

# Preparation of Aluminium Modified Zeolite and Experimental Study on Its Treatment of Fluorine-containing Water

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**Abstract.** Aluminium modified zeolite was prepared by acids, bases and their salts and it was used in the adsorption experiments of fluorine-containing water. Through the experimental study on the treatment of fluorine-containing drinking water by modified zeolite, the optimal preparation conditions of modified zeolite and the treatment effect of zeolite fluoride removal were explored. The results show that the Al-modified zeolite has a better adsorption effect on fluorine. When the Al-modified zeolite is used to treat the water which has a fluorine concentration of 1.63 mg/L, the fluoride ion can be reduced to less than 1 mg/L to meet the national drinking water standard.

## 1. Introduction

Fluorine is one of the essential trace elements in the human body. However, excessive intake of fluoride can affect human health. So it is necessary to find a cost-effective method to remove fluorine<sup>[1]</sup>. Zeolite is cheap and easy to obtain, but the adsorption capacity of natural zeolite is not ideal, so it is of practical value to modify the zeolite to enhance its adsorption capacity<sup>[2]</sup>. In this paper, the natural zeolite was modified by acid, base and aluminium sulfate, the influencing factors of preparing Al-modified zeolite were studied. The Al-modified zeolite was analysed by electron microscopy. Al-modified zeolite was used to treat different concentrations of fluorine-containing drinking water and its treatment effect was investigated.

## 2. Test section

### 2.1 Test Water

The raw water required for the test simulates groundwater in Kangping County, the fluorine content is about 1.63 mg / L.

### 2.2. Preparation of Al-Modified Zeolites

A certain amount of natural zeolite was placed in a beaker, soaked in 1 mol/L of sodium hydroxide solution for 12 hours, then washed with deionized water until neutral, and then immersed in 3 mol/L of hydrochloric acid solution for 10 hours, washed and dried. It is further immersed in a certain concentration of aluminium sulfate solution for a certain period of time, washed and dried to form an Al-modified zeolite.



### 2.3. Experiment Method

The modified zeolite was added to 100 ml of experimental water and stirred with a magnetic stirrer for a while. A suitable amount of the solution was centrifuged; the supernatant was taken for measurement.

### 2.4. Determination of fluorine

Measurement of fluoride ion by spectrophotometry

## 3. Results and discussion

### 3.1 Effect of Aluminium Salt Concentration and Its Time on Fluoride Removal

#### 3.1.1 Selection of aluminium sulfate solution concentration

The zeolite was further treated with aluminium sulfate on the basis of modification with hydrochloric acid. The reaction conditions of this test are: under normal temperature conditions, 5.0 g of zeolite was firstly immersed in 3 mol/L of hydrochloric acid for 10 h, washed and dried at 110 °C, then soaked for 6h with different concentrations of aluminium sulfate solution, washed and dried. Then, it was added into 100 mL water which has the fluorine concentration of 1.63 mg/L to carry out a stirring adsorption test. The remaining fluoride ion concentration was measured at intervals. The effect of different concentrations of aluminium sulfate modified zeolite on the treatment of fluorine-containing water is shown in Figure 1.

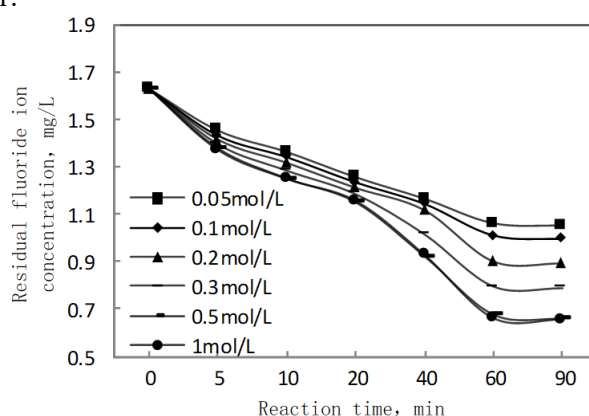


Figure 1. Effect of different aluminium sulfate concentrations on the effect of fluoride removal

According to Figure 1, it can be seen that as the concentration of aluminum sulfate increases, the fluoride removal capacity of the zeolite increases, the remaining fluorine ion concentration decreases. When the concentration of aluminum sulfate is 0.2 mol/L, the residual fluorine concentration at which the reaction reaches equilibrium has dropped below 1 mg/L. When the concentration of aluminum sulfate reaches 0.5 mol/L, the fluoride ion concentration continues to drop to 0.676 mg/L. When the concentration is increased, the concentration of fluoride ions is not significantly reduced. This is because the concentration of aluminium sulfate increases, excessive aluminium ions may precipitate with hydroxide to form iron hydroxide, covering the surface of the zeolite, blocking the pores of the zeolite, hindering the adsorption of fluoride ions. Although the concentration of aluminium sulfate is increased to 0.5 mol/L when treating fluorine-containing water, the concentration of fluoride ion can be lowered to a lower level than that of 0.2 mol/L of aluminium sulfate, there is no risk to health, but the amount of aluminium sulfate is more than twice that of the latter, which increases the cost. Therefore, the optimum concentration of modified zeolite was determined by selecting 0.2 mol/L of aluminium sulfate.

#### 3.1.2 Selection of soaking time of aluminium sulfate solution

In order to determine the appropriate soaking time, under normal temperature conditions, 5.0 g of zeolite was firstly immersed in 3 mol/L of hydrochloric acid for 10 h, washed and dried at 110 °C,

then soaked for different times with 0.2 mol / L of aluminium sulfate solution, washed and dried. Then, it was added into 100 mL of water which has the fluorine concentration of 1.63 mg/L to carry out a stirring adsorption test. The remaining fluoride ion concentration was measured at intervals. The effect of different concentrations of aluminium sulfate modified zeolite on the treatment of fluorine-containing water is shown in Figure 2. It can be seen that as the soaking time prolongs, the adsorption properties of zeolites are also gradually increasing. Before 9 hours, the fluoride ion concentration decreases to a great extent. When the soaking time is 7 hours, the reaction reaches equilibrium, the remaining fluoride ion concentration has been already below 1 mg/L, as time goes on, the fluoride ion concentration continues to decrease. When the time reaches 9h, the fluoride ion concentration drops to 0.673mg/L. After 9 h, the fluoride ion concentration did not change substantially. This is because at the beginning of the reaction, the surface of the zeolite is relatively empty and can adsorb fluorine well, but as time goes on, more and more fluorine adheres to the surface of the zeolite, most of the surface of the zeolite is already occupied, so the fluoride ion concentration no longer drops significantly with time. Therefore, the optimum modification time of modified zeolite was selected by immersing aluminium sulfate for 7h.

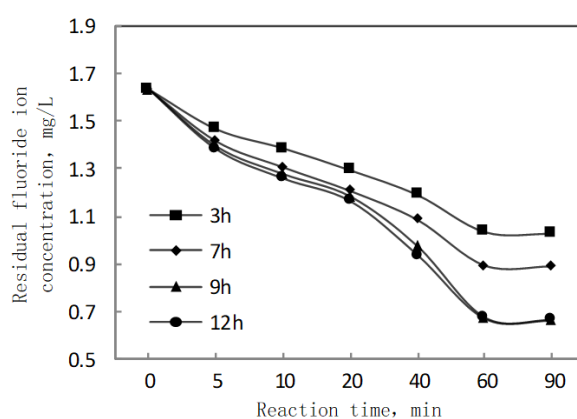
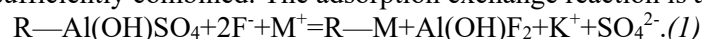


Figure 2 Effect of different soaking time on the effect of fluoride removal

Aluminium sulfate immersion treatment is a critical step. After the natural zeolite is treated with hydrochloric acid, the impurities in the pores are removed, the active surface area is increased, then activated by aluminium sulfate, which can better adsorb the aluminium salt and become a good carrier of the aluminium salt.  $\text{Al}^{3+}$  exchanges with metal ions in the zeolite to modify the zeolite, which gives the zeolite a well-developed microporous structure [3]. The zeolite structure increases the adsorption activity point, so that it has good ion exchange performance and adsorption performance, the aluminium sulfate treatment does not saturate the coordination of the aluminium ions, which is more favourable for adsorbing the anion  $\text{F}^-$  [4-5]. In the process of removing fluorine, aluminium ions and fluoride ions can be sufficiently combined. The adsorption exchange reaction is as follows:



It can be seen from the formula that chemisorption plays a major role, so that aluminium ions and fluoride ions combine to form a complex, thereby achieving the effect of removing fluoride ions.

### 3.2 Characterization of Al Modified Zeolite Materials

A certain amount of zeolite was first soaked in 3mol/L of hydrochloric acid for 10h, washed and dried, then immersed in 0.2mol/L of aluminium sulfate solution for 7h, washed and dried to make Al modified zeolite. Electron microscopic scanning of natural zeolite and Al modified zeolite is shown in Figure 3.

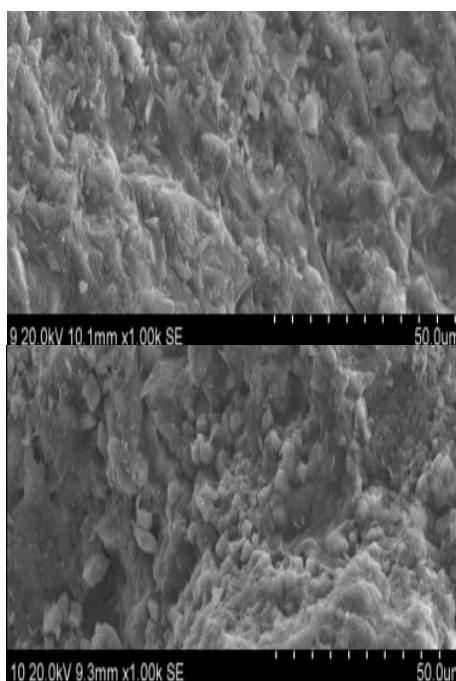


Figure 3 Natural zeolite surface and Al modified zeolite surface

It can be seen from Fig. 3 that the surface of the natural zeolite is relatively smooth and dense, the surface of the Al-modified zeolite changes greatly, the surface becomes rough and the convex portion is formed into a block shape, so that the surface is relatively loose. Moreover, the surface forms a microporous structure, which increases the specific surface area, the larger the specific surface area, the stronger the adsorption capacity of the zeolite, which fully demonstrates that the modification of the zeolite by this method can change the structure of the original zeolite and enhance the fluorine removal ability of the zeolite.

### 3.3 Experimental Study on Treatment of Fluorine-containing Water by Al Modified Zeolite

5g of Al modified zeolite was added to 100ml of different concentrations of fluorine-containing water for 60min. The treatment effect of Al-modified zeolite on different concentrations of fluorine-containing water is shown in Table 1. It can be seen from the table that the Al-modified zeolite has a certain fluorine removal effect on water with different fluorine concentration. The water with a fluorine concentration of 1.63 mg/L, the fluorine concentration can be reduced to below 1 mg/L. This indicates that not only the surface structure of the modified zeolite was changed, but also the fluorine removal ability of the modified zeolite was confirmed. For the fluorine water with higher concentration, although the fluorine concentration after the primary adsorption treatment of the Al-modified zeolite cannot reach the national drinking water standard, it also has a certain degree of reduction. Therefore, for a higher concentration of fluorine-containing water, multiple adsorption treatments can be considered depending on the actual situation.

Table 1. Effect of Al Modified Zeolite on Fluorine Removal of Different Concentrations of Fluorine-containing Water.

| Fluorine concentration (mg/L) | Residual fluoride ion concentration (mg/L) |
|-------------------------------|--------------------------------------------|
| 1.63                          | 0.893                                      |
| 2                             | 1.012                                      |
| 4                             | 2.613                                      |
| 8                             | 6.339                                      |

|    |       |
|----|-------|
| 10 | 8.189 |
|----|-------|

### 3.4 Al-modified zeolite adsorption isotherm fitting

5 g of Al modified zeolite was prepared and added into 100 mL of water which containing different initial fluorine concentrations. The reaction was continuously stirred at 25°C. When the fluorine concentration measured is constant, we calculate the adsorption amount to obtain an adsorption isotherm. As shown in Fig. 3. The data of the adsorption isotherm is fitted, the Langmuir isotherm is used to draw the isotherm as shown in Fig. 4. The results show that the adsorption isotherm of the modified zeolite is consistent with the Langmuir isotherm, the regression coefficient of the linear equation is 0.9916. The Langmuir adsorption isotherm is:

$$q_e = \frac{0.063 C_e}{1 + 2.529 C_e} \quad (2)$$

It can be seen that the adsorption of fluoride ions by the modified zeolite conforms to the Langmuir adsorption isotherm and it belongs to the monolayer adsorption model, which has typical chemisorption properties.

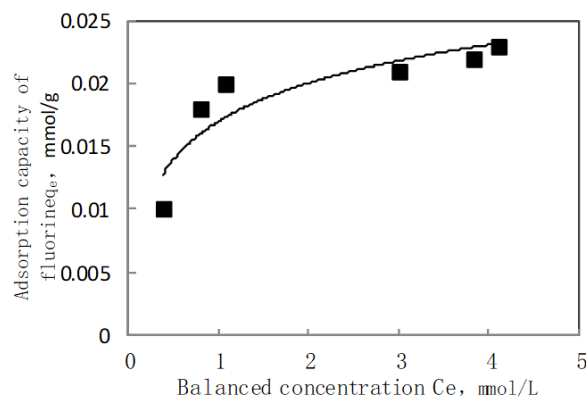


Figure 4 Adsorption isotherms

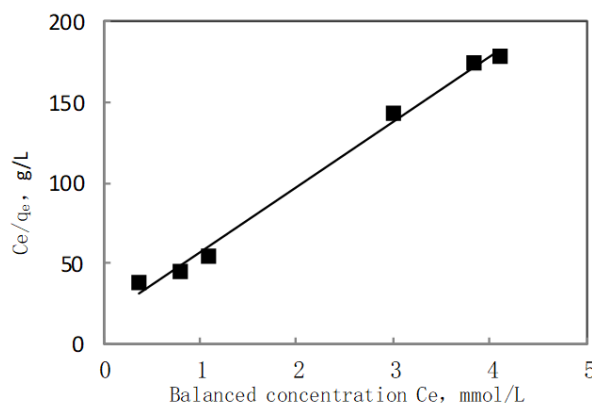


Figure 5 Linearization by Langmuir adsorption isotherm

## 4. Conclusions

(1) The optimal preparation conditions of Al modified zeolite are: The zeolite was immersed in 3mol/L of hydrochloric acid for 10h, rinsed and dried, then immersed in 0.2mol/L of aluminium sulfate for 7h, washed and dried to obtain Al-modified zeolite.

(2) Electron microscopic analysis of the Al-modified zeolite showed that the zeolite modified by aluminium exhibited a microporous structure, and since the acid dissolved the blocked impurities, the

specific surface area of the zeolite was larger than that of the natural zeolite, and the fluorine removal ability of the zeolite was improved.

(3) For fluoride-containing water with a fluorine concentration of 1.63 mg/L, the Al-modified zeolite can reach the national drinking water standard after a single adsorption treatment, the Al modified zeolite can not only handle low-concentration fluorine-containing water, but also high concentrations of fluorine-containing water also have a certain effect of fluoride removal.

#### **References:**

- [1] Li Yongfu, Meng Fanping, Yao Ruihua. Technology of Water Treatment,**36**(2010)
- [2] Gao Peng. Heilongjiang Hydraulic Science and Technology,**40**(2012)
- [3] YU Hua-long, ZHOU Li-dai, JIANG Jun. Liaoning Chemical Industry,**40**(2011)
- [4] Ma Yongxian, Zhang Huanzhen, Fan Yupeng. Technology of Water Treatment,**37**(2011)
- [5] Liu Wenzhi, Zhang Yujie. Technology of Water Treatment,**03**(1995).