Modeling physical and oxidative removal properties of Fenton process for treatment of landfill leachate using response surface methodology (RSM)

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ABSTRACT

In this study, the Fenton process was found to be successful to treat landfill leachate rejected after reverses osmose treatment. Central composite design (CCD) and response surface method (RSM) were applied to evaluate and optimize the interactive effects of three operating variables, initial pH and dosages of H_2O_2 and Fe^{2+} on physical and oxidative performances of Fenton process. Six dependent parameters such as overall chemical oxygen demand (COD) removal, COD removals of oxidation and coagulation, mineralization, humic substances (HS) removal and sludge volume ratio (SVR) were either directly measured or calculated as responses. According to analysis of variances (ANOVA) results, six proposed models could be used to navigate the design space with high regression coefficient R^2 varied from 0.9489 to 0.9988. It was found that initial pH, H_2O_2 and Fe^{2+} dosage had significant effects on the overall COD removal, mineralization and HS removal due to their respective effects on the oxidation and coagulation removals. Synergies effect of oxidation and coagulation during Fenton process controlled the treatment. The visual search of overlaying critical response contours plot was demonstrated. The results indicated the optimum conditions to be 3.64 of initial pH, 100 mM of Fe^{2+} and 240 mM of H_2O_2 dosage, respectively. The experimental data and model predictions agreed well. The overall COD removal, COD removals of oxidation and coagulation, mineralization, HS removal and SVR of 71.81%, 46.22%, 25.80%, 63.81%, 91.53% and 3.50 ml/mM were demonstrated.

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1. Introduction

Landfill leachate is a complex wastewater, and it always contains high concentration organic pollutants. The most popular treatments of landfill leachate in the past were biological treatments [1]. However, the biological treatments were known to be inadequate in handling such a difficult treatment task, because the refractory organic pollutants in landfill leachate inhibitted the biomass activity and/or were recalcitrant to biodegradation [2,3]. Recently, growing interests have been focused on Fenton treatment of landfill leachate either as a post- or a pre-treatment step [1,4–8]. As one of advanced oxidation processes (AOPs), Fenton process can achieve two alternative goals exploiting the strong oxidation potential of hydroxyl radicals (•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 with the aim of making their subsequent biological treatment possible [3,9]. Generally, Fenton process is composed of following stages: pH adjustment, oxidation reaction, neutralization, coagulation and solid–liquid separation [2]. Under acidic condition, the organic substances are degraded by reactive free radicals •OH produced in the H_2O_2/Fe^{2+} mixture, and removed by means of coagulation with formation of ferric hydroxy complexes after neutralization. Both oxidation and coagulation play important roles in the removal of organics.It is important to understand the mutual relationships between reaction parameters in terms of hydroxyl radical production and consumption, in order to understand better and improve Fenton reaction. Kang and Hwang [2] mentioned that COD removal efficiency by oxidation was greatly affected by the pH value and the most effective oxidation reaction was observed below pH 4.0. Deng [3] indicated that at high peroxide dosages, higher Fe^{2+} dosage led to higher efficiency of coagulation due to higher concentrations of ferric coagulant after neutralization; however, this effect was not obvious at low peroxide dosages where low oxidation effi-

ciency occurred. And, Zhang et al. [7] found the favorable H_2O_2 to Fe^{2+} molar ratio was 1.5, and organic removal increased as dosage increased at the favorable H_2O_2 to Fe^{2+} molar ratio. However, the effects of variable mentioned above are studied independently, whilst keeping the others constant [6,7,10]. These one-factor-at-a-time screening designs of the reaction conditions are time consuming and not efficient, besides, the interactions between variables and their effects in the process are not determined by these ways.

Moreover, landfill leachate is known to contain significant quantities of humic substances (HS), which pose a variety of problems in treatment operations and distribution systems [11]. HS may accelerate the transport of hydrophobic pollutants from the landfills side into the environment due to binding with heavy metals and organic pollutants present in leachates [12,13]. In addition, HS are the precursors of numerous chlorination byproducts that can cause certain cancers [14,15]. They also impart a brown/yellow colour to the water [11,16]. Extensive studies had been carried out elsewhere to characterize HS in landfill leachate [11,12,15,16]. However, no more removal relationship between the individual pollutant (such as HS) and the overall contaminants (denoted as COD and/or total organic carbon (TOC)) has been reported. It is therefore crucial that the degradation characteristics of HS in landfill leachate during treatment process should be well understood, and this would lead to better insights into the underlying degradation mechanisms responsible for treatment technology.

The statistical method of response surface methodology (RSM) has been proposed to include the influences of individual factors as well as their interactive influences [17]. It is an empirical statistical modeling technique employed for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multivariable equations and evaluate simultaneously the relative significance of several affecting factors even in presence of complex interaction. A further benefit of using the RSM design is the reduction of the number of experiments needed compared to a full experimental design at the same level. In addition, the eventual objective of RSM is to determine the optimum operating conditions for the system, or to determine the region, which satisfies the operating specifications [17]. In the last few years, RSM has been applied to optimize and evaluate the interactive effects of independent factors in Fenton's and Fenton-like processes for wastewater treatment such as humic acid (HA), herbicides aqueous or laboratory wastewaters [4,18,19]. However, only Zhang et al. [20] applied a two-level-factorial-design to optimize Fenton treatment of landfill leachate. Zhang et al. [20] proposed that pH, initial COD and their interaction gave negative effects whilst Fe^{2+} dosage and H_2O_2/Fe^{2+} mole ratio showed positive effect on COD removal. However, using RSM, the effect estimation of the interaction of various operating conditions on the organics removal performances by the oxidation and coagulation, as well as the sludge performance generated in Fenton process has not been reported.

In the present paper, the Fenton treatment of landfill leachate rejected by reverse osmosis (RO) was firstly evaluated in terms both of oxidation and coagulation removal efficiency with a Box–Behnken design of RSM. Quadratic models were used to adjust the studied experimental results, considering only the variables that presented significant effects. The effects of initial pH, dosages of Fenton's reagents and the interaction between these factors on (1) the oxidation and coagulation performance on removal of organics, (2) the mineralization characterization and (3) the removal characterization of HS in leachate were studied in this evaluation. Six interrelated parameters such as overall COD removal, COD removals by oxidation and coagulation, mineralization, HS removal, as well as sludge volume ratio (SRV) were evaluated as responses. Moreover, a continuous response surface of the main parameters was developed to provide an optimal region to satisfy the operating specifications.

2. Materials and methods

Landfill leachate rejected by RO was collected from Guangzhou Domestic Landfill site (600 m^3/d), South China. The landfill leachate was treated by a combined process, the treatment sequence is up-flow anaerobic sludge blanket (UASB), sequencing batch reactor (SBR), continuous micro-filtration (CMF) and reverse osmos (RO). The leachate effluent rejected by RO is known as concentrated leachate and its characteristics presented as follows: COD (4284 mg/l), TOC (2583 mg/l), biological oxygen demand (BOD) (28.5 mg/l), NH_3–N (62.9 mg/l), pH 7.88, turbidity (19.0 NTU), conductivity (39.2 ms/cm). The ratio of BOD_5/COD was about 0.01, which indicated that the concentrated leachate is difficult to treat biologically.

Concentrated leachate was prefiltered through a 0.45 μm glass fiber filter to remove large particles and debris, and maintain uniformity of tested samples. Experiments were carried out in 2 l beakers with 1 l wastewater under vigorous magnetic stirring at room temperature. The initial pH values were 2.0, 4.0 and 6.0; the dosages of H_2O_2 were 40, 180 and 320 mM; the dosages of Fe^{2+} were 20, 100 and 180 mM. Table 1 shows experimental conditions for all the experiments. The initial solution pH was adjusted to the desired value by using concentrated H_2SO_4 or NaOH solutions. Following the pH adjustment, granular ferrous sulfate ($FeSO_4 \cdot 7H_2O$) were quickly added and the reactions were initiated by adding hydrogen peroxide solution (H_2O_2, 30%, w/w) all at once. After 120 min reaction time, NaOH pellets were added to increase the pH to approximately 6.5 and a solution of 10 M NaOH solution was then added dropwise to a pH of 8.0 to terminate the reaction and precipitate residual ferric ions. Two samples of 100 ml aliquot solutions were immediately dispensed to graduated glass cylinders and heated in a 50 °C water bath for 30 min to remove residual H_2O_2 in solution. Subsequently, the two samples were brought to the room temperature, and one of two samples was settled for 30 min sedimentation, another was mixed uniformly under continuous magnetic stirring. The volume of the settled iron sludge was recorded. The supernatant solution and the mixed solution were taken for COD and TOC measurements and for determination of HS isolated from samples.

The dissolved organic matter (DOM) in leachate was fractionated into humic acid (HA), fulvic acid (FA) and hydrophilic (HyI) fractions, and the HA and FA was denoted as HS. The samples were prefiltered through a 0.45 μm glass fiber filter and acidified to pH 1.5 by addition of concentrated sulfuric acid (H_2SO_4, 96%). The precipitate (HA) and the supernatant (FA + HyI) were separated by centrifuging at 4500 rpm for 15 min. Supelite^{TM} DAX-8 resin (40–60 mesh, Sigma–Aldrich, USA) was used to isolate FA and HyI. The cleaning method of DAX-8 and the fractionation procedure for DOM from wastewater are described elsewhere [11,21]. The study used number 732 cation exchange resin (20–50 mesh, ZhengGuang, China) to protonate the FA and HyI. The concentrations of HS were monitored by measuring their TOC values. All experiments were carried out in duplicate in order to ensure data repeatability.

The overall COD removal, COD removals by oxidation and coagulation were measured by a slight modification of the methods of Kang and Hwang [2] and Deng [3], respectively. The COD value of supernatant was considered as the value of overall decontamination process (as $COD_{overall}$)—Fenton's oxidation plus coagulation. The COD value of mixed uniformly solution was considered as the value of oxidation process (as COD_{oxid}). The value of coagulation process was the difference between the overall value and the oxidation value as following:

$$COD_{coag} = COD_{overall} - COD_{oxid} \qquad (1)$$

COD was analyzed following the standard method with potassium dichromate and BOD_5, NH_4–N was measured according to

Table 1
Three-factor and three-level Box–Behnken central composite design and experimental results.

Coded Unit	Variables			Experimental responses					
	X_1 –	X_2 mM	X_3 mM	Y_1 %	Y_2 %	Y_3 %	Y_4 %	Y_5 %	Y_6 ml/mM
1	2.00(−1)	40.0(−1)	100.0 (0)	58.40	20.60	37.80	33.38	55.80	22.0
2	2.00(−1)	320.0(+1)	100.0 (0)	64.20	45.00	19.20	57.21	72.50	21.6
3	2.00(−1)	180.0 (0)	20.0 (−1)	52.10	39.40	12.70	34.26	63.60	11.5
4	2.00(−1)	180.0 (0)	180.0 (+1)	67.80	25.20	42.60	54.07	68.00	31.3
5	4.00(0)	40.0 (−1)	20.0 (−1)	49.00	25.10	23.90	24.18	54.40	13.7
6	4.00(0)	320.0 (+1)	20.0 (−1)	59.00	40.20	18.80	45.70	73.20	12.9
7	4.00(0)	40.0 (−1)	180.0 (+1)	54.50	17.40	38.10	34.75	57.60	27.9
8	4.00(0)	320.0 (+1)	180.0 (+1)	69.40	34.20	34.80	57.64	82.10	22.2
9	4.00(0)	180.0 (0)	100.0 (0)	68.80	43.40	25.40	57.99	88.90	11.5
10	4.00(0)	180.0 (0)	100.0 (0)	71.50	44.10	27.40	58.92	89.50	12.1
11	4.00(0)	180.0 (0)	100.0 (0)	69.60	43.50	26.10	59.38	88.10	10.6
12	4.00(0)	180.0 (0)	100.0 (0)	67.80	42.90	26.10	57.46	89.60	10.7
13	4.00(0)	180.0 (0)	100.0 (0)	71.30	43.20	28.10	59.49	89.80	11.2
14	6.00(+1)	40.0 (−1)	100.0 (0)	46.00	22.80	21.00	12.02	41.70	13.7
15	6.00(+1)	320.0 (+1)	100.0 (0)	51.80	29.90	21.90	30.52	65.10	8.1
16	6.00(+1)	180.0 (0)	20.0 (−1)	45.30	27.30	18.00	16.03	55.10	11.9
17	6.00(+1)	180.0 (0)	180.0 (+1)	45.00	25.10	19.90	16.10	58.60	14.8

X_1: first variable, initial pH, X_2: second variable, H_2O_2 dosage, X_3: third variable, Fe^{2+} dosage; Y_1: overall COD removal efficiency, Y_2: oxidation COD removal, Y_3: coagulation COD removal, Y_4: mineralization, Y_5: HS removal, Y_6: SVR.

standard methods [22]. The TOC values of samples were measured with TOC analyzer (Shimadzu, Germany). The pH value, turbidity and conductivity of samples were measured with a pH meter pHs-25 (Rex, China), turbidimeter WGZ-1A (Xinrui, China) and conductivimeter DDS-11A (Rex, China), respectively.

Sludge volume ratio (SVR) was calculated using the following equation:

$$\text{Sludge volume ratio(SVR)} = \frac{\text{sludge volume(ml)} \times 10}{\text{ferrous sulfate dosage(mM)}} \quad (2)$$

Experimental data were analyzed using the RSM procedure of the statistical analysis system and fitted to a second-order polynomial model. Quadratic equation for the variable was as follows [23]:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum_i \sum_j \beta_{ij} X_i X_j \quad (3)$$

Y is the predicted response, β_0 a constant; β_i the first-order model coefficient; β_{ii} the squared coefficient for the factor i; and β_{ij} the linear model coefficient for the interaction between factors i and j. X_i is the coded value of the main effect. The Design Expert Software (version 7.1.6, Stat-Ease, Inc., Minneapolis, MN) was used for the statistical design of experiments and data analysis. Analysis of variances (ANOVA) was used for graphical analyses of the data to obtain the interaction between the process variables and the responses. 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. Model terms were selected or rejected based on the P value (probability) with 95% confidence level. Three-dimensional (3D) plots and their respective contour plots were obtained based on effects of the two factors at three levels. Moreover, the perturbation plot would help to compare the effect of all the factors at a particular point in the design space. Furthermore, the optimum region was identified based on the main parameters in the overlay plot. The adequacy of the regression equations was checked by comparing the experimental data with predicted values obtained from the equations. Detail analysis on the model is presented in the following sections.

3. Results and discussion

3.1. Fitting the response surface models to significant independent variables

Central composite Box–Behnken experimental design was chosen for finding out the relationship between the response function (Y) and variables (X). Values of the independent variables (X_1–X_3) as well as their variation limits, and the experimental data obtained for six responses (Y_1–Y_6) are presented in Table 1. In this table the independent variables levels are presented in terms of the original unit in addition to coded levels (in parentheses). The coded values for initial pH (X_1), hydrogen peroxide and ferrous ion dosages (X_2 and X_3) were set at three levels: −1 (minimum), 0 (central) and +1 (maximum). Experimental results are shown as overall COD removal efficiency (Y_1), COD removal by oxidation (Y_2) and coagulation (Y_3), mineralization (Y_4), HS removal (Y_5), SVR (Y_6).

Tables 2 and 3 illustrate the reduced quadratic models in terms of coded factors with significant terms and also show other statistical parameters. In Table 2, six models (Y_1–Y_6) F-values of 34.01, 657.43, 47.17, 295.60, 423.32 and 1090.25 with a very low probability value ($P < 0.0001$) implied that terms were significant in all models. There was only 0.01% chance that a model F-value could occur due to noise. The ANOVA results for six parameters (Y_1–Y_6) showed that the significant ($P < 0.05$) response surface models with high R^2 value varied from 0.9489 to 0.9988 were obtained. These high R^2 coefficients ensured a satisfactory adjustment of the quadratic models to the experimental data [17]. The values of the adjusted R^2 of 0.9489, 0.9973, 0.9629, 0.9940, 0.9958 and 0.9984, respectively, for six model Y_1–Y_6 were also high to advocate high significance of the models [24]. Therefore, the response surface models were accurately employed for predicting variation percentage of these six parameters.

As also shown in Table 2, the lack of fit (LOF) F-values of all six models implied the variation of the data around the fitted model were not significant relative to the pure error. There were 14.08%, 30.75%, 13.13%, 10.43%, 12.55% and 10.25% chance for Y_1–Y_6 that the LOF F-value could occur due to noise, respectively. The value of probability of lack of fit (PLOF) higher than 0.05 show that the F-statistic was insignificant, implying significant model correlation between the variable and process response. Adequate precision (AP) compared the range of the predicted values at the design points to the average prediction error. The ratios of six models

Table 2
ANOVA results for response parameters.

Response	Final modified equations in terms of coded factors with significant terms	F	P	LOF	PLOF	R^2	$AdjR^2$	AP	SD	CV	PRESS
Y_1	$69.80 - 6.80X_1 + 4.56X_2 + 3.91X_3 - 4.00X_1X_3 - 10.06X_1{}^2 - 4.64X_2{}^2 - 7.19X_3{}^2$	34.01	<0.0001	3.28	0.1408	0.9776	0.9489	15.153	2.24	3.77	416.27
Y_2	$43.42 - 3.14X_1 + 7.93X_2 - 3.76X_3 - 4.33X_1X_2 + 3.00X_1X_3 - 6.91X_1{}^2 - 6.93X_2{}^2 - 7.26X_3{}^2$	657.43	<0.0001	1.68	0.3075	0.9988	0.9973	71.999	0.50	1.51	17.11
Y_3	$26.62 - 3.94X_1 - 3.26X_2 + 7.75X_3 + 4.87X_1X_2 - 7.00X_1X_3 - 3.62X_1{}^2 + 1.98X_2{}^2$	47.17	<0.0001	3.45	0.1313	0.9838	0.9629	24.452	1.57	6.05	207.42
Y_4	$58.65 - 13.03X_1 + 10.84X_2 + 5.30X_3 - 4.93X_1X_3 - 17.91X_1{}^2 - 7.46X_2{}^2 - 10.62X_3{}^2$	295.60	<0.0001	4.07	0.1043	0.9974	0.9940	46.073	1.36	3.25	160.04
Y_5	$89.18 - 4.92X_1 + 10.43X_2 + 2.50X_3 + 1.67X_1X_2 + 1.42X_2X_3 - 17.95X_1{}^2 - 12.45X_2{}^2 - 9.90X_3{}^2$	423.32	<0.0001	3.57	0.1255	0.9982	0.9958	61.784	1.00	1.43	84.66
Y_6	$3.21 - 1.30X_1 - 0.49X_2 - 7.16X_3 - 0.31X_1X_2 - 0.41X_1X_3 + 0.32X_1{}^2 + 1.25X_2{}^2 + 6.73X_3{}^2$	1090.25	<0.0001	4.12	0.1025	0.9993	0.9984	89.894	0.25	3.56	5.61

X_1: first variable, initial pH, X_2: second variable, H_2O_2 dosage, X_3: third variable, Fe^{2+} dosage; Y_1: overall COD removal efficiency, Y_2: oxidation COD removal, Y_3: coagulation COD removal, Y_4: mineralization, Y_5: HS removal, Y_6: SVR; P: probability of error, LOF: Lack of Fit F-value, PLOF: probability of lack of fit, R^2: determination coefficient, Adj. R^2: adjusted R^2, AP: adequate precision, SD: standard deviation, CV: coefficient of variation, PRESS: predicted residual error sum of squares.

Table 3
Results for the reduced cubic model of the variable effects on the response.

Source	Sum of squares						Mean square						F						P					
	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
X_1	369.92	78.75	124.03	1358.44	194.04	180.43	369.92	78.75	124.03	1358.44	194.04	180.43	73.56	309.61	50.13	739.01	193.69	224.05	<0.0001	<0.0001	0.0002	<0.0001	<0.0001	<0.0001
X_2	166.53	502.45	85.15	940.71	869.45	19.61	166.53	502.45	85.15	940.71	869.45	19.61	33.11	1975.35	34.41	511.76	867.83	24.35	0.0007	<0.0001	0.0006	<0.0001	<0.0001	0.0017
X_3	122.46	113.25	480.50	224.49	50.00	266.66	122.46	113.25	480.50	224.49	50.00	266.66	24.35	445.25	194.19	122.13	49.91	331.12	0.0017	<0.0001	<0.0001	<0.0001	0.0002	<0.0001
X_1X_2	0.000	74.82	95.06	7.11	11.22	6.69	0.000	74.82	95.06	7.11	11.22	6.69	0.000	294.16	38.42	3.87	11.20	8.31	1.0000	<0.0001	0.0004	0.0900	0.0123	0.0236
X_1X_3	64.00	36.00	196.00	97.38	0.20	70.85	64.00	36.00	196.00	97.38	0.20	70.85	12.73	141.53	79.21	52.98	0.20	87.98	0.0091	<0.0001	<0.0001	0.0002	0.6666	<0.0001
X_2X_3	6.00	0.72	0.81	0.46	8.12	6.34	6.00	0.72	0.81	0.46	8.12	6.34	1.19	2.84	0.33	0.25	8.11	7.87	0.3108	0.1358	0.5851	0.6312	0.0248	0.0263
$X_1{}^2$	426.33	201.04	55.25	1350.73	1357.02	11.64	426.33	201.04	55.25	1350.73	1357.02	11.64	84.78	790.40	22.33	734.82	1354.50	14.46	<0.0001	<0.0001	0.0021	<0.0001	<0.0001	0.0067
$X_2{}^2$	90.55	202.50	16.47	234.09	652.90	50.45	90.55	202.50	16.47	234.09	652.90	50.45	18.01	796.13	6.65	127.35	651.69	62.64	0.0038	<0.0001	0.0365	<0.0001	<0.0001	<0.0001
$X_3{}^2$	217.52	221.93	0.39	475.16	412.88	85.37	217.52	221.93	0.39	475.16	412.88	85.37	43.25	872.5	0.16	258.50	412.12	106.00	0.0003	<0.0001	0.7049	<0.0001	<0.0001	<0.0001
Residual	35.20	1.78	17.32	12.87	7.01	5.64	5.03	0.25	2.47	1.84	1.00	0.81												

X_1, X_2 and X_3 represent the main effect of initial pH, H_2O_2 concentration and Fe^{2+} concentration, respectively.

Y_1: overall COD removal efficiency, Y_2: oxidation COD removal, Y_3: coagulation COD removal, Y_4: mineralization, Y_5: HS removal, Y_6: SVR.

X_1X_2, X_1X_3 and X_2X_3 represent the interaction between initial pH and H_2O_2 concentration, interaction between initial pH and Fe^{2+} concentration and interaction between H_2O_2 concentration and Fe^{2+} concentration, respectively.

$X_1{}^2$, $X_2{}^2$ and $X_3{}^2$ represent the quadratic effect of initial pH, H_2O_2 concentration and Fe^{2+} concentration, respectively.
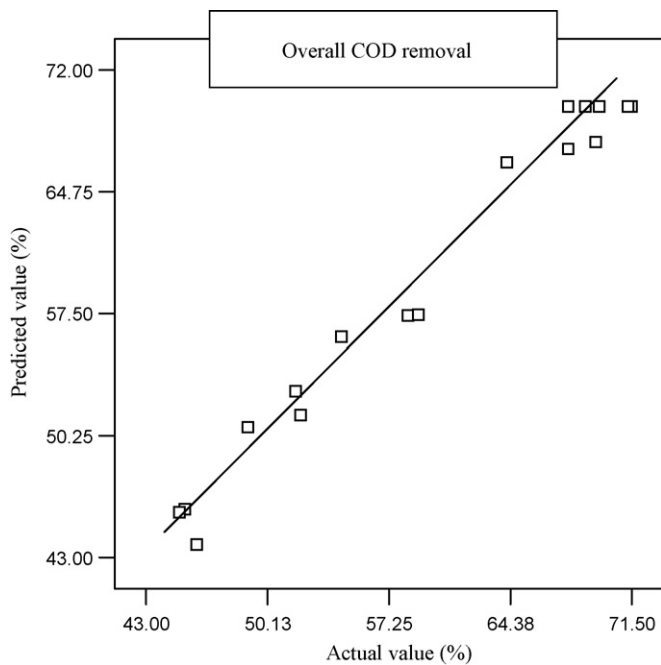
Fig. 1. Predicted vs. actual value plot for overall COD removal.

(15.153–89.894) were greater than 4, which indicated adequate signals [17]. So these six models could be used to navigate the design space. Simultaneously, low values of the coefficient of variation (CV) (1.43–6.05%) indicated good precision and reliability of the experiments [17]. Besides, the plot of the comparison of actual and predicted values for overall COD removal (Y_1) indicated an adequate agreement between real data and the ones obtained from the model (Fig. 1). The other predicted vs. actual value plots for other five responses (Y_2–Y_6) were similar to Fig. 1, therefore, they were not shown in this paper.

3.2. Overall COD removal

Previous researchers [2,3,9] had reported that initial pH significantly influenced the COD removal. Fig. 2(a) is a perturbation plot, which illustrates the effect of all the factors at the center point in the design space. It was apparent that initial pH (X_1) had significant negative effect (linear + quadratic) on overall COD removal (Y_1) (Fig. 2 and Table 2). Here positive effect means that the corresponding response (Y) increases as the effect factor (X) level increases, whereas negative effect means that the corresponding response (Y) decreases as the level increases. 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 [6]. 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 •OH radical production resulting in the reduction of COD removal [6]. Moreover, the scavenging effect of H^+ on •OH can inhibit the reaction between Fe^{3+} and H_2O_2 [3,9]. On the other hand, a pH above optimal, the removal of overall COD reduced with the formation of ferric oxyhydroxide [6]. As also seen in Fig. 2(a) and Table 2, the dosages of H_2O_2 (X_2) and Fe^{2+} (X_3) had positive linear effect and negative quadratic effect on Y_1. The 3D surface graphs for the same have been represented in Fig. 2(b). The response surface of overall COD removal showed a clear peak, suggesting that the optimum condition for maximum overall COD removal was well inside the design boundary. The individual optimization procedure exhibited that initial pH 3.05, H_2O_2 dosage
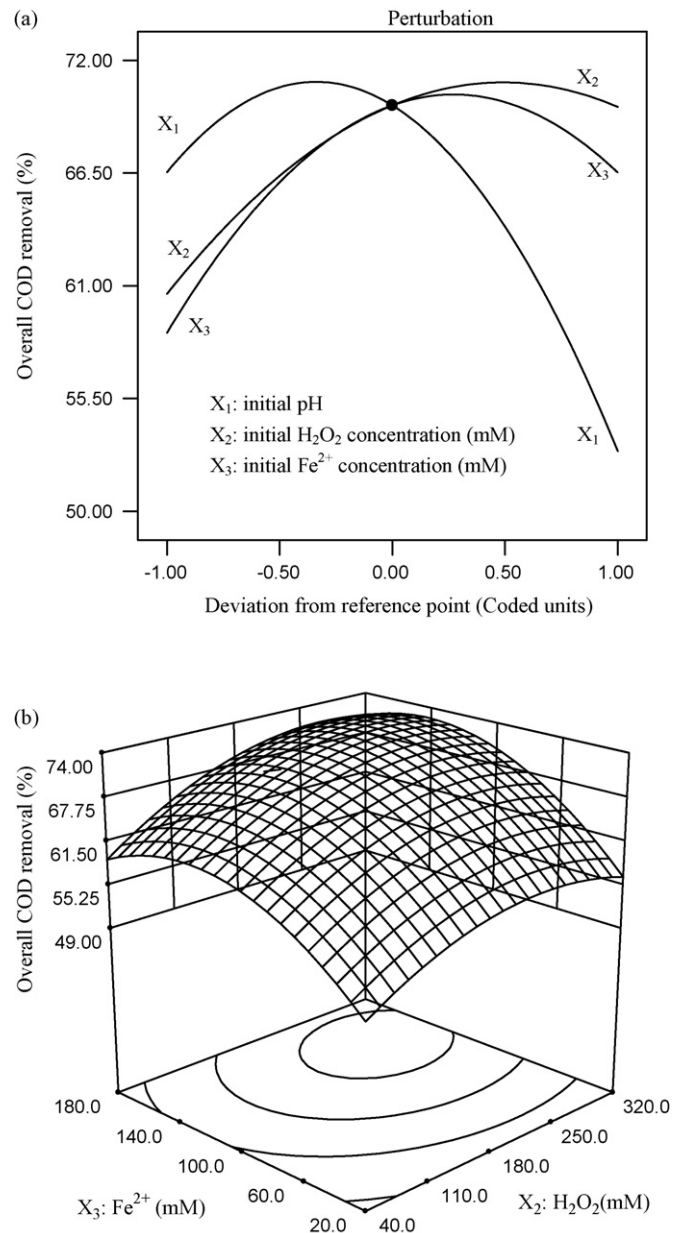
Fig. 2. (a) Perturbation graph and (b) three-dimensional surface graphs for overall COD removal.

152.7 mM and Fe^{2+} concentration 137.2 mM were predicted to provide the highest overall COD removal (70.73%). The results were consistent with the earlier observation that the Fenton process had the highest efficiency when the pH was around 3.0 [9].

3.3. The roles of oxidation and coagulation

The typical Fenton wastewater treatment process includes four stages: pH adjustment, oxidation, neutralization and coagulation, as well as solid–liquid separation. The organics are removed by both oxidation and coagulation [3]. The perturbation plots (Fig. 3) showed that initial pH significantly influenced importance of oxidation relative to coagulation [3], where the effects of all the factors at the center point in the design space are compared. Except for the interaction term X_2X_3, the other linear terms (X_1, X_2 and X_3), quadratic terms ($X_1{}^2$, $X_2{}^2$ and $X_3{}^2$) and the interaction terms (X_1X_2 and X_1X_3) were statistically significant for oxidation COD removal (Table 3). The addition of H_2O_2 (X_2) had an expected linear positive
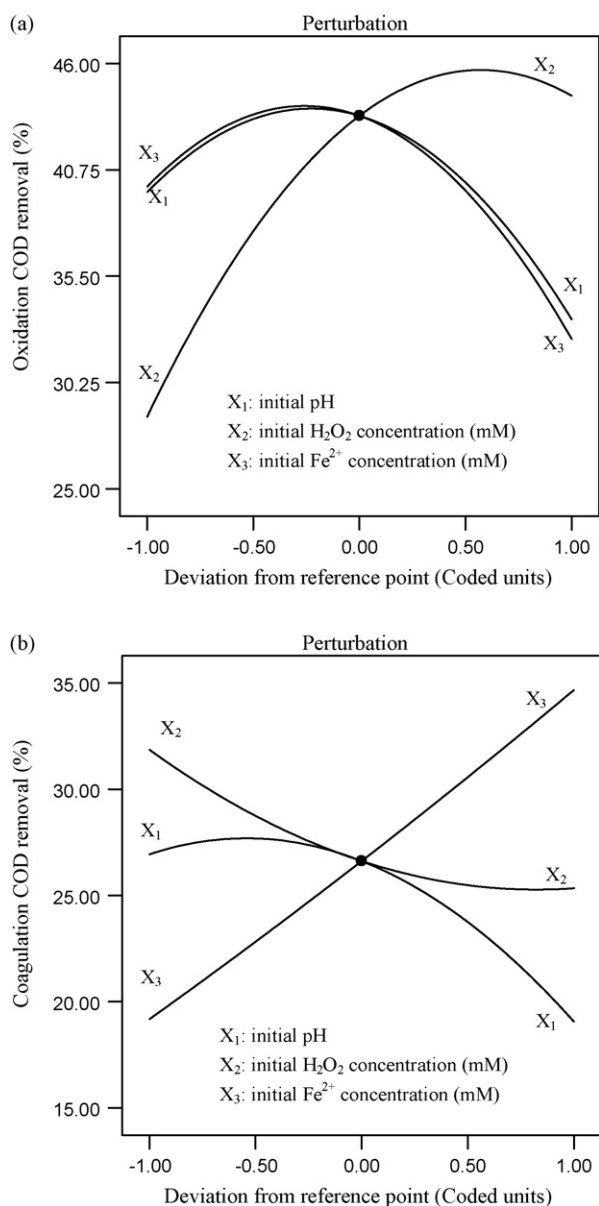
(a)

(b)

Fig. 3. Perturbation graphs for (a) oxidation and (b) coagulation COD removal.

(a)

(b)

Fig. 4. (a) Three-dimensional surface graph for oxidation removal and (b) two-dimensional contour plot for coagulation COD removal.

effect and a quadratic negative effect on oxidation COD removal (Y_2), whilst the addition of Fe^{2+} (X_3) and the increase of initial pH (X_1) had negative effect (linear + quadratic) on Y_2 (Fig. 3(a) and Table 2). The results shown in Fig. 4(a) confirm again the expected positive influence of H_2O_2 dosage on the oxidation removal efficiency. The oxidation COD removal increased with increasing Fe^{2+} dosage by 100 mM, then started to decrease due to Fe^{2+} which started to act as a scavenger of hydroxyl radicals [4,9]. These observations were consistent with those of Kang and Hwang [2]. In conclusion, it is desirable to run Fenton process at low pH, low Fe^{2+} dosage, and high H_2O_2 dosage, because in terms of hydroxyl radical production and consumption, there were negative effect of pH and Fe^{2+} dosage, positive effect of H_2O_2 dosage on the oxidation removal [2,3]. However, it was not necessary to increase the H_2O_2 dosage excessively because parallel inefficient decomposition routes contributed to wastage of hydrogen peroxide at excessive H_2O_2 dosage, resulting in insignificant increase of oxidation. Hence, this enabled identification of a maximum point of oxidation COD removal as a function of these factors.
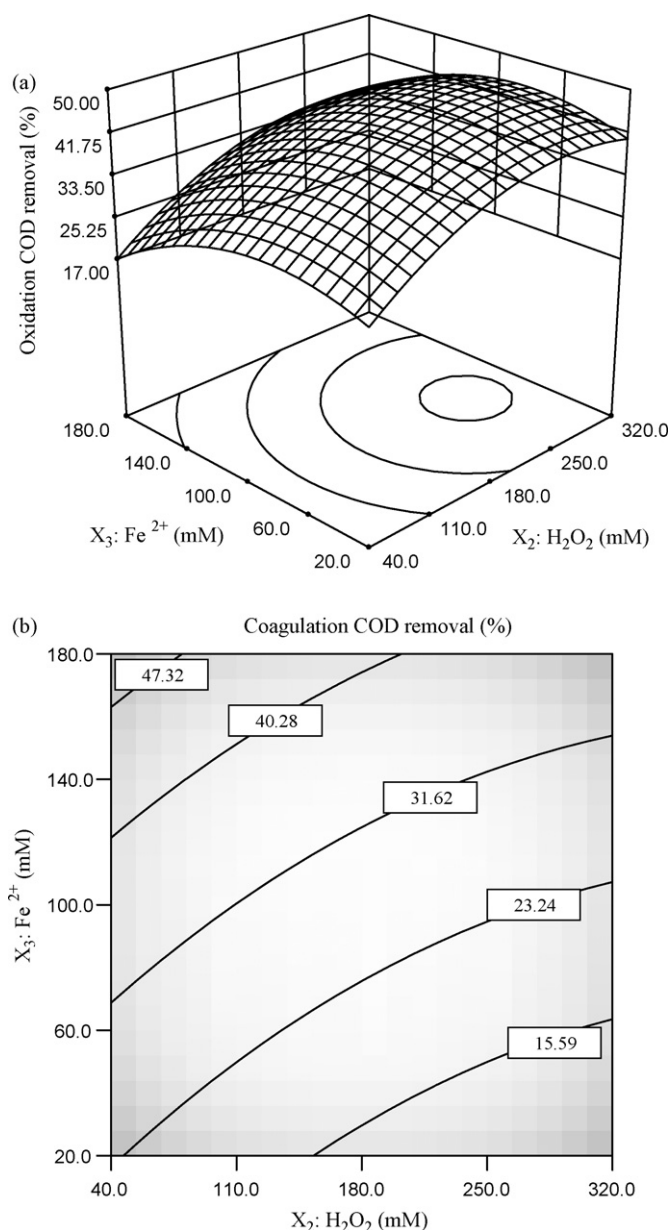
The individual optimum region led to the desirable oxidation COD removal (the highest value, $Y_2 = 45.60\%$) was estimated to be achieved by a set level of 3.97, 267.7 mM and 57.1 mM for initial pH, H_2O_2 and Fe^{2+} dosages, respectively. On the contrary, the COD removal by oxidation was predicted to provide the weakest behavior at 2.03 initial pH, 41.6 mM H_2O_2 and 131.7 mM Fe^{2+} (the least oxidation removal, $Y_3 = 16.98\%$).

For the coagulation COD removal (Y_2), the main effects of initial pH, H_2O_2 and Fe^{2+} dosage (X_1, X_2, X_3), two-level interaction (X_1X_2, X_1X_3) effects and quadratic effects ($X_1{}^2, X_2{}^2$) were significant model terms (Table 3). The addition of Fe^{2+} (X_3) had an expected positive overall effect (linear + quadratic), whilst the addition of H_2O_2 (X_2) had a linear negative effect and a quadratic positive effect and the increase of initial pH (X_1) had overall negative effect (linear + quadratic) on Y_2 (Fig. 3(b) and Table 2). The contour plot of the effect of variables on coagulation COD removal (Fig. 4(b)) showed that high coagulation removal can achieve at higher Fe^{2+} dosage and lower H_2O_2 concentration with proper initial pH. The identi-

fied optimum conditions of maximum coagulation COD removal (44.31%) was obtained as follows: 2.45 initial pH, 61.2 mM H_2O_2 and 157.9 mM Fe^{2+}.

It can be noted that there are opposite effects of X_2, X_3, X_1X_2, X_1X_3 and $X_2{}^2$ for oxidation removal (Y_2) and coagulation removal (Y_3), respectively (Fig. 3). The observed results showed that the effects of Y_2 and Y_3 were inversely related, and high oxidation efficiency might cause relatively low coagulation efficiency. Because both the oxidation and coagulation stages of Fenton process removed high molecular weight organics preferentially [3,10], the remaining oxidative byproducts were not as amenable to coagulation. Accordingly, the reason the reduction of overall COD at extremely high H_2O_2 dosage was that slightly increase of oxidation COD removal did not compensate the significant decrease of COD coagulation removal.

3.4. Mineralization

A common method for characterizing Fenton process is to determine the mineralization of leachate. Measurements of TOC removal were carried out to evaluate the mineralization of leachate. Except for the interaction terms X_1X_2 and X_2X_3, the other linear terms (X_1, X_2 and X_3), quadratic terms ($X_1{}^2$, $X_2{}^2$ and $X_3{}^2$) and the interaction terms (X_1X_3) were statistically significant (Table 3). Addition of H_2O_2 and Fe^{2+} had positive linear effects (X_2 and X_3) and negative quadratic effects ($X_2{}^2$ and $X_3{}^2$) (Table 2). The perturbation plot (Fig. 5(a)), which was observed to be similar to that of overall COD removal, also showed the mineralization was largely controlled by the initial pH, followed by the level of Fe^{2+} and H_2O_2 dosages. The results enabled identification of a point of maximum mineralization as a function of these two factors (X_2 and X_3) involved in a determined initial pH.

As depicted for the same in Fig. 5(b), percentage of mineralization increased with hydrogen peroxide dose up to 240 mM for all Fe^{2+} doses between 20 and 180 mM indicating peroxide limitations at low hydrogen peroxide dosages. An insignificant impact of increasing H_2O_2 dosage on mineralization was observed at peroxide dosages over 240 mM. This is due to hydroxyl ion ($^{\bullet}OH$) scavenging effect by excess H_2O_2 and consequent formation of the less reactive radical $HO_2{}^{\bullet}$ [9]. It should be noted here that overall TOC removal also includes both oxidation and coagulation removals. The addition of Fe^{2+} dosage had an expected positive effect on TOC removal probably due to higher concentrations of ferric coagulant after neutralization resulted in the increase of coagulation performance. However, there has a negative effect on overall TOC removal at extremely addition of Fe^{2+}. The explanation, which was similar to that of overall COD removal, was that larger hydroxyl ion scavenging effects of overdose of Fe^{2+} on oxidation behavior were more significant than the increase of coagulation performance.

The optimization results indicated that combined level of 3.73 initial pH, 288.9 mM H_2O_2 and 162.2 mM Fe^{2+} was estimated to result in the optimum mineralization behavior (the highest mineralization, $Y_5 = 62.54\%$), whilst 71.12% overall COD removal, 38.76% oxidation COD removal, 32.44% coagulation COD removal, 86.76% HS removal and 2.35 ml/mM SVR were achieved. Percent TOC removals were much lower than overall COD and HS removals. The results indicated that the organic pollutants including HS in leachate were degraded incompletely and some intermediate products were produced during Fenton process.

3.5. Removal of humic substances

The concentrated leachate presents a high content of organic matter. The ratio of dissolved organic carbon (DOC) to total organic carbon (TOC) concentration was as high as 85.4%, indicating that the
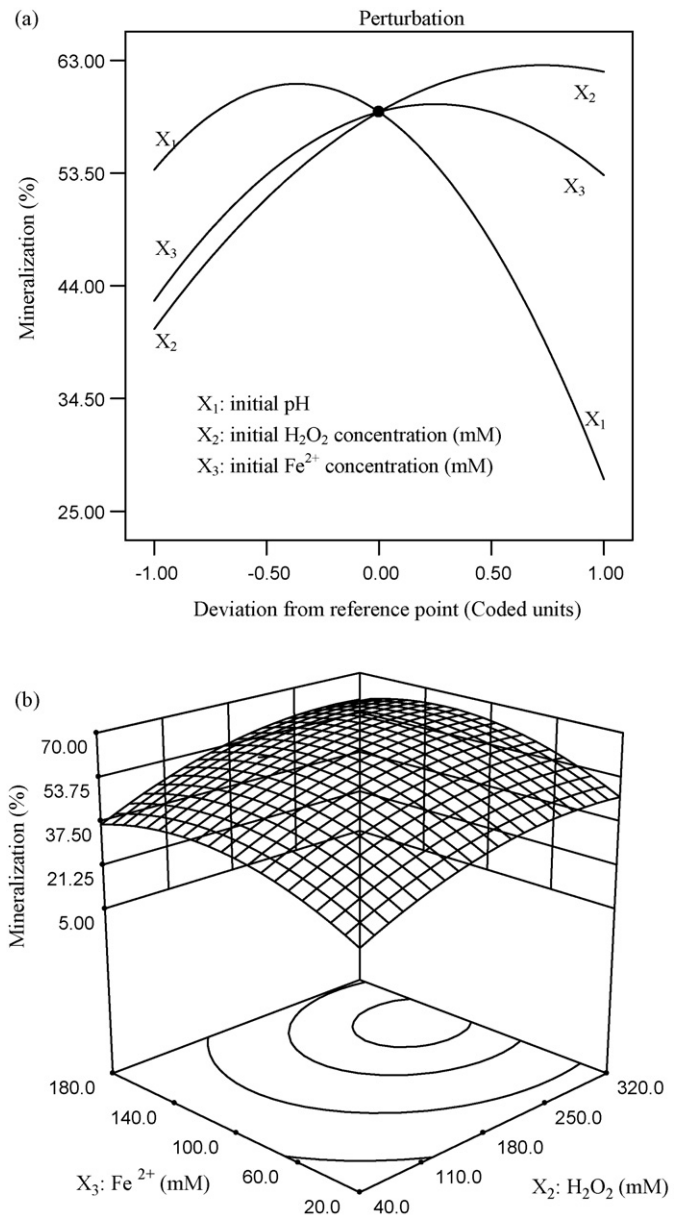

Fig. 5. (a) Perturbation graph and (b) three-dimensional surface graphs for mineralization.

DOM comprised a majority of the organic substances in wastewater. The fractionation results of DOM revealed that HS composed 83.3% of DOC. Hence, the removal of HS from concentrated leachate should be received specific attention. To better evaluate the treatment efficiency of Fenton process, the removal of HS isolated from supernatant of reaction samples were taken as one treatment parameter (Y_6).

Table 3 shows that the other linear terms (X_1, X_2 and X_3), quadratic terms ($X_1{}^2$, $X_2{}^2$ and $X_3{}^2$) and the interaction terms (X_1X_2 and X_2X_3) were statistically significant, except for the interaction term X_1X_3. The effects comparison of all the factors at the center point in perturbation plot (Fig. 6(a)) also shows the steep curvatures in initial pH (X_1), dosages of H_2O_2 (X_2) and Fe^{2+} (X_3) factors. The results indicated that the response of HS removal was very sensitive to these three factors. HS was removed by both oxidation and coagulation, which would explain why HS removal was influenced by these three factors. In practice, this mean that the increase of HS removal (Y_5) resulted in the increase of COD (Y_1) and TOC
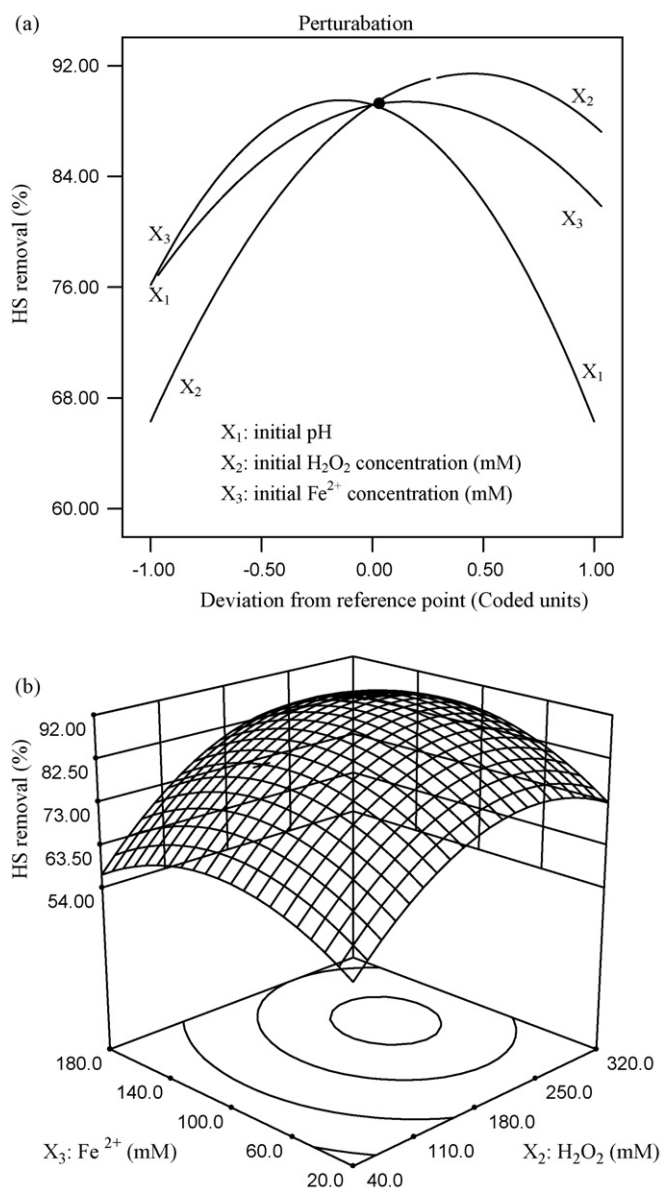
Fig. 6. (a) Perturbation graph and (b) three-dimensional plots for HS removal.

Fig. 7. (a) Perturbation graph and (b) three-dimensional plots for SVR.

(Y_4) removals due to (1) low pH and higher H_2O_2 dosage increased oxidation performance, and/or (2) the addition of Fe^{2+} increased the coagulation efficiency. Accordingly, the three responses (Y_1, Y_4 and Y_5) gave very similar perturbation plots (Fig. 2, Fig. 5(a) and Fig. 6(a)).

Fig. 6(b) confirmed again that HS removal increased with increasing H_2O_2 dosage by 180 mM due to H_2O_2 limitations at low peroxide doses. Further increase of peroxide dose resulted in the decrease of HS removal probably due to hydroxyl radical scavenging effects of high peroxide doses. Similar trend was also observed at other Fe^{2+} dosages. The highest percentage 89.87% of HS removal was achieved at 4.15 initial pH, 208.5 mM H_2O_2 and 90.6 mM Fe^{2+}.

3.6. Sludge generated by Fenton process

A large amount of flocs of various sizes in the leachate were observed during Fenton process. According to Walling and Kato [25], the small flocs were ferric hydroxo complexes, which formed by complex chain reactions of ferrous and hydroxide ions and resulted in the generation of high amount of ferric-based sludge.
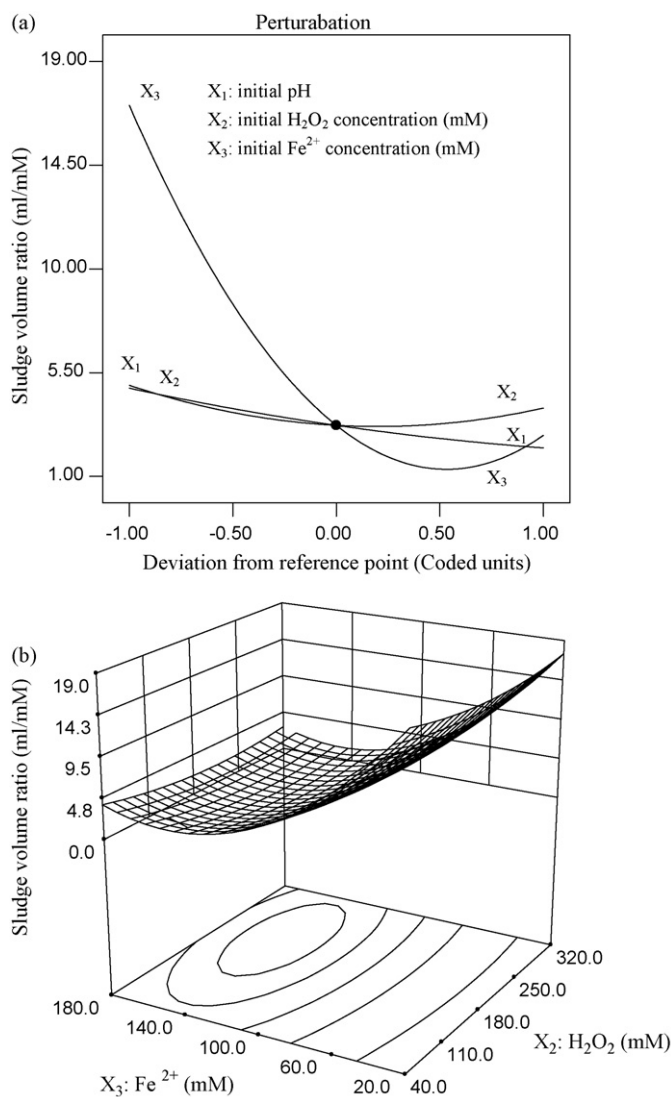
The removal of the sludge containing iron ions produced during Fenton treatment is expensive in labor, reagents and time [26]. In this study, SVR is proposed as a simple but useful indicator to evaluate coagulation performance in Fenton treatment. It was carried out to determine the characteristics of the sludge produced by iron ion at various operating conditions. The steepest curvature in Fe^{2+} dosage (X_3) in perturbation plot (Fig. 7) showed the increase of Fe^{2+} has a positive effect on the reduce amount of SVR. SVR rapidly decreased with increasing ferrous sulfate dosage due to higher precipitation performance occurred at higher Fe^{2+} dosage after neutralization. However, SVR value increased at extremely higher Fe^{2+} dosage. The results were according with the observation of Benatti et al. [19] that the higher COD removal after

Table 4
The optimization criteria for chosen responses.

Response		Unit	Limits
Y_1	Overall COD removal	%	>70
Y_2	COD removal by oxidation	%	>45
Y_3	COD removal by coagulation	%	>25
Y_4	Mineralization	%	>60
Y_5	HS removal	%	>88
Y_6	SVR	ml/mM	<3.5

Table 5
Verification experiments at optimum conditions.

Conditions	Response					
	Y_1 (%) Overall COD removal	Y_2 (%) Oxidation COD removal	Y_3 (%) Coagulation COD removal	Y_4 (%) Overall TOC removal	Y_5 (%) HS removal	Y_6 (ml/mM) SVR
Experimental value	71.81	46.22	25.80	63.81	91.53	3.50
Model response	70.18	46.07	23.34	61.98	89.66	3.40
Error	1.63	0.15	2.46	1.83	1.87	0.10
STDEV	±1.63	±0.15	±2.46	±1.83	±1.87	±0.10

oxidation stage, the lower quantity of chemical sludge resulting from the Fenton process. The initial pH (X_1) did not appear to have a direct effect on SVR because sludge precipitated at neutralization condition. Moreover, at fixed Fe^{2+} dosage and initial pH, the SVR reduced slightly with increasing H_2O_2 dosage (Fig. 7(b)) likely due to the synergistic roles of oxidation and coagulation in Fenton treatment. An opposite trend was obtained whilst increasing H_2O_2 dosage over 180 mM due to the iron sludge flotation caused by the autodecomposition of excess H_2O_2 into O_2 [27].

The minimum SVR of 1.3 ml/mM was obtained at initial pH of 4.67, H_2O_2 dosage of 152.0 mM and Fe^{2+} dosage of 126.7 mM. Conversely, the SVR at 2.64 initial pH, 42.1 mM H_2O_2 and 20.3 mM Fe^{2+} was predicted to provide the weakest coagulation sludge volume behavior (the highest, Y_6 = 19.3 ml/mM).

3.7. Optimization of Fenton process for concentrated leachate treatment

The main objective of the optimization is to determine the optimum values of variables for concentrated leachate treatment with Fenton process from the models obtained using experimental data. With multiple responses, the optimum condition where all parameters simultaneously meet the desirable criteria can visually be searched by superimposing or overlaying critical response contours on a contour plot. Graphical optimization displays the area of feasible response values in the factor space and the regions that do fit the optimization criteria would be shaded. The Fig. 8 shows the optimum region, which is identified based on six critical responses

(Y_1–Y_6). The criteria of optimum region were adopted as shown in Table 4.

An additional experiment was conducted applying the optimum conditions with 3.64 initial pH, 240 mM H_2O_2 and 100 mM Fe^{2+} dosage to confirm the agreement of the results achieved from models and experiments. As shown in Table 5, experimental findings for all responses parameters were in close agreement with the model prediction. Low errors 1.63%, 0.15%, 2.46%, 1.83%, 1.87% and 0.10 ml/mM and low standard deviations ±1.63%, ±0.15%, ±2.46%, ±1.83%, ±1.87% and ±0.10% for six responses (Y_1–Y_6) respectively were achieved.

4. Conclusions

Fenton process is an effective method to treat the concentrated leachate with high HS components rejected from RO. The RSM results demonstrated significant effects of three operating variables (initial pH, H_2O_2 and Fe^{2+} dosage) as well as their interactive effects on six responses (overall COD removal, removal by oxidation and coagulation, mineralization, HS removal and sludge volume ratio). The factors most strongly affecting overall COD removal, mineralization and HS removal are initial pH, H_2O_2 and Fe^{2+} dosages, due to their respective effects on the removal efficiency of oxidation and coagulation. The dosages of H_2O_2 and Fe^{2+} were the most significant factors for the increment contribution of oxidation and coagulation removal efficiency respectively.

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.

Fig. 8. Overlay plot for optimal region.

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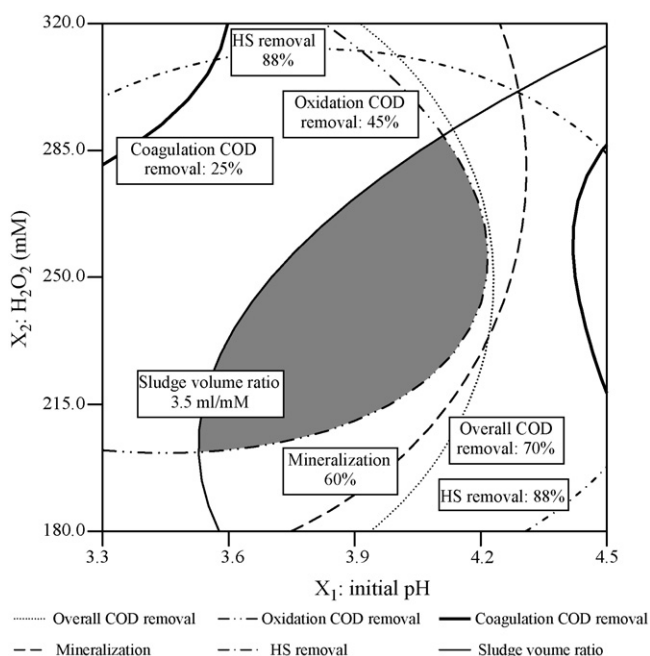
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