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Multivariate approach to the Fenton process for the treatment of landfill leachate

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ABSTRACT

Fenton process has been widely used to treat landfill leachate. The "design of experiments" methodology was used to study the main variables affecting the Fenton process as well as their most relevant interactions. Results of two-level-factorial-design indicated that pH, COD, and the interaction of pH and COD gave negative effects, but Fe(II) dosage and H_2O_2/Fe(II) mole ratio showed positive effect, respectively. The quadratic model was derived based on the results of both two-level-factorial-design experiment and further runs of star points and center points. The response surface plots of quadratic model were obtained accordingly and the optimal conditions were derived from the quadratic model.

1. Introduction

Recently there are numeral reports about the treatment of landfill leachate by the Fenton process either as a post- or a pre-treatment step [1]. In the Fenton process, iron and hydrogen peroxide are the two major chemicals that determine not only the operation costs but also the treatment efficacy. To understand better and improve the Fenton process, numerous studies have been conducted to determine the optimal reaction conditions [2]. 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 [3].

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 will have better reliability. For example, technique such as two-level-factorial-design can be used to overcome the problem of inter-variable interaction [4]. There are a few advantages in two-level-factorial-design over the one-factor-at-a-time method [3,4]. By initially restricting the tests to only two levels, the number of experiments can be minimized. The two-level-factorial-design requires only two runs per factor studied, e.g., low and high levels. This statistics-based method involves simultaneous adjustment of experimental factors at only two levels, assuming linearity in the factor effects. The effect of a factor can be estimated at several levels of the other factors, yielding conclusions that are valid over a range of experimental conditions. Even though two-level-factorial-design is unable to explore fully a wide range in the factor space, it can indicate major trends. A promising direction for further experimentation can be determined because the few critical factors are separated from the insignificant factors. Further investigation of critical factors generates a response surface that can be used to approach the process to the optimum condition. Furthermore, they can detect and estimate interactions among variables. Although there are many reports on the application of response

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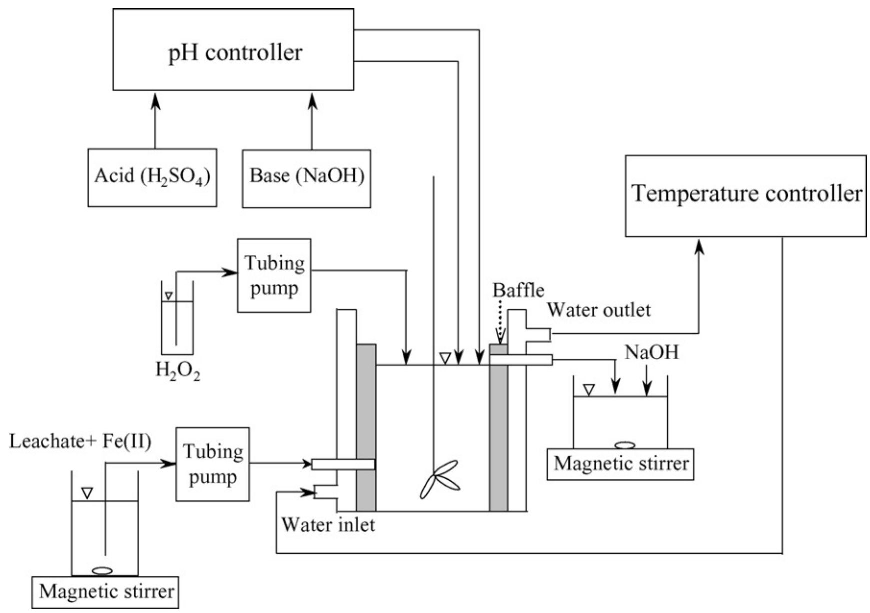

Fig. 1. Experimental set-up.

surface methodology (RSM) to Fenton type reaction (including photo-Fenton and electro-Fenton) for the treatment of wastewater [5–21], the application to the treatment of landfill leachate was few [22]. Therefore, in this paper, the treatment of landfill leachate using Fenton process was first evaluated in terms of COD removal efficiency with two-level-factorial-design. H_2O_2/Fe(II) mole ratio, Fe(II) dosage, pH and initial COD as the key parameters affecting COD removal were studied in this evaluation. The quadratic model depicting the response surface was then determined with further experiments to the star points and center point, and the favorable conditions were derived from the model.

2. Materials and methods

Leachate samples were taken with polyethylene bottles from the Central Solid Waste Management Center (CSWMC) at Sandtown, Delaware, USA. Samples were preserved in refrigerator at 4 °C in accordance with the Standard Methods [23]. Prior to the experiments, large particles and debris were removed by centrifuge to minimize particulate effects in oxidation reactions. The leachate samples were centrifuged for 10 min at 10000 rpm (or 12200 g) using Sorvall superspeed refrigerated centrifuge (Dupont Co., Wilmington, DE, Model RC-5). The characteristics of the centrifuged leachate were pH 6.65–6.69, COD 8298–8894 mg L^{-1}, TOC 2040–2207 mg L^{-1}, and alkalinity as $CaCO_3$ 3500–4600 mg L^{-1}.

All chemicals used were ACS (American Chemical Society) certified grade and obtained from Fisher Scientific Company, Springfield, NJ, or Aldrich Chemical Company, Milwaukee, WI.

The completely-stirred tank reactor (CSTR) experiments were carried out using a one-liter double jacket spherical plastic reactor with four baffles to minimize vortexing and rotational flow (Fig. 1). Mixing was provided by a variable speed motor connected to an epoxy-coated steel shaft and Teflon standard three-blade propeller. It was vertically mounted above one propeller diameter from the tank bottom. Mixing speed was about 1750 rpm, which was measured by strobotac electronic stroboscope (General Readi Co., West Concord, MA, Type 1531). The acidic condition on the reactor was controlled with an automatic pH controller (New Brunswick Scientific Co., Model pH-2) using 1-M sulfuric acid and 10-M sodium hydroxide. The reactor temperature was maintained 25 ± 1 °C by a water circulator.

Leachate samples were diluted to the desired COD strengths with distilled water, and then ferrous iron was dissolved into the 6.5-liter diluted leachate. Apply 1-liter leachate-iron solution into the reactor. Concentrated sulfuric acid was used to adjust pH around the operating value. The remaining 5.5-liter leachate-iron solution was stocked in a cylindrical tank. A magnetic stirred bar was used to keep the stock solution homogenized. To initiate the experiment, two peristaltic pumps were switched on and the hydrogen peroxide solution and the leachate-iron solution were separately injected into the reactor. Samples from the overflow were taken for the analysis of residual COD by both Hach vials and a closed reflux, colorimetric method at 600 nm with Hach spectrophotometer (Hach DR/2000, Loveland, CO.) according to the Standard Methods [23].

3. Results and discussion

Major factors that affect the performance of the Fenton process were as follows: (1) hydraulic retention time, (2) reaction time, (3) reaction pH, (4) hydrogen peroxide to ferrous iron mole ratio, (5) initial COD, (6) ferrous iron dosage, (7) temperature, (8) final pH and (9) age of leachate. Based on the protocol of two-level-

Table 1
Variable levels for two levels, and star and center points

Variables	Symbol	−2	−1	0	1	2
Reaction pH: A	X_1	2	3	4	5	6
H_2O_2/Fe(II) mole ratio: B	X_2	0.625	1.750	2.875	4.000	5.125
Fe(II) dosage (mol/L): C	X_3	0.0125	0.0250	0.0375	0.0500	0.0625
COD (mg/L): D	X_4	500	2450	4400	6350	8300

Table 2
Design matrix for the 2^4 factorial design of Fenton's process

Observation number	pH	H_2O_2/Fe(II) mole ratio	Fe(II) dosage (mol/L)	COD (mg/L)	COD removal efficiency (%)
1	–1	–1	–1	–1	47.1
2	+1	–1	–1	–1	27.6
3	–1	+1	–1	–1	62.1
4	+1	+1	–1	–1	22.1
5	–1	–1	+1	–1	72.4
6	+1	–1	+1	–1	50.1
7	–1	+1	+1	–1	81.4
8	+1	+1	+1	–1	44.1
9	–1	–1	–1	+1	24.5
10	+1	–1	–1	+1	19.1
11	–1	+1	–1	+1	32.3
12	+1	+1	–1	+1	17.7
13	–1	–1	+1	+1	41.4
14	+1	–1	+1	+1	30.2
15	–1	+1	+1	+1	60.8
16	+1	+1	+1	+1	26.2

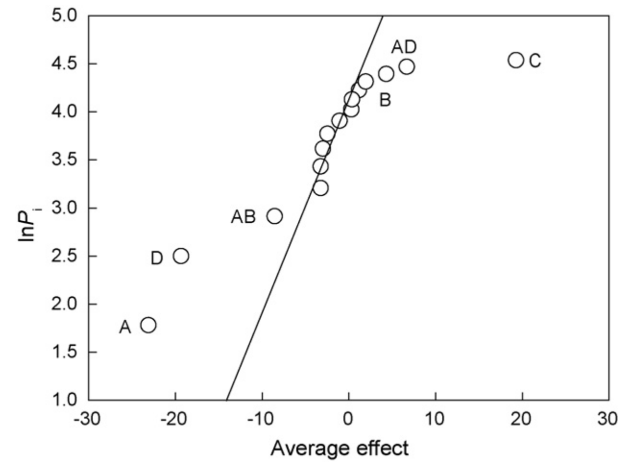

Fig. 2. ln P_i versus average effect.

Table 3
Design matrix for star points and center point of the 2^4 factorial design of Fenton's process

Observation number	pH	H_2O_2/Fe(II) mole ratio	Fe(II) dosage (mol/L)	COD (mg/L)	COD removal efficiency (%)
17	–2	0	0	0	55.8
18	+2	0	0	0	18.6
19	0	–2	0	0	17.1
20	0	+2	0	0	43.9
21	0	0	–2	0	22.8
22	0	0	+2	0	64.3
23	0	0	0	–2	87.8
24	0	0	0	+2	32.1
25	0	0	0	0	45.5
26	0	0	0	0	45.0
27	0	0	0	0	45.1
28	0	0	0	0	45.6

factorial-design, in single replicate, the total number of experiment run is 2^9. In a case including a third level for in-depth investigation, the number of runs becomes excessive. Therefore, first, several factors were pre-selected based on the results of one-factor-at-a-time experiment [24] and excluded from two-level-factorial-design experiment. These factors were: (1) hydraulic retention time, (2) reaction time, (3) temperature, (4) pH, and (5) leachage age. Since the half-life was 60 min as determined from batch experiments, the hydraulic retention time was fixed at 60 min. It was assumed that the steady state was obtained at three times of the hydraulic retention time; so that the reaction time was fixed at 180 min. In field conditions, temperature would not be controlled, so was excluded from the factor of two-level-factorial-design experiment and fixed at $25 \pm 1\,^{\circ}C$. Temperature effect can be obtained from Arrhenius equation. Final pH was fixed at 7.5–8.0, which was confirmed as optimal [25]. It does not seem reasonable to quantify the effect of leachate age because the characteristics change continuously according to the burial age. It was excluded from the factor of two-level-factorial-design experiment, and young leachate from area D-phase 1 (burial age 3–5 years) on the Central Solid Waste Management Center at Sandtown, Delaware was used [26].

Table 1 shows the levels of the four major factors tested in two-level-factorial-design study. The notations of (–1) and (+1) illustrate the low level and the high level of two-level-factorial-design experiment, respectively. The notations of (–2) and (+2), and (0) are those levels of star points and center point used in-depth investigation.

At first, 16 (=2^4) runs of two-level-factorial-design experiment for four parameters were performed randomly. The response was the removal efficiencies of COD. Table 2 shows a design matrix for the experiment. The combination of experimental conditions

Table 4
The calculation of average effects by the contrast coefficients

COD removal (%)	A	B	AB	C	AC	BC	ABC	D	AD	BD	ABD	CD	ACD	BCD	ABCD
47.1	–	–	+	–	+	+	–	–	+	+	–	+	–	–	+
27.6	+	–	–	–	–	+	+	–	–	+	+	+	+	–	–
62.2	–	+	–	–	+	–	+	–	+	–	+	+	–	+	–
22.1	+	+	+	–	–	–	–	–	–	–	–	+	+	+	+
72.4	–	–	+	+	–	–	+	–	+	+	–	–	–	+	–
50.1	+	–	–	+	+	–	–	–	–	+	+	–	+	+	+
81.4	–	+	–	+	–	+	–	–	+	–	+	–	–	–	+
44.1	+	+	+	+	+	+	+	–	–	–	–	–	+	–	–
24.4	–	–	+	–	+	+	–	+	–	–	+	–	–	+	–
19.1	+	–	–	–	–	+	+	+	+	–	–	–	+	+	+
32.3	–	+	–	–	+	–	+	+	–	+	–	–	–	–	+
17.7	+	+	+	–	–	–	–	+	+	+	+	–	+	–	–
41.4	–	–	+	+	–	–	+	+	–	–	+	+	–	–	+
30.2	+	–	–	+	+	–	–	+	+	–	–	+	+	–	–
60.8	–	+	–	+	–	+	–	+	–	+	–	+	–	+	–
26.2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Average effect	–23.1	4.3	–8.5	19.3	–3.2	0.3	–1.1	–19.4	6.7	1.2	0.4	–3.0	–3.2	1.9	–2.5
Rank	1	13	3	15	4	9	8	2	14	11	10	6	5	12	7

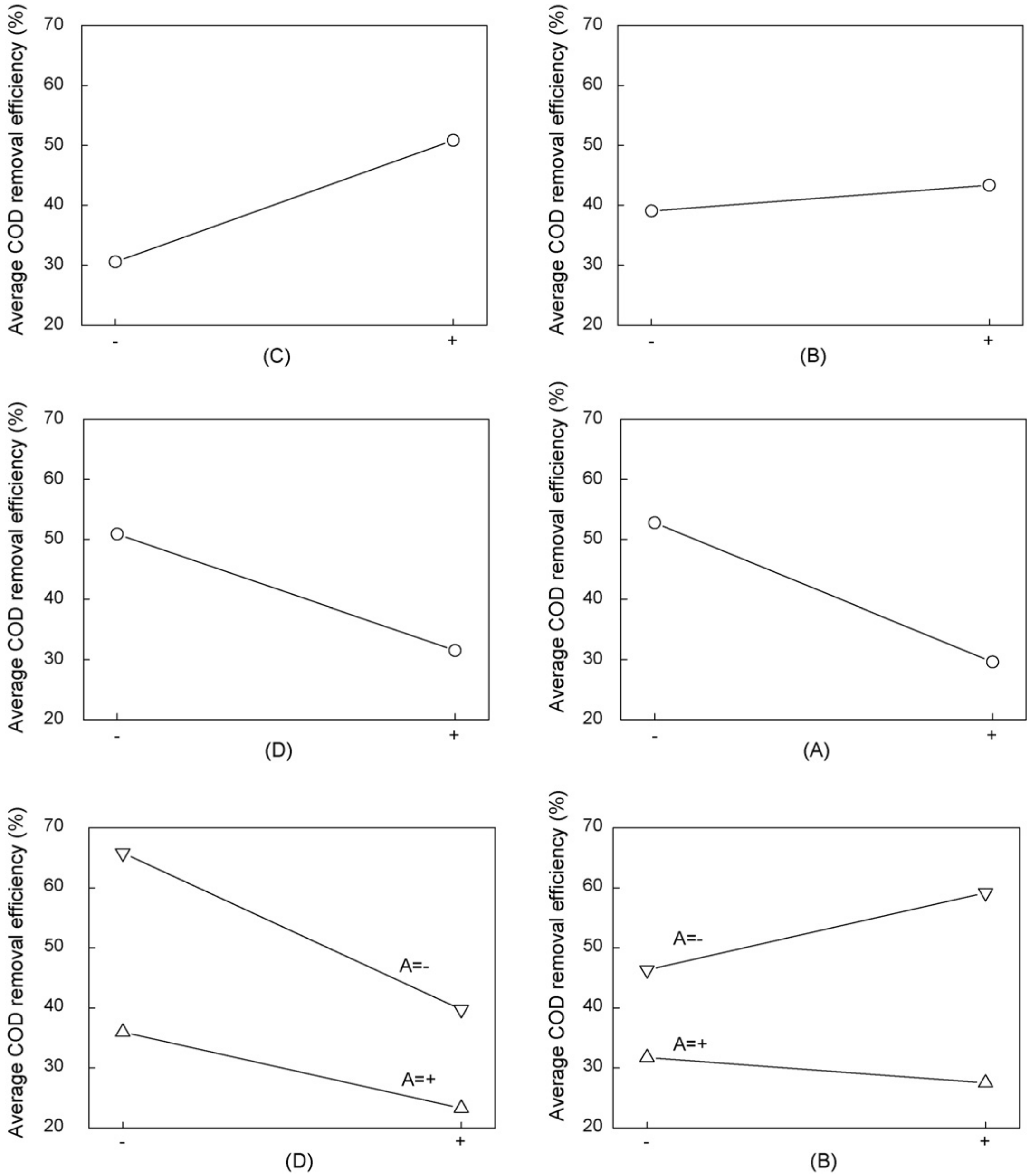

Fig. 3. The average effect of the significant factors.

with the levels is shown together. A (−1) sign and a (+1) sign for a quantitative variables represent the low level and the high level, respectively.

In order to check the assumption of linearity in the factor effects, further experiments to the star points and center point were performed randomly based on the conditions illustrated in Table 3. A (−2) sign, a (+2) sign, and a (0) sign for a quantitative variables rep-

Table 5
Analysis of variance for the model

Source	Degrees of freedom	Sum of squares	Mean Square	*F*-value
Model	14	9974.29	712.45	27.52
Error	13	336.52	25.89	Prob > *F* < 0.0001
Total	27	10310.81		

Table 6
The estimated coefficients and the corresponding *t*-values

Term	Coefficient	Standard error	*t*-value	Prob > |*t*|
Intercept	45.3	2.5439	17.81	<0.0001
X_1	−10.80	1.0385	−10.40	<0.0001
X_2	3.67	1.0385	3.53	0.0037
X_3	9.88	1.0385	9.51	<0.0001
X_4	−11.10	1.0385	−10.68	<0.0001
X_1X_1	−2.29	1.0385	−2.21	0.0459
X_2X_1	−4.27	1.2720	−3.36	0.0052
X_2X_2	−3.97	1.0385	−3.82	0.0021
X_3X_1	−1.62	1.2720	−12.7	0.2254
X_3X_2	0.14	1.2720	0.11	0.9117
X_3X_3	−0.70	1.0385	−0.68	0.5090
X_4X_1	3.34	1.2720	2.63	0.0208
X_4X_2	0.58	1.2720	0.46	0.6552
X_4X_3	−1.49	1.2720	−1.17	0.2613
X_4X_4	3.39	1.0385	3.27	0.0061

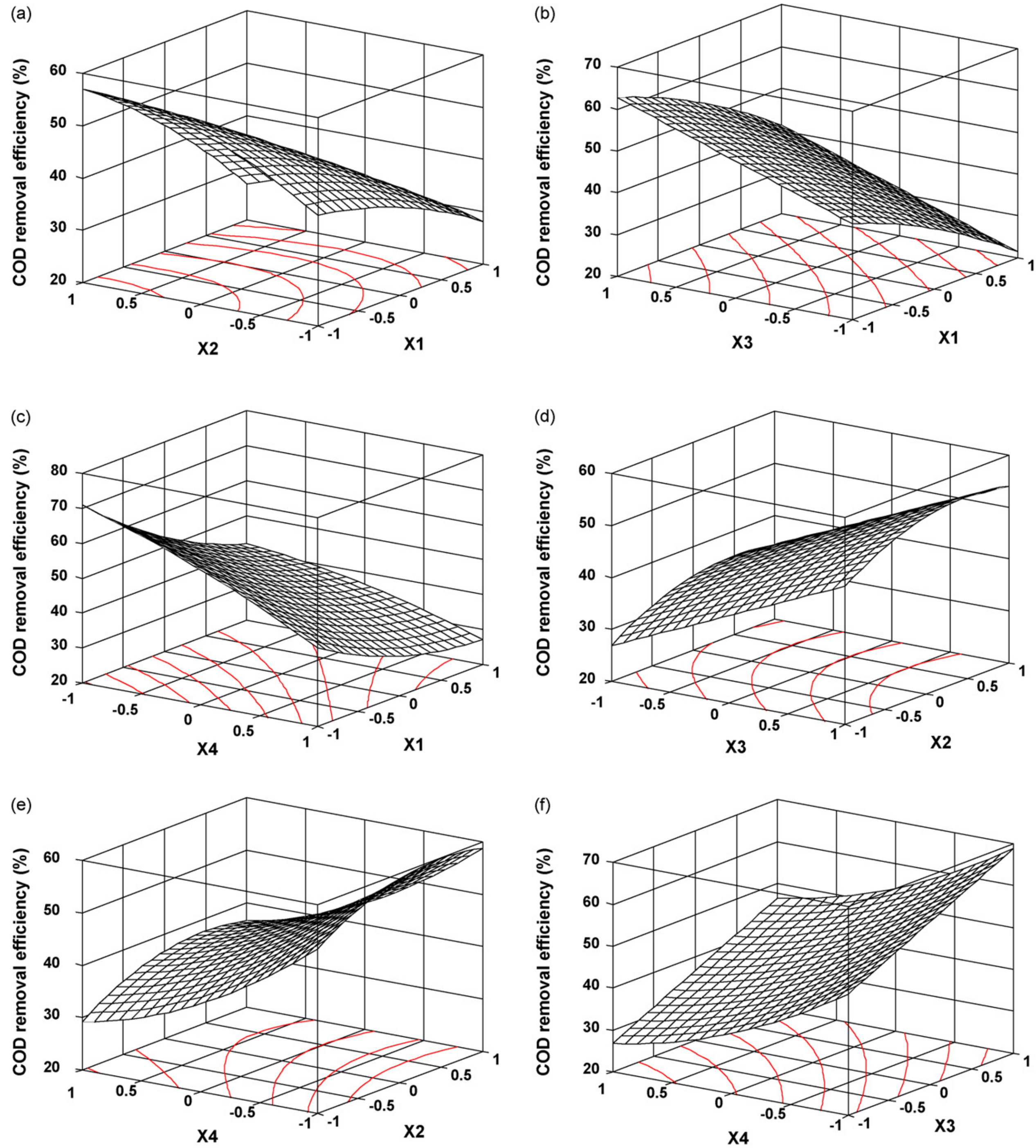

Fig. 4. (a) Response surface plot of the effect of reaction pH and H_2O_2/Fe(II) mole ratio on COD removal efficiency ($X_3 = X_4 = 0$), (b) response surface plot of the effect of reaction pH and Fe(II) dosage on COD removal efficiency ($X_2 = X_4 = 0$), (c) response surface plot of the effect of reaction pH and initial COD value on COD removal efficiency ($X_2 = X_3 = 0$), (d) response surface plot of the effect of H_2O_2/Fe(II) mole ratio and Fe(II) dosage on COD removal efficiency ($X_1 = X_4 = 0$), (e) response surface plot of the effect of H_2O_2/Fe(II) mole ratio and initial COD value on COD removal efficiency ($X_1 = X_3 = 0$) and (f) response surface plot of the effect of Fe(II) dosage and initial COD value on COD removal efficiency ($X_1 = X_2 = 0$).

resent the star point of the low level, the star point of the high level, and the center point, respectively.

Tables 2 and 3 summarize the results from the two-level-factorial-design experiments, and star and center points experiment.

The removals of COD from the two-level-factorial-design experiment were between 17.7% and 81.4%. At first, various effects should be calculated to begin the analysis of the results using the table of contrast coefficients and Yates' algorithm. The average effect of one variable or interaction between/among variables overall conditions of the other variables were calculated using the table of contrast coefficients as shown in Table 4. In order to screen several vital significant factors from those insignificant, a half-normal plot was drawn. The average effects were simply ranked according to the absolute value from low to high. Also, they were assigned cumulative half-normal probability values, P_i, according to the following

Table 7
F-ratios of the parameters

Source	Number of parameter	Degrees of freedom	Sum of squares	*F*-ratio	Prob > *F*
X_1	1	1	2801	108.2	<0.0001
X_2	1	1	323.4	12.49	0.0037
X_3	1	1	2342	90.48	<0.0001
X_4	1	1	2955	114.1	<0.0001
X_1X_1	1	1	126.2	4.874	0.0459
X_2X_1	1	1	291.6	11.26	0.0052
X_2X_2	1	1	377.8	14.60	0.0021
X_3X_1	1	1	41.92	1.620	0.2254
X_3X_2	1	1	0.3306	0.0128	0.9117
X_3X_3	1	1	11.94	0.4611	0.5090
X_4X_1	1	1	178.9	6.911	0.0208
X_4X_2	1	1	5.406	0.2088	0.6552
X_4X_3	1	1	34.70	1.379	0.2613
X_4X_4	1	1	276.6	10.69	0.0061

formula:

$$\ln P_i(\%) = \ln\left\{100\left[\frac{(i-0.05)}{m}\right]\right\} \quad (1)$$

where *i* is the rank and *m* is the number of the effects.

Fig. 2 shows the plots of the effects versus their assigned half-normal probability. A line was drawn to find the group of near-zero effects. Some factors that gave near-zero effects fell on the straight line, but significant factors fell off the line. Significant factors were labeled on the plots, which were found as follows: (1) Fe(II) dosage, (2) pH and COD interaction, (3) H_2O_2/Fe(II) mole ratio, (4) pH and H_2O_2/Fe(II) mole ratio, (5) COD, and (6) pH. The average effects of the significant factors were calculated and shown in Fig. 3. The pH, COD, and the interaction of pH and COD gave negative effects, but Fe(II) dosage and H_2O_2/Fe(II) mole ratio showed positive effects, respectively. The interaction of pH and H_2O_2/Fe(II) mole ratio showed positive effect or negative effect depending on the pH levels. Here positive effect means that the average effect increases as the level increases, whereas negative effect means that the average effect decreases as the level increases. The negative effect of COD and the positive effect of Fe(II) dosage mean that more dosage is necessary to achieve better COD removal for a higher strength leachate. The interaction of pH and COD showed different impacts, depending on the pH level. Even though the higher pH gave a less negative effect than the lower pH, clearly it was better to use a low pH considering the negative effect of pH.

In conclusion, it is desirable to run the process at a low pH and a high H_2O_2/Fe(II) mole ratio from the negative effect of pH, the positive effect of high H_2O_2/Fe(II) mole ratio, and their interaction.

The results of both two-level-factorial-design experiment (16 runs) and further runs (12 runs) of star points and center point were used to optimize the process. By adding these points to the factorial, it is possible to include second-order terms for interactions and to check the curvature in the response. Standard statistical analyses were performed to validate the overall results and individual effects using a statistical software package of JMP 3.2 (SAS Institute Inc.). The analysis of variance is summarized in Table 5. They show a reliable confidence in the estimation of COD removal efficiency ($R^2 = 0.9674$).

Significant factors selected were almost same as obtained from two-level-factorial- design. When selecting significant factors, both *t*-ratio (Table 6) and *F*-ratio (Table 7) were used. These tables showed comparable results. The negative effects of pH and COD, and the positive effects of H_2O_2/Fe(II) mole ratio and Fe(II) dosage were confirmed, and have been discussed in our previous study when one-factor-at-a-time experiment was conducted [24]. When the non-significant coefficients were dropped from the model, the model was reduced as follows,

$$\begin{aligned}\text{COD removal efficiency}(\%) = {} & 44.24 - 10.80X_1 + 3.67X_2 + 9.88X_3 \\ & -11.10X_4 - 2.12X_1^2 - 4.27X_1X_2 \\ & -3.79X_2^2 + 3.34X_1X_4 + 3.57X_4^2 \quad (2)\end{aligned}$$

The corresponding response surface plots were obtained from the above quadratic equation and illustrated in Fig. 4a–f. Some interactions between/among variables were significant so that the curvature of three-dimensional surfaces was obvious, as showed in Fig. 4a–f.

As can be seen in Fig. 4a,d and e, there existed an optimum H_2O_2/Fe(II) mole ratio (X_2) for COD removal. This means that regardless of the magnitude of H_2O_2/Fe(II) mole ratio it would cause the decrease in COD removal. Too low the H_2O_2/Fe(II) mole ratio, it would lead to faster disappearance rate of ferrous ion as well as hydroxyl radical via reaction (3),

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (3)$$

On the other hand, too high the H_2O_2/Fe(II) mole ratio, the low COD removal efficiency was brought by the side reaction between hydrogen peroxide and hydroxyl radical via reaction (4),

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2{}^{\bullet} + H_2O \quad (4)$$

The above reaction results in the consumption of hydrogen peroxide as well hydroxyl radical, and the production of hydroperoxyl radical, a species with much weaker oxidizing power compared with hydroxyl radical.

It is interesting to note that the optimal H_2O_2/Fe(II) mole ratio (X_2) was independent of initial COD and ferrous iron dosage (Fig. 4d and e). However, the optimal value was related to pH and decreased with pH (Fig. 4a). Specifically, the optimal H_2O_2/Fe(II) mole ratio was 4.7, 4.4, 4.0, 3.7, and 3.4 when the reaction pH was fixed at 2, 2.5, 3, 3.5, and 4, respectively.

4. Conclusion

The two-level-factorial-design was used to design the Fenton process for the purpose of treating landfill leachate from area D-phase 1 on the Central Solid Waste Management Center at Sandtown, Delaware. Using the two level experiment results, average effects were calculated and plotted a half-normal probability plot. COD, pH, and the interaction of pH and COD gave negative effects, but Fe(II) dosage and H_2O_2/Fe(II) mole ratio showed positive effect, respectively. Conclusively, it is desirable to run the process at a low pH and a high H_2O_2/Fe(II) mole ratio from the negative effect of pH, the positive effect of high H_2O_2/Fe(II) mole ratio, and their interaction.

The results of both two-level-factorial-design experiment and further runs of star points and center points were used to optimize the process. The coefficients of quadratic model were derived and the corresponding response surface plots were obtained.

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References

[1] Y. Deng, J.D. Englehardt, Treatment of landfill leachate by the Fenton process, Water Res. 40 (2006) 3683–3694.
[2] J. Yoon, Y. Kim, J. Huh, Y. Lee, D. Lee, Roles of oxidation and coagulation in Fenton process for the removal of organics in landfill leachate, J. Ind. Eng. Chem. 8 (2002) 410–418.
[3] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experiments, Wiley, New York, 1978.
[4] M.J. Anderson, P.J. Whitcomb, Optimize your process-optimization effects, Chem. Eng. Prog. 92 (1996) 51–60.
[5] V. Sarria, S. Kenfack, O. Guillod, C. Pulgarin, An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants, J. Photochem. Photobiol. A159 (2003) 89–99.
[6] M. Ahmadi, F. Vahabzadeh, B. Bonakdarpour, E. Mofarrah, M. Mehranian, Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation, J. Hazard. Mater. B123 (2005) 187–195.
[7] W.C. Paterlini, R.F.P. Nogueira, Multivariate analysis of photo-Fenton degradation of the herbicides tebuthiuron, diuron and 2,4-D, Chemosphere 58 (2005) 1107–1116.
[8] F. Martinez, G. Calleja, J.A. Melero, R. Molina, Heterogeneous photo-Fenton degradation of phenolic aqueous solutions over iron-containing SBA-15 catalyst, Appl. Catal. B60 (2005) 181–190.
[9] V. Arantes, C. Baldocchi, A.M.F. Milagres, Degradation and decolorization of a biodegradable-resistant polymeric dye by chelator-mediated Fenton reactions, Chemosphere 63 (2006) 1764–1772.
[10] C.T. Benatti, C.R.G. Tavares, T.A. Guedes, Optimization of Fenton's oxidation of chemical laboratory wastewaters using the response surface methodology, J. Environ. Manage. 80 (2006) 66–74.
[11] W. Gernjak, M. Fuerhacker, P. Fernandez-Ibanez, J. Blanco, S. Malato, Solar photo-Fenton treatment – process parameters and process control, Appl. Catal. B64 (2006) 121–130.
[12] R. Molina, F. Martinez, J.A. Melero, D.H. Bremner, A.G. Chakinala, Mineralization of phenol by a heterogeneous ultrasound/Fe-SBA-15/H_2O_2 process: multivariate study by factorial design of experiments, Appl. Catal. B66 (2006) 198–207.
[13] R. Oliveira, M.F. Almeida, L. Santos, L.M. Madeira, Experimental design of 2,4-dichlorophenol oxidation by Fenton's reaction, Ind. Eng. Chem. Res. 45 (2006) 1266–1276.
[14] M.P. Ormad, R. Mosteo, C. Ibarz, J.L. Ovelleiro, Multivariate approach to the photo-Fenton process applied to the degradation of winery wastewaters, Appl. Catal. B66 (2006) 58–63.
[15] A.G. Trovo, W.C. Paterlini, R.F. Pupo Nogueira, Evaluation of the influences of solution path length and additives concentrations on the solar photo-Fenton degradation of 4-chlorophenol using multivariate analysis, J. Hazard. Mater. B137 (2006) 1577–1582.
[16] E.C. Catalkaya, F. Kargi, Effects of operating parameters on advanced oxidation of diuron by the Fenton's reagent: a statistical design approach, Chemosphere 69 (2007) 485–492.
[17] M. Sleiman, D. Vildozo, C. Ferronato, J.-M. Chovelon, Photocatalytic degradation of azo dye Metanil Yellow: optimization and kinetic modeling using a chemometric approach, Appl. Catal. B77 (2007) 1–11.
[18] S. Hammami, N. Oturan, N. Bellakhal, M. Dachraoui, M.A. Oturan, Oxidative degradation of direct orange 61 by electro-Fenton process using a carbon felt electrode: application of the experimental design methodology, J. Electroanal. Chem. 610 (2007) 75–84.
[19] A.G. Chakinala, D.H. Bremner, P.R. Gogate, K.C. Namkung, A.E. Burgess, Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing, Appl. Catal. B78 (2007) 11–18.
[20] A.K. Abdessalem, N. Oturan, N. Bellakhal, M. Dachraoui, M.A. Oturan, Experimental design methodology applied to electro-Fenton treatment for degradation of herbicide chlortoluron, Appl. Catal. B 78 (2008) 334–341.
[21] J. Herney-Ramirez, M. Lampinen, M.A. Vicente, C.A. Costa, L.M. Madeira, Experimental design to optimize the oxidation of Orange II dye solution using a clay-based Fenton-like catalyst, Ind. Eng. Chem. Res. 47 (2008) 284–294.
[22] H. Zhang, C.-P. Huang, Treatment of landfill leachate by Fenton oxidation process, Chin. J. Chem. Eng. 10 (2002) 128–131.
[23] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 18th edition. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington DC, 1992.
[24] H. Zhang, H.J. Choi, C.P. Huang, Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor, J. Hazard. Mater. B136 (2006) 618–623.
[25] H.-J. Choi, Evaluation of Fenton's Process for the Treatment of Landfill Leachate, Ph.D. Dissertation, University of Delaware, 1998.
[26] Delaware Solid Waste Authority, Meeting the Needs of Future Generations, Annual report, Dover, Delaware, 1997.