.72 and 99 min reaction time. The results obtained by the predicted model were 70, and 54% removal for COD and UV_{254}, respectively, with optimum conditions. The predicted results fitted well with the results of the laboratory experiment. A wide range of analysis was conducted for micropollutants and some volatile organic compounds, pharmaceuticals, pesticides, plasticizers, polycyclic aromatic hydrocarbons and heavy metals were detected. Removal efficiencies of some micropollutants including bis(2-ethylhexyl) phthalate, anthracene, benzene hexachloride, dieldrin, diuron, chlorpyriphos and diclofenac were between 90% and 99% with Fenton oxidation at the optimum condition. It was also determined that heavy metals decreased as a result of co-precipitation after oxidation.

Keywords: Leachate; Advanced oxidation; Optimization; Central composite design; Micropollutants; COD; UV_{254}

1. Introduction

Landfill method has been used for disposing of a remarkable amount of municipal solid waste throughout the world. However, sanitary landfill generates a large amount of heavily polluted leachate [1]. Landfill leachate commonly contains high concentrations of organic compounds, heavy metals, sulfate (SO_4^{2-}), sulfide (S^{2-}), ammonium (NH_4^+), phosphate (PO_4^{2-}), chloride and many other hazardous chemicals lead to failure in traditional treatment methods and are characterized by very high chemical oxygen demand (COD) value as well as strong color. Furthermore, landfill leachate has been reported to contain a wide variety of organic compounds such as volatile organic compounds (VOCs), pharmaceuticals, pesticides, plasticizers and polycyclic aromatic hydrocarbons [2]. The characterization of waste and their quality, the hydrogeological factors, and age of the landfill such as young, middle-aged and mature have affected the composition and concentration of contaminants [3,4]. Therefore, leachate is a potential source of contamination for groundwater, surface water and effluents, in which pollution is far above the discharge standards [5–7]. Therefore, efficient treatment of landfill leachate is mandatory to protect environment and water sources. High concentration of COD and refractory hazardous organics is the main problem of

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the traditional treatment process for achieving the discharge standards [8].

There are several leachate treatment methods, including biological, physical and chemical processes. Some biological methods such as aerobic, anaerobic and anoxic processes are used in combination or alone for leachate treatment [9]. Air stripping and adsorption are major physical methods and coagulation, flocculation and chemical oxidation are examples of effective chemical treatment methods especially for COD removal from landfill leachate [10–13]. Advanced oxidation processes have been studied in landfill leachate treatment because of its oxidation potential and ability to convert and reduce the non-biodegradable organics [14–17].

Transition metal salts and H_2O_2 have the ability to initiate the oxidation reaction to form hydroxyl radicals [18–20]. Among these materials, ferrous iron and hydrogen peroxide are commonly known as Fenton's reagent. The hydroxyl radicals whose oxidation potential (2.8 V) is higher than ozone (2.07 V) and H_2O_2 (1.8 V) can easily provide degradation of the organic components. The reaction characteristics and reagent conditions have strongly affected the efficiency of Fenton oxidation. Therefore, determination of the relationship between these parameters is important to increase the overall reaction efficiency [20].

Response surface methodology (RSM) is a statistics-based method and widely used to optimize the process parameters with a limited number of experimental run and increase the yield of the processes without increasing the cost [21,22]. The method used for this purpose is called optimization. RSM computes the relationships between input variables (X) and their responses (Y). Coefficient estimation of the mathematical models, response prediction and examination of the adequacy of the model are the main advantages of RSM.

The main objective of this study was to determine optimum conditions for the removal of high COD concentration and UV_{254} reduction from landfill leachate by using Fenton oxidation. RSM was used to optimize each parameter in order to determine the combined effect of different parameters. Additionally, owing to the presence of the pharmaceutical species and pesticides that are non-degradable, the proposed system was utilized. As a result of literature review, a limited number of works has been published dealing with the application of RSM to Fenton oxidation of landfill leachate.

2. Materials and methods

2.1. Leachate sampling and characterization

The landfill leachate samples used in the current study were collected from the active detention pond of municipal landfill area and 706 tons of waste were collected per year, located in Konya region, in the middle of Turkey. All samples were collected manually in 20 L plastic containers, and then transferred, characterized and refrigerated immediately in accordance with the Standard Methods for the Examination of Water and Wastewater [23]. Table 1 shows some characteristics of the leachate sample.

All experimental runs were conducted at laboratory temperature/pressure conditions. COD, BOD_5, sulfate, phosphate–phosphorus, ammonium–nitrogen, pH and metals (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Pt and Zn) were analyzed according to internationally accepted procedures and Standard Methods. Agilent GC/MS 7890B with HP-5MS (30 m × 250 µm × 0.25 µm) column and Agilent GC/MS 6850 with DB-VRX (60 m × 250 µm × 1.40 µm) column were used for determining semi-VOCs and VOCs following the US-EPA Method 8270D and 8260C, respectively. Triple Quad LC-MS-MS (Agilent 6460 A) with Zorbax Extend C-18 (3.0 mm inner diameter (I.D.) × 100 mm × 3.7 µm particle size) column for alkali compounds and Poroshell 120 SB C-18 (4.6 mm I.D. × 150 mm × 2.7 µm particle size) column for acidic compounds were used to analyze some other micropollutants including pharmaceuticals and pesticides: 2,4-dimethylphenol, acenaphthylene, acenaphthene, 4-nitrophenol, 2-methyl-4,6-dinitrophenol, benzene hexachloride (BHC) alpha isomer, BHC beta isomer, phenanthrene, anthracene, di-*n*-butyl phthalate, isodrin, endosulfan I, dieldrin, endrin ketone, bis(2-ethylhexyl) phthalate, acetonitrile, diethyl ether, 2-chloro-1,3-butadiene, 2-nitropropane, formetanate, aminocarb, propamocarb, thiamethoxam, monocrotophos, carbendazim, dimethoate, acetamiprid, metamitron, chloridazon, thiacloprid, pirimicarb, metalaxyl, lenacil, diuron, terbutryn, alachlor, diclofenac and chlorpyriphos.

2.2. Chemicals

All chemicals used in characterization study were purchased from Sigma-Aldrich (Turkey). Hydrogen peroxide (H_2O_2) 30% (w/v) and ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) 99.5%, both from Merck (Turkey), were used for the Fenton oxidation. For all experiments, deionized water was used to prepare the required solutions. Acidic and alkaline conditions were ensured using either HCl or NaOH.

2.3. Fenton oxidation

To reduce the high organic loading from landfill leachate, free hydroxyl radicals were obtained in situ by Fenton's reagent at room temperature and pressure. Samples of 200 mL of landfill leachate with COD concentration of 43,200 mg/L were continuously stirred at 200 rpm/30 rpm, and defined quantities of $FeSO_4.7H_2O$ were added to the samples. The extent of oxidation (and therefore the degree of direct COD reduction) typically depends on the amount of hydrogen peroxide used. By stoichiometric balance (Eqs. (1) and (2)) of the direct oxidation with hydrogen peroxide, it is assessed to be necessary to spend 2.125 mg (as 100%) of H_2O_2 to abate 1 mg of COD [24].

Table 1
Characterization of the raw landfill leachate

pH	7.50
COD (mg/L)	43,200
BOD (mg/L)	17,500
SO_4^{2-} (mg/L)	1,970
PO_4–P (mg/L)	23
NH_4–N (mg/L)	3,900
UV_{254} (Absorbance)	0.504

$$COD + H_2O_2 \xrightarrow{\text{With } Fe^{2+}} \text{partially oxidized species} \quad (1)$$

$$\text{partially oxidized species} + H_2O_2 \rightarrow CO_2 + H_2O + \text{inorganic salts} \quad (2)$$

In many cases, however, complete digestion of the organic compounds to carbon dioxide and water is not needed. Partial oxidation of intermediate compounds minimizes chemical consumption and often results in substantial reductions in COD and toxicity. In this study, the required theoretical H_2O_2 doses of 70% (64,000 mg H_2O_2/L) and 0.2% (250 mg H_2O_2/L) were selected as the maximum and minimum doses for the COD mineralization, respectively. Furthermore, the extreme doses were also selected to optimize the process in a wide range. Different responses were observed in order to optimization. Ferrous iron doses were selected to maintain Fe^{2+}/H_2O_2 ratio as 0.1. The reaction was initiated by adding different amounts of hydrogen peroxide to the reactor after the pH and Fe^{2+} doses were adjusted. The pH of the solution significantly affects the efficiency of the Fenton oxidation process and is generally studied at the pH range of 2–6. Working at alkaline pH was not preferred because of scavenging effect of OH^- and carbonate ions [25,26].

Aliquots were withdrawn from the sample, before and during the experiment, to determine the initial and the remaining COD concentration and UV_{254} absorbance in the sample. The residual H_2O_2 may cause interference to the standard COD test due to the dichromate ions react with H_2O_2 in an acidified solution [27]. However, hydrogen peroxide is unstable and rapidly decomposes in high pH values and loses its oxidation ability [25,28]. Therefore, the residual H_2O_2 was destroyed in the sample before COD measurement by adding 6 N NaOH to prevent the interference reaction [29]. The oxidation-reduction potential (ORP) values were analyzed before and after NaOH addition for determining oxidation potential of the reaction medium. Negative ORP values demonstrated that NaOH addition destroyed the residual H_2O_2. After all, residual H_2O_2 was also determined according to the iodometric method for correction of hydrogen peroxide interference on COD test [27]. The pH, temperature, ORP and conductivity of the solution were measured by a digital ion analyzer with various electrodes (Multi 340i, WTW, Germany).

2.4. Response surface methodology

Response surface methods are designs and models for working with continuous treatments when finding the optimal or describing the response is the goal. RSM is an experimental methodology that allows the optimal conditions of a process to be found when the experimental region is delimited by the experimentation range of each factor. It defines the effect of the independent variables, alone or in combination, on the processes [30].

Since RSM makes it possible to study a large number of factors and to detect possible interactions between them, it provides a considerable reduction in the number of the experiments and easy interpretation [31]. Using this experimental design methodology, it was possible to design and optimize the removal efficiency of COD and UV_{254} using the Fenton process and to construct a prediction model for the response.

2.5. Central composite design and data analysis

A central composite design (CCD) was used in the RSM, and the codec factors and corresponding levels for the oxidation efficiency with the Fenton process are shown in Table 2. The data were evaluated by the analysis of variance (ANOVA) using Design Expert Version 9.0.1 trial version (Stat-Ease, USA). ANOVA is similar to regression in that it is used to investigate and model the relationship between a response variable and one or more independent variables. The design was performed with 30 runs: 16 factorial points, 3 central points and 11 axial points and a 95% confidence interval. The factors (variables) were: the initial concentration of Fe^{2+}, the initial concentration of H_2O_2, initial pH of the solution and the reaction time. The range of pH values was selected based on the best performance of Fe^{2+} (pH = 2–6). The dosages of Fe^{2+} were chosen on the basis of preliminary experiments.

After selection of the design, the model equation was defined and coefficients of the model equation were predicted. RSM postulates the functional relationship between the controllable input parameters and the obtained response surfaces. For evaluation of experimental data, the response variable was fitted by a second-order model in the form of quadratic polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where i is the linear coefficient, j is the quadratic coefficient, β is the regression coefficient, k is the number of factors studied and optimized in the experiment and e is the random error. The analysis was focused on verifying the influence of individual parameters on the percentage of COD and UV_{254} removal. The actual design parameters of experiments and their responses for Fenton oxidation are given in Table 3.

The ANOVA and least squares techniques were used for graphical analyses of the data to obtain the interaction between the process variables and the responses. The goodness of the fit polynomial model was expressed by the coefficient of determination R^2, and its statistical significance was checked by the Fisher's F test in the same program. The significance and the magnitude of the estimated coefficients of each variable and all their possible interactions on the response variable(s) were determined. Such coefficients for each variable represent the improvement in the response, that is, to expect as the variable setting is changed from low to high. Effects with a confidence level less than 95% (effects with a p value higher than 0.05) were discarded and pooled into the error term and a new ANOVA was performed for the reduced model.

3. Results and discussion

Optimization of COD and UV_{254} removal by Fenton oxidation under laboratory conditions was investigated using RSM. The physical (time and pH) and chemical (Fe^{2+} and

H_2O_2 dosage) parameters have been optimized using CCD. Besides increasing the remediation and biodegradability of the landfill leachate by Fenton oxidation, it is also important to increase the yield of the process without raising the cost. This method used for this purpose is called optimization.

3.1. Evaluation of statistical analysis

Optimization process was carried out in two sections: (1) performing the statistically designed experiments, (2) estimating coefficients in the proposed model and predicting the response of process. The desired goal was determined for each variable and response in the optimization step of the Design Expert software.

Experimental data were analyzed by using the response surface regression procedure. For evaluation of experimental data, the response variable was fitted by second-order model in the form of quadratic polynomial model. The final mathematical model equation in terms of actual factors, which was obtained by Design Expert software, is given below:

Table 2
Experimental design of leachate treatment by Fenton oxidation

Independent process variables	Factor	Real values of coded levels				
		Minimum	–1	0	+1	Maximum
Fe^{2+} concentration	A	50	1,662.5	3,275	4,887.5	6,500
H_2O_2 concentration	B	250	16,187.5	32,125	48,062.5	64,000
pH	C	2	3	4	5	6
Time	D	5	50	95	140	185

Table 3
The actual design parameters of oxidation experiments and removal efficiencies

Experimental no.	Fe^{2+}, mg/L (x_1)	H_2O_2, mg/L (x_2)	pH (x_3)	Time, min (x_4)	COD removal (%)	UV_{254} removal (%)
1	3,275	32,125	2	95	66.8	43.85
2	4,887.5	48,062.5	3	50	70.5	62.90
3	3,275	32,125	5	140	63.1	41.87
4	3,275	32,125	6	95	55.7	28.77
5	6,500	32,125	5	140	66.7	33.13
6	1,662.5	48,062.5	3	50	59.7	62.90
7	1,662.5	16,187.5	5	50	55.7	46.83
8	1,662.5	16,187.5	4	95	66.8	38.49
9	4,887.5	16,187.5	3	50	52.0	62.10
10	3,275	32,125	3	140	70.5	29.56
11	50	32,125	5	140	54.0	28.77
12	4,887.5	48,062.5	5	50	63.2	64.48
13	1,662.5	48,062.5	3	140	66.9	63.29
14	4,887.5	16,187.5	4	95	70.6	33.93
15	3,275	250	4	95	45.2	4.76
16	4,887.5	48,062.5	5	50	63.2	72.62
17	3,275	32,125	4	95	66.9	55.75
18	1,662.5	48,062.5	3	140	70.5	71.23
19	1,662.5	48,062.5	4	95	63.3	65.67
20	3,275	32,125	4	5	59.5	53.77
21	3,275	64,000	3	140	59.8	56.35
22	3,275	32,125	4	95	78.0	63.69
23	3,275	32,125	4	95	77.8	63.49
24	4,887.5	48,062.5	4	95	85.3	65.28
25	1,662.5	16,187.5	4	95	63.1	29.37
26	1,662.5	16,187.5	4	95	63.1	39.68
27	4,887.5	16,187.5	3	50	55.7	29.17
28	4,887.5	16,187.5	5	50	70.5	34.92
29	3,275	32,125	5	140	74.3	62.50
30	3,275	32,125	4	185	70.7	58.93

$$\text{COD removal (\%)} = -87.89516 + [3.06758 \times 10^{-003} \times (\text{Fe})] + [2.89526 \times 10^{-003} \times (H_2O_2)] + [41.49208 \times (\text{pH})] + [0.52160 \times (\text{Time})] + [9.68318 \times 10^{-008} \times (\text{Fe}) \times (H_2O_2)] + [9.99122 \times 10^{-004} * (\text{Fe}) \times (\text{pH})] - [3.01002 \times 10^{-005} \times (\text{Fe}) \times (\text{Time})] - [3.52330 \times 10^{-004} \times (H_2O_2) \times (\text{pH})] + [2.92842 \times 10^{-007} \times (H_2O_2) \times (\text{Time})] - [0.021609 \times (\text{pH}) \times (\text{Time})] - [6.87104 \times 10^{-007} \times (\text{Fe})^2] - [2.69951 \times 10^{-008} \times (H_2O_2)^2] - [4.13674 \times (\text{pH})^2] - [1.57015 \times 10^{-003} \times (\text{Time})^2]$$

Table 4 shows that the model to predict COD removal was significant at the 5% confidence level since *p* value was below 0.05. Fisher's *F* test is used to compute both *p* and the lack of fit (LOF) values that describes the variation of the data around the fitted model. The large LOF values (>0.05) indicate the model is insignificant. Only insignificant LOF together with significant *p* value indicate good model correlation between the process variables and the response.

A high R^2 coefficient, close to 1, is desirable and this ensures a satisfactory adjustment of the quadratic model to the experimental data [31]. A low value (7.25%) of the coefficient of variance (CV) indicates a very high degree of precision and good reliability of experimental values. Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination. In this study, AP values of the model showed signal-to-noise ratios of 9.15 and 9.06 which indicated an adequate signal.

Table 4
ANOVA results for response parameters

Response	COD removal	UV_{254} removal
p	0.0010	0.0083
LOF	0.4162	0.2257
R^2	0.8399	0.7759
AP	9.152	9.065
SD	4.71	0.92
CV	7.25	13.36
Press	2,404.51	100.570

Table 5 summarized some similar studies in the technical literature. The application of RSM with four factors for optimization of Fenton oxidation in landfill leachate treatment was not present in literature. Most of the studies were focused on conventional responses such as COD and color removal. The capability of the proposed models was evaluated in terms of fitness and prediction. A negative predicted R^2 implies that the overall mean is a better predictor of the response than the current model.

The response surface contour plots of the quadratic model with two variables kept at a central level and the other two variables within the experimental ranges are demonstrated in Figs. 1–5. Different surfaces can be obtained by adjusting constant variable.

It was concluded from Fig. 1 that maximum COD removal was obtained far above the average H_2O_2 and Fe^{2+} concentrations (the central part of the contour). However, the lowest and the highest values of H_2O_2 and Fe^{2+} concentration did not affect the Fenton oxidation performance significantly. As shown in Fig. 2, the influence of H_2O_2 on COD removal was important by the change of pH. Higher COD removal efficiency was observed at relatively lower pH values and at higher H_2O_2 concentration. In Fig. 3, average H_2O_2 concentration and relatively higher reaction times had a positive effect on COD removal. H_2O_2 concentration has more influential parameter than time on the removal efficiency due to rapid reaction characteristics of Fenton. Fig. 4 also shows that interactive effects of Fe^{2+} concentration and time on the removal efficiency was not important than the other variables.

Table 5
Comparison of recent studies on the application of response surface methodology in modeling of Fenton responses in landfill leachate treatment

Variables		Target responses		Proposed model capability					References
X	Opt. Con.	*Y*	Optimized response	Fitness		Prediction			
				R^2	Adj. R^2	Pre. R^2	AP	*F* Ratio	
H_2O_2 (g/L)	17.2	COD removal	85%	0.986	0.974	NA	29.44	NA	[32]
pH	5.7	COD removal	69.1%	0.968	0.951	0.909	25.26	18.17	[33]
$[H_2O_2]/[Fe^{2+}]$	17.7	SIR	2.4 l/mol	0.948	0.911	0.760	18.02	8.31	
Fe^{2+} (mM)	195	ORSR	16.6 g/L	0.945	0.915	0.793	22.71	10.21	
pH	5.9	COD removal	72.47%	0.932	0.906	NA	20.90	36.11	[34]
Fe^{2+} (mM)	9.6	Color removal	95.19%	0.954	0.930	NA	21.26	39.25	
$[H_2O_2]/[Fe^{2+}]$	2.38								
Time (h)	5.52								
Fe^{2+} (g/L)	1.76	COD removal	70.35%	0.840	0.690	–0.16	9.152	7.25	Current study
H_2O_2 (g/L)	26.4	UV_{254} reduction	53.73%	0.776	0.570	–0.79	9.065	13.36	
pH	3.72								
Time (min)	99.2								

Opt. Con., optimum condition; NA, not available; R^2, determination coefficient; Adj. R^2, adjusted R^2; Pre. R^2, prediction R^2; AP, adequate precision; *F* ratio, model *F* value to critical value in *F* table; SIR, sludge iron ratio; ORSR, organics removal to sludge ratio.

The effect of functional variables as pH, Fe^{2+} dosage, H_2O_2 dosage and time, on the removal of COD and UV_{254} reduction demonstrated in Figs. 6 and 7, respectively. As shown in Figs. 6 and 7, the colormap based on removal efficiency of COD and transparency was introduced in the scatters. The scatter size was proportional to time. The other variables are expressed on graphs.

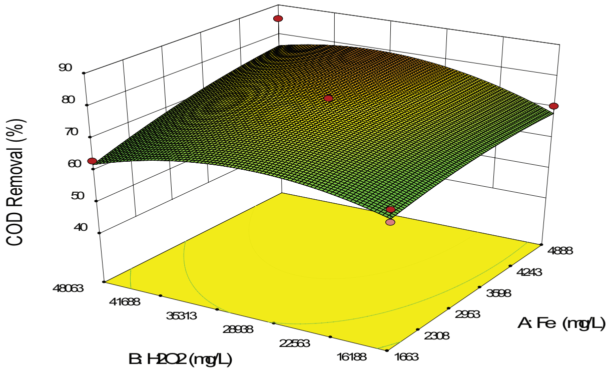

Fig. 1. The effect of H_2O_2 and Fe(II) concentration on COD removal (pH: 4 and time: 95 min).

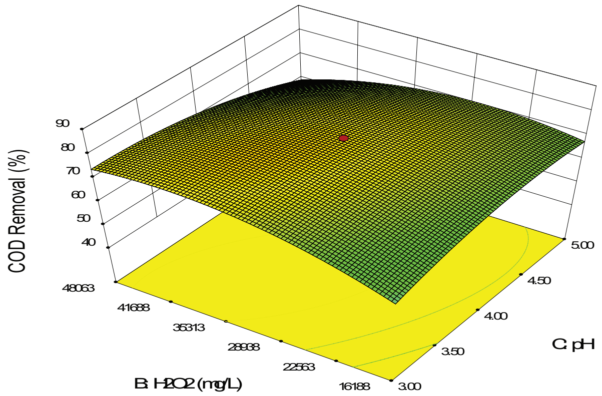

Fig. 2. The effect of H_2O_2 and pH on COD removal (Fe(II): 3,275 mg/L and time: 95 min).

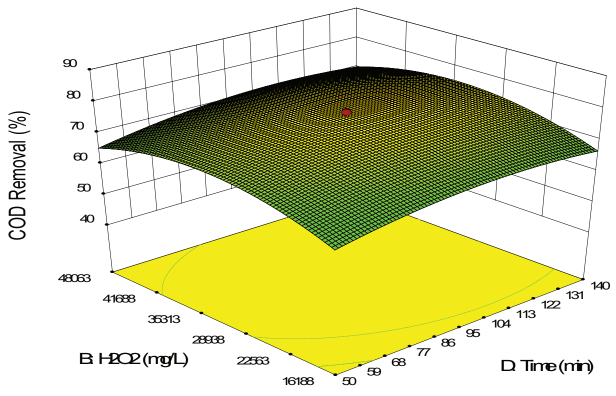

Fig. 3. The effect of H_2O_2 and time on COD removal (Fe(II): 3,275 mg/L and pH: 4).

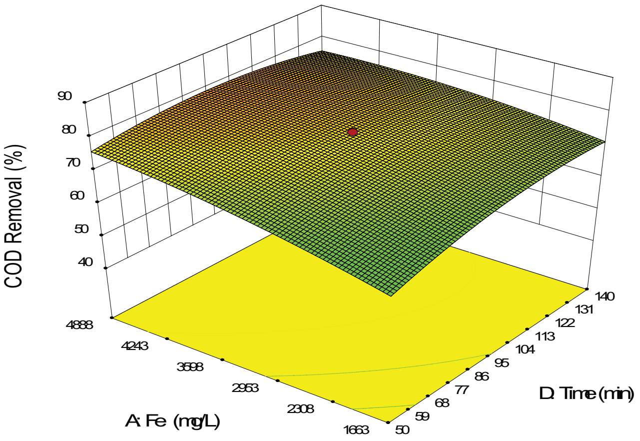

Fig. 4. The effect of Fe(II) and time on COD removal (H_2O_2: 32,125 mg/L and pH: 4).

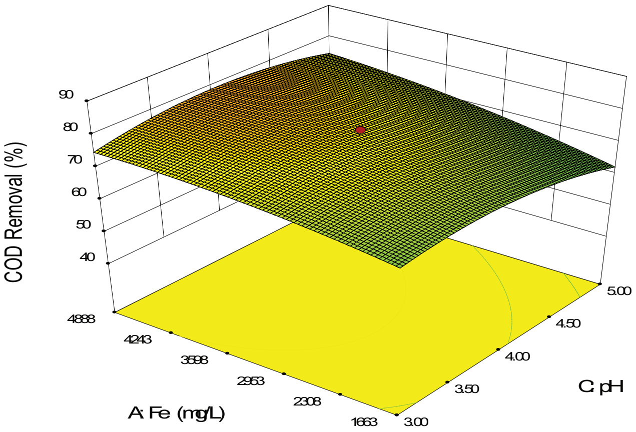

Fig. 5. The effect of Fe(II) and pH on COD removal (H_2O_2: 32,125 mg/L and time: 95 min).

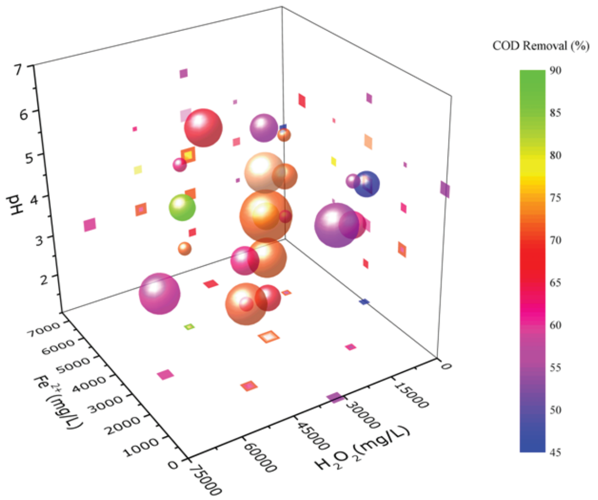

Fig. 6. The 3D scatter plot of COD removal.

3.2. Optimization of the process parameters

The process parameters were optimized using the numerical optimization option in the software. In the optimization step of the software, the desired goal for the response was selected, Fe^{2+} and H_2O_2 concentrations were minimized and the other parameters were selected to be within the study range. The optimization results of the process variables and the selection constraints for each parameter were summarized in Table 6.

The cost of the treatment process is the most important parameter for applying the results to the pilot and real plant scale. Although high removal efficiencies have been obtained in different methods as in this study, the cost of chemicals and equipment could limit the applicability. Therefore, cost optimization of the process in terms of chemicals ($FeSO_4$, H_2O_2, $Ca(OH)_2$ and H_2SO_4) and treatment time were also obtained in this study. Treatment cost of 97.65 \$/m^3 water and COD removal of 61% were obtained under the conditions given in Table 6. It was also observed that treatment cost increased from 98\$ to 115\$ while the importance of cost changed from 5 to 3. The desirability function can be used to combine multiple responses into one response called the "desirability function" which changes between 0 (one or more independent variables are unacceptable) and 1 (all independent variables are on target). In this study, desirability function values for COD optimization and cost optimization were found to be 0.602 and 0.665, respectively.

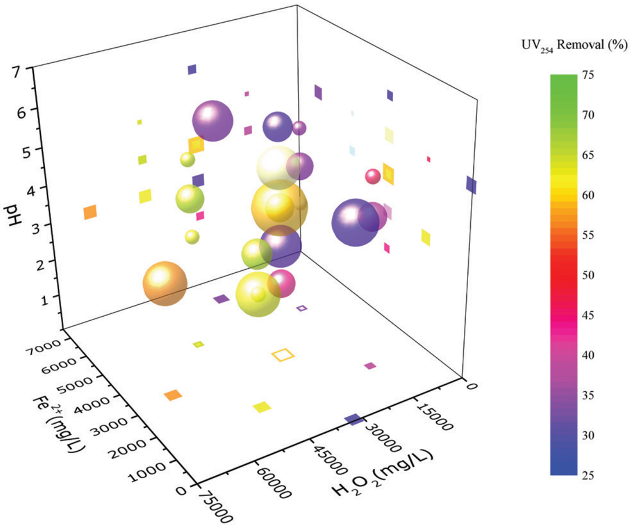

Fig. 7. The 3D scatter plot of UV_{254} reduction.

3.3. Effect of Fenton on the removal of micropollutant species

Micropollutants of leachate sample were analyzed before (raw sample) and after oxidation at the optimum Fenton condition obtained by RSM.

Results indicated that Fenton oxidation could be useful for removal of refractory microorganic pollutants from leachate. Some detected micropollutants have been presented in Table 7. It was also observed that Fenton oxidation at the optimum condition was able to reduce bis (2-etylhexyl) phthalate (DEHP), anthracene, BHC, dieldrin, diuron, chlorpyriphos and diclofenac with the removal efficiencies higher than >95%, >97%, >91%, >99%, >98%, >98% and >99%, respectively. The lowest removal efficiency was obtained for endosulfan as 4.5% and the others were carried out above 70% removal. Some heavy metals also decreased via co-precipitation after oxidation (Table 8). The maximum removal efficiency of 99% was obtained for Pb removal.

4. Conclusion

A wide application of RSM in treatment processes was observed in the literature. In most of the RSM studies reported, there was not enough preliminary work about independent parameters. The maximum (or minimum) value of the response without stationary point had been given as the optimum point. On the other hand, previously developed models are not applied on a global scale, so there is a need to develop local-scale models. The present study demonstrated the applicability of Fenton oxidation method for removal of the high organic load from the landfill leachate. Fenton process appears to be a promising technology for degradation of either COD or refractory micropollutants. Further to what has been applied within the framework of this study, more research is now performed in trying to apply a statistical approach to confirm the set of optimum conditions obtained from the varied experiments. The CCD was used to develop a reasonable mathematical model for predicting the optimum removal efficiency. The value of R^2 for the obtained quadratic model showed a high correlation between actual and predicted data. The satisfactory

Table 6
Selection constraints for optimization and obtained results

Parameter	Lower limit	Upper limit	Optimization for maximum COD removal			Optimization for minimum cost		
			Goal	Importance	Opt. cond.	Goal	Importance	Opt. cond.
Fe^{2+} (mg/L)	50	4,888	Minimum	3	1,755	Minimum	3	2,066
H_2O_2 (mg/L)	250	48,063	Minimum	4	26,422	Minimum	4	16,997
pH	3	5	In range	3	3.72	In range	3	4.39
Time	50	140	In range	3	99.2	Minimum	3	56.05
Response (% COD removal)	45.22	85.33	**Maximum**	**5**	**70.4**	Maximum	4	61.3
Response (% UV_{254} removal)	4.762	72.62	Maximum.	4	53.7	–	–	–
Response (Cost; \$/m^3 water)	15.87	798.79	–	–	–	**Minimum**	**5**	**97.65**

Maximum removal efficiency and minimum removal cost are indicated in bold font.

Table 7
Effects of Fenton oxidation on some micropollutants at the optimum conditions (H_2O_2 = 26,422 mg/L, Fe^{2+} = 1,755 mg/L, pH = 3.72, time = 99 min)

Compound (μg/L)	Raw	Final	Compound (μg/L)	Raw	Final
2,4-Dimethylphenol	21.1	<1	Formetanate	737.9	<10
Acenaphthylene	137.8	<1	Aminocarb	3,516.6	745.6
Acenaphthene	5.1	<1	Propamocarb	37,551.5	10,150.9
4-Nitrophenol	588.5	169.5	Thiamethoxam	879.9	<10
2-Methyl-4,6-dinitrophenol	25.3	<1	Monocrotophos	4,351.9	<10
BHC alpha isomer	368.2	<1	Carbendazim	27,619.1	2,961.9
BHC beta isomer	11.9	<1	Dimethoate	1,490.0	<10
Phenanthrene	16.9	<1	Acetamiprid	38,015.6	9,418.3
Anthracene	41.9	<1	Metamitron	356.0	<10
Di-*n*-butyl phthalate	16.1	<1	Chloridazon	26,220.7	4,148.9
Isodrin	11	<1	Thiacloprid	1,664.1	<10
Endosulfan I	760.4	726.5	Pirimicarb	1,774.7	<10
Dieldrin	130.6	<1	Metalaxyl	33,842.1	9,608.6
Endrin ketone	48.1	<1	Lenacil	1,073.1	<10
Bis(2-ethylhexyl) phthalate	20	<1	Diuron	815.3	<10
Acetonitrile	994.75	35.15	Terbutryn	<10	<10
Diethyl ether	409.46	<1	Alachlor	<10	<10
2-Chloro-1,3-butadiene	73.01	4.59	Diclofenac	1,708.7	<10
2-Nitropropane	739.19	69.33	Chlorpyriphos	985.0	<10

Table 8
Effects of Fenton oxidation on some metals at the optimum conditions (H_2O_2 = 26,422 mg/L, Fe^{2+} = 1,755 mg/L, pH = 3.72, time = 99 min)

Metal (mg/L)	Raw	Final
Na	5,823.9	39,879
Mg	776.74	616.78
Al	4.4105	1.8743
K	19,842	12,004
Ca	2,399.1	566.49
Cr	3.3745	0.9448
Mn	24.626	51.294
Fe	208.81	175.14
Co	0.1020	0.0746
Ni	1.3261	0.8548
Cu	0.7186	0.7005
Zn	3.8180	2.6958
As	0.3081	0.1179
Cd	0.0064	0.0054
Pt	0.0683	0.0133
Pb	1.3414	0.0704

prediction equation was derived for COD removal using RSM. All these results show that the Fenton process is a promising and efficient technology for the treatment of landfill leachate.

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Conflict of interest

The authors have declared no conflict of interest.

References

[1] S.S.A. Amr, H.A. Aziz, M.J. Bashir, Application of response surface methodology (RSM) for optimization of semi-aerobic landfill leachate treatment using ozone, Appl. Water Sci., 4 (2014) 231–239.

[2] B.O. Clarke, T. Anumol, M. Barlaz, S.A. Snyder, Investigating landfill leachate as a source of trace organic pollutants, Chemosphere, 127 (2015) 269–275.

[3] J.L. De Morais, P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, J. Hazard. Mater., 123 (2005) 181–186.

[4] H. Sari, K. Yetilmezsoy, F. Ilhan, S. Yazici, U. Kurt, O. Apaydin, Fuzzy-logic modeling of Fenton's strong chemical oxidation process treating three types of landfill leachates, Environ. Sci. Pollut. Res., 20 (2013) 4235–4253.

[5] T.M. Alslaibi, Y.K. Mogheir, S. Afifi, Analysis of landfill components in estimating the percolated leachate to groundwater using the HELP model, Water Sci. Technol., 62 (2010) 1727–1734.

[6] T.H. Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, J.B. Christensen, A. Baun, H.-J. Albrechtsen, G. Heron, Biogeochemistry of landfill leachate plumes, Appl. Geochem., 16 (2001) 659–718.

[7] G. Schrab, K. Brown, K. Donnelly, Acute and genetic toxicity of municipal landfill leachate, Water Air Soil Pollut., 69 (1993) 99–112.

[8] G. Percheron, N. Bernet, R. Moletta, Start-up of anaerobic digestion of sulfate wastewater, Bioresour. Technol., 61 (1997) 21–27.

[9] O.N. Ağdağ, D.T. Sponza, Anaerobic/aerobic treatment of municipal landfill leachate in sequential two-stage up-flow anaerobic sludge blanket reactor (UASB)/completely stirred tank reactor (CSTR) systems, Process Biochem., 40 (2005) 895–902.

[10] J. Derco, A.Ž. Gotvajn, J. Zagorc-Končan, B. Almásiová, A. Kassai, Pretreatment of landfill leachate by chemical oxidation processes, Chem. Pap., 64 (2010) 237–245.

[11] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, Treatment of leachate by electrocoagulation using aluminum and iron electrodes, J. Hazard. Mater., 154 (2008) 381–389.

[12] D. Trebouet, J. Schlumpf, P. Jaouen, F. Quemeneur, Stabilized landfill leachate treatment by combined physicochemical–nanofiltration processes, Water Res., 35 (2001) 2935–2942.

[13] T. Yilmaz, A. Aygün, A. Berktay, B. Nas, Removal of COD and colour from young municipal landfill leachate by Fenton process, Environ. Technol., 31 (2010) 1635–1640.

[14] D.M. Bila, A.F. Montalvao, A.C. Silva, M. Dezotti, Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement, J. Hazard. Mater., 117 (2005) 235–242.

[15] A. Goi, Y. Veressinina, M. Trapido, Combination of ozonation and the Fenton processes for landfill leachate treatment: evaluation of treatment efficiency, Ozone Sci. Eng., 31 (2009) 28–36.

[16] S. Huang, V. Diyamandoglu, J. Fillos, Ozonation of leachates from aged domestic landfills, Ozone Sci. Eng., 15 (1993) 433–444.

[17] R.G. Rice, Applications of ozone for industrial wastewater treatment—a review, Ozone Sci. Eng., 18 (1996) 477–515.

[18] D.-H. Ahn, W.-S. Chang, T.-I. Yoon, Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process, Process Biochem., 34 (1999) 429–439.

[19] K. Ikehata, M.G. El-Din, Aqueous pesticide degradation by hydrogen peroxide/ultraviolet irradiation and Fenton-type advanced oxidation processes: a review, J. Environ. Eng. Sci., 5 (2006) 81–135.

[20] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater., 98 (2003) 33–50.

[21] A. Aygün, Tekstil endüstrisi reaktif ve dispers boya banyo atıksularının elektrokoagülasyon prosesi ile arıtımı: Yanıt yüzey yöntemi ile optimizasyon, Selçuk Univeristy Science Institute, 2012.

[22] P. Sudamalla, S. Pichiah, M. Manickam, Responses of surface modeling and optimization of Brilliant Green adsorption by adsorbent prepared from *Citrus limetta* peel, Desal. Wat. Treat., 50 (2012) 367–375.

[23] American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 21th ed., APHA, Washington, 2005.

[24] A. Lopez, M. Pagano, A. Volpe, A.C. Di Pinto, Fenton's pre-treatment of mature landfill leachate, Chemosphere, 54 (2004) 1005–1010.

[25] M.E. Argun, M. Karatas, Application of Fenton process for decolorization of reactive black 5 from synthetic wastewater: kinetics and thermodynamics, Environ. Prog. Sustain. Energy, 30 (2011) 540–548.

[26] E. Basturk, M. Karatas, Advanced oxidation of Reactive Blue 181 solution: a comparison between Fenton and Sono-Fenton Process, Ultrason. Sonochem., 21 (2014) 1881–1885.

[27] Y.W. Kang, M.-J. Cho, K.-Y. Hwang, Correction of hydrogen peroxide interference on standard chemical oxygen demand test, Water Res., 33 (1999) 1247–1251.

[28] I. Gulkaya, G.A. Surucu, F.B. Dilek, Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater, J. Hazard. Mater., 136 (2006) 763–769.

[29] P. Bautista, A. Mohedano, M. Gilarranz, J. Casas, J. Rodriguez, Application of Fenton oxidation to cosmetic wastewaters treatment, J. Hazard. Mater., 143 (2007) 128–134.

[30] D. Baş, İ.H. Boyacı, Modeling and optimization I: usability of response surface methodology, J. Food Eng., 78 (2007) 836–845.

[31] S. Ghafari, H.A. Aziz, M.H. Isa, A.A. Zinatizadeh, Application of response surface methodology (RSM) to optimize coagulation–flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum, J. Hazard. Mater., 163 (2009) 650–656.

[32] P. Kirmizakis, C. Tsamoutsoglou, B. Kayan, D. Kalderis, Subcritical water treatment of landfill leachate: application of response surface methodology, J. Environ. Manage., 146 (2014) 9–15.

[33] A. Amiri, M.R. Sabour, Multi-response optimization of Fenton process for applicability assessment in landfill leachate treatment, Waste Manage., 34 (2014) 2528–2536.

[34] H. Li, S. Zhou, Y. Sun, J. Lv, Application of response surface methodology to the advanced treatment of biologically stabilized landfill leachate using Fenton's reagent, Waste Manage., 30 (2010) 2122–2129.