Optimization of the aluminum based compound flocculant preparation conditions and fluorine removal performance validation by response surface method

Lixiang Zheng¹,* and Xufeng Xu¹

¹Hangzhou Research Institute of China Coal Technology & Engineering Group, Hangzhou 311201, P. R. China

*Corresponding author’s e-mail: zhenglx117@126.com
*Corresponding author’s ORCID: https://orcid.org/0000-0003-0046-2515

Abstract. The aluminum based compound flocculant was prepared with components such as polyaluminum chloride (PAC), calcium oxide (CaO) and polyaluminosilicate ferric oxide (PSAF) by adopting mixed and compound method. On the basis of single factor experiment, the main factors affecting the preparation of aluminum based compound flocculant were selected, and the preparation conditions were optimized through Box-Behnken design experiment and response surface analysis. The results showed that the quadratic polynomial model had significant regression, but the loss of fit term was not noticeable. The determination coefficient $R^2$ is 0.9603, which indicated that the model had good fit. The optimum preparation condition of the aluminum based compound flocculant was as follows: the mass ratio of PAC:CaO:PSAF was 8:4:5. When the influent initial fluorine content was 4.0~6.0mg/L, the dosage of the flocculant was 0.85mg/L, and the initial pH value was 7.5, the removal rate of fluoride ion (F⁻) reached 92.95%, the fluoride ion content in the supernatant was less than 1.0mg/L, and the relative error with the predicted value of the model was 2.31%. The response surface curve optimization model was reliable.

1. Introduction
Fluoride content in groundwater is greater than 1.0mg/L in most areas of northwest, north and northeast China, exceeding the limit of fluoride content which is less than 1.0mg/L stipulated in China's Sanitary Standard for Drinking Water (GB 5749-2006)[1,2]. At present, the single coagulant sedimentation method used to treat low concentration fluorine-containing water has limitations such as low fluoride removal rate, high reagent cost and the effluent fluoride content is greater than 1.0mg/L[3-6]. In this study, polyaluminum chloride (PAC), calcium oxide (CaO) and polyaluminum ferric silicate (PSAF) were selected as the components, and the aluminum based compound flocculant was prepared by adopting the mixed and compound method, which was used as the defluorine agent for the treatment of fluorinated mine water with low content (4.0-6.0 mg/L) and large amount of water (more than 10000m³/d).

Response surface analysis (RSM) is one of the effective methods to optimize the process parameters, reduce the number of experiments, and evaluate the level and interaction of various influencing factors. This method is an optimized experiment which combines experimental design, mathematical model and statistical method[7-9]. The Box-Behnken module of Design Expert 11 software was used to study the interaction among various factors and its significance. At the meantime the corresponding
regression equation and response surface curve were obtained, so as to optimize and predict the optimal conditions and the corresponding response values. This analysis method is characterized by its less experiment times, short period and high precision of regression equation. In this study, on the basis of single factor experiment, RSM was adopted to optimize the preparation conditions of aluminum complex flocculant, determine the best preparation conditions, and conduct fluoride removal performance evaluation test, thus providing technical guidance for industrial production and engineering application.

2. Materials and Methods

2.1. Reagents and instruments

2.1.1. Reagents. Polyaluminum chloride (PAC, effective content 35%, a chemical company in Gongyi, Henan); anhydrous calcium oxide (CaO, effective content 94%, an environmental protection company in Zhengzhou, Henan); aluminum ferric silicate (PSAF, effective content 36%, a chemical company in Zhengzhou, Henan); hydrochloric acid (HCl); sodium carbonate (Na₂CO₃); sodium hydroxide (NaOH); sodium fluoride (NaF, AR); deionized water, etc.

2.1.2. Instruments. Electronic balance (Ohaus AR224CN, USA); magnetic stirrer (ShangYi SN-MS-1D, China); water bath temperature oscillators (SHA-B, China); coagulation test six league mixer (ZR4-6, China); desktop fluorine meter (utility F090, USA); desktop pH meter (ray magnetic PHS-3E, China); peristaltic pump (Rongbo BT600LC, China); electric fluorine furnace (SX-4-10, China); electric blower type constant temperature drying oven (101A-1, China), etc.

2.2. Test methods

First, a single factor test was carried out. The compound flocculant was accurately weighed with an analytical balance and added to a beaker containing 1L simulated fluorine waste (5mg/L F⁻). The beakers were placed in a six-bladed agitator for coagulation defluorination. After the reaction was finished according to the set stirring procedure, the fluoride ion concentration in the supernatant was measured by the fluorine ion compound electrode method. The fluoride removal rate was calculated, and the single factor parameters such as components in the compound flocculant were obtained. Then RSM was used to determine the optimal ratio prediction and fluoride removal effect verification of the compound flocculant.

3. Results and Discussion

3.1. Response surface experiment design and analysis

In the single factor, fluoride removal experiment of the aluminum compound flocculant, the composition of components were PAC 0.4mg, CaO 0.15mg, PSAF 0.20mg, and the reaction pH value was 8.0. Before each experiment, the reagent was mixed according to the composition, and then the compound flocculant was added to the simulated wastewater (5mg/L F⁻). The pH value was adjusted with 0.1mol/L NaOH and HCl. In the experiment, four factors including PAC dosage, CaO dosage, PSAF dosage and initial pH value were investigated. The Box-Behbken module in DE-11 software was used to design a four-factor and three-level response surface experiment, with a total of 27 experimental schemes. The factor levels are listed in Table 1. Response surface experimental design and fluoride removal evaluation results are listed in Table 2.

| Factors            | Unit | Levels |
|--------------------|------|--------|
| PAC dosage(A)      | mg/L | -0.3   |
|                    |      | 0.4    |
|                    |      | 0.5    |
### Table 2. Response surface experimental design and test results table

| Number | PAC(A)mg/L | CaO(B)mg/L | PSAF (C)mg/L | pH (B) | Fluoride removal rate(%) | Fluorine content in supernatant(mg/L) |
|--------|------------|------------|--------------|--------|--------------------------|--------------------------------------|
| 1      | 0          | -1         | 0            | -1     | 84                       | 0.8                                  |
| 2      | 1          | 0          | 0            | 1      | 82                       | 0.9                                  |
| 3      | 0          | 0          | -1           | -1     | 84                       | 0.8                                  |
| 4      | 0          | 0          | 0            | 0      | 90                       | 0.5                                  |
| 5      | -1         | 0          | 0            | -1     | 74                       | 1.3                                  |
| 6      | 1          | 0          | 0            | 1      | 86                       | 0.7                                  |
| 7      | 0          | 0          | 0            | 0      | 90                       | 0.5                                  |
| 8      | 0          | 1          | -1           | 0      | 84                       | 0.8                                  |
| 9      | 0          | 0          | 0            | -1     | 92                       | 0.4                                  |
| 10     | 1          | 0          | 0            | 0      | 92                       | 0.4                                  |
| 11     | 0          | -1         | -1           | 0      | 88                       | 0.6                                  |
| 12     | 0          | 1          | 0            | 1      | 82                       | 0.9                                  |
| 13     | 1          | 1          | 0            | 0      | 84                       | 0.8                                  |
| 14     | 0          | -1         | 0            | 1      | 86                       | 0.7                                  |
| 15     | 0          | 0          | 1            | -1     | 92                       | 0.4                                  |
| 16     | 0          | 1          | 1            | 0      | 92                       | 0.4                                  |
| 17     | 1          | 0          | -1           | 0      | 84                       | 0.8                                  |
| 18     | 1          | -1         | 0            | 0      | 86                       | 0.7                                  |
| 19     | -1         | 0          | 1            | 0      | 82                       | 0.9                                  |
| 20     | -1         | 0          | 0            | 1      | 76                       | 1.2                                  |
| 21     | -1         | -1         | 0            | 0      | 80                       | 1                                    |
| 22     | 0          | -1         | 1            | 0      | 92                       | 0.4                                  |
| 23     | 0          | 0          | 0            | 0      | 90                       | 0.5                                  |
| 24     | -1         | 1          | 0            | 0      | 82                       | 0.9                                  |
| 25     | 0          | 0          | -1           | 1      | 84                       | 0.8                                  |
| 26     | 0          | 0          | 0            | 0      | 92                       | 0.4                                  |
| 27     | 0          | 0          | 1            | 1      | 88                       | 0.6                                  |
| 28     | 0          | 0          | 0            | 0      | 90                       | 0.5                                  |
| 29     | -1         | 0          | 0            | -1     | 78                       | 1.1                                  |

### 3.2. Model variance analysis and significance test

The design principle of the Box-Behnken experiment in DE-11 software and the least square method were used to perform regression fitting optimization analysis on the data obtained in Table 2, and the quadratic polynomial regression equation of the model was obtained.

Fluoride removal rate(%) = -1064 + 776A + 1044B + 588C + 215D - 200AB - 300AC - 10AD + 400BC - 120BD - 40CD - 720A^2 - 280B^2 - 380C^2 - 11D^2

(1)

As shown in Equation 1, the coefficient of each linear effect is positive, indicating that the positive change of the impact factor results in the increase of the response value. Meanwhile, the quadratic
effect coefficient is negative, indicating that the paraboloid opening of the quadratic polynomial equation is downward, and the response value has a maximum point. Therefore, the response surface experiment can be optimized and analyzed to obtain the optimal value. Variance analysis and significance test were conducted to obtain the response values of the model, and the results are listed in Table 3.

**Table 3. Variance analysis of the model and significance test of regression coefficients**

| Source | Sum of Squares | df | Mean Square | F-value | P-value |
|--------|----------------|----|-------------|---------|---------|
| Model  | 650.37         | 14 | 46.46       | 24.21   | <0.0001 |
| A-PAC  | 108.00         | 1  | 108.00      | 56.28   | <0.0001 |
| B-CaO  | 25.00          | 1  | 0.00        | 0.00    | 1.0000  |
| C-PSAF | 96.33          | 1  | 96.33       | 50.20   | <0.0001 |
| D-pH   | 27.00          | 1  | 27.00       | 14.07   | 0.0021  |
| AB     | 4.00           | 1  | 4.00        | 2.08    | 0.1708  |
| AC     | 9.00           | 1  | 9.00        | 4.69    | 0.0481  |
| AD     | 1.00           | 1  | 1.00        | 0.52    | 0.4823  |
| BC     | 4.00           | 1  | 4.00        | 2.08    | 0.1708  |
| BD     | 36.00          | 1  | 36.00       | 18.76   | 0.0007  |
| CD     | 4.00           | 1  | 4.00        | 2.08    | 0.1708  |
| A²     | 336.26         | 1  | 336.26      | 175.22  | <0.0001 |
| B²     | 3.18           | 1  | 3.18        | 1.66    | 0.2190  |
| C²     | 5.85           | 1  | 5.85        | 3.05    | 0.1026  |
| D²     | 56.45          | 1  | 56.45       | 29.41   | <0.0001 |
| Residual | 26.87      | 14 | 1.92        |         |         |
| Lack of Fit | 23.67  | 10 | 2.37  | 2.96 | 0.1537 not significant |
| Pure Error | 3.20    | 4  | 0.80 |     |         |
| Cor Total | 677.24    | 28 | 28.00     |         |         |

**Figure 1. Fitting between predicted and actual values**

As can be seen from Tab.3, the F-value of the regression model is 24.21, and the corresponding P-value is less than 0.0001, that is, the response value has highly to do with the quadratic multinomial regression equation, which is of statistical significance. The F-value of the loss of fit term is 2.96, and the corresponding P-value is 0.1537>0.05, which shows that the loss of fit term is not obvious, that is,
there is no loss of fit factor. This model fits with the experiment well and can replace the real point to analyze the experiment, thus the regression model has a high credibility. The model determination coefficient $R^2$ was 0.9603, and the correction determination coefficient $R_{adj}^2$ was 0.92107. As can be seen from Fig. 1, the correlation coefficient $R^2$ of the fitting line is 0.9904, and the slope is 0.9904, both close to 1, indicating that this model can be used to replace the actual value for optimization analysis. Individual significance was determined by T test. The results showed that the influence of primary term on fluoride removal rate was extremely significant, and the order of influence of various factors on fluoride removal rate was: A(PAC)>C(PSAF) >D(initial pH value) >B(CaO).

3.3. Response surface diagram and analysis

Response surface diagram is a three-dimensional space fitting surface diagram which shows the influencing factors of response value. From this diagram, the interaction among the factors can be observed directly. Based on the fitting equation and regression analysis, the response surface relationship diagram among PAC, CaO, PSAF, initial pH value and fluoride removal rate was drawn by DE-11 software, as shown in Fig. 2.

![Figure 2. 3D response surface diagram of each factor](image)

It can be seen from Fig. 2 that each figure represents the influence of the interaction of the other two factors on the fluoride removal rate when 2 of the four factors are set at the zero level. The contour line in the response surface indicates the strength of the interaction between the two factors, and the ellipse indicates the significant interaction between the two factors. The more flattened it is, the more significant the interaction is. In addition, the circle indicates that the interaction between the two factors is not obvious. It can be seen from the analysis that the mixture amount of PAC is the most significant influencing factor. With the increase of the mixture amount of PAC, the fluoride removal firstly increases and then decreases, and the surface changes steeply. The fluoride removal rate reached the highest point when the PAC mixture was 0.4mg. Other factors can also reach corresponding peaks. The order of influence of each factor on fluoride removal rate was A>PAC>C>PSAF>D>pH>B(CaO). This is consistent with the previous significance analysis table. Therefore, it is necessary to optimize the values of each parameter from the response surface to make the prepared the aluminum based compound flocculant to treat fluorine wastewater optimally.
3.4. Optimal prediction and verification experiments

According to variance analysis and response surface analysis, DE-11 software was used to optimize the parameters which affects the fluoride removal rate. The optimal process parameters were obtained as follows: PAC dosage was 0.407mg/L, CaO was 0.2000mg/L, PASF was 0.2500mg/L and initial pH value was 7.53. Under the optimal conditions, the predicted value of the optimal fluoride removal rate was 95.18%.

Five parallel tests were carried out under the above optimal conditions, and the fluoride removal rates were 92.3%, 94.6%, 91.8%, 93.4% and 92.8%, respectively. The mean value was 92.98%, and the relative error was 2.31%<5%. It can be seen from Fig. 3 that the response surface curve optimization model is consistent with the predicted model, indicating that the optimized optimal compound parameters are more accurate and reliable, which is of great significance to guide the preparation process optimization of aluminum based compound flocculant.

![Figure 3. Comparison of experimental verification and theoretical prediction](image)

4. Conclusion

Through experimental research and lab analysis, the following conclusions are reached.

First, the model regression equation and statistical coefficient were obtained through the optimal design of response surface experiment. The optimal process parameters after optimization were as follows: PAC dosage was 0.407mg/L, CaO was 0.2000mg/L, PASF was 0.2500mg/L and initial pH value was 7.53.

Second, under the optimal conditions, the predicted value of the optimal fluoride removal rate of the model was 95.18%. At this point the predicted value of fluoride removal rate was 95.18%. The average value of the five verification experiments was 92.98%, and the relative error was 2.31%<5%, indicating that the response surface curve optimization model was reliable.

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