Treatment of tetrahydrofuran wastewater by the Fenton process: response surface methodology as an optimization tool

Xianzhong Cao, Huiqing Lou, Wei Wei and Lijuan Zhu

ABSTRACT

In this study, the Box-Benkhen design and response surface method (RSM) were applied to evaluate and optimize the operating variables during the treatment of tetrahydrofuran (THF) wastewater by Fenton process. The four factors investigated were initial pH, Fe^{2+} dosage, H_2O_2 dosage and reaction time. Statistical analysis showed the linear coefficients of the four factors and the interactive coefficients such as initial pH/Fe^{2+} dosage, initial pH/H_2O_2 dosage and Fe^{2+} dosage/H_2O_2 dosage all significantly affected the removal efficiency. The RSM optimization results demonstrated that the chemical oxygen demand (COD) removal efficiency could reach up to 47.8% when initial pH was 4.49, Fe^{2+} dosage was 2.52 mM, H_2O_2 dosage was 20 mM and reaction time was 110.3 min. Simultaneously, the biodegradability increased obviously after the treatment. The main intermediates of 2-hydroxytetrahydrofuran, γ-butyrolactone and 4-hydroxybutanoate were separated and identified and then a simple degradation pathway of THF was proposed. This work indicated that the Fenton process was an efficient and feasible pre-treatment method for THF wastewater.

Key words | degradation mechanism, Fenton process, response surface method (RSM), tetrahydrofuran (THF)

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INTRODUCTION

Tetrahydrofuran (THF) is used extensively in the manufacture of many polymers and other products such as certain adhesives and pharmaceuticals. As an inhibitor to cytochrome P450-dependent enzymes, THF can invade an organism through the respiratory tract, enteron and skin (Draper *et al.* 1997). Based on a series of toxicity tests, it was concluded that exposure to THF could induce central nervous system irritation, narcosis, edema and colonic muscle spasms in animals (Malley *et al.* 2001). Therefore, wastewater containing THF should be safely treated before being discharged into the environment. Recently, THF has been observed in groundwater at a concentration exceeding the water quality criteria and guidelines set by different states of the US (Isaacson *et al.* 2006). In addition, it has also been detected in river and drinking surface water in China (Li *et al.* 2007).

THF in wastewater was commonly chemically oxidized to γ-butyrolactone by using strong oxidizing agents such as sodium bromate, due to the stable chemical characteristics of THF (Metsger & Bittner 2000). Alternatively, biological treatment technology using activated sludge was generally performed using less energy under ordinary temperature and pressure, attributed to the aerobic microorganisms in the sludge that could metabolize the organic waste (Oh *et al.* 2010). However, THF had a negative impact on the performance of the activated sludge system, even in a short time. As an inhibitor of enzyme activities, it dramatically decreased the number and diversity of cultivable microorganisms, and thus made a great change to the microbial community structure (Yao *et al.* 2012). It was reported that the activity of dehydrogenase, phosphatase, urease and catalase was seriously inhibited at relatively high THF concentrations ranging from 1.13 to 4.37 M (Lv *et al.* 2008). Anaerobic microbes also noticeably suffered and the quantity of gas generation was abruptly reduced when wastewater containing THF was released into an anaerobic bioreactor (Ray *et al.* 2009). Although several degrading microorganisms had been isolated, only a few strains could degrade high-concentrations of THF (more than 10 mM) (Tajima *et al.* 2012). Therefore, it was impracticable

doi: 10.2166/wst.2014.017

to degrade high-concentrations of THF wastewater by biological treatment technology.

Advanced oxidation processes (AOPs) were considered as competitive water treatment technologies for degradating organic micropollutants which were not removed by biological treatments (Oller *et al.* 2011). AOPs were used in combination with biological treatments for wastewater remediation to follow partial oxidation and increase the biodegradability as a pre-treatment, or to degrade persistent compounds as a post-treatment (Bandara *et al.* 1997). One of the most effective AOPs mainly consisted of utilizing a Fenton's reagent such as a conjunction of H_2O_2 and Fe^{2+}. Generally, Fenton treatment of wastewater was conducted via four stages: oxidation, neutralization, coagulation/flocculation and solid-liquid separation (Deng 2007). Both the oxidation and coagulation were able to remove target contaminants, so the application of Fenton's reagent as an oxidant for wastewater treatment was attractive; however, in recent years, the goal when performing the Fenton process has been converted from one step elimination to partial degradation of the pollutants. This was aimed at enhancing the biodegradability and generating a new effluent able to be degraded by biological treatments (Estrada *et al.* 2012).

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for experimental design, model development and process optimization. It is capable of statistical investigation of single-factor and interactive effects synchronously (Lou *et al.* 2013), and allows fewer experimental runs while providing sufficient information for statistically acceptable results compared to full-factorial experiments (Izquierdo *et al.* 2013). This approach complies with a sequential order, including screening the independent variables and corresponding levels, constructing a surface model by a proper and appropriate experimentally designed method, estimating the coefficients of the fitted approximation model as well as evaluating the adequacy and validity of the surface model (GilPavas *et al.* 2009).

As mentioned above, biological treatment technology is impracticable for treating THF wastewater, especially high-concentration wastewater. Strong oxidizing agents could obtain better treatment results, but the higher cost restricted application. So, AOPs as a pre-treatment technology to improve the biodegradability of THF wastewater might be a better choice. In this paper, a Box-Benkhen design (BBD) was employed to investigate the effect of parameters (initial pH, Fe^{2+} dosage, H_2O_2 dosage and reaction time) on the removal efficiency of THF wastewater (the response variable), and to find out the optimized parameters in the Fenton process. In addition, the main intermediate products were identified by the gas chromatography–mass spectrometry (GC–MS) technique and a simple degradation pathway of THF was proposed. The biodegradability of the wastewater was also investigated.

MATERIALS AND METHODS

Chemicals

$FeSO_4 \cdot 7H_2O$ (99%), H_2O_2 (30%), H_2SO_4 (98%) and NaOH (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals used were of analytical reagent grade. All chemicals were prepared using high-purity water from a Millipore system with a resistivity of 18.2 $M\Omega \cdot cm$.

Wastewater characteristics

The samples were taken directly from the wastewater stream of the THF industrial plant. Before analysis and treatment in the laboratory, they were kept refrigerated according to the standard procedures to avoid compound degradation during their storage and transportation (APHA *et al.* 2005). The wastewater characteristics were presented as follows: chemical oxygen demand (COD) 24,571 mg/L, biological oxygen demand (BOD) 3,108 mg/L, BOD/COD 0.126, pH 8.52. The ratio of BOD/COD (B/C) was used to express the biodegradability of wastewater. When the ratio was higher than 0.35, the wastewater was considered to be biodegradable. In this study, the ratio of B/C was only 0.126, which indicated that the THF wastewater was difficult to be treated biologically.

Experimental procedure

The initial pH of the THF wastewater was adjusted to the desired value with H_2SO_4 (50%, v/v) and NaOH solution (10 M). Approximately 500 mL THF wastewater was first added into 1,000 mL Erlenmeyer flasks followed by the designed amount of $FeSO_4$ and H_2O_2, and then the Fenton reaction was initiated. The reagents were mixed by a magnetic stirrer to ensure complete homogeneity. After a certain period of reaction, the Fenton oxidation process was stopped by adding NaOH solution to regulate the pH value to around 8.5, and then a small amount of polyacrylamide (PAM, 0.1%, w/w) was added to enhance the flocculation performance. The treated wastewater was filtered through a 0.45 μm filter for water quality measurements. All the experiments and measurements were conducted at least three times to obtain the average with an accuracy of ±5%. The experiment was carried out at room temperature (25 ± 2 °C) and atmospheric pressure.

Experimental design and statistical analysis

RSM analysis was adopted and implemented to establish the optimal operational conditions of the Fenton process. A BBD was applied to investigate the effects of the four independent variables on the response functions. The independent variables were: initial pH (A), Fe^{2+} dosage (B), H_2O_2 dosage (C) and reaction time (D). The low, centre and high levels of each variable were designated as −1, 0 and +1, respectively. Three different actual levels of the four variables were chosen from preliminary experiments: initial pH 2, 4 and 6; Fe^{2+} dosage 1, 2 and 3 mM; H_2O_2 dosage 10, 15 and 20 mM; and reaction time 60, 90 and 120 min. Twenty-nine BBD experiments were randomly made to avoid any systematic error. Experiment results were analyzed by multiple regressions to fit the full second-order polynomial model. The typical quadratic response surface model for four factors was proposed as Equation (1).

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} X_i X_j + \xi \quad (1)$$

where Y is the response, X_i is the independent variables and β_0 is the intercept parameter; β_i, β_{ii} and β_{ij} are the linear coefficients, squared coefficients and interaction coefficients, respectively. ξ is the random error.

Three-dimensional (3D) surface plots were generated using Design Expert Software (version 8.0.6). Thus, the effects of all the factors at a particular point in the design space were compared directly. Furthermore, the optimum region was identified based on the main parameters in the overlay plot. The quality of the fitted polynomial model was expressed by analysis of variances (ANOVA), the coefficient of determination R^2 and adjusted R^2 (R^2_{adj}). The statistical significance of each source of terms (linear, two-factor interaction and quadratic) and the regression coefficients of the fitted model was checked by Fisher's F-test in the same programme. Model terms were accepted or rejected based on the P-value (probability) with a 95% confidence level (Wu *et al.* 2010). The adequacy of the regression equations was checked by comparing the experimental data with predicted values obtained from the equations.

RESULTS AND DISCUSSION

Fitting the response surface model and analysis of variance

The experimental conditions and results are shown in Table 1. Based on the results shown in Table 1, the COD

Table 1 | Box–Behnken design and experimental results

	Coded independent variable levels				
Exp.no.	A	B	C	D	Response value Removal efficiency (%)
1	4	2	15	90	43.2
2	2	2	10	90	36.1
3	4	1	15	60	30.0
4	2	2	15	60	40.4
5	2	2	15	120	43.8
6	4	3	20	90	47.8
7	4	1	20	90	35.6
8	4	2	15	90	42.3
9	6	2	15	120	35.4
10	6	2	10	90	25.0
11	6	2	20	90	38.3
12	4	1	15	120	32.6
13	4	2	10	120	35.2
14	2	1	15	90	28.4
15	4	2	15	90	42.8
16	4	3	15	60	37.9
17	2	3	15	90	44.6
18	4	3	10	90	31.2
19	4	2	15	90	43.9
20	6	1	15	90	25.7
21	4	2	10	60	31.3
22	6	2	15	60	30.8
23	2	2	20	90	44.1
24	4	2	15	90	43.5
25	4	1	10	90	25.6
26	4	2	20	60	44.4
27	6	3	15	90	31.8
28	4	3	15	120	42.4
29	4	2	20	120	46.7

removal efficiency explained by an RSM model of second order polynomial equation was as follows:

$$Y = -48.03 + 7.11917 \times X_1 + 27.155 \times X_2 + 3.20233 \times X_3 + 0.29817 \times X_4 - 1.2625 \times X_1X_2 + 0.1325 \times X_1X_3 + 0.005 \times X_1X_4 + 0.33 \times X_2X_3 + 0.015833 \times X_2X_4 - 0.002667 \times X_3X_4 - 1.14146 \times X_1^2 - 5.91583 \times X_2^2 - 0.09813 \times X_3^2 - 0.0013926 \times X_4^2 \quad (2)$$

where Y is the removal efficiency of COD (%), X_i ($i = 1, 2, 3, 4$) is the actual independent variable, X_1 is the initial pH, X_2 is the Fe^{2+} dosage (mM), X_3 is the H_2O_2 dosage (mM) and X_4 is the reaction time (min).

Table 2 presents the results of ANOVA, which was used to screen the important operational variables influencing the removal efficiency. The statistical significance of the model and the four independent variables was evaluated by their *F*- and *p*-values. The model regression is highly significant with an *F*-value of 121.82 and *P*-value of <0.0001.

Table 2 | ANOVA for response of the fitted full quadratic polynomial model

Source	SS	DF	MS	*F*-value	*P*-value
Model	1324.33	14	94.60	121.82	< 0.0001[a]
A	211.68	1	211.68	272.60	< 0.0001[a]
B	278.40	1	278.40	358.53	< 0.0001[a]
C	438.02	1	438.02	564.09	< 0.0001[a]
D	37.81	1	37.81	48.69	< 0.0001[a]
AB	25.50	1	25.50	32.84	< 0.0001[a]
AC	7.02	1	7.02	9.04	0.0094[a]
AD	0.36	1	0.36	0.46	0.5070
BC	10.89	1	10.89	14.02	0.0022[a]
BD	0.90	1	0.90	1.16	0.2992
CD	0.64	1	0.64	0.82	0.3793
A^2	135.22	1	135.22	174.14	< 0.0001[a]
B^2	227.01	1	227.01	292.34	< 0.0001[a]
C^2	39.04	1	39.04	50.28	< 0.0001[a]
D^2	10.19	1	10.19	13.12	0.0028[a]
Residual	10.87	14	0.78		
Lack of Fit	9.34	10	0.93	2.44	0.2024
Pure Error	1.53	4	0.38		
Cor Total	1335.20	28			

SD = 0.88; CV = 2.36%; $R^2 = 0.9919$; $R^2_{adj} = 0.9837$;
$R_{pred} = 0.9579$; Adeq Precision = 24.97.
SS: sum of square; DF: degree of freedom; MS: mean square; *P*-value: a statement describing *F*.
[a]Values are statistically significant (at 5% level of significance).

Equation (2) and Table 2 show the four factors, square items and the interactive items of initial pH/Fe^{2+} dosage, initial pH/H_2O_2 dosage, Fe^{2+} dosage/H_2O_2 dosage which all show statistically significant at the confidence level of 95%. ANOVA also displays that H_2O_2 dosage is the most important operating variable, followed by Fe^{2+} dosage, initial pH and reaction time. As seen from Table 2, The R^2 is calculated as 0.9919, indicating good agreement between the experimental and predicated values. The R^2_{pred} of 0.9579 is in reasonable agreement with the R^2_{adj} of 0.9837. Adeq Precision measures the signal to noise ratio, and a ratio greater than 4 is desirable; in this case, the ratio of 24.97 indicates an adequacy of signal. CV indicates the degree of precision with which different treatments are compared; the lower CV of 2.36% demonstrates that the performed experiments are highly reliable. The *P*-value of 'Lack of Fit' is 0.2024 ($p > 0.05$, *F*-test), which implies that the lack of fit was not significant relative to the pure error.

Response surface analysis

The 3D surface plots of the response variable (average removal efficiency of COD) as a function of the selected factors (two-factors-at-a-time) are demonstrated in Figure 1((a)–(f)). The 3D surface plots, showing the graphical display of the fitted regression model, were shaped by combining points of identical response values.

Effect of H_2O_2 dosage

Figure 1((b), (d), (f)) shows the effect of H_2O_2 dosage on removal efficiency of COD. Raising H_2O_2 concentration is conducive to the degradation of organic substances, so higher COD removal efficiency was achieved with increased H_2O_2 dosage. Zhong *et al.* (2012) reported that removal efficiency decreased with H_2O_2 concentration up to 20 mM. This was attributed to the fact that excess H_2O_2 reacted with $^{\bullet}OH$ to form $HO_2^{\bullet}$ and the oxidation potential of $HO_2^{\bullet}$ was much lower than that of OH. However, the observation in this experiment is different from the previous research, which may be due to the high COD concentration. The effect of H_2O_2 dosage on the THF wastewater treatment is influenced by the initial pH and Fe^{2+} dosage. At lower pH values (pH 2–4), increasing H_2O_2 dosage obviously increases the removal efficiency, while at high pH values (pH 5–6), the enlargement of H_2O_2 dosage slightly decreases the removal efficiency because higher pH causes the invalid decomposition of H_2O_2 and then decreases the

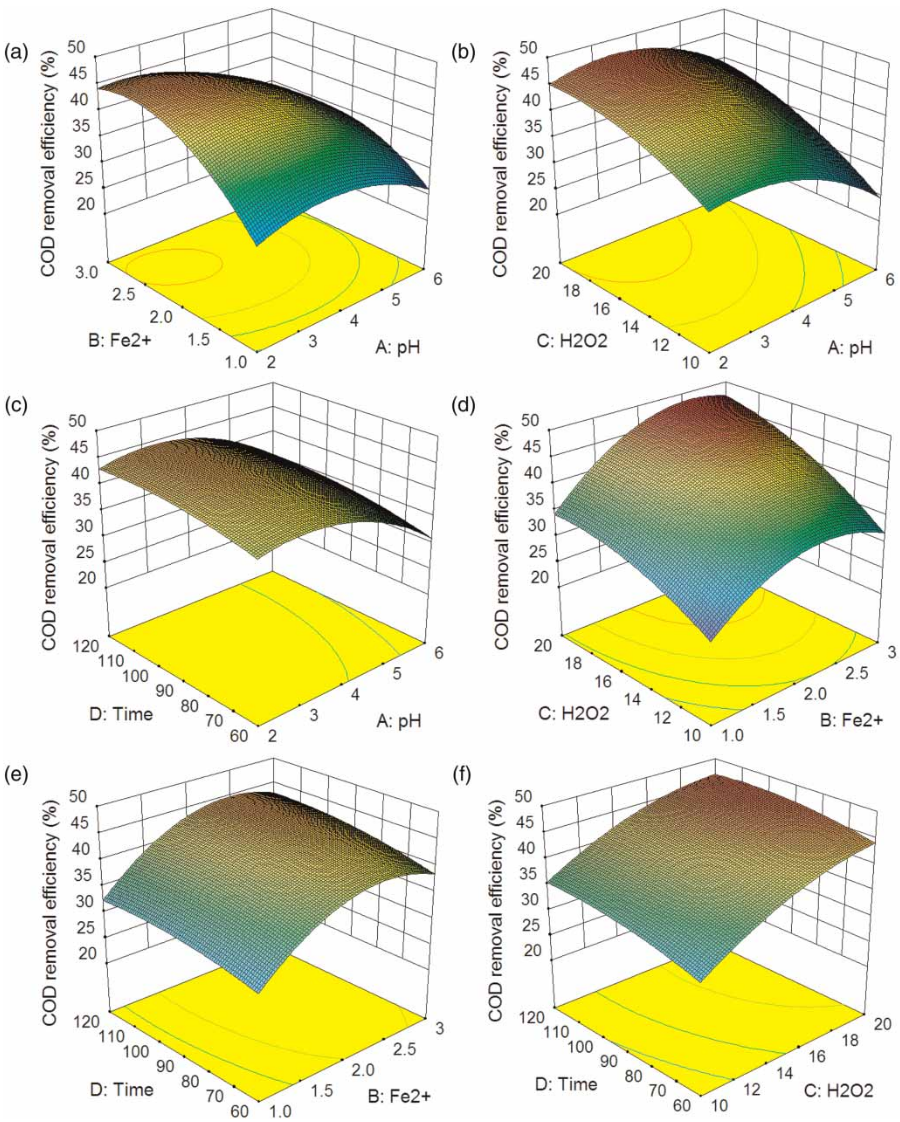

Figure 1 | Response surface showing removal efficiency of COD as a function of two independent variables: (a) initial pH and Fe^{2+} dosage (H_2O_2 dosage 15 mM, reaction time 90 min); (b) initial pH and H_2O_2 dosage (Fe^{2+} dosage 2 mM, reaction time 90 min); (c) initial pH and reaction time (Fe^{2+} dosage 2 mM, H_2O_2 dosage 15 mM); (d) Fe^{2+} dosage and H_2O_2 dosage (initial pH 4, reaction time 90 min); (e) Fe^{2+} dosage and reaction time (initial pH 4, H_2O_2 dosage 15 mM); (f) H_2O_2 dosage and reaction time (initial pH 4, Fe^{2+} dosage 2 mM).

oxidation efficiency. Higher Fe^{2+} dosage generates more $^{\bullet}OH$ which results in higher COD removal efficiency. However, decreasing the H_2O_2/Fe^{2+} molar ratio does not help to increase COD removal efficiency, which is presumably due to the direct reaction of $^{\bullet}OH$ with the high concentration of Fe^{2+} or the recombination of $^{\bullet}OH$.

Effect of Fe^{2+} dosage

Fe^{2+} is also an important component of the Fenton process because Fe^{2+} can catalytically decompose H_2O_2 and yield $^{\bullet}OH$. The effect of Fe^{2+} dosage on the removal efficiency of COD is shown in Figure 1((b), (d), (e)). Initial oxidation rate is a function of the Fe^{2+} concentration, therefore increasing the Fe^{2+} dosage increases the removal efficiency of COD. However, if Fe^{2+} is overdosed, the excess Fe^{2+} starts to compete for the $^{\bullet}OH$ with organic pollution and thus decreases the removal efficiency. The coagulation process is also initiated in addition to producing extra sludge and increasing total dissolved solids (TDS) of effluent at higher Fe^{2+} dosage (Neyens & Baeyens 2003). The effect of Fe^{2+} dosage on the treatment is constrained by the initial pH which has an effect on the iron solubility, complexation, and redox cycling between states (II) and (III) of iron (Brillas *et al.* 2009). Thus the viability of the Fe^{2+} depends on the pH of the solution, a lower concentration of Fe^{2+} results in a decrease of removal efficiency because Fe^{2+} acts as a catalyst to enhance the conversion of H_2O_2 into $^{\bullet}OH$.

Effect of pH

According to the major components of the Fenton reagents and the overall reaction, the initial pH was important for the efficiency of the Fenton process. The influence of initial pH on removal efficiency of COD is illustrated in Figure 1((a), (b), (c)). The removal efficiency increased slightly with increasing initial pH from 2.0 to 4.0; however, the removal efficiency decreased seriously as the initial pH varied from 4.0 to 6.0. The underlying reason is attributed to two aspects: on the one hand, the generation of $^{\bullet}OH$ is constrained when pH is below 3, which decreases the efficiency of Fenton oxidation; on the other hand, higher pH values with more $^{\bullet}OH$ reduce the activity of the Fenton reagent (Liu *et al.* 2013).

Effect of reaction time

The reaction time is depended on the rate of the reaction and the production of $^{\bullet}OH$ is a rate-limiting step. As seen from Figure 1((c), (e), (f)), the removal efficiency of COD increases as the reaction time is prolonged, but the amount of variation is relatively small. The impacts of initial pH value (Figure 1(c)), Fe^{2+} dosage (Figure 1(e)) and H_2O_2 dosage (Figure 1(f)) on the COD removal efficiency are independent of time, so prolonging the reaction time under certain conditions does not obviously improve the removal efficiency. Table 2 also shows that the interaction between initial pH/reaction time, Fe^{2+} dosage/reaction time and H_2O_2 dosage/reaction time were not significant.

Response optimization and validation of the experimental model

The main objective of the RSM optimization was to determine the optimum values of variables for THF wastewater treatment with the Fenton process. The regression model of the maximum removal efficiency shows that predicted COD removal reaches up to 47.8% under the optimum operating conditions of initial pH 4.49, Fe^{2+} dosage 2.52 mM, H_2O_2 dosage 20 mM and reaction time 110.3 min.

The prediction capability of the RSM model was validated by conducting three additional independent experiments. The predicted values are compared with the experimental results in Table 3, which shows that the experimental values agreed well with the predicted values with a deviation of 0.74–2.62%. This validation also confirms that the RSM is effective and reliable for optimizing the COD removal efficiency of Fenton oxidized THF wastewater.

Biodegradability tests

In general, chemical oxidation can change the molecular structure of non-biodegradable compounds and rupture them into smaller molecules; but intermediates usually have better aerobic biodegradability than the original compounds (Katayana & Matsumara 1991). The biodegradability of organic pollutants in wastewater can be explained and evaluated by the B/C ratio, which is used to express the biodegradability of wastewater. Wastewater with a B/C ratio below 0.30, between 0.30–0.45 and over 0.45 was considered to be poorly-biodegradable, biodegradable and easily-biodegradable, respectively (Gerke & Jwsaki 1981). As a way to explain that the Fenton effluent could meet the requirement of biological treatment, the B/C ratio is appropriate for examining the biodegradability of

Table 3 | Validation of model prediction against experimental outcomes for factors under consideration

Exp. no.	pH	Fe^{2+} dosage (mM)	H_2O_2 dosage (mM)	Reaction time (min)	Removal efficiency (%) Experimental	Predicted
1	4.5	2.5	20	110	45.24	47.73
2	3.5	1.5	12.5	120	38.91	37.06
3	2.5	2.5	17.5	90	49.82	47.92
4	5.5	2.0	20	120	39.73	42.35
5	2.0	2.5	15	60	41.05	42.00
6	4.0	1.5	12.5	100	37.21	36.47

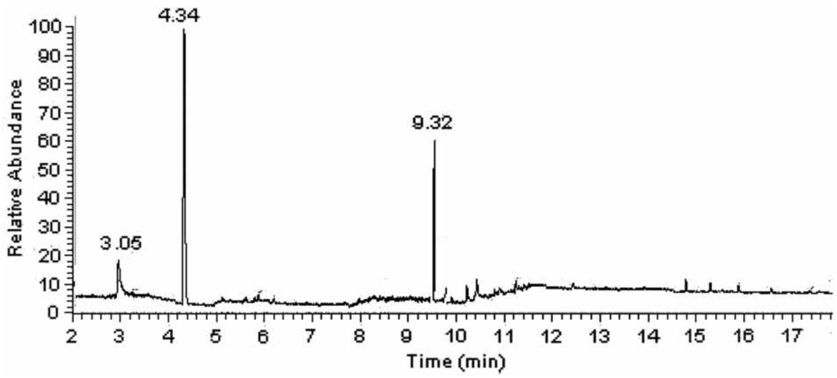

Figure 2 | Chromatogram from GC-MS of samples taken after Fenton treatment.

the wastewater oxidized by the Fenton process. After Fenton treatment under the above-mentioned optimum operating conditions determined by RSM, the approximate concentration of COD decreases from 25,000 to 14,000 mg/L, and BOD increases from 3,200 to 6,000 mg/L. The corresponding B/C ratio increases from 0.13 to 0.43, which indicates that the characteristics of the wastewater were transferred from poorly-biodegradable to easily-biodegradable after the Fenton process. The improved biodegradability of the wastewater could be explained by (1) a part of the organic compounds is mineralized and (2) part of the poorly biodegradable organic compounds are transformed into easily biodegradable organics.

Products of THF degradation by Fenton

In order to further investigate the degradation mechanism of THF, the organic components of the wastewater after Fenton treatment were analyzed by the GC–MS technique. As shown in Figure 2, three major peaks at retention times of 3.05, 4.34 and 9.32 min are detected in the gas chromatogram. Compared with standard mass spectra, these peaks correspond to 2-hydroxytetrahydrofuran, *γ*-butyrolactone and 4-hydroxybutanoate.

According to the analysis of intermediates, a general pathway for degradation of THF by the Fenton process is proposed in Figure 3. The degradation process is initiated by direct hydroxylation to create 2-hydroxytetrahydrofuran. Then *γ*-butyrolactone is continuously formed from the oxidation of OH. Further degradation leads to a ring cleavage reaction generating 4-hydroxybutanoate. The ultimate carboxylic acid is slowly converted to CO_2 and H_2O. As far as we know, the proposed degradation pathway of THF during the Fenton process has not been reported in the literature.

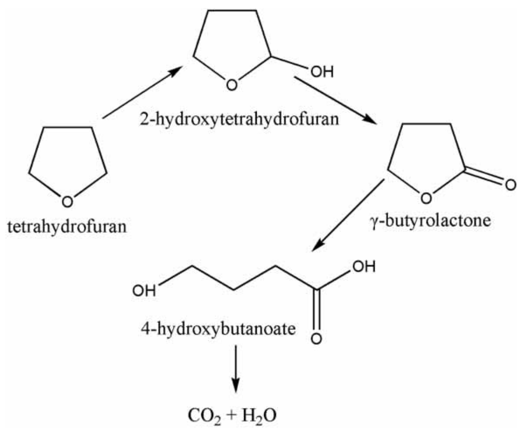

Figure 3 | The degradation pathway of THF during the Fenton process.

CONCLUSIONS

A response surface model based on the BBD technique was successfully applied to investigate the relationship between the COD removal efficiency of Fenton oxidation to treat THF wastewater and the operating parameters, to optimize the experiment process and predict the removal efficiency. ANOVA and response surface analysis showed that the selected four factors and the interactive items of initial pH/Fe^{2+} dosage, initial pH/H_2O_2 dosage as well as Fe^{2+} dosage/H_2O_2 dosage were statistically significant. The predicted removal efficiency agreed well with the outcomes observed experimentally, and maximum removal efficiency was obtained under the optimum conditions. Verification experiments confirmed the accuracy of the response surface model, which was proved to be a feasible and efficient method for the treatment of THF wastewater. The biodegradability of the wastewater increased after the Fenton oxidation process. The degradation mechanism was obtained by analyzing the three different intermediates.

The results of this study clearly indicated the potential and versatility of RSM based on BBD, which was capable of investigating the optimum conditions in the wastewater treatment process. This study has shown that Fenton pretreatment is an attractive alternative method for treating high-concentration THF wastewater.

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First received 31 July 2013; accepted in revised form 3 January 2014. Available online 21 January 2014