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Modeling and optimization of the coagulation of highly concentrated coking wastewater by ferrous sulfate using a response surface methodology

Chong Lin[a], Jianbo Liao[a], Chaohai Wei[a,b,*]

[a]*College of Environment and Energy, South China University of Technology, Guangzhou 510006, China, Tel./Fax: +86 20 39380588; emails: huagong246@gmail.com (C. Lin), 393805509@qq.com (J. Liao), cechwei@scut.edu.cn (C. Wei)*
[b]*Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

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ABSTRACT

The coagulation process by ferrous sulfate was used to pretreat coking wastewater prior to a subsequent biological treatment. The central composite Box–Behnken experimental design and response surface method were applied to evaluate and optimize the interactive effects of three operating variables, namely the initial pH, dosage of ferrous sulfate, and interaction time, on the physical and chemical performances of coagulation. Four dependent parameters, namely COD removal, cyanide removal, sulfide removal, and total oil removal, were either directly measured or calculated as responses. According to analysis of variances results, the four models proposed in this work can be used to navigate the design space, with the high regression coefficient R^2 varying from 0.9158 to 0.9877. The initial pH, ferrous sulfate dosage, and interaction time had significant effects on the COD removal, cyanide removal, sulfide removal, and total oil removal due to their respective effects on chemical precipitation and coagulation removal. The synergies effect of chemical precipitation and coagulation during ferrous sulfate coagulation process controlled the treatment. A visual search of the overlaying critical response contours plot was carried out, and the results indicated the optimum conditions to an initial pH 11, ferrous sulfate dosage of 1.5 g/L, and reaction time of 120 min. The experimental date and models' predictions agreed well. COD removal, cyanide removal, sulfide removal, and total oil removal of 15.25, 93.82, 73.36, and 4.73%, respectively, were demonstrated. The results of a B/C analysis and cost evaluation show that $FeSO_4$ coagulation is an appropriate technology for coking wastewater pretreatment.

Keywords: Coking wastewater; Ferrous sulfate; Coagulation; Response surface methodology (RSM)

1. Introduction

Coking wastewater is generated from coal coking, coal gas purification, and the by-product recovery processes of coking. This wastewater includes some inorganic pollutants, such as ammonium, sulfate, cyanide, and thiocyanate, and organic contaminants, such as phenolic compounds, nitrogen-, oxygen-, and sulfur-containing heterocyclic compounds, and polynuclear aromatic hydrocarbons [1]. Most of these constituents are refractory, toxic, mutative, and carcinogenic. Coking wastewater is a serious environmental

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*Corresponding author.

problem all over the world, especially in developing countries like China and India, where coal is the main energy source [2]. Conventional treatment of coking wastewater includes solvent extraction of phenolic compounds, steam stripping of ammonia and biological treatment, mostly in the form of the activated sludge process [3]. Due to the presence of many refractory and toxic inorganic compounds including ammonia, sulfate, cyanide, thiocyanate, the activated sludge process is not efficient for the removal of organic pollutants, as they can extend the hydraulic retention time, and negatively impact the stability of biological system when the concentrations of inorganic compound are changed suddenly. In general, dilution water and recirculation water are used to solve this problem [4], but this then raises the volume of wastewater being treated along with the initial investment and operating costs. Therefore, more work is required to develop better ways to pretreat the inorganic compounds in coking wastewater, such as ammonia, sulfate, cyanide, and thiocyanate.

Physical or chemical pretreatment processes are usually needed to improve the performance of biological systems [5]. Techniques such as chemical oxidation by Fenton’s reagent, ultrasonic irradiation, catalytic oxidation, and activated carbon or bottom ash adsorption have been used or studied for the pretreatment of coking wastewater prior to its treatment by biological systems [6–9]. Because the concentration of suspended matter is low in raw coking wastewater, the flocculating agents in common use, such as polymeric aluminum chloride (PAC) [10], polymeric ferric sulfate (PFS) [11,12], polymeric aluminum ferric chloride [13], and polyferric silicate sulfide [14] which often used with pulp and paper mill wastewater [15,16], textile and dyeing wastewater [17,18], tannery wastewater [19], yeast wastewater [20], municipal wastewater [6], and so on, are not used in coking wastewater treatment plants. In contrast, chemical precipitation to remove ammonium nitrogen by adding magnesium salt and phosphate to form magnesium ammonium phosphate hexahydrate (MAP) is a useful method that has been applied to coking wastewater treatment [21]. Moreover, a number of researchers have examined how to recycle MAP for ammonium nitrogen removal. Ferrous sulfate as a commonly used environmental benign agent is applied in Fenton oxidation and flue gas desulfurization [12]. But it has not yet been applied to the flocculation of sulfate, cyanide, and thiocyanate in coking wastewater. It is well known that cyanide can form stable complex compounds with ferrous ion such as ferrous blue $Fe_2[Fe(CN)_6]$ ($K_{sp} = 10^{-39}$) and Prussian blue $Fe_4[Fe(CN)_6]_3$ ($K_{sp} = 10^{-42}$) because of its strong complexation ability, which is used when electroplating wastewater to reduce toxicity. The related reaction process can be expressed as Eqs. (1) and (2) [22]. Ferrous sulfide FeS ($K_{sp} = 6.3 \times 10^{-18}$) is a compound that is difficult to dissolve in water also [23]. One of the characteristics of coking wastewater is its strong alkalinity. Before biological treatment, its pH must thus adjust to neutral so that the system can run effectively. Ferrous sulfate solution is acidic, and thus coagulation pretreatment with this can not only precipitate the organic compounds in coking wastewater but also adjust the pH value. However, the performance and optimal operating conditions of the coagulation pretreatment process using ferrous sulfate need to be evaluated, and this is the main aim of the current work.

$$3FeSO_4 \cdot 7H_2O + 6CN^- \rightarrow Fe_2[Fe(CN)_6] \downarrow + 3SO_4^{2-} + 2H_2O \quad (1)$$

$$3Fe_2[Fe(CN)_6] + 4H^+ + O_2 \rightarrow Fe_4[Fe(CN)_6]3 \downarrow + 2Fe^{2+} + 2H_2O \quad (2)$$

Many factors can influence the efficiency of the coagulation–flocculation process, such as the type and dosage of coagulant, pH, mixing speed and time, temperature, and retention time. The optimization of these factors may significantly increase the process efficiency. The statistical method of response surface methodology (RSM) has been proposed to determine the influences of individual factors as well as their interactive influences [16]. It is an empirical statistical modeling technique employed for multiple regression analysis using quantitative data obtained from properly designed experiments, in order to solve multivariable equations and simultaneously evaluate the relative significance of several influencing factors even in presence of complex interactions. RSM can reduce the number of experiments needed to determine the optimum operating conditions of a system. In the last few years, RSM has been applied to optimize and evaluate the interactive effects of independent factors in the dye removal process, as well as the treatment of paper-recycling wastewater, pulp and paper mill effluent, and manufacturing wastewater [6,16,24–29]. However, RSM has not yet been applied to examine the effects of the interactions of various operating conditions on the removal of COD, sulfide, cyanide, and total oil by ferrous sulfate coagulation.

The coagulation pretreatment of coking wastewater by ferrous sulfate was first evaluated in this work using the Box–Behnken approach to RSM. Quadratic models were then used to adjust the experimental results, considering only the variables that presented significant effects. The effects of initial pH, dosage of ferrous sulfate, and interaction time between these factors on (1) the coagulation performance on removal of organic, (2) the removal characterization of cyanide, (3) the removal characterization of sulfide, and (4) the removal of total oil were studied. Four interrelated parameters, namely overall COD removal, cyanide removal, sulfide removal, and total oil removal, were evaluated as responses. The continuous response surface of the main parameters was developed to provide an optimal region to satisfy the operating specifications. Moreover, BOD/COD and cost were evaluated to assess the practicality of applying $FeSO_4$ coagulation for coking wastewater pretreatment.

2. Materials and methods

2.1. Materials

The coking wastewater used in the experiments was collected from Jinniu-Tiantie coking plant in Handan, Hebei province of China. The coking wastewater was treated by a combined process, an O/H/O biological system, secondary coagulation, and ozonation technology. The effluent quality can meet the integrated wastewater discharge standard (GB8978-1996). The major physicochemical characteristics of the raw coking wastewater are summarized in Table 1 and these indicate that it is difficult to treat biologically.

The laboratory reagent ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) (molecular mass of 278.5 g mol^{-1}, purity >99%) was purchased from Aladdin Reagents compound in China. Ferrous sulfate solutions were prepared fresh everyday by dissolving appropriate amounts of powdered ferrous sulfate in Milli-Q Plus (Millipore) water.

2.2. Experimental procedure

A six-beaker jar-test apparatus was used to simulate the coagulation–flocculation process. Each beaker contained 250 mL of the coking wastewater. The coagulation–flocculation procedure involved 2 min of rapid mixing at 100 rpm, followed by 30 min of slow mixing at 40 rpm, and 15 min of setting. Additional centrifuging (5,000 rpm for 5 min) was then performed to obtain a clear liquid for all samples before analysis. The pH adjustment was carried out by vigorous stirring with a glass rod using solutions of 2 M HCl and 2 M NaOH. The temperature of the raw wastewater was kept constant at 35℃. The experiments were all carried out in triplicate to test their reproducibility. The percentage of response parameter removal was calculated using Eq. (3), where *Cr* and *Ct* are the concentrations in raw and treated solution, respectively.

$$\text{Response removal } (\%) = \frac{Cr - Ct}{Cr} \times 100 \qquad (3)$$

COD_{Cr}, CN^-, and S^{2-} were analyzed according to the Chinese State Environment Protection Agency (SEPA) Standard Methods (Chinese SEPA, 2002). The TOC of the raw and treated solution was measured after filtration thought 0.45 μm membrane by a TOC analyzer (TOC-VCPH, Shimazdzu, Japan). The pH was measured with a pH meter (pHS-3C, China).

2.3. Experimental design and data analysis

The central composite Box–Behnken experimental design was used for the RSM in this work. The experimental data were analyzed using the RSM procedure of the statistical analysis system and fitted to a second-order polynomial model. The quadratic equation used in this is as follows:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum_i \sum_j \beta_{ij} X_i X_j \qquad (4)$$

In which Y is the predicted response, β_0 is a constant, β_i is the first-order model coefficient, β_{ii} is 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, Star-Ease, Inc., Minneapolis, MN) was used for the statistical design of the 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 fit of the polynomial model was expressed by the coefficient of

Table 1
Quality of raw coking wastewater

	pH	COD (mg L^{-1})	NH_4-N (mg L^{-1})	S^{2-} (mg L^{-1})	CN^- (mg L^{-1})	Volatile phenol (mg L^{-1})	Chroma	SS (mg L^{-1})
Raw coking wastewater	9.5–10.5	6,000 ± 540	85.7 ± 20.4	52.4 ± 16	20.1 ± 10	1,180 ± 120	450 ± 70	70 ± 20

determination R^2 and Adj R^2, and its statistical significance was checked by the Fisher's *F*-test in the design expert software. Model terms were selected or rejected based on the *p* value (probability) with a 95% confidence level. Three-dimensional (3D) plots and their respective contour plots were obtained with regard to the effects of the two factors at three levels. A perturbation plot was used to compare the effects of all the factors at a particular point in the design space. Furthermore, the optimum region was indentified based on the main parameters in the overlay plot. The adequacy of the regression equations was checked by comparing the experimental data with the predicted values obtained from the equations. A detail analysis of the model is presented in the following sections.

3. Results and discussion

3.1. Fitting the response surface models to significant independent variables

The central composite Box–Behnken experimental design was chosen to find out the relationship between the response function (*Y*) and variables (*X*). The values of the independent variables (*X*1–*X*3) as well as their variation limits, and the experimental data obtained for four responses (*Y*1–*Y*4) 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), $FeSO_4$ dosage, and reaction time (*X*2 and *X*3) were set at three levels: −1(minimum), 0(central), and +1(maximum) (Table 2). The experimental results are shown as overall COD efficiency (*Y*1), S^{2-} removal (*Y*2), CN^- removal (*Y*3), and total oil removal (*Y*4).

Tables 3 and 4 show the reduced quadratic models in terms of coded factors with significant terms, and also show other statistical parameters. In Table 3, the four models (*Y*1–*Y*4) *F*-values of 8.46, 63.03, 28.70, and 10.93 with very low probability values ($p < 0.0001$) imply that the terms were significant in all models. There was only a 0.01% chance that a model's *F*-value could occur due to noise. The ANOVA results for the four parameters (*Y*1–*Y*4) showed that significant ($p < 0.05$) response surface models were obtained with high R^2 value ranging from 0.9158 to 0.9909. The high R^2 coefficients indicate that the quadratic models had a satisfactory fit with the experimental data. The values of adjusted R^2 of 0.8075, 0.9722, 0.9736, and 0.8481, for the models *Y*1–*Y*4, respectively, were also high, which again supports the significance of the models [30]. The response surface models could thus be used to accurately predict the percentage variation of these four parameters.

As also shown in Table 3, the lack of fit (LOF) F-values of all four models imply that the variations of the data around the fitted model were not significant relative to the pure error. There were 10.24, 93.45, 94.09, and 73.13% chance for the models *Y*1–*Y*4 that the LOF F-value could occur due to noise, respectively. The values of probability of lack of fit (PLOF) higher than 0.05 show that the *F*-statistic was insignificant, implying significant correlations between the variables and process responses in all four models. Adequate precision (AP) was used to compare the range of the predicted values at the design points to the average prediction error. The ratios of the four models ranged from 9.030 to 20.474 all greater than 4, indicating AP. These models could thus be used to navigate the design space. Simultaneously, the low values of the coefficient of variation (ranging from 6.61 to 25.38%) indicated the good precision and reliability of the experiments. In addition, the plot comparing the actual and predicted values for total COD removal (*Y*1) indicates an adequate agreement between real data and that obtained from the models shown in Fig. 1. The other predicted vs. actual value plots for the other three responses (*Y*2–*Y*4) were similar to those in Fig. 1, therefore, and they are not shown in this paper.

3.2. Total COD removal

Previous researchers reported that the composition of COD in coking wastewater is mainly soluble organic matter, total oils, and inorganic substances. Conventional flocculants such as PAC and PFS cannot be applied to COD removal because of low concentration of suspended solids. However, the oxidation and hydrolysis of $FeSO_4$ could lead to precipitation of ferric hydroxide, and then cause ferrous hydroxide to coagulate the total COD, depending on the dosage and initial pH. On the other hand, when the dosage of $FeSO_4$ was above optimal level, the removal of overall COD removal reduced with the ferrous ion for COD product. Fig. 2(a) shows a perturbation plot which illustrates the effects of all the factors at the center point in the design space. It is apparent that the dosage (*X*2) has significantly negative effects (linear and quadratic) on the overall COD removal (*Y*1), as also shown in Table 3. Here, a positive effect means that the corresponding response (*Y*) increases as the effect factor (*X*) level increases, whereas a negative effect means that the corresponding response decreases as the level increases. As also shown in Fig. 2(a) and

Table 2
Three-factor and three-level Box–Behnken central composite design and experimental results

	Variables			Experimental responses			
Coded unit	$X1$	$X2$ (g/L)	$X3$ (min)	$Y1$ (%)	$Y2$ (%)	$Y3$ (%)	$Y4$ (%)
1	7.00(0)	1.10(0)	62.50(0)	11.56	78.52	64.45	3.59
2	7.00(0)	1.10(0)	62.50(0)	11.86	74.66	66.51	3.43
3	7.00(0)	0.20(−1)	120.00(+1)	1.01	24.86	6.01	1.15
4	11.00(+1)	1.10(0)	5.00(−1)	17.56	89.56	74.88	3.86
5	11.00(+1)	0.20(−1)	62.50(0)	1.03	21.36	6.88	1.23
6	3.00(−1)	0.20(−1)	62.50(0)	0.87	20.88	4.75	1.09
7	7.00(0)	1.10(0)	62.50(0)	13.65	84.87	72.53	3.67
8	3.00(−1)	2.00(+1)	62.50(0)	9.56	85.82	69.67	4.12
9	7.00(0)	0.20(−1)	5.00(−1)	0.94	23.52	6.75	1.29
10	3.00(−1)	1.10(0)	5.00(−1)	10.68	82.86	68.75	3.26
11	7.00(0)	2.00(+1)	120.00(+1)	14.14	91.22	69.54	4.51
12	3.00(−1)	1.10(0)	120.00(+1)	7.65	81.94	65.94	4.21
13	7.00(−1)	1.10(0)	62.50(0)	14.89	89.56	70.21	4.41
14	11.00(+1)	1.10(0)	120.00(+1)	16.89	92.36	72.52	5.02
15	7.00(0)	1.10(0)	62.50(0)	15.08	85.31	49.53	4.84
16	7.00(0)	2.00(+1)	5.00(−1)	9.66	88.53	77.31	3.96
17	11.00(+1)	2.00(+1)	62.50(0)	11.63	94.33	73.48	4.48

Notes: $X1$: first variable, initial pH, $X2$: second variable, $FeSO_4$ dosage, $X3$: third variable, reaction time; $Y1$: overall COD removal efficiency, $Y2$: S^{2-} removal, $Y3$: CN^- removal, $Y4$: total oil removal.

Table 3, the initial pH and reaction time have positive linear effect on $Y1$. The 3D surface graphs for the same results are shown in Fig. 2(b). The response surface of overall COD removal shows a clear peak, suggesting that the optimum conditions for maximum overall COD removal are well inside the design boundary. The results of the individual optimization procedure show that an initial pH 11.01, $FeSO_4$ dosage of 1.5 g/L, and reaction time of 120 min were predicted to provide the highest overall COD removal of 14.93%.

3.3. Sulfide removal

Desulfurized liquid wastewater is an important part component of coking wastewater, which has the characteristics of low quantity flow, high concentration, and strong toxicity. When sulfide is placed in an aerobic bioreactor it consumes dissolved oxygen to produce sulfate ions, suppressing the subsequent hydrolysis reaction. The sulfide removal process can improve the efficiency of the bioreactor. In the experiment, the linear terms ($X1$ and $X2$), quadratic term ($X22$), and the interaction terms ($X1X2$) were all statistically significant, as shown in Table 4. The addition of Fe^{2+} had positive linear effect ($X2$) and negative quadratic affect ($X2^2$), as shown in Table 3. The perturbation plot, which is similar to that of overall COD removal, also shows that the removal of sulfide is largely controlled by the $FeSO_4$ dosage, followed by the initial pH and reaction time. The results show that sulfide removal is a function of the two factors ($X1$ and $X3$) involved in determining the $FeSO_4$ dosage.

As shown in Fig. 3(b), the percentage of sulfide removal increased along with the $FeSO_4$ dosage, up to 1.5 g/L for an initial pH between 3 and 11 indicating that the $FeSO_4$ dosage is the limiting factor for sulfide removal. An insignificant impact of increasing the $FeSO_4$ dosage on sulfide removal was observed at level over 1.5 g/L. This is because the hydrolysis reaction of ferrous sulfide can easily occur under acid conditions. The addition of Fe^{2+} had the expected positive effect with regard to reducing pH. The explanation for this, similar to that for overall COD removal, is that the hydrolysis and reducing reaction associated with Fe^{2+} were more significant than the increase of coagulation performance due to an overdose of Fe^{2+}.

The optimization results indicate that the combination of an initial pH 11.03, $FeSO_4$ dosage of 1.5 g/L, and reaction time of 120 min leads to the optimum sulfide removal behavior, with the highest sulfide removal being $Y2 = 94.46\%$.

3.4. Cyanide removal

Coking wastewater is also called phenol-cyanogen wastewater, and the toxicity of cyanide inhibits the metabolism of microbes. To better improve the

Table 3
ANOVA results for the response parameters

Response	Final modified equations in terms of coded factors with significant terms	*F*	*p*	LOF	PLOF	R^2	Adj R^2	AP	SD	CV	PRESS
*Y*1	$13.41 + 2.31X1 + 5.14X2 + 0.12X3 + 0.48X1X2 + 0.61X1X3 + 1.10X2X3 - 0.43X1^2 - 7.21X2^2 + 0.24X3^2$	8.46	<0.0001	4.12	0.1024	0.9158	0.8075	9.030	2.52	25.38	554.13
*Y*2	$82.58 + 3.26X1 + 33.66X2 + 0.74X3 + 2.01X1X2 + 0.93X1X3 + 0.34X2X3 + 1.33X1^2 - 28.32X2^2 + 2.77X3^2$	63.03	<0.0001	0.13	0.9345	0.9878	0.9722	20.474	4.70	6.61	446.71
*Y*3	$64.65 + 2.33X1 + 33.20X2 - 1.71X3 + 0.42X1X2 + 0.11X1X3 - 1.76X2X3 + 2.33X1^2 - 28.29X2^2 + 3.54X3^2$	28.70	<0.0001	0.063	0.9409	0.9736	0.9397	13.796	6.90	12.75	635.19
*Y*4	$3.99 + 3.26X1 + 33.66X2 + 0.74X3 + 2.01X1X2 + 0.93X1X3 + 0.34X2X3 + 1.33X1^2 - 28.32X2^2 + 2.77X3^2$	10.93	<0.0001	0.45	0.7313	0.9336	0.8481	9.202	0.53	15.50	10.26

Notes: *X*1: first variable, initial pH, *X*2: second variable, $FeSO_4$ dosage, *X*3: third variable, reaction time; *Y*1: overall COD removal efficiency, *Y*2: S^{2-} removal, *Y*3: CN^- removal, *Y*4: total oil removal. *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 4
Results for the reduced cubic model of the variables effects on the response parameters

	Sum of squares				Mean square				*F*				*p*			
Source	*Y*1	*Y*2	*Y*3	*Y*4	*Y*1	*Y*2	*Y*3	*Y*4	*Y*1	*Y*2	*Y*3	*Y*4	*Y*1	*Y*2	*Y*3	*Y*4
*X*1	42.50	85.22	43.48	0.41	42.50	85.22	43.48	0.41	6.70	3.85	0.91	1.44	0.0361	0.0904	0.3710	0.2696
*X*2	211.56	9,063.96	8,818.58	18.94	211.56	9,063.96	8,818.58	18.94	33.33	409.83	185.34	67.23	0.0007	<0.0001	<0.0001	<0.0001
*X*3	0.11	4.37	23.39	0.86	0.11	4.37	23.39	0.86	0.017	0.20	0.49	3.07	0.8988	0.6702	0.5058	0.1233
*X*1*X*2	0.91	16.12	0.71	0.012	0.91	16.12	0.71	0.012	0.14	0.73	0.015	0.043	0.7159	0.4215	0.9065	0.8417
*X*1*X*3	1.50	3.46	0.051	0.002500	1.50	3.46	0.051	0.002500	0.24	0.16	0.001064	0.008873	0.6417	0.7042	0.9749	0.9276
*X*2*X*3	4.86	0.46	12.36	0.12	4.86	0.46	12.36	0.12	0.77	0.021	0.26	0.42	0.4105	0.8899	0.6260	0.5356
$X1^2$	0.77	7.45	22.95	0.018	0.77	7.45	22.95	0.018	0.12	0.34	0.48	0.063	0.7378	0.5798	0.5098	0.8095
$X2^2$	218.74	3,376.22	3,368.71	7.37	218.74	3,376.22	3,368.71	7.37	34.46	152.66	70.80	26.15	0.0006	<0.0001	<0.0001	0.0014
$X3^2$	0.24	32.20	52.82	0.016	0.24	32.20	52.82	0.016	0.037	1.46	1.11	0.058	0.8523	0.2668	0.3270	0.8167
Residual	44.43	154.81	333.07	1.97	6.36	22.12	47.58	0.28								

Notes: *X*1, *X*2, and *X*3 represent the effect of initial pH, $FeSO_4$ dosage, and reaction time, respectively. *X*1*X*2, *X*1*X*3, and *X*2*X*3 represent the interaction between initial pH and $FeSO_4$ dosage, interaction between initial pH and reaction time, and interaction between $FeSO_4$ dosage and reaction time, respectively. *Y*1: overall COD removal efficiency, *Y*2: S^{2-} removal, *Y*3: CN^- removal, *Y*4: total oil removal. $X1^2$, $X2^2$, and $X3^2$ represent the quadratic effect of initial pH, $FeSO_4$ dosage, and reaction time, respectively.

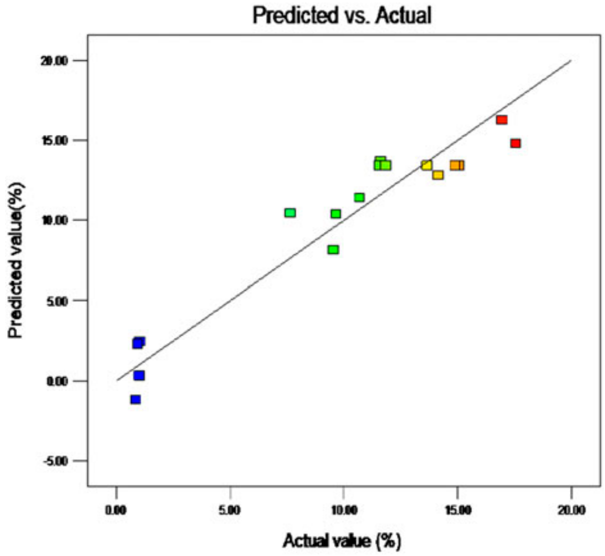

Fig. 1. Predicted vs. actual values for overall COD removal.

treatment efficiency of the related biological process, the removal of cyanide from coking wastewater was adopted as one treatment parameter (*Y*3).

Table 4 shows that the linear term (*X*2) and quadratic term ($X2^2$) were statistically significant. The steepest curvature in the $FeSO_4$ dosage (*X*2) in the perturbation plot shown in Fig. 4(a) indicates than an increase in the $FeSO_4$ dosage has a positive effect with regard to reducing the amount of cyanide. The amount of cyanide rapidly decreased as $FeSO_4$ dosage increased, due to the greater precipitation performance that occurred at a higher Fe^{2+} dosage following $Fe_2[Fe(CN)_6]$ oxidization. The reaction time and pH did not appear to have any obvious effects on cyanide removal, because the precipitation process occurred rapidly at a wide pH range. Moreover, at a fixed initial pH and Fe^{2+} dosage, the amount of cyanide reduced slightly with increasing reaction time likely due to the balance between precipitation and dissolution.

The maximum cyanide removal rate of 78.9% was obtained at an initial pH 11.34, $FeSO_4$ dosage of 1.5 g/L, and reaction time of 120 min.

3.5. Total oil removal

The content of total oil in coking wastewater is mainly coal tar, which can be divided into floating oil, dispersed oil, emulsified oil, dissolve oil, and heavy oil. The chemical composition of total oil is extremely complicated, and represented about 10% as total COD_{Cr} of the total pollutant concentration. The compounds of coal tar have the characteristics of biological toxicity and poor degradability, which significantly influence microbial proliferation and inhibit the activity of microbial enzymes. Moreover, the adhesion effect of coal tar in coking wastewater limits the transfer of oxygen molecules, and also can inhibit the activity of micro-organisms. Total oil removal is thus proposed as a significant and useful indicator to evaluate coagulation performance in this study. Experiments were carried out to determine the concentration of the total oil isolated from the supernatant of reaction samples by iron ions at various operating conditions.

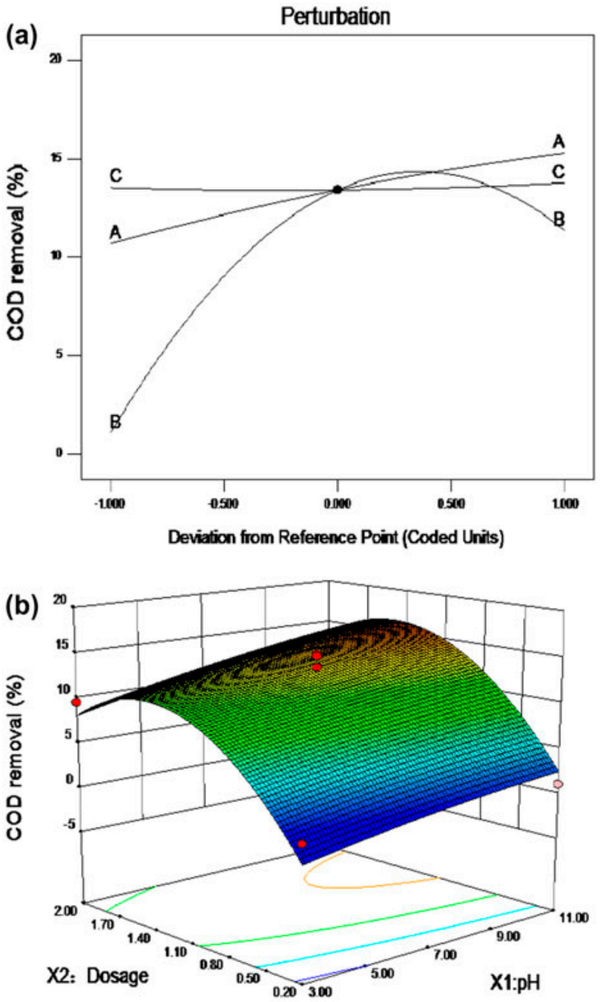

Fig. 2. (a) Perturbation graph and (b) 3D surface graphs for overall COD removal (A: initial pH, B: $FeSO_4$ dosage, C: reaction time).

Table 4 shows that the linear term (*X*2) and quadratic term ($X2^2$) were statistically significant. A comparison of the effects of all the factors at the center point in the perturbation plot in Fig. 5(a) also shows the steepest curvature in $FeSO_4$ dosage (*X*2). The

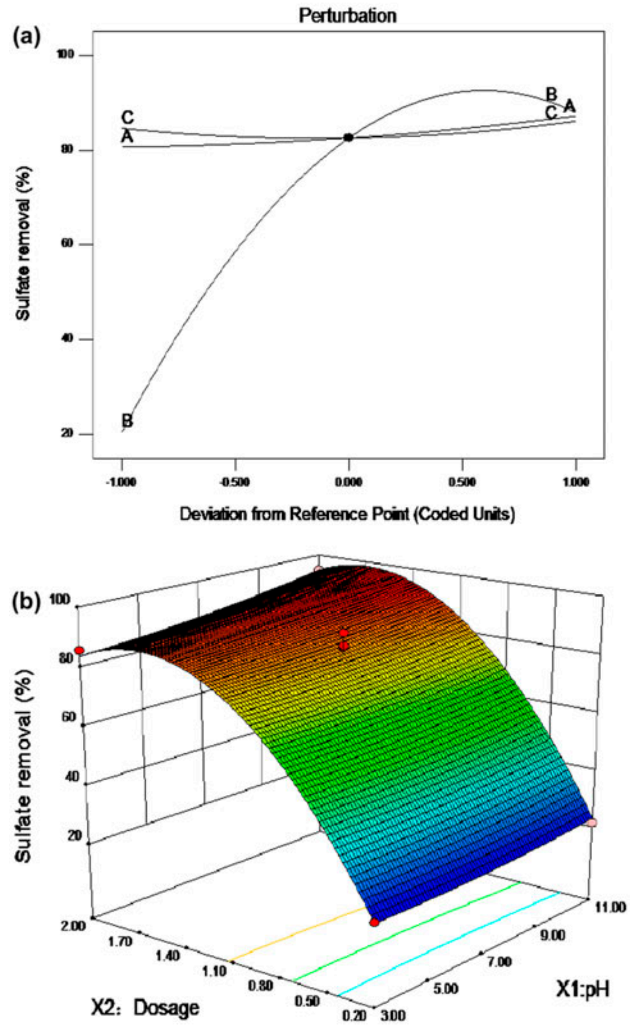

Fig. 3. (a) Perturbation graph and (b) 3D surface graphs for sulfide removal (A: initial pH, B: $FeSO_4$ dosage, C: reaction time).

results indicate that the response of total oil removal was very sensitive to the $FeSO_4$ dosage. The total oil was removed by both electrolyte demulsification and coagulation, which would explain why the total oil removal was especially influenced by the dosage. In practice, this means that the increase in total oil removal resulted in increases in both sulfide removal ($Y2$) and cyanide removal ($Y3$), as the high pH, long reaction time, and addition of $FeSO_4$ increased coagulation efficiency. Accordingly, the three responses ($Y2$, $Y3$, and $Y4$) gave very similar perturbation plots.

Fig. 5(b) again confirmed that the total oil removal increased when the $FeSO_4$ dosage was increased to 1.56 g/L. Further increases in the $FeSO_4$ dosage resulted in the balance of total oil removal probably due to the charge neutralization equilibrium that

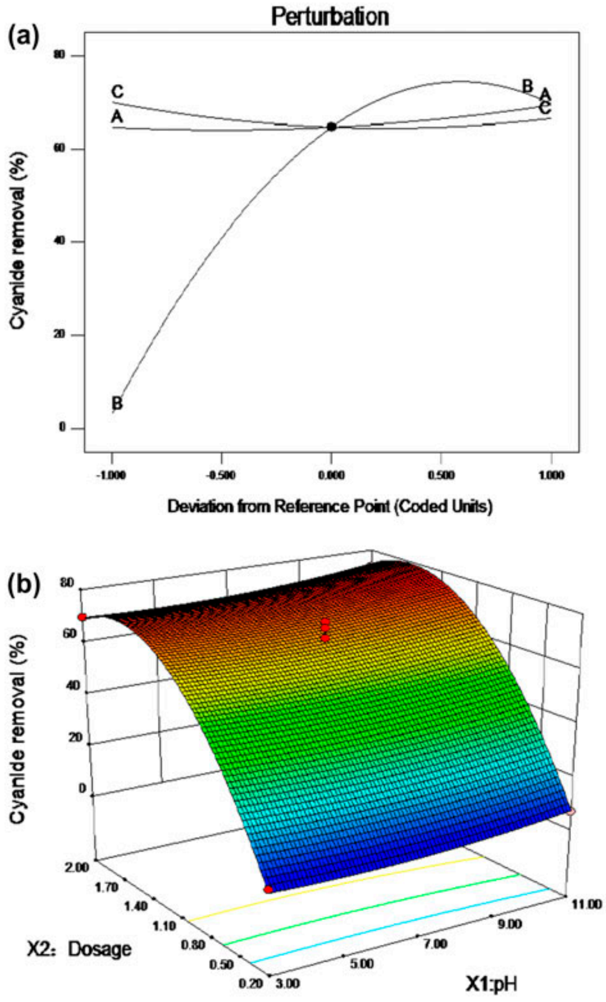

Fig. 4. (a) Perturbation graph and (b) 3D surface graphs for cyanide removal (A: initial pH, B: $FeSO_4$ dosage, C: reaction time).

occurs in the coking wastewater. The highest level of 4.75% total oil removal was achieved at an initial pH 11, $FeSO_4$ of 1.53 g/L, and reaction time of 120 min.

3.6. Optimization of $FeSO_4$ coagulation for coking wastewater

The main objective of optimization is to determine the optimum values of variables for concentrated coking wastewater treatment with $FeSO_4$ coagulation based on the models proposed in this work and using experimental data. With multiple responses, the optimum conditions where all the parameters simultaneously meet the desirable criteria can visually be searched for by superimposing or overlaying the critical response contours on a contour plot. Among the optimum conditions, the coagulation efficiency was

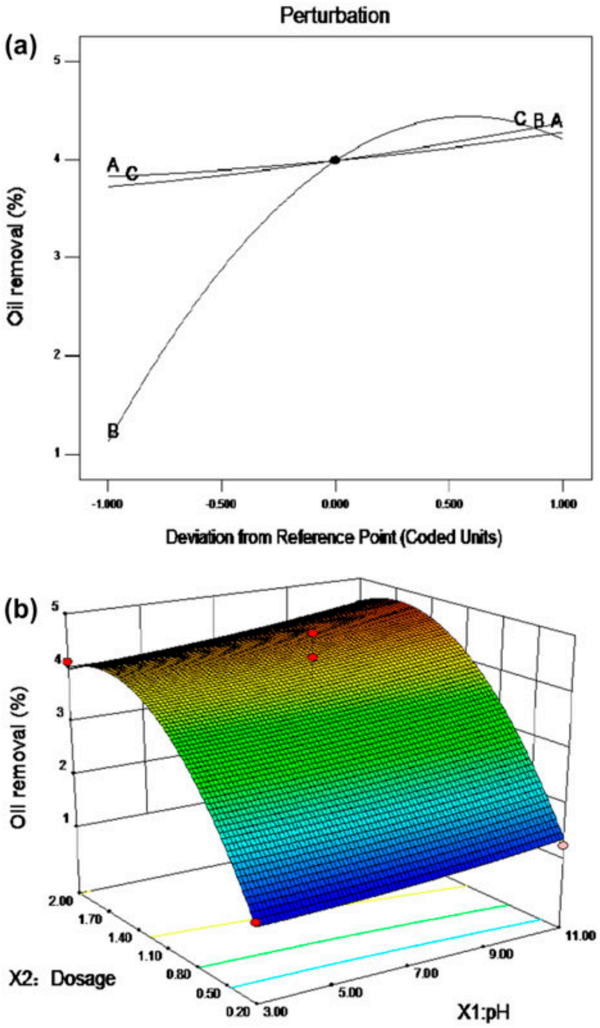

Fig. 5. (a) Perturbation graph and (b) 3D surface graphs for total oil removal (A: initial pH, B: $FeSO_4$ dosage, C: reaction time).

influenced by the dosage of $FeSO_4$, initial pH, and reaction time, and the significance of these factors was in this same order, from most to least. It can be explained as follows: the $FeSO_4$ solution is acidic, and thus the initial pH changed when $FeSO_4$ was added. Cyanide and sulfide were precipitated more thoroughly when the dosage was increasing. And the sediment which formed was able to adsorb the oil component of the coking wastewater. A $FeSO_4$ dosage of about 1.5 g/L was the inflection point of COD removal. The $FeSO_4$ solution's contribution of the COD value is higher than the coagulation precipitate removing COD, leading to the removal rate of COD decrease. An additional experiment was thus conducted applying the optimum conditions of an initial pH 11, $FeSO_4$ dosage of 1.53 g/L, and reaction time of 120 min to confirm the agreement of the results obtained from the models and experiments. As shown in Table 5, the experimental findings for all the response parameters were in close agreement with the models' predictions. Low errors of 2.51, 4.70, 6.86, and 0.53% and low standard deviations ± 2.51%, ± 4.70%, ± 6.86%, and ± 0.53% were obtained for *Y*1–*Y*4, respectively.

3.7. BOD_5 analysis and cost evaluation

The results for the BOD_5 measurements before and after treatment by $FeSO_4$ coagulation were set out. The BOD_5 value of effluent was 1,735.4 ± 125.6 mg/L, which was lower than the 2,255.5 ± 168.5 mg/L found for the raw wastewater. With regard to the coagulation process, the BOD_5/COD increased from 0.27 ± 0.04 to 0.41 ± 0.05, which contributed to the biodegradability of the effluent. Some poisonous and harmful substances in the coking wastewater, such as sulfide and cyanide, were removed in the coagulation process by chemical precipitation and complexation, and some refractory compounds, such as oil and POPs were removed by physical reactions such as adsorption–neutralization and sweeping.

Chemicals may account for the largest individual share of operating costs in chemical treatment processes. The appropriate determination of the type and dosage of chemicals to be used will not only improve the process, but also influence the running costs of using the different coagulants at the optimum operating conditions. With a coking wastewater treatment system, an increase in B/C would improve the treatment efficiency of biological systems and reduce the hydraulic retention time. The reduction in the aeration rate can offset the greater reagent cost. Total operation cost has been calculated for a coking treatment plant with a capacity of 2,400 m^3 wastewater per day in Handan, Hebei province of China. It includes costs of electrical energy, chemicals, maintenance, and sludge dewatering and disposal costs. Fortunately, the sludge contains an amount of heavy oil, which has a

Table 5
Verification experiments at optimum conditions

	Response			
Conditions	*Y*1	*Y*2	*Y*3	*Y*4
Experimental value	15.25	93.82	73.36	4.73
Model response	17.76	98.52	80.22	5.26
Error	2.51	4.70	6.86	0.53
STDEV	±2.51	±4.70	±6.86	±0.53

Table 6
Cost evaluation of $FeSO_4$ coagulation process

Item	Unit	Value
Influent flow	m^3/h	100
$FeSO_4$ dosage	kg/m^3	1.5
Wholesale $FeSO_4$ price	USD/kg	0.08063
Power consumption	kw/h	2.2
Industrial electricity price	USD/kw	0.1074
Cost	USD/m^3	0.1233

collection value. The cost of dewatering and disposal costs could be saved. Electrical energy and material costs were taken into account as major cost items in the calculation of the operating cost (USD m^{-3} of coking wastewater) in the form:

$$\text{Operating cost} = a \cdot C_{\text{energy}} + b \cdot C_{\text{chemicals}} \tag{5}$$

Coefficient *a*: industrial electrical energy price.
Coefficient *b*: wholesale chemical $FeSO_4$ price.
where C_{energy} (kwh/m^3) and $C_{\text{chemicals}}$ (kg/m^3) are consumption quantities for treating coking wastewater. *a* and *b* coefficients for China market in 2014 are as follows in Table 6. Based on the design specifications and experimental date, Table 6 shows that the estimated cost of using the $FeSO_4$ coagulation process was about 0.1233 USD per cubic meter. The whole operation cost of the coking wastewater treatment plant is about 3.5 USD per cubic meter. Given that the financial and environmental benefits of this process, the proposed $FeSO_4$ coagulation is a promising approach for the pretreatment of coking wastewater.

4. Conclusions

The $FeSO_4$ coagulation process is an effective method to pretreat high concentration coking wastewater. The RSM results obtained in this work demonstrated the significant effects of three operating variables (initial pH, $FeSO_4$ dosage, and reaction time), as well as their interactive effects on four responses (overall COD removal, sulfide removal, cyanide removal, and total oil removal). The factors most strongly affecting overall COD removal, sulfide removal, cyanide removal, and total oil removal are initial pH and $FeSO_4$ dosage, due to their effects on the removal efficiency of chemical precipitation and complexation, respectively. The dosage of $FeSO_4$ is the most significant factor with regard to coagulation removal efficiency. The optimum operating conditions were obtained by applying RSM. The experimental findings were in close agreement with the models' predictions. It is evident that the use of a statistical optimization approach, namely RSM, helped to evaluate the use of $FeSO_4$ coagulation with coking wastewater in an efficient with minimum effort and time.

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