Optimization of defluorination and iron reduction effect of manganese-loaded activated alumina by Response Surface Methodology

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ABSTRACT: Influenced by geological environment, both fluoride ion and iron ion exceed the standard in underground drinking water sources in some areas. Aiming at this problem, the experiment was designed by Response Surface Methodology (RSM). With the goal that fluoride ion in the effluent meets the Standards for Drinking Water quality (GB 5749-2006) and the concentration of iron ion in the effluent drops significantly, the adsorption time, pH value and temperature were taken as independent variables, and the primary and secondary relationship of influencing factors on fluoride and iron reduction of manganese-loaded activated alumina was explored, then the process parameters were optimized. The remarkable relationships are A_F (adsorption time) > B_F (pH value) > C_F (temperature), B_Fe (pH value) > C_Fe (temperature) > A_Fe (adsorption time). Under the conditions of adsorption time 8h, pH value 4 and temperature 25℃, when the mass concentrations of iron and fluoride in raw water are 2mg/L, the removal rates of fluoride and iron can reach 68% and 59.5%, and the mass concentrations of effluent are 0.61mg/L and 0.81mg/L respectively.

1. Introduction
As the main drinking water source, the problem of excessive intake of fluoride ion and iron ion in groundwater will be harmful to human health[1,2]. The fluoride removal methods are precipitation[3,4], ion exchange[5], membrane filtration[6] and adsorption[7]. Adsorption is widely used for its low operation cost and simple operation. The commonly used adsorbent, activated alumina, has the disadvantages of small saturated adsorption capacity and large adsorbent consumption, so the removal effect is not ideal[8]. In order to solve this problem, scholars begin to study the modification
of activated alumina. The modified manganese-loaded activated alumina has better porosity, larger specific surface area and more adsorption sites, which enhances the adsorption capacity of fluoride ions. RSM is widely used in academic papers as a method to guide experimental design based on statistics.

In this study, in order to solve the problem that fluoride and iron in the underground exceed the standard at the same time, the influence of manganese-loaded activated alumina dosage, pH value, temperature and other factors on fluoride removal and iron reduction was analyzed by RSM. The primary and secondary relations of influencing factors were determined, and the optimal operation parameters were determined, so as to improve the fluoride removal efficiency and reduce the operation cost.

2. Materials and methods

2.1. Experimental water quality
More than 80 million people in China drink water with fluoride ion exceeding the standard, and most of the fluoride ion content in groundwater is 2~5 mg/L. Upon this, a certain amount of fluoride and iron ion solution are added to laboratory pure water to prepare experimental water with the concentration of 2 mg/L.

2.2. Preparation of manganese-loaded activated alumina
Activated alumina particles were pretreated with Al2(SO4)3 solution to prepare sulfate activated alumina. Then was prepared by impregnation method, 100g of them were added into 500mL MnSO4 solution with a molar concentration of 0.06 mol/l, stirred continuously, 10.2mL H2O2 with a concentration of 30% was added, heated to 95℃, and 150mL NH3·H2O with a molar concentration of 0.2mol/L was added. At this time, the brown precipitate formed on the surface of activated alumina particles was MnOOH. Then drying at 100℃ for 2h, washing with hot deionized water for 8 times, drying for 4h, and cooling to room temperature.

2.3. Response Surface Methodology experiment

2.3.1. Establishment of Response Surface Methodology model
RSM is a statistical method to fit the functional relationship between factors and response values by multivariate quadratic Return equation. This method can analyze the interaction between variables, and obtain the optimal parameters with the least amount of experiments. After establishing the model, the Analysis of Variance is used to test it, and the statistical significance is tested by F test and correlation coefficient test, and the interaction of each factor is analyzed by three-dimensional surface graph.

2.3.2. Code of box behnken design model
Box Behnken Design model was adopted, and three independent variables, adsorption time (4h, 6h, 8h), pH value (4, 5, 6) and temperature (15℃, 20℃, 25℃), were selected for experimental design. 17 groups of test schemes are designed by Design-Expert 8.0 software.

2.4. Index detection method
According to the Standard Test methods for drinking water (GB/T 5750-2006), fluoride (F-) is determined by fluorimetric reagent spectrophotometry, and total iron is determined by phenanthroline spectrophotometry. The effluent water quality hygiene standards are in accordance with the limits of Standards for Drinking Water quality (GB5749-2006). Fluoride is 1.0 mg L-1 and total iron is 0.3 mg L-1.
3. Results and analysis

3.1. Response Surface Methodology scheme and results

17 groups of test schemes were designed by Design-Expert 8.0 software, and the data after the test were fitted. Taking the removal rate of fluoride ions and iron ions as double response values, the removal effect was analyzed. The specific scheme and results of RSM test are shown in Table 1 below.

| Number | Absorption time/h | pH  | Temperature/°C | Removal rate of fluoride ion/% | Removal rate of iron ion/% |
|--------|-------------------|-----|----------------|-------------------------------|----------------------------|
| 1      | 8                 | 5   | 15             | 56.98                         | 62.82                      |
| 2      | 6                 | 4   | 25             | 66.02                         | 45.58                      |
| 3      | 6                 | 4   | 15             | 60.03                         | 43.04                      |
| 4      | 4                 | 5   | 25             | 49.10                         | 75.21                      |
| 5      | 8                 | 6   | 20             | 58.71                         | 87.57                      |
| 6      | 4                 | 4   | 20             | 48.92                         | 22.73                      |
| 7      | 6                 | 5   | 20             | 52.55                         | 73.65                      |
| 8      | 4                 | 5   | 15             | 39.97                         | 84.43                      |
| 9      | 6                 | 6   | 15             | 42.64                         | 65.16                      |
| 10     | 6                 | 5   | 20             | 51.74                         | 67.85                      |
| 11     | 8                 | 4   | 20             | 63.27                         | 49.15                      |
| 12     | 4                 | 6   | 20             | 43.28                         | 53.60                      |
| 13     | 8                 | 5   | 25             | 63.18                         | 84.09                      |
| 14     | 6                 | 6   | 25             | 51.24                         | 92.01                      |
| 15     | 6                 | 5   | 20             | 40.30                         | 59.09                      |
| 16     | 6                 | 5   | 20             | 44.53                         | 62.34                      |
| 17     | 6                 | 5   | 20             | 41.04                         | 33.55                      |

3.2. Significance test of Response Surface Methodology model

3.2.1. Analysis of variance of Return equation

The multivariate quadratic model was used to fit the results in Table 1 by Return, and the adsorption time, pH value and temperature were recorded as A, B and C. The response results of adsorption time, pH value and temperature to the removal rate were obtained, and the regression equation was established.

According to Table 2 and Table 3, the FF value of Return equation of fluoride ion is 7.39, PF value =0.0194<0.05, FFe value of iron ion is 43.53, PFe value=0.0003<0.01, which shows that Return equation has certain significance and credibility, and the FF value of mismatch term of fluoride ion in the model is 0.014. The FFe value of iron ion mismatch term is 0.005, and the PFe value is 0.9461 > 0.1, which indicates that the mismatch term of the model is not significant. The model can be used to predict the removal rate of fluoride ion and iron ion, and the model has a high degree of fitting.
According to the P values of various influencing factors of fluoride ions in table 2, the P values of A (adsorption time) and B (pH value) in the primary term are all < 0.01, indicating that adsorption time and pH value have a significant impact on fluoride removal, while the P value of C (temperature) is < 0.1, indicating that B2 and A2B in the secondary term have a significant impact on fluoride removal.

Table 3 Analysis of variance of regression equation of iron ions

| Variance source | Sum of squares | Variance | Mean square | F F | P Fe |
|-----------------|----------------|----------|-------------|-----|------|
| Model           | 5157.20        | 11       | 468.84      | 43.53| 0.0003*** |
| A               | 40.52          | 1        | 40.52       | 3.76 | 0.1101 |
| B               | 2375.07        | 1        | 2375.07     | 220.52| <0.0001*** |
| C               | 215.95         | 1        | 215.95      | 20.05| 0.0065*** |
| AB              | 14.26          | 1        | 14.26       | 1.32 | 0.3019 |
| AC              | 232.47         | 1        | 232.47      | 21.58| 0.0056*** |
| BC              | 147.77         | 1        | 147.77      | 13.72| 0.0139** |
| A²              | 0.44           | 1        | 0.44        | 0.041| 0.8478 |
| B²              | 930.81         | 1        | 930.81      | 86.42| 0.0002*** |
| C²              | 305.02         | 1        | 305.02      | 28.32| 0.0031*** |
| A²C             | 37.57          | 1        | 37.57       | 3.49 | 0.1208 |
| AB²             | 668.38         | 1        | 668.38      | 62.06| 0.0005*** |
| Residual        | 53.85          | 5        | 10.77       |     |      |
| Misfitting term | 0.070          | 1        | 0.070       | 0.005180| 0.9461 |
| Pure error      | 53.78          | 4        | 13.45       |     |      |
| Sum             | 5211.05        | 16       |             |     |      |

According to the P values of various influencing factors of iron ions in table 3, the P value of B (pH value) and C (temperature) in the primary term is 0.01, which indicates that the pH value and temperature of solution have the most obvious influence on the removal effect of iron ions. The P values of B², C² in the quadratic term and AC, BC and A2B in the interactive term are less than 0.01, which indicates that they have a significant influence, while other terms have less influence. The results show that the pH value and temperature have a greater influence on the iron removal effect of manganese-loaded activated alumina.

Comparing the P and F value in table 2 and table 3, it can be seen that the relationship between each factor of the removal rate is as follows: A (adsorption time) > B (pH value) > C (temperature) > AFe (adsorption time). Therefore, the pH value has the most significant influence.

3.2.2. Significance analysis of Return model

Design Expert is used to fit the experimental data by Return, which further verifies the significance of Return equation. According to the analysis in table 4, Adeq Precision of fluoride ion is 8.843 > 4, Adeq Precision of iron ion is 25.128 > 4, the C.V. of fluoride ion is 6.70% < 10%, and the C.V. of iron ion is 5.05% < 10%, which shows that this model is consistent with the actual situation. The correlation coefficients between the actual and predicted removal rates of fluoride and iron ions are 0.9421 and 0.9897, respectively, both of which are greater than 0.8, indicating that the correlation between them is high with small errors. The predicted value of the model is in a straight line with actual value, with
good consistency. The RSM model can describe and predict the response value well and analyze the best test conditions.

| Element | Mean   | C.V. % | R-Squared | Adj R-Squared | Adeq Precision |
|---------|--------|--------|-----------|---------------|----------------|
| F       | 51.98  | 6.70   | 0.9421    | 0.8147        | 8.843          |
| Fe      | 64.97  | 5.05   | 0.9897    | 0.9669        | 25.128         |

### 3.2.3. Factor interaction analysis

According to the data of Return model, the order of the influence of each factor in the interaction is adsorption time and temperature > pH value and temperature > adsorption time and pH value. The influences of various factors and their interactions on response values are shown in Figure 1~ Figure 6 below.

The effect of adsorption time and temperature is shown in Figure 1 and Figure 2. The slope of RSM diagram is large, which indicates that adsorption time and temperature have great influence. When the temperature is 25°C and the adsorption time is 4h, the removal rate of fluoride ion is 56% and that of iron is 68%. With the increase of adsorption time to 8h, the removal rate of fluoride ion increased by 13%, reaching 69%, and the removal rate of iron ion increased by 32%.

The influence of temperature on the removal rates of fluoride and iron ions is related to adsorption time. When the adsorption time deviates from the optimal value, even if the temperature is increased, the removal rates of fluoride and iron ions cannot be effectively improved. Therefore, ensuring sufficient adsorption time is the prerequisite to ensure the removal rate. When the adsorption time is fixed, the removal rate gradually increases with the increase of temperature, because the process belongs to endothermic process.

With the increase of pH value and temperature, the removal rate of fluoride ion increases gradually. This may be because the ionic equilibrium constant of hydrofluoric acid in aqueous solution is small, and when the solution is acidic, there are more free fluoride ions, and the fluoride removal ability is enhanced. However, under alkaline conditions, OH- in the solution will compete for the limited adsorption sites on the adsorbent, which leads to the reduction of fluoride removal efficiency. When pH is 4, the removal rate of iron ions is 60%, which is lower than raw water. When pH is increased to 5.6, all iron ions in water can be removed.
3.2.4. Optimization and verification of process parameters

Under the optimal parameters of adsorption time 8h, pH value 4 and temperature 25℃, the model predicted that removal rates of fluoride and iron ions were 68.8% and 60.3%, respectively. At this time, the actual removal rates of fluoride and iron ions were 68% and 59.5%, and the actual effluent concentrations of fluoride and iron ions were 0.64mg/L and 0.81mg/L, respectively. The difference between the measured value and the predicted value obtained by RSM model is less than 1%, which shows that the fitting degree between the experimental value and the predicted value is good.

4. Conclusion

Under the optimal parameters of adsorption time 8h, pH value 4 and temperature 25℃, the predicted removal rates of fluoride and iron ions were 68.8% and 60.3%, and the measured removal rates of
them were 68% and 59.5%, respectively. The difference between the measured and predicted value of the model is less than 1%. The pH value has the most significant influence on fluorine and iron removal efficiency of manganese-loaded activated alumina. In the interaction, adsorption time and temperature > pH value and temperature > adsorption time and pH value.

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