Research on high efficiency coagulation process of poly-silicic-ferric by response surface methodology

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Abstract. The Box-Behnken response surface methodology was used to optimize the coagulation and sedimentation processes using poly-silicic-ferric (PSF) as coagulant. The quadratic regression equation with the dosage, flocculation time and precipitation time as the independent variables and the turbidity removal rate as the response value was established to determine the optimal process conditions of the PSF. The response surface results showed that the dosage of the agent, the flocculation time, the precipitation time and the interaction between them all had significant effects on the coagulation properties of the PSF. The optimal turbidity removal rate of PSF was 99.2% when the dosage of the agent, the flocculation time and the precipitation time were 7.2 mg/L, 5 min and 3 min, respectively. In addition, the predicted values were in good agreement with the measured values, and the model had high credibility. This indicated that PSF can coagulate and precipitate the impurity particles in a short time, which can shorten the time of the coagulation and sedimentation processes.

1. Introduction
Coagulation process is a low-cost, significant and widely used treatment method in the water and wastewater treatment processes [1], and its treatment effect has a profound impact on the subsequent processes. With the rapid development of the economy, the coagulation process of traditional water plants has exposed limitations in rural areas and temporary water supply (natural disasters such as earthquakes and floods). However, the equipmentized water treatment facilities have become the trend of future development, which have the characteristics of short construction period and high flexibility [2]. The efficient and short-term coagulation and sedimentation process has become an inevitable requirement for equipmentized water treatment facilities. In recent years, domestic and foreign scholars have carried out more research on high-efficiency coagulation and sedimentation processes. Lijun Zhu et al. found that the sludge settling performance of loading flocculation process was superior to the traditional process [3]. Han Xiao et al. upgraded the plate flocculating tank using micro-vortex, and the performance of flocculation tank improved 15% [4]. The above efficient water treatment methods are optimized from the treatment process and reactor to shorten the reaction time, nevertheless, the research on the optimization of coagulation and sedimentation process based on high-efficiency coagulant has rarely been reported.

PSF is a kind of composite high-efficiency inorganic coagulant, which exhibits excellent properties such as large fractal dimension and easy settlement in the process of coagulation [5]. The response surface methodology is an effective method to analyze the significance of the factors and the interaction, optimize the experimental conditions, and reduce the number of experiments. This paper aims to study the efficient coagulation and sedimentation process of PSF. Based on the response
surface experiment, the treatment effect under the condition of shorter time is explored, and the interaction between the influencing factors is analyzed, and the process conditions of PSF coagulation and sedimentation are optimized.

2. Materials and methods

2.1. Chemicals and materials

Kaolin, humic acid and sodium hydroxide (NaOH) were purchased from Shengkai Co., Ltd., Jinan, China. All chemicals were of analytical grade and used as received without further purification. Polyferric aluminum was obtained from Yuqing Water Plant, Jinan, China, which ferric-aluminum content of 10.26%. Poly-silicic-ferric was homemade (preparation method refers to references [10]).

The experimental water sample was simulated water of kaolin and humic acid. The simulated water which called humic acid simulation water was mixed by 1.0 g/L of humic acid stock solution and kaolin stock solution. The characteristics of humic acid simulation water are as follows: temperature 21.4 ~ 28.2 °C, pH 8.60 ~ 8.92, turbidity 25 ~ 35 NTU, chroma 0.333 ~ 0.438 A, permanganate index 7.67 ~ 9.7 mg/L.

2.2. Experimental procedure

2.2.1. Jar test. First of all, the 1 L humic acid simulation water was placed on a coagulation test mixer (ZR4-6, Zhongrun, Shenzhen, China), and was rapid mixed at 200 r/min for 1 min. It's worth noting that 6 mg/L PSF (measured in Fe) was added at the beginning of the mixing. Then the duration flocculation time was set as 10 min with the stirring speed of 40 r/min. After 10 minutes' standing, the turbidity of water sample which taken from 4 cm below the liquid level was measured by a turbidimeter (2100AN, HACH, Shanghai, China).

2.2.2. Response surface experiment design. The dosage, flocculation time and precipitation time were selected for optimization. The level of each factor in the experiment was determined by single factor experiment: the dosage was 4~8 mg/L, the flocculation time was 3~5 min, and the precipitation time was 2~4 min. The Box-Behnken response surface experimental design with 3 factors and 3 levels is used. The coding of each factor and level is shown in Table 1.

| Independent variable     | Coding | Horizontal coding |
|--------------------------|--------|-------------------|
| Dosage /(mg/L)           | X₁     | -1 0 1            |
| Flocculation time /min   | X₂     | 3 4 5             |
| Precipitation time /min  | X₃     | 2 3 4             |

3. Results and Discussion

3.1. Design and results of response surface experiments

The removal effect of PSF on humic acid simulation water in a short time is explored with the turbidity removal rate as the response value Y. The experimental program and results are shown in Table 2, in which the experimental serial numbers are generated by Design Expert V8.0.6 software.

Modeling and analysis were performed using the Design Expert software for the data in Table 2. The turbidity removal rate was used as the response value Y of the model, and the dosage, flocculation time and precipitation time were used as independent variables to obtain the regression model (1).

\[
Y=0.9+0.13X₁+0.17X₂+0.1X₃-0.089X₁X₂-0.068X₁X₃-0.063X₂X₃-0.065X₁²-0.11X₂²-0.09X₃²
\]  

(1)

X₁,X₂,X₃ are the encoded values.
Table 2. Design and results of response surface experiments.

| Serial number | X1  | X2  | X3  | Y  | Turbidity removal rate (%) |
|---------------|-----|-----|-----|----|----------------------------|
|               |     |     |     |    | Predictive value | Actual value |
| 1             | 0   | -1  | 1   | 70.48 | 69.41 |
| 2             | 0   | 0   | 0   | 90.39 | 91.82 |
| 3             | 0   | 0   | 0   | 90.39 | 90.53 |
| 4             | 0   | 0   | 0   | 90.39 | 89.50 |
| 5             | 1   | -1  | 0   | 78.45 | 79.24 |
| 6             | 0   | -1  | -1  | 37.75 | 36.18 |
| 7             | 0   | 1   | -1  | 83.89 | 84.97 |
| 8             | -1  | -1  | 0   | 34.67 | 36.51 |
| 9             | 0   | 0   | 0   | 90.39 | 89.00 |
| 10            | 1   | 1   | 0   | 94.28 | 92.43 |
| 11            | 0   | 0   | 0   | 90.39 | 91.10 |
| 12            | 0   | 1   | 1   | 91.53 | 93.09 |
| 13            | -1  | 0   | -1  | 45.01 | 44.74 |
| 14            | -1  | 0   | 1   | 78.83 | 78.06 |
| 15            | -1  | 1   | 0   | 86.03 | 85.23 |
| 16            | 1   | 0   | -1  | 84.66 | 85.43 |
| 17            | 1   | 0   | 1   | 91.20 | 91.48 |

Table 3. Analysis of variance and significance of parameters for regression model.

| Source          | sum of squares | df | F value | P value |
|-----------------|----------------|----|---------|---------|
| Model           | 0.61759        | 9  | 219.41  | < 0.0001 a |
| Residual        | 0.00219        | 7  | 0.0001  |         |
| Lack of Fit     | 0.00166        | 3  | 4.19    | 0.1001 c |
| Pure Error      | 0.00053        | 4  | 0.0001  |         |
| Cor Total       | 0.61978        | 16 |         |         |
| X1              | 0.13532        | 1  | 432.67  | < 0.0001 a |
| X2              | 0.22571        | 1  | 721.68  | < 0.0001 a |
| X3              | 0.08145        | 1  | 260.44  | < 0.0001 a |
| X1 X2           | 0.03155        | 1  | 100.89  | < 0.0001 a |
| X1 X3           | 0.01859        | 1  | 59.44   | 0.0001 b |
| X2 X3           | 0.01575        | 1  | 50.35   | 0.0002 b |
| X1 X1           | 0.01785        | 1  | 57.07   | 0.0001 b |
| X2 X2           | 0.04663        | 1  | 149.11  | < 0.0001 a |
| X3 X3           | 0.03375        | 1  | 107.92  | < 0.0001 a |

a extremely significant at P<0.0001.
b significant at 0.0001<P<0.05.
c not significant at P>0.05.

Table 3 describes the variance analysis results of the regression model (1). The P value represents the significance of the regression coefficient, and the smaller the P value is, the more significant the regression coefficient is [6]. It can be seen from Table 3 that the F value of the model is 219.41, and the P value is <0.0001, indicating that the model has significant significance and can well fit with the experimental results; the lack of fit is not significant (P= 0.1001>0.05), indicating that there is no
missing factor, and the experimental results can be analyzed by the regression equation instead of the actual experimental point; the correction decision coefficient $R_{adj}^2 = 0.9916$ reflects that the regression model can account for 99.16% of the response change. The above analyses make clear that the model can be used to analyze and predict the influence of various factors.

As we can see from the model parameters in Table 3 that the dosage, flocculation time and precipitation time have significant effects on the removal rate of turbidity in the first term. The order of influence of each factor on the PSF turbidity rate is: flocculation time $>$ dosage $>$ precipitation time; and in the interaction term, the interaction between dosage, flocculation time and precipitation time all remarkably influenced the removal of turbidity.

3.2. Analysis of Response Surface Interaction

![Response surface of turbidity removal](image)

(a)  
(b)  
(c)

Figure 1. Response surface of turbidity removal.
The three-dimensional surface and contour distribution of the regression model (1) are shown in Figure 1. The medium-high lines of the figure have an elliptical distribution, that is, the interaction between the dosage, flocculation time and precipitation time have significant impacts on the turbidity removal effect using PSF. It's clear from Figure 1(a) that the slope of the surface is large, indicating that the interaction between flocculation time and dosage is more obvious. It can be seen from Figure 1(a) that in the case of fixed flocculation time, the turbidity removal rate increases with the increase of the dosage, while the turbidity removal rate first increases and then stabilizes as flocculation time increases under circumstance of same dosage. This indicates that the turbidity removal of by PSF can achieve better results when adopting a shorter flocculation time at a better dosage (usually the flocculation time of the jar tests is about 10-20 min [1,5,7]). Figure 1(b) and Figure 1(c) illustrate that in the case of fixed dosage or flocculation time, the turbidity removal rate first increases with the increase of the precipitation time, but turbidity removal rate tends to be stable when the precipitation time increases to no less than 3 min. This indicates that most of the flocs sink faster during the PSF coagulation and sedimentation process and it can be precipitated in 3 min, while the precipitation time of the general jar tests is about 10~20 min, as in the literature [5,7]. It is concluded from Figure 1 that PSF with high coagulation performance can achieve better treatment effect in a shorter flocculation time. PSF is formed by copolymerization of polysilicic acid and iron ions, in which iron and silicon inhibit each other during polymerization, so that the polymer is mainly in low and medium state and the activity and the adsorption capacity of low and medium state polymer are stronger [8,9]. This enables PSF to quickly adsorb and aggregate impurity particles in raw water to form flocs in a relatively short time. In a previous study [10], PSF exhibits a fractal structure with a large fractal dimension under transmission electron microscopy, and its particle size is 11 times that of a common coagulant composite aluminum iron, which increases the probability of PSF collision adhesion suspended matter and colloid. The structure makes it possible to adsorb a large amount of suspended solids and colloidal particles to form a larger flocs group in a short time, and the precipitation can be completed in a shorter time. According to the high-efficiency coagulation performance of PSF, the time of the traditional coagulation and sedimentation process can be shortened.

3.3. Parameter optimization and model verification
According to the analysis of variance and interaction analysis, the regression model with turbidity removal rate as the response value can accurately analyzes and predicts the relationship between variables and the turbidity removal rate. The optimization parameters of the coagulation and sedimentation processes of PSF in a short time are obtained by calculating the first and second derivatives of the regression equation Y and considering the turbidity removal effect and the actual operating conditions: the dosage is 7.2 mg/L, the flocculation time is 5.0 min, and the precipitation time is 3.0 min. The theoretical value of the turbidity removal rate under the optimized parameters can reach 99.2%. In order to further verify the credibility of the model, the above optimization parameters are taken for jar tests. The average value of the turbidity removal rate in the three parallel experiments is 96.3%, which is little different from the theoretical prediction value, indicating that it is feasible to optimize the PSF coagulation sedimentation by the response surface methodology.

4. Conclusions
1) The results of Box-Behnken response surface methodology showed that the dosage, flocculation time, precipitation time and their interaction have significant influences on the turbidity removal rate using PSF. In the first term, the flocculation time is the most obvious influence factor. In the interaction term, the interaction between the dosage and the flocculation time has the most significant effect.
2) When the dosage, flocculation and precipitation time are 7.2 mg/L, 5 min and 3 min, respectively, the turbidity removal rate using PSF can reach up to 99.2%. The difference between theoretical value and measured value is small, which indicates that the reliability of the model is high.
The optimal parameters can be obtained by optimizing the PSF coagulation sedimentation process through the response surface methodology.

3) PSF coagulant can shorten the traditional coagulation and sedimentation process time, correspondingly reduce the volume of flocculation and sedimentation equipment, and promote the development of equipmentized water treatment facilities.

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