Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2016.1157707

57 (2016) 25520–25531
November

A combined process of chemical precipitation and flocculation for treating phosphating wastewater

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Received 5 October 2015; Accepted 13 February 2016

ABSTRACT

A combined process that involves adjusting pH value, adding calcium chloride and flocculation was used for the removals of zinc (Zn), total phosphorus (TP), and chemical oxygen demand (COD) from phosphatizing wastewater. The result of single-factor experiment showed that the optimum process conditions used for precipitation were phosphating wastewater pH (pHI) of 10.0 and $CaCl_2$ dosage of 25.0 g L^{-1}, and for flocculation were cationic polyacrylamide (CPAM) dosage of 20.0 mg L^{-1} and pH (pHII) of 8.0. Using the optimum process conditions to treat phosphating wastewater, Zn, TP, and COD were reduced to 0.44, 0.33, 38.0 mg L^{-1}, respectively. Response surface methodology (RSM) was employed to optimize the factors of pHI, $CaCl_2$ dosage, CPAM dosage, and pHII to maximize COD removal efficiency. The significant order of factors that affect COD removal efficiency was as CPAM dosage > pHI > $CaCl_2$ dosage > pHII. The interactions between CPAM dosage and pHII, pHI and pHII are relatively significant. The optimization results of RSM experiment showed that the COD removal efficiency of 82.1% could be achieved with the optimal conditions: pHI of 9.5, $CaCl_2$ dosage of 29.0 g L^{-1}, CPAM dosage of 25.2 mg L^{-1}, and pHII of 7.5.

Keywords: Flocculation; Chemical precipitation; Phosphating wastewater; Response surface methodology

1. Introduction

Compared with other metal surface treatment technologies in the mechanical processing industry, the zinc phosphate coating process is more widely employed in metal surface treatment to improve the corrosion resistance and wear resistance because of its low cost, excellent quality, and strong adhesive ability [1,2]. Large quantities of phosphating wastewater are generated annually from the metal polishing and coating industry. For example, Shanghai Baosteel Group Corporation has an annual production of over 4,000 tons of phosphating wastewater [3], which contains

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high concentrations of phosphate, zinc, and chemical oxygen demand (COD). Phosphating wastewater will lead to a serious damage when discharged directly into the environment [4,5]. For example, the addition of phosphorus compounds into surface water systems will promote the rapid growth of algae (eutrophication) [6,7]. Hence, effective treatment for the removal of zinc (Zn), total phosphorus (TP), and COD from phosphating wastewater is necessary to meet the discharge limit and control environmental pollution.

Many treatment methods, such as flocculation, chemical precipitation, adsorption, membrane separation, ion-exchange, and electrocoagulation, have been employed to remove Zn, TP, and/or COD from phosphatizing wastewater [3,8,9]. All these technologies have some drawbacks. For example, the elimination of pollutants is incomplete and/or they are not cost-effective [10,11]. Among these technologies, flocculation and chemical precipitation are the commonly adopted methods because of their economy and convenience [12–14]. However, given that the water quality of phosphating wastewater is highly complex, using a single method for treatment and for the accomplishment of drainage requirements is difficult. Furthermore, flocculation using ferric chloride, aluminum ferric sulfate, or lime will result in large quantities of secondary waste such as hydroxyapatite [15–17]. Thus, many scholars have suggested treatment of phosphating wastewater using combined method.

RSM offers the best test in optimizing and verifying the scientific researches and industrial studies [18]. It uses the multivariate quadratic regression equation to fit the relationship between index and influencing factors through regression equation analysis; this method aims to find the most excellent process parameters and has the ability to provide maximum information with minimum experience [19,20]. The Box–Behnken design (BBD), a kind of RSM design, is the most frequently used design in pioneering studies because of its scientificity compared with other designs in RSM [21,22].

Despite the existence of many studies on the treatment of phosphating wastewater, combined methods remain rare. The optimization of phosphating wastewater by BBD is not well-reported in literature [1,3,23]. In this study, the effect of the combination process of chemical precipitation and flocculation on the removal of Zn, TP, and COD from phosphating wastewater was investigated. First, preliminary studies, namely, single-factor experiment, were conducted to limit the extreme values of the variables. The effects of parameters including pH, precipitation reagent ($CaCl_2$ dosage), and flocculant (CPAM dosage) on the removal efficiencies of contaminants were analyzed and explained to obtain better levels of each factor. Then, RSM experiment with the fixed factor levels was conducted to optimize combined process and further improve COD removal efficiency. Finally, the ingredients of CPAM flocs were observed and analyzed through a microscope.

2. Materials and methods

2.1. Test materials

The phosphating wastewater samples were obtained from Pushi Co., Ltd (China, Yibin). They were collected from a specific storage pool containing phosphating wastewater without adding any chemical reagent. The samples were immediately transported to the laboratory within 30 min after sampling and subsequently stored at 4℃ in the refrigerator. The measured initial characteristics of the phosphating wastewater were shown in Table 1.

Cationic polyacrylamide (CPAM) with intrinsic viscosity of 2.0 dL g^{-1} and cationic degree of 40% was synthesized in the laboratory; of which the detailed synthetic process and characterization have been reported [24,25]. Other chemicals, such as calcium chloride (AR), sodium hydroxide (NaOH), hydrochloricacid (HCl), and ammonium molybdate (AR), were also used during the experiment. All aqueous solutions and standard solutions were prepared with distilled water.

2.2. Treatment method

The method for the treatment of phosphating wastewater was carried out by adjusting pHI, adding calcium chloride for precipitation, adding CPAM for flocculation, and adjusting pHII for optimizing flocculation. All tests were conducted in beakers in the laboratory at room temperature. Each result was an average of three repeated tests under similar experimental condition. All test studies can be divided into two parts, namely, single-factor experiment and RSM experiment.

Table 1
Initial characteristics of phosphating wastewater

Pollutant	Unit	Value
Turbidity	(NTU)	46.5
Chemical oxygen demand (COD)	(mg L^{-1})	181.6
Zn	(mg L^{-1})	47.8
Total phosphorus (TP)	(mg L^{-1})	67.1
Total suspended solids (TSS)	(mg L^{-1})	76.3
pH		3.3

2.2.1. Single-factor experiment

The procedures of single-factor experiment involve the following steps: adjusting phosphating wastewater to different pH (pHI) for precipitation, adding different dosages of $CaCl_2$ into the wastewater treated by the optimum pHI, adding different dosages of homemade CPAM into the wastewater treated by the optimum $CaCl_2$ dosage, and adjusting the phosphating wastewater treated by the optimum CPAM dosage to different pH (pHII). The procedure also involves measuring the concentrations of Zn, TP, and COD in the supernatant of wastewater after completing each step, researching the influence of pHI, $CaCl_2$ dosage, CPAM dosage, and pHII on the treatment result and the fixed optimum parameter values for each factor.

2.2.2. RSM experiment

The factors of pHI, $CaCl_2$ dosage, CPAM dosage, and pHII had a significant influence on the efficiency of contaminants removals from phosphating wastewater according to the results of the single-factor experiment. Accordingly, the relationship between every two factors was investigated to find the optimal combination of these variables for the maximal COD removal efficiency by employing RSM. The BBD is widely employed in statistical modeling to obtain response surface models that set the mathematical relationships between response and variables [23,26]. Based on the BBD, the four factors of pHI value, adding $CaCl_2$ dosage, adding CPAM dosage, and pHII value with three levels, namely, high (+1), low (−1), and central points (basic level 0), were set up using the Design-Expert 8.0.5 software. Table 2 shows the experimental level and values of independent variables.

The quadratic equation model (Y) in terms of linear, quadratic, and cross terms was constructed according to Eq. (1) [27]:

$$Y = a_0 + \sum_{i=1}^{f} a_i X_i + \sum_{i=1}^{f} a_{ii} X_i^2 + \sum_{i}^{i<j}\sum_{j} a_{ij} X_i X_j + \varepsilon \qquad (1)$$

Table 2
Experimental levels and values of independent variables

		Level and value		
Factors code	Factors	−1	0	1
A	pHI	8.0	9.0	10.0
B	$CaCl_2$ dosage (g L^{-1})	20.0	25.0	30.0
C	CPAM dosage (mg L^{-1})	15.0	20.0	25.0
D	pHII	7.0	8.0	9.0

where Y is the response variable (COD removal efficiency) to be modeled; X_i and X_j are the factors which influence predicted response Y; a_i is the linear coefficient; a_{ii} is the squared coefficient for factor i; a_{ij} is the model coefficient for the interaction effect between factors i and j; f is the number of factors investigated in the experiment; and ε is the random error.

According to the response results of the model, analysis of variance (ANOVA) was applied to establish the feasibility of the quadratic equation model between the variables and the responses [28]. To check for the statistical significance of the quadratic equation model and test variables, F-test and p-values at 95% confidence level were used. The modeling quality of the model was tested based on the coefficient of determination R^2 and adjusted R^2 [19,22]. Additionally, the interaction effect of the factors (AB, AC, AD, BC, BD, and CD) on the response value was analyzed using three-dimensional plots. Finally, the predicted COD removal efficiency and the measured value were compared to investigate the adequacy of the regression equation.

2.3. Analytical methods

The turbidity measurements using a turbidimeter (HACH 2100Q, USA). Zn concentration was measured using a PerkinElmer AAS 1100 spectrophotometer. The determination of TP was conducted using the ammonium molybdate spectrophotometric method. COD concentration was measured by a UV–vis spectrophotometer (DR/5000 UV spectrophotometer, HACH). All reagents used in this study were of analytical grade, except for CPAM. The removal efficiency was calculated using Eq. (2):

$$\text{Removal } (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (2)$$

where C_i and C_f are the initial and final concentrations of Zn, COD, and TP, respectively.

3. Results and discussion

3.1. Single-factor experiment

3.1.1. Effect of pHI

The effect of phosphating wastewater pHI on the removal efficiency of Zn and TP was investigated. Fig. 1 showed that the pHI significantly affected the removal efficiencies of Zn and TP. The residual Zn in supernatant markedly decreased at pHI of 4.0–9.0,

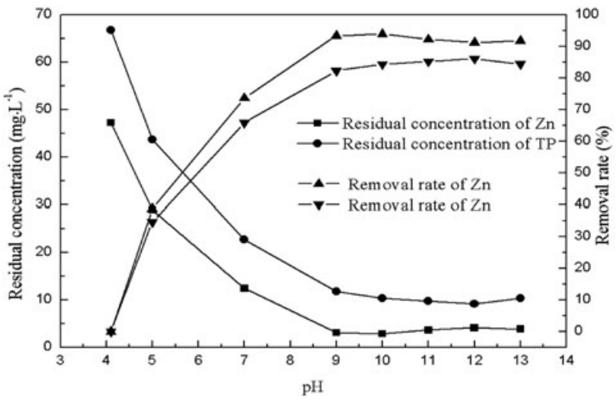

Fig. 1. Effect of pHI on the removals of Zn and TP.

maintained stability at pHI of 9.0–10.0, and increased slightly at pHI of 10.0–13.0. The change rule of Zn removal efficiency was opposite to that of residual Zn concentration. The residual concentration and removal efficiency of Zn reach the minimal value of 2.87 mg L^{-1} and maximum value of 93.9% respectively, at pHI of 9.0–10.0. The residual TP in supernatant sharply decreased at pHI of 4.0–9.0, slowed down at pHI of 9.0–12.0, and increased slightly at pHI of 12.0–13.0. The change rule of TP removal efficiency demonstrated an opposite behavior to that of residual TP concentration. The residual concentration of TP and its removal efficiency reached the minimum value of 10.42 mg L^{-1} and maximum value of 84.4%, respectively, at pHI of 10.0–12.0. By synthetically considering the test results, the optimal pHI was fixed at 10.0.

Changing the pHI of phosphating wastewater could remove Zn and TP from wastewater because the increase of pHI can cause Zn and phosphorus precipitation [29]. A series of reactions occurring during the precipitation can be expressed as follows:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow \quad K_{sp}\ (Zn(OH)_2) = 1.2\times10^{-17} \tag{3}$$

$$3Zn^{2+} + 2PO_4^{2-} \rightarrow Zn_3(PO_4)_2\downarrow \quad K_{sp}\ (Zn_3(PO_4)_2) = 9.1\times10^{-33} \tag{4}$$

According to the chemical reaction, Zn^{2+} and PO_4^{3-} are converted into $Zn(OH)_2$ and $Zn_3(PO_4)_2$ precipitation and removed when hydroxyl ion concentration in phosphating wastewater is gradually increased [30]. The residual Zn and TP increased slightly when the phosphating wastewater is adjusted to a strong alkaline condition because $Zn(OH)_2$ and $Zn_3(PO_4)_2$ are partially converted into soluble ZnO^{2-} and orthophosphate when wastewater is in strong alkaline condition [31].

3.1.2. Effect of $CaCl_2$ dosage

Fig. 2 shows that the $CaCl_2$ dosage significantly affected the removal efficiencies of Zn and TP, especially TP. Increasing $CaCl_2$ dosage initially increased the removal efficiencies of Zn and TP, and then tended to stabilize afterwards. The presence of $CaCl_2$ at a dosage of 25.0 g L^{-1} could enable the residual concentration and removal efficiency of TP to reach the minimum value of 3.23 mg L^{-1} and maximum value of 69.0%, respectively. The good removal efficiency was attributed to the reaction of phosphate and $CaCl_2$ (see Eq. (5)) which produced a variety of calcium phosphate precipitation, such as $CaHPO_4{\cdot}2H_2O$, $Ca_4H(PO_4)_3{\cdot}2.5H_2O$, $Ca_3(PO_4)_2$, $Ca_5(PO_4)_3OH$, and $Ca_{10}(OH)_2(PO_4)_6$. Among these compounds, $Ca_{10}(OH)_2(PO_4)_6$ is the most stable.

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(OH)_2(PO_4)_6\downarrow \tag{5}$$

The presence of $CaCl_2$ at dosage of 20 g L^{-1} could enable the residual concentration and removal efficiency of Zn to reach 1.76 mg L^{-1} and 38.7%, respectively, and then stabilized afterward. One possible explanation for this phenomenon was that a certain amount of Zn was adopted on calcium phosphate settling [32]. The optimal $CaCl_2$ dosage was fixed at 25.0 g L^{-1} to achieve the best treating effect.

3.1.3. Effect of CPAM dosage

The experiment was conducted to further improve the removal efficiencies of zinc, TP, and COD. The CPAM used in the test is an organic polymer

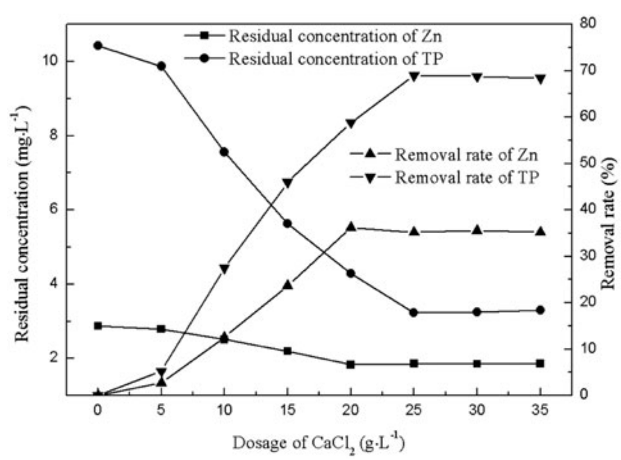

Fig. 2. Effect of $CaCl_2$ dosage on the removals of pollutants.

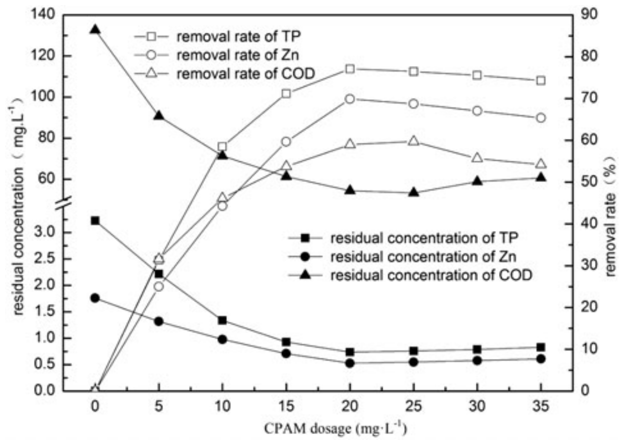

Fig. 3. Effect of CPAM dosage on the removals of pollutants.

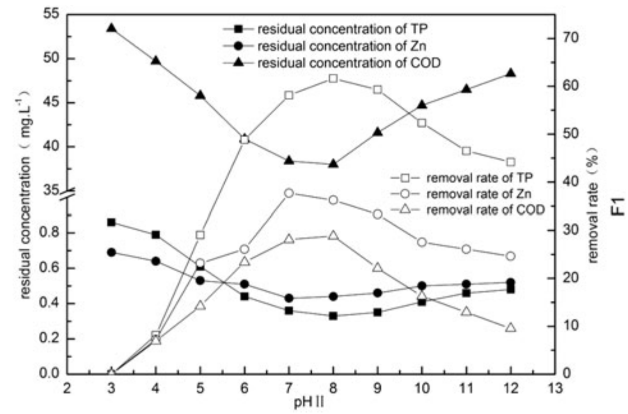

Fig. 4. Effect of pHII on the flocculant performance of CPAM.

Table 3
The Box–Behnken response surface design and corresponding response values

Run	$CaCl_2$ dosage (mg L^{-1})	pHI	CPAM dosage (mg L^{-1})	pHII	Residual concentration of COD (mg L^{-1})		Removal rate of COD (%)	
					Actual value	Predicted value	Actual value	Predicted value
1	0	0	0	0	44.3	44.3	75.6	75.6
2	1	0	0	1	42.9	43.2	76.4	76.2
3	0	1	−1	0	52.3	53.6	71.2	70.5
4	0	−1	0	−1	52.1	53.6	71.3	70.5
5	−1	0	0	1	51.2	49.8	71.8	72.6
6	0	−1	0	1	48.3	49.8	73.4	72.6
7	1	−1	0	0	47.2	46.3	74	74.5
8	0	0	−1	−1	66.6	66.5	63.3	63.4
9	0	0	0	0	44.3	44.3	75.6	75.6
10	0	0	0	0	44.3	44.3	75.6	75.6
11	0	1	0	1	46.7	45.0	74.3	75.2
12	0	0	0	0	44.3	44.3	75.6	75.6
13	0	1	0	−1	49.6	47.9	72.7	73.6
14	0	1	1	0	34.0	35.6	81.3	80.4
15	0	0	1	1	44.5	44.7	75.5	75.4
16	0	0	−1	1	51.8	55.9	71.5	69.2
17	1	0	1	0	33.1	33.1	81.8	81.8
18	0	−1	−1	0	60.5	59.2	66.7	67.4
19	−1	0	0	−1	51.2	51.2	71.8	71.8
20	1	0	0	−1	46.9	48.7	74.2	73.2
21	−1	−1	0	0	47.9	48.3	73.6	73.4
22	1	0	−1	0	55.8	54.8	69.3	69.8
23	−1	1	0	0	44.7	45.6	75.4	74.9
24	−1	0	1	0	40.3	40.9	77.8	77.5
25	1	1	0	0	39.2	38.7	78.4	78.7
26	−1	0	−1	0	56.3	56.1	69	69.1
27	0	−1	1	0	41.2	40.3	77.3	77.8
28	0	0	0	0	44.3	44.3	75.6	75.6
29	0	0	1	−1	39.6	38.1	78.2	79.0

Table 4
ANOVA results for response parameters

Source	Sum of squares	Df	Mean squares	F value	p-value Prob. > F	Remark
Model	393.55	14	28.11	7.38	0.0003	Significant
A-$CaCl_2$	17.04	1	17.04	4.47	0.0529	
B-pHI	29.14	1	29.14	7.65	0.0152	
C-CPAM	247.52	1	247.52	64.97	<0.0001	
D-pHII	9.19	1	9.19	2.41	0.1428	
AB	2.25	1	2.25	0.59	0.455	
AC	3.42	1	3.42	0.90	0.3593	
AD	1.21	1	1.21	0.32	0.582	
BC	11.9	1	11.9	3.12	0.0989	
BD	0.04	1	0.04	0.01	0.9198	
CD	29.7	1	29.7	7.80	0.0144	
A^2	0.3	1	0.30	0.08	0.7815	
B^2	0.35	1	0.35	0.093	0.7653	
C^2	3.1	1	3.10	0.81	0.3821	
D^2	37.88	1	37.88	9.94	0.007	
Residual	53.34	14	3.81			
Lack of fit	53.34	10	5.33			
Pure error	0	4	0			
Cor total	447.33	28				
R^2	0.9801					
R^2_{adj}	0.9602					

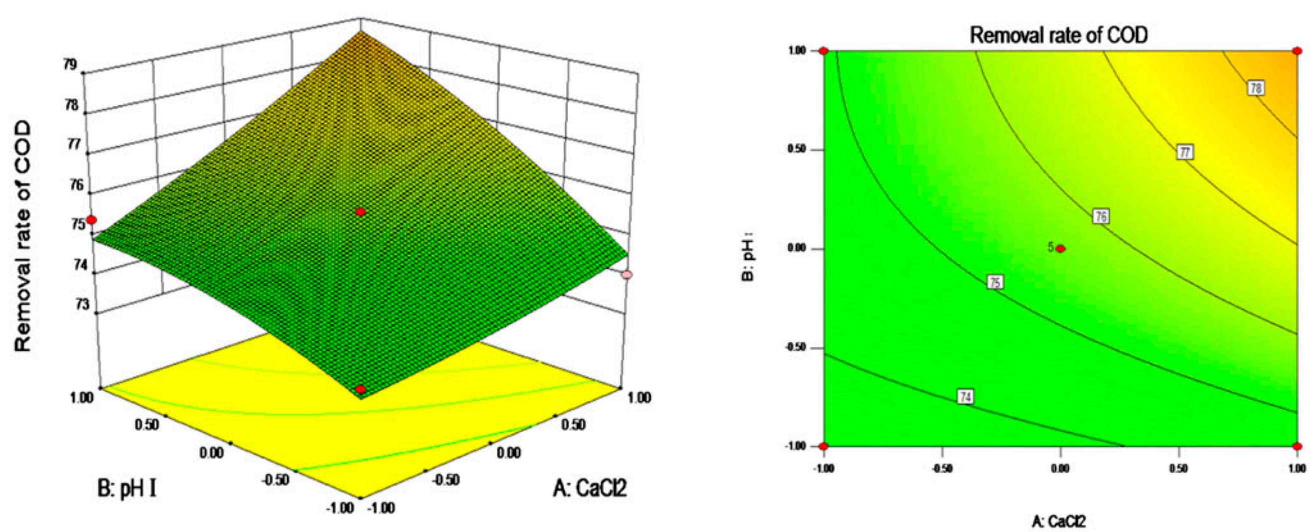

Fig. 5. 3D surface plots and 2D contour plots of COD removal efficiency for $CaCl_2$ dosage vs. pHI.

flocculant, which can prompt suspended particles in phosphating wastewater to destabilize, gather, and facilitate flocculant precipitation by bridging adsorption and electric neutralization [33,34]; this process can also net PO_4^{3-}, Zn^{2-}, and COD in phosphating wastewater with the active groups in its own molecules, thereby improving the removal efficiencies of Zn, TP, and COD [35,36].

As shown in Fig. 3, increasing the CPAM dosage initially decreased and then slightly affected the residual concentrations of Zn, TP, and COD. The presence of CPAM at dosage of 15.0–35.0 mg L^{-1} resulted in high removal efficiencies of Zn, TP, and COD. Their maximum removal efficiencies were 69.9, 77.1, and 59.7%, respectively, whereas their minimum residual concentrations were 0.53, 0.74, 53.4 mg L^{-1}, respectively. When CPAM dosage was increased continuously, the removal efficiencies of Zn, TP, and COD all decreased in different degrees; the main reason for the decrease was attributed to flocculant overdose, gradual increase of flocculant also increased the positive charge of the colloidal system; electrostatic repulsion causes floc to recover stability [25,37]. Given that the flocculant costs should be kept as low as possible, the optimal CPAM dosage was fixed at 20.0 mg L^{-1}.

3.1.4. Effect of pHII

To determine the pHII that is most beneficial to CPAM flocculation, the experiment on pHII influence on flocculant performance was conducted. Fig. 4 showed that the pHII significantly affected flocculation performance. Increasing the pHII initially decreased the residual concentrations of Zn, TP, and COD in wastewater before increasing them. When the pHII was of 8, the residual concentrations of Zn, TP, and COD reached the minimum, namely, 0.44, 0.33, 38.0 mg L^{-1}, respectively. The variations of the removal efficiencies of Zn, TP, and COD demonstrated opposite results to their residual concentrations. The maximum removal efficiencies of Zn, TP, and COD were 55.6, 76.6, and 44.7%, respectively. These results are attributed to the fact that H^+ enhances the positive charges of the colloidal surface at low pH, which

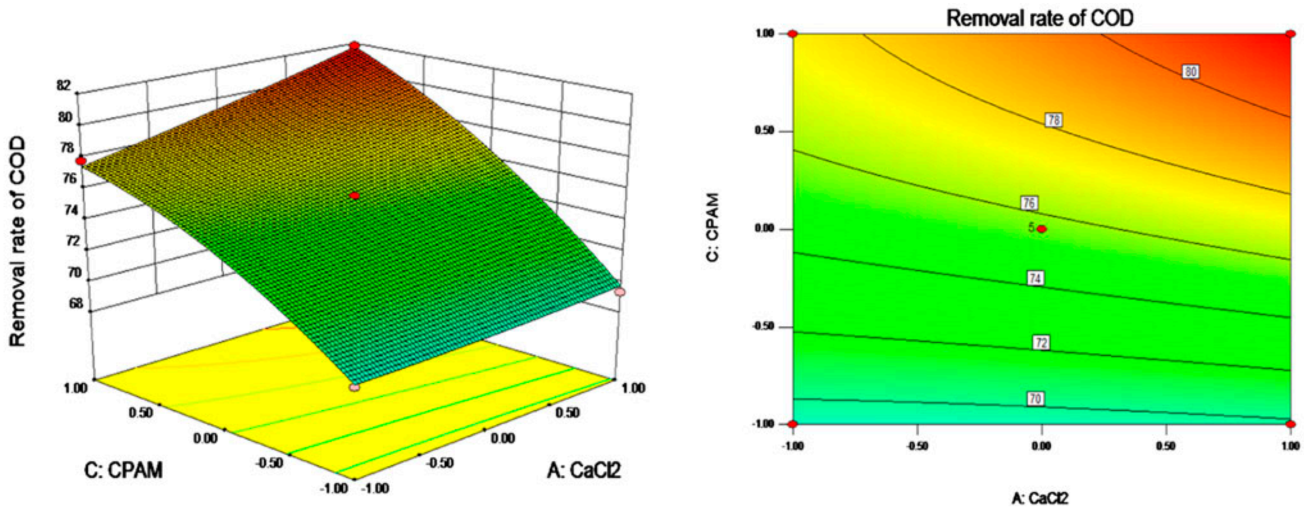

Fig. 6. 3D surface plots and 2D contour plots of COD removal efficiency for $CaCl_2$ dosage vs. CPAM dosage.

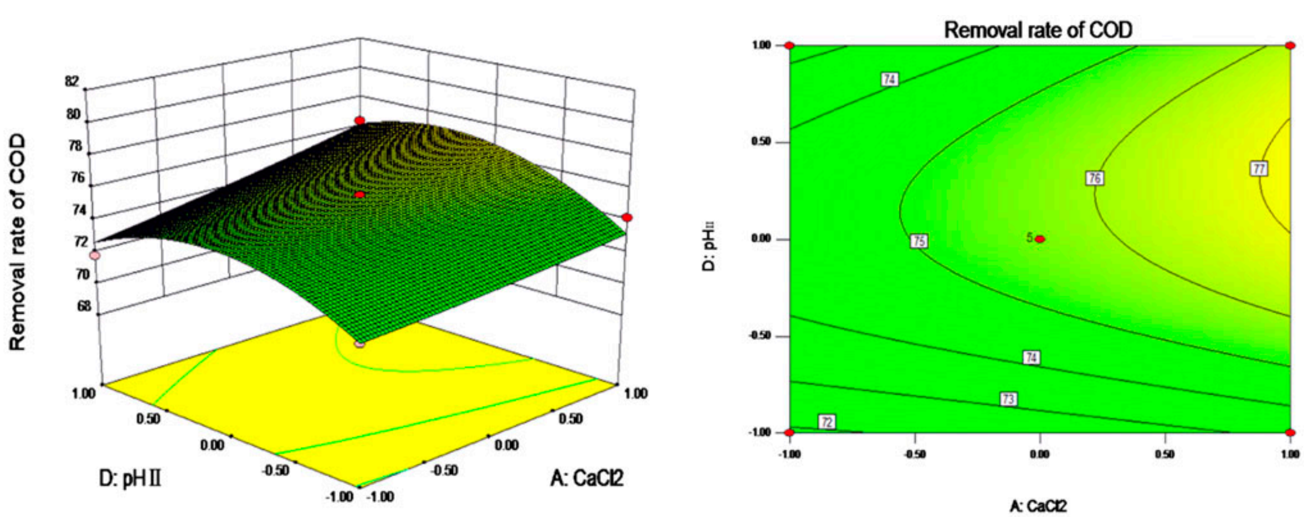

Fig. 7. 3D surface plots and 2D contour plots of COD removal efficiency for $CaCl_2$ dosage vs. pHII.

results in an increased electrostatic repulsion and colloidal stability [38,39]. The negative charges of solution increased at higher pH; these charges could not be fully neutralized by CPAM at a fixed dosage, thereby reducing the electricity neutralization of CPAM [24,40,41]. Moreover, strong acid and alkaline conditions caused a certain amount of CPAM to hydrolyze, which reduced the concentration and deteriorated the performance of CPAM [42,43]. The optimal pHII was thus fixed at 8.0.

3.2. RSM experiment

3.2.1. Model fitting

The responses (COD removal efficiency) of the combined process were correlated with four factors of pHI, $CaCl_2$ dosage, CPAM dosage, and pHII by using the second-order polynomial model according to Eq. (1). From the experimental data (Table 3), the following quadratic regression models were generated for COD removal efficiency:

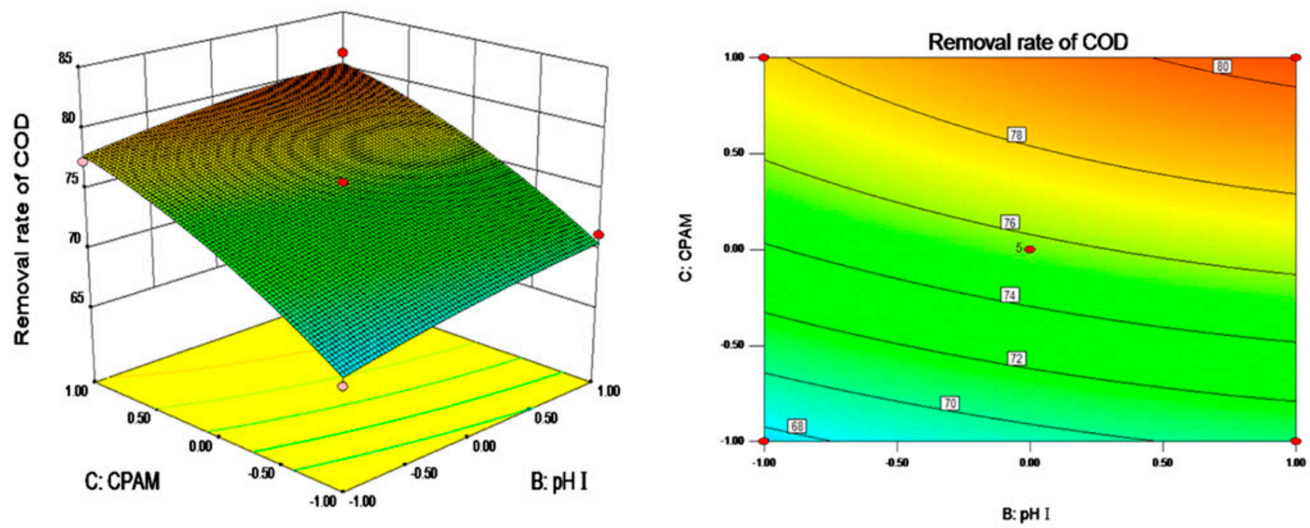

Fig. 8. 3D surface plots and 2D contour plots of COD removal efficiency for CPAM dosage vs. pHI.

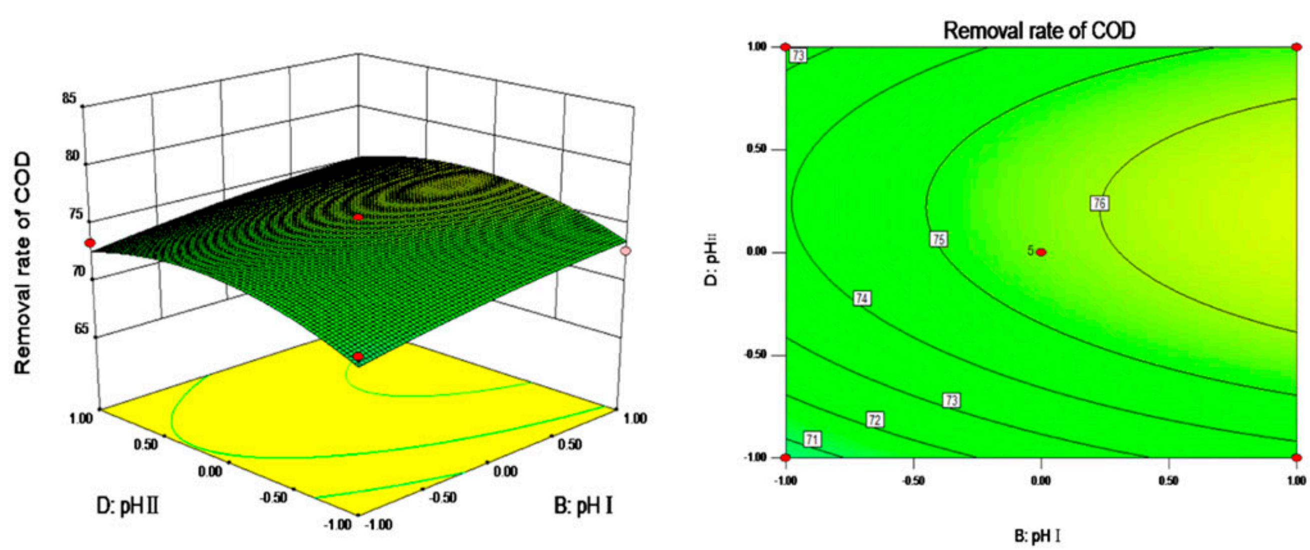

Fig. 9. 3D surface plots and 2D contour plots of COD removal efficiency for pHI vs. pHII.

$$R1 = 75.60 + 1.22A + 1.42B + 5.07C + 0.95D + 0.65AB + 0.93AC + 0.55AD - 0.13BC - 0.13BD - 2.73CD + 0.13A^2 - 0.36B^2 - 1.20C^2 - 2.26D^2 \quad (6)$$

Eq. (5) shows the quadratic regression model for COD removal efficiency from phosphating wastewater using the combined process.

The responses were analyzed by employing ANOVA to estimate the goodness of fit. The results were presented in Table 4. It showed that the p-value of CPAM dosage was less than 0.0001, which implied that CPAM dosage was the most significant influence factor. The significant order of factors effect on the treatment result is CPAM dosage > pHI > $CaCl_2$ dosage > pHII. Table 4 also shows lack of fit is non-significant, and the R^2 value of 97.65%, which indicate that the second-order polynomial model fits the experimental results well and can be employed to predict and conduct optimization analysis on the test condition of treating phosphating wastewater.

3.2.2. Response surface analysis of COD removal efficiency

According to data shown in Tables 1 and 2, three-dimensional (3D) response surface plots and two-dimensional (2D) contour plots for COD removal efficiency which provided the interaction effect between every two variables were drawn and shown in Figs. 5–10. If the response surface slope is relatively flat, the factors have little effect on COD removal efficiency; conversely, if the response surface slope is steep, the factors have a significant influence on COD removal efficiency [44]. Figs. 5–10 show that the interactions between CPAM dosage and pHII, pHI, and pHII are relatively significant. The significant order is CPAM dosage > pHI > $CaCl_2$ dosage > pHII. To obtain the optimal process parameters for COD removal, Eq. (3) was taked the first-order partial derivative and solved through making it equal zero [45]. The calculating results indicated that the optimal conditions were as follows: pHI of 9.51, $CaCl_2$ dosage of 29.03 mg L^{-1}, CPAM dosage of 25.22 mg L^{-1}, and pHII of 7.52. Under the optimal conditions, the predicted value of COD removal efficiency is 82.9%.

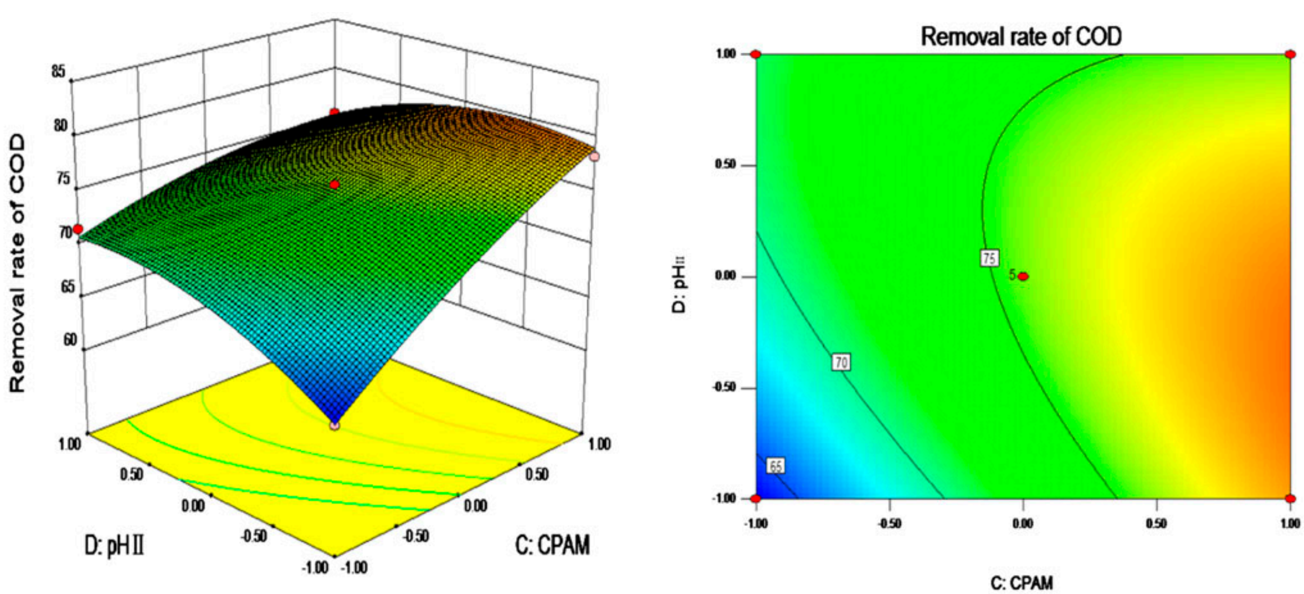

Fig. 10. 3D surface plots and 2D contour plots of COD removal efficiency for CPAM dosage vs. pHII.

Table 5
Measured and predicted values of COD removal efficiency for the confirmation experiments

Conditions				Removal efficiency of COD (%)	
pHI	$CaCl_2$ dosage (mg L^{-1})	CPAM dosage (mg L^{-1})	pHII	Measured values	Predicted value
9.5	29.0	25.2	7.5	82.1	82.9

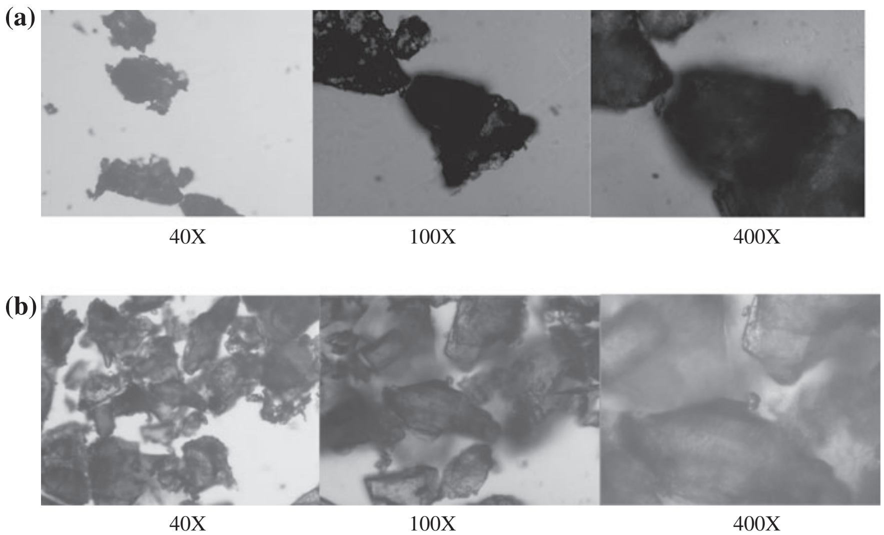

Fig. 11. Microscopic images of CPAM flocs: (a) Microscopic images of wet flocs and (b) Microscopic images of baked flocs.

3.2.3. Model validation

Model validation is essential for RSM. Therefore, three runs of additional experiments were conducted to confirm the validity of the model. According to the practical situation, the optimal conditions were modified as follows: pHI of 9.5, $CaCl_2$ dosage of 29.0 mg L^{-1}, CPAM dosage of 25.2 mg L^{-1}, and pHII of 7.5. The confirmation experimental results were shown in Table 5.

As shown in Table 5, the average of measured COD removal efficiencies is 82.1%. The error between measured COD removal efficiency and the predicted value is only 0.8%. The measured value of confirmation experiments is very close to the predicted values of the regression models. Thus, the RSM approach was successfully applied for modeling and optimizing the treatment process in COD removal [46].

3.3. Microphotograph analysis of flocs

Biological microscope instrument was employed to observe and analyze the structure and morphology of flocs, which were obtained from CPAM treatment of phosphating wastewater. The microscopic images of (a) wet flocs and (b) baked flocs are shown in Fig. 11. As shown in Fig. 11, the wet floc is loose and composed of crystals located at the center of the flocs. A small amount of velvet floc is observed, which adheres to the surface of the crystals. The baked floc is mainly composed of close-grained crystals. According to the composition of phosphating wastewater and the reaction during the treatment process, the main ingredients of floc should be chemical sediment of $Zn(OH)_2$ and $Ca_3(PO_4)_2$ [15].

4. Conclusions

In this study, a combined process of adjusting pH, adding calcium chloride for precipitation and flocculation was used for the removals of Zn, TP, COD from phosphating wastewater. RSM was employed to optimize the factors of pHI, $CaCl_2$ dosage, CPAM dosage, and pHII to maximize the efficiency of COD removal. The following conclusions were obtained from the analysis of the test results:

(1) The result of the single-factor experiment showed that the optimum process conditions for phosphating wastewater treatment is pHI of 10.0, $CaCl_2$ at a dosage of 25.0 g L^{-1}, CPAM at a dosage of 20.0 mg L^{-1}, and pHII of 8.0. Under the optimal process conditions, the residual concentrations of Zn, TP, COD in phosphating wastewater were 0.44, 0.33, 38.0 mg L^{-1}, respectively. The total removal efficiencies of Zn, TP, COD reached 99.1, 99.3, and 80.0%, respectively.

(2) The result of the experiment using RSM showed that the significant order of factors that affected COD removal efficiency was as CPAM dosage > pHI > $CaCl_2$ dosage > pHII. The interactions between CPAM dosage and pHII, pHI, and pHII are relatively significant. The

optimization results of the RSM experiment indicated that a COD removal efficiencies of 82.1% could be achieved under pHI of 9.5, $CaCl_2$ dosage of 29.0 mg L^{-1}, CPAM dosage of 25.2 mg L^{-1}, and pHII of 7.5. The microphotograph of CPAM flocs showed that the main ingredients of floc should be chemical sediments of $Zn(OH)_2$ and $Ca_3(PO_4)_2$.

Acknowledgments

The authors are grateful for the financial support provided by the National Science Foundation of China (Project no. 21477010; 21401163), Application of membrane separation technology on Zhacai wastewater treatment (Project no. 2009KFJ002), Soil biological technology application research on ecological restoration of Xiangjiaba Reservoir area (Project no. 09ZA152), Fundamental research funds for the central universities (Project no. 106112014CDJZR210004).

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