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Research Article

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Preparation of polymeric phosphate aluminum-ferric chloride (PPAFC) and response surface methodology approach to optimize coagulation-flocculation process

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ABSTRACT

A composite flocculant, polymeric phosphate-aluminum ferric chloride (PPAFC), in this study was synthesized through hydrolytic polymerization of PAC, $FeCl_3.6H_2O$ and Na_2HPO_4, which was used to coagulate humic acid. Scanning Electron Microscope (SEM) was employed to characterize the PPAFC. Humic acid being an important component of the aquatic environment has posed a potential threat to human health thus receiving wide attention. Therefore, the purpose of this study was also focused on removing humic acid from water by the coagulation-flocculation process, especially with the PPAFC. Since the flocculation performance was often determined both by the added flocculants and the operational parameters such as rapidly mixing time, rapidly mixing speed and pH, the response surface methodology (RSM) with humic acid removal efficiency as response value, was herein used to analyze the mutual effects of these parameters so that a better flocculation efficiency could be obtained under an optimum conditions. As a result, the RSM model was significant and for flocculation at a rapidly mixing time, pH and rapidly mixing speed of 2 min, 7.07 and 350 rpm, respectively, the humic acid removal efficiency was 94.28%.

Key words: Flocculant, polymeric phosphate-aluminum ferric chloride, humic acid, response surface methodology

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INTRODUCTION

Humic acid is the major component of humic substances which is a mixture of many molecules, dominating 50-90% of organic matters in the aquatic environment [1-2]. According to their solubility, the humic acid can be divided into three fractions being humic acid, fulvic acid and humin. The humic acid is difficult to dissolve at pH lower than 2, which is largely affected by pH [3-4]. In contrary, the fulvic acid is easy to dissolve since the solubility of which is not largely dependent on pH. However, the humin is extensively insoluble without influence by pH. In native water resource system, the concentration of humic acid is only between 1 and 12 mg/L, but it is possible to result in higher level hazardous materials such the disinfection byproducts (DBPs) by reacting with the chlorine. Some of the DBPs such as the trihalomethanes (THMs) and haloacetic acids (HAAs), have posed an adverse effect on human health [5]. Therefore, reducing humic acid will be contributive to the control of the formation of DBPs. There are many methods for removing humic acid, such as adsorption, membrane separation, advanced oxidation and coagulation-flocculation process [6-10]. Among these methods, the coagulation-flocculation process is relatively cost-effective technique in reducing the dissolved organic compounds during water treatment [11-12].

The coagulation-flocculation is a process of removing the colloids, which is often assessed by measuring the turbidity removal from water as well as others such as the organic compounds, chemical oxygen demand (COD) and heavy metals. In the process, the chemicals that are called flocculants played a key function in destabilizing the colloids thus forming the flocs through some known mechanisms such as neutralization and adsorption-bridging. At present, many flocculants containing organic coagulant, inorganic coagulant and biological coagulant have been widely used. The high molecular flocculant, PPAFC, has a better combined effect of the iron and aluminium-based flocculants on improving flocculation performance [13-14], which can be used with less dosage in broader range of pH without significant influence by the salts. Therefore, the PPAFC would be one of the best solutions to remove the humic acid from aquatic environment [15].

The present work aimed to synthesize the PPAFC through the solution polymerization of PAC, $FeCl_3.6H_2O$ and Na_2HPO_4 and to study the humic acid removal by PPAFC. The PPFC was prepared and characterized by the FTIR and SEM techniques, respectively. In order to obtain better flocculation performance, the response surface methodology (RSM) was used to optimize the flocculation conditions in which the Box-Behnken model was used to design the flocculation experiment with the humic acid removal efficiency as the response values. Some parameters affecting the flocculation performance, such as the independent variables, rapidly mixing time, pH and rapidly mixing speed, were investigated.

EXPERIMENTAL SECTION

2.1 Material and instruments

The commercial humic acid used in this study was purchased from Sinopharm Chemical Reagent Co., Ltd. The other analytical grade materials such as disodium hydrogen phosphate (Na_2HPO_4), hydrochloric acid (HCl), sodiumhydroxide (NaOH) and hexahydrated ferric chloride($FeCl_3.6H_2O$) were used in this study. In addition, the conmercial flocculant, Polyaluminum Chloride (PAC), was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. The instruments used in this study were as follows:

- The scanning electron microscope (SEM) (JSM-6380LV, JEOL Company, Japan)
- Jar Tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd. China)
- UV-Vis spectrophotometer (TU-1910, Beijing Purkinje General Instrument Co., Ltd, China)

2.2 Preparation of PPAFC

The reaction of the PPAFC preparation occurred in a 250 mL beaker, which was put in a thermostatic water bath. With deionized water as a solvent, PAC and $FeCl_3.6H_2O$ were mixed by slowly stirring at 50 ˚C for 20 min until a thin uniform paste was obtained. Then, Na_2HPO_4 was added as a stabilizing agent in order to increase the degree of polymerization with a slowly stirring for 10 min, followed by addition of 1 mol /L NaOH solution to adjust the alkalify degree and by a slowly stirring for 1 h at temperature of 50 ˚C. Finally, a thick liquid flocculant PPAFC in reddish-brown color was produced. This flocculant could be used after at least 24 h at room temperature.

2.3 Characteristics of PPAFC

The morphology of the PPAFC was observed through the SEM. The electron samples were prepared by shattering and planishing, and sputtering Au. The electron samples were dried and the SEM images were taken through scanning electronic microscope.

2.4 Humic acid solution preparation

1 g/L humic acid solution was prepared by dissolving 1.0 g humic acid in 1000 mL volumetric flask in which 1.0 mol/L NaOH solution was used to adjust the solubility of humic acid. The soluton was strored in dark at 4 ^{o}C for later use.

2.5 Flocculation test

Flocculation test was performed using a program controlled jar test apparatus. 500 mL of wastewater was transferred into a beaker. Flocculants were dosed at medium stirring speed of 350 rpm for 2 min and slow speed of 40 rpm for 10 min. After a quiescent settling of 25 min, the samples were collected from 2 cm below the surface for the measurement of ultraviolet absorbance at 254 nm (UV254). The absorbance values were transferred into the concentration. The removal efficiency of humic acid were as the percentage rate was calculated.

2.6 RSM model

RSM in this study was used to explore the relationships between several explanatory variables and the humic acid removal efficiency as the response variable. The RSM model was established with a 3-factors Box–Behnken design. The explanatory variables included rapidly mixing time, pH value and rapidly mixing speed. Three significant levels of each of the variables were selected. Among which, the upper level corresponded to +1, the lower level to -1 and the basic level to zero. The Box–Behnken design was performed using a scientific software (MINITAB 16). The 3-factors Box-behnken design and the experimental results were shown in Table 1 and Table 2.

Table 1. Ranges and levels of the explanatory variables

Variables	Ranges and levels		
	-1	0	+1
Rapidly mixing time (X_1) (s)	60	90	120
pH (X_2)	6	7	8
Rapidly mixing speed (X_3) (rpm)	250	300	350

Table 2. The experimental results of 3-factors Box-behnken design

No.	Coded variables			Uncoded variables			Humic acid removal efficiency(%) (Y)	
	X_1	X_2	X_3	X_1	X_2	X_3	Measured value	Predicted value
1	0	0	0	90	7	300	0.871	0.860
2	1	1	0	120	8	300	0.891	0.897
3	-1	0	-1	60	7	250	0.853	0.850
4	1	0	1	120	7	350	0.952	0.937
5	0	0	1	90	7	350	0.853	0.869
6	1	0	-1	120	7	250	0.890	0.889
7	-1	1	0	60	8	300	0.721	0.722
8	-1	0	1	60	7	350	0.814	0.806
9	-1	-1	0	60	6	300	0.878	0.883
10	0	0	0	90	7	300	0.854	0.862
11	0	0	0	90	7	300	0.879	0.863
12	0	1	1	90	8	350	0.806	0.808
13	0	-1	1	90	6	350	0.892	0.882
14	1	-1	0	120	6	300	0.883	0.880
15	0	-1	-1	90	6	250	0.870	0.868

RESULTS AND DISCUSSION

3.1 SEM characterization

The SEM images of PPAFC was depicted in Figure 1. It can be seen that the surface of PPAFC was a rough and microporous structure, which would increase the more adsorption sites of flocculant thus improving its bridging ability. The crystal structure of PPAFC was indefinite form.

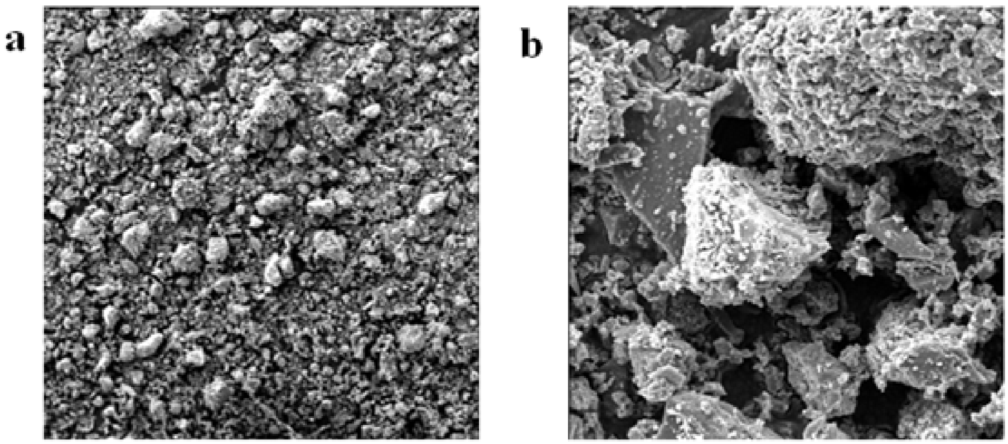


Figure 1. SEM microphotographs: (a) ×50 and (b) ×500

3.2 RSM analysis

According to the experimental results, a quadratic regression model was created using the design expert V8.0.6 software as shown in Eq.:

$$Y=1.24 - 0.0146\ X_1 + 0.174\ X_2 - 0.00184\ X_3 + 0.00140\ X_1X_2 + 0.000016\ X_1X_3 - 0.000079\ X_2X_3 + 0.000009\ X_{12} - 0.0222\ X_{22} + 0.000002\ X_{32}$$

The adequacy of the model was investigated using the analysis of variance (ANOVA) and the results were shown in Table 3. *F*-value of the model was 16.87 and the *P*-value was less than 0.01, indicating that the model was significant.

In addition, the value of the determination coefficient, R^2= 0.9796, indicated that only 3.19% of the total variations could not be explained by the model, suggesting a strong correlation between the predicted and observed values. Furthermore, the result indicated a better precision and reliability of the experiments being carried out. From the above investigation, it showed that the model was adequate for the prediction of humic acid removal efficiency. Therefore, the model was feasible for modeling the humic removal efficiency.

The coefficient and standard error were shown in Table 4. The results showed that X_1, X_1X_2, X_1X_3, X_2^2 were significant variable terms because their P values were all less than 0.05. The degree of their significance was listed here in decrease order: $X_1X_2 > X_1 > X_1X_3 > X_2^2$. This implied that the rapidly mixing time played an important role in flocculating humic acid.

Table 3. Analysis of ANOVA

Source	df	SS	MS	*F*	*P*
Regression	9	0.0351703	0.0039078	16.87	0.003
Residual error	5	0.0011582	0.0002316		
Sum	4	0.0363284			

S = 0.0152195; R^2 = 96.8%; Adj. R^2= 91.1%

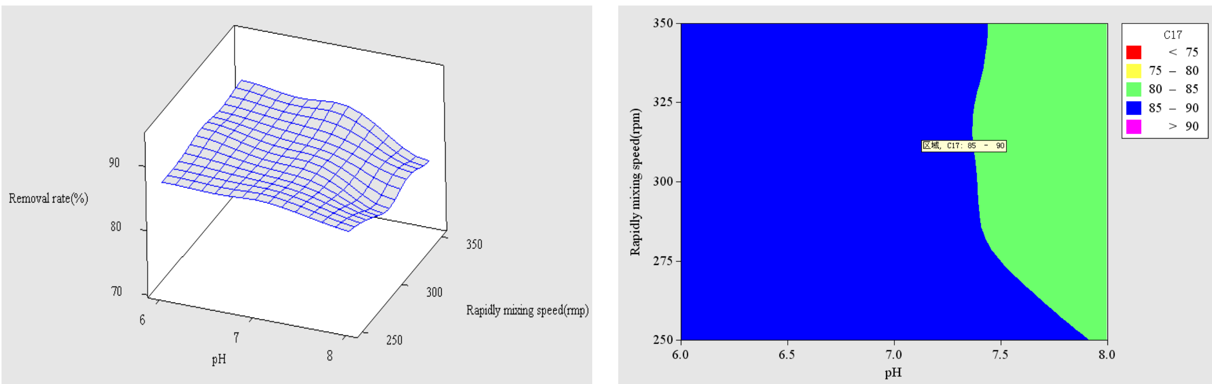
Table 4. The coefficient and standard error

Variables	Coefficient	Standard Error	*T*	*P*
Constant	1.2355	0.6324	0.95	0.108
X_1	-0.014646	0.002907	-5.04	0.004
X_2	0.1736	0.1194	1.45	0.206
X_3	-0.001836	0.002211	-0.83	0.444
X_1X_2	0.0014010	0.0002537	5.52	0.003
X_1X_3	0.00001577	0.00000507	3.11	0.027
X_2X_3	-0.0000793	0.0002152	-0.37	0.728
X_1^2	0.00000888	0.00000954	0.93	0.395
X_2^2	-0.022196	0.008584	-2.59	0.049
X_3^2	0.00000169	0.00000347	0.49	0.648

3.3 Flocculation optimization

In order to investigate the mutual effects of the explanatory variables on the humic acid removal efficiency. The MINITAB 16 was used to plot the three-dimension response surfaces and the corresponding contour plots. The response surface plots display the response as a function of two factors by keeping the third factor constant, and two-dimensional response surface contours were plotted to investigate the mutual effect of the operational variables. The results were shown in Figure 2.

Figures 2 (a-b) show the humic acid removal efficiency as a function of rapidly mixing speed and pH value. Figures 2 (c-d) show the humic acid removal efficiency as a function of rapidly mixing speed and rapidly mixing time, and Figures 2 (e-f) show the humic acid removal efficiency as a function of pH value and rapidly mixing time. Figures 2 (a-f) show the mutual effect of rapidly mixing time, pH value and fast mixing speed on the humic acid removal efficiency. It has been found that if a response surface slope was relatively smooth, it meaned that this factor in a certain range of humic acid removal efficiency was less affected. In contrary, if a response surface slope was very steep, it meaned that the mutual factors effects on the removal efficiency were sensitive. It indicated that the increase in rapidly mixing time and rapidly mixing speed led to an increase in the level of the humic acid removal efficiency, especially under the condition that larger rapidly mixing speed and longer rapidly mixing time were used.



（a） （b）

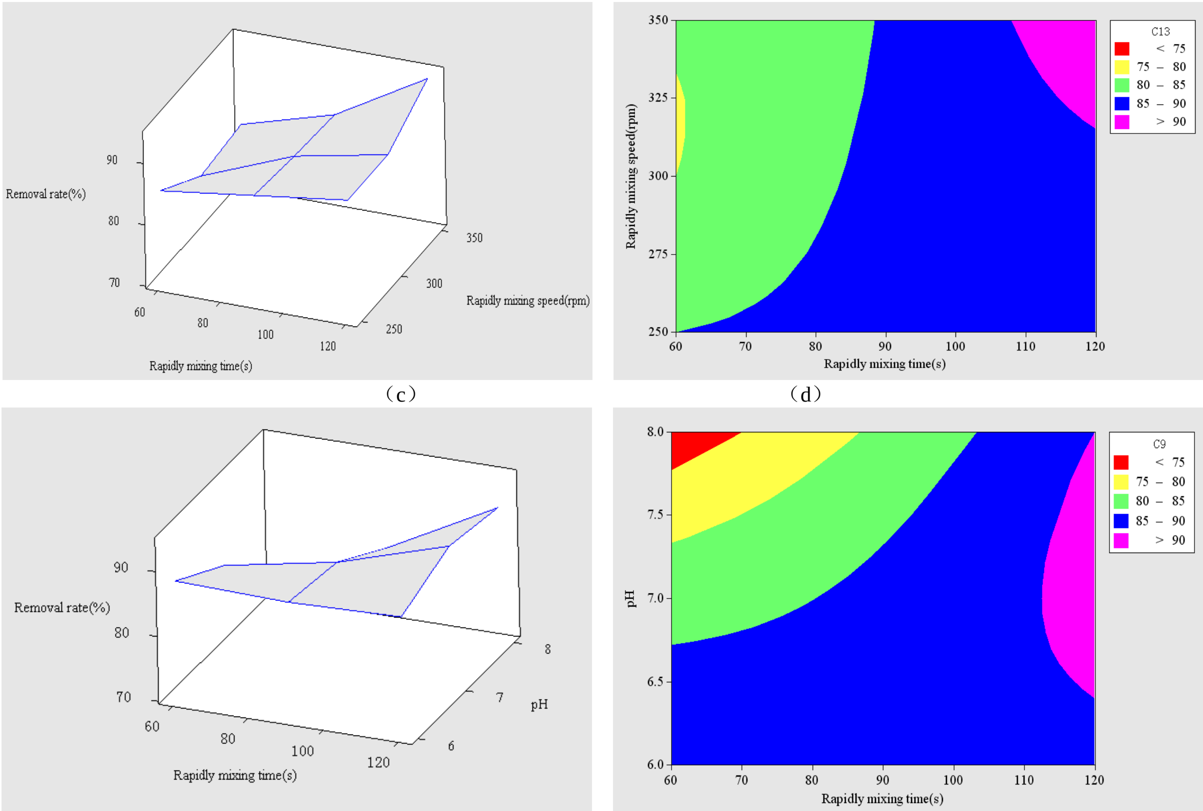


Figure 2. Mutual effect of rapidly mixing time, pH value and rapidly mixing speed on the removal efficiency

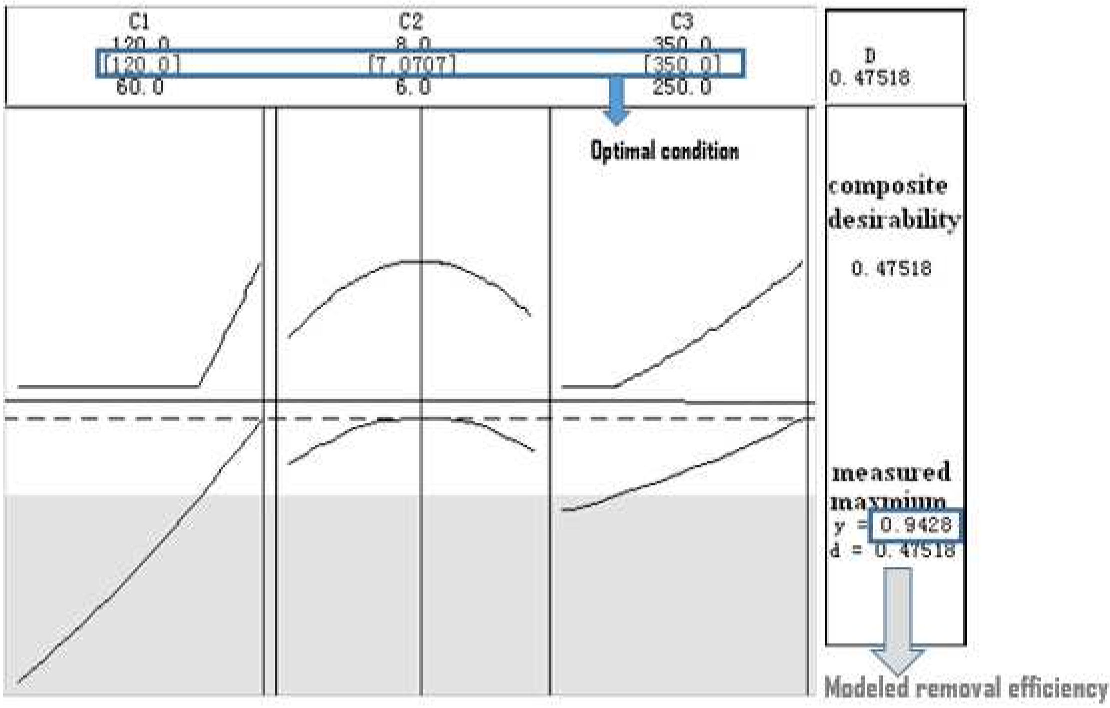


Figure 3. The most advantage of theory calculation

In order to obtain the optimum flocculation conditions, MINITAB 16 optimizer was used in this study. The results were shown in Figure 3. Figure 3 showed an optimum conditions (rapidly mixing time of 2 min, the pH value at 7.07 and rapidly mixing speed at 350 rpm under which the humic acid removal efficiency of 94.28% was achieved. The practical operation result was 95.2%, which was similar to the simulation value. The result showed that the model has a strong maneuverability. Although there was slight difference between the theoretical and the actual values of the rapidly mixing speed when achieving the highest removal efficiency, the rapidly mixing time and pH values were very similar and the similar humic acid removal efficiencies also resulted. The results showed that the model could reflect the optimization removal conditions of humic acid, and that using the response parametric surface method to optimize the experimental conditions for treatment of wastewater was feasible.

CONCLUSION

A composite flocculant, PPAFC, in this study was synthesized through an aqueous solution polymerization with PAC, $FeCl_3.6H_2O$ and Na_2HPO_4. The results indicated that PPAFC had many significant characteristic functional groups. The RSM model used to optimize the flocculation conditions showed that for flocculation at rapidly mixing time of 2 min, pH value of 7.07 and rapidly stirring speed of 350 rpm, the humic acid removal efficiency was up to 94.28%. The measured humic acid removal efficiency under the modeled conditions was 95.2%. Therefore, the predicted humic acid removal efficiency by the RSM model was in agreement with the measured, thus indicating that the RSM model could be as a new method for investigating the PPAFC effect on humic acid removal.

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