Study on adsorption characteristics and regeneration effect of iron - based alumina composites

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Abstract: In this paper, an iron-based alumina composite was synthesized by modifying activated alumina with ferric chloride. The adsorption performance of iron-based alumina composite modified with 15% ferric chloride solution reached a certain peak. At lower initial fluoride concentration, the amount of fluoride treated by this composite is much more than that of water samples with higher initial fluoride concentration. To some degree, the slower flow rate of fluoride solution, the better adsorption performance of adsorbent. The iron-based alumina composite expressed a better performance of fluoride adsorption at pH=6.5. The adsorbent treated with aluminum potassium sulfate had the best adsorption performance.

1 Introduction

The concentration of fluoride in drinking water has a significant impact on human health. If human body uptake of fluoride in the right concentration is good for preventing tooth decay, however, too much of it would lead to tooth and bone disease. According to the standards of the World Health Organization (WHO), the appropriate concentration of fluorine ion in drinking water is 0.5-1.5mg/L^[1], while the Chinese safe drinking water standard stipulates that the concentration of fluorine ion prohibited exceed 1.0mg/L^[2]. Fluoride-bearing groundwater is widely distributed in China, there were still about 70 million people drink excessive fluoride water, especially in northeast, north and northwest China^[3]. In the past 20 or 30 years, there have been a lot of studies on the treatment of fluorine-containing water at home and abroad. At present, the removal methods of fluoride in fluorine-containing water mainly include nanofiltration^[4, 5], sedimentation^[6, 7], coagulation^[8, 9], electrodialysis^[10, 11], reverse osmosis^[12, 13], adsorption^[14, 15] and ion exchange. Among the commonly used methods for removing fluorine, the adsorption method is one of the most widely used because of its simple operation, low cost, high selectivity and efficiency, and the wide variety of adsorbent. The activated-alumina (AA) grains are considered as spherical and porous, with constant diameter and with adsorption sites uniformly distributed throughout the grains, it was strongly showed that activated-alumina has a excellent adsorption properties. Therefore, in this paper, activated alumina was improved performance with ferric

chloride was used to remove fluoride, and adsorption experiments under different conditions were studied and discussed according to using and regeneration of regenerant.

2 Materials and methods

2.1. Reagents and instruments

The reagents were used in the experiments were mainly about aluminum hydroxide, potassium aluminum sulfate, sodium sulfate, sodium hydroxide, hydrochloric acid, sodium fluoride and Hexahydrate ferric chloride. The above reagents were analytical pure and Sinopharm group chemical reagent co. LTD. The instruments were used in the experiments mainly include AL-204 balance, multi-function constant temperature and speed magnetic stirrer, low-speed large-capacity multi-tube centrifuge, electric constant temperature drum box, fluorine ion selective electrode, PHS-3C pH meter, automatic specific surface aperture distribution analyzer and measuring straw.

2.2. Materials preparation

In the preparation procedure, 15g of ferric chloride powder was dispersed in a 200mL of beaker with 100mL of distilled water to prepare 15% concentration of ferric chloride solution. Then, 10g of activated alumina were added and soaked into 15% concentration of ferric chloride solution for modification. At the same time, the

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various concentrations of ferric chloride solution were prepared to obtain the optimal concentration, and the optimal soaking time was also studied.

2.3. Adsorption experiments

Effect of concentration of ferric chloride solution on adsorption performance. The activated alumina was modified with 0%, 5%, 10%, 15% and 25% concentration of ferric chloride solution respectively, the unmodified activated alumina was added for experiment, and compared with the modified activated alumina of these concentrations. The initial fluoride concentration was set as 10ppm, the flow rate ratio was 1:6, and the pH value was 7. The fluoride solution was adsorbed with modified adsorbents of different concentrations of ferric chloride solution. Finally, chose the optimally modified activated alumina for the rest of experiments. Effect of initial fluoride concentration, flow rate ratio, pH and regenerated solutions, on adsorption performance would also be considered, respectively.

3 Results and discussion

Figure 1. a. Effects of various concentrations of modifiers on fluoride removal, b. effects of two different concentrations of modifiers on fluoride removal effect. (Where, BV is the multiple column ratio and c is the effluent concentration.)

As shown in fig.1. a, the line B is unmodified activated alumina experiment to get the adsorption curve, and the line J, H, D and F were obtained with 5%, 10%, 15% and 25% concentration of modified activated alumina adsorption curve, respectively. In Fig. 1.b, the line D is the adsorption curve after modification with 15% concentration, and the line F is the adsorption curve after modification with 25% concentration. As can be seen from the figure, the adsorption performance of activated

alumina after modification with 15% concentration of iron chloride solution reached a certain peak, and the adsorption performance was better than that after modification with 0%, 5% and 10% concentration. However, when the concentration of 15% increased to 25%, the adsorption effect did not change significantly, perhaps the modified effect of activated alumina reached saturation. Therefore, the experiment should be modified with 15% concentration of ferric chloride on activated alumina, so as to continue the experiment.

Figure 2. Effects of various initial concentrations on fluoride removal

As shown in fig. 2, both line B and D of adsorption curve were obtained when the initial fluoride concentration are 10ppm and 3ppm. As can be seen from the figure, when the initial fluoride concentration was 3ppm, the adsorption effect reached the peak at $BV=80$. After that, the adsorption effect changed significantly. When the initial fluoride concentration was 10ppm, the BV did not reach its peak at around 400. Comparison shows that at lower initial fluoride concentration, the amount of fluoride treated by this adsorbent is much more than the higher initial fluoride concentration, and had a better adsorption properties. This may be due to the high concentration of fluoride in the solution, and the limited ability of the adsorbent to deal with the high concentration of fluoride in a certain contact time. Therefore, in this experiment, the adsorption effect was better when the initial fluorine concentration was 3ppm.

Figure 3. Effects of various flow rate ratio on fluoride removal

As shown in fig. 3, both line B and line D were obtained in the experiment when the flow rate ratio are 1:6 and 1:3. When the flow rate ratio of 1:6 reaches about 200 BV , the fluoride removal effect changed greatly and reached a certain peak value, while the flow rate of 1:3 did not reached the peak value when the BV

was above 800. It can be seen that adsorption devices with different flow rate ratios had a great influence on the defluoride performance of adsorbent, and the flow rate of 1:3 was better than that of 1:6. This might caused by the retention time of the original fluoride solution in the adsorbent was shorter, which made the adsorbent adsorbed the fluoride solution incompletely. So the relatively slower flow rate ratio it is, the better adsorption performance would have.

Figure 4. Effects of various pH on fluoride removal.

As shown in fig. 4, the line B, D and F of adsorption curve represented the effect of various pH on fluoride removal at 7, 6.5 and 8, respectively. As can be seen from the figure, when pH=6.5 and BV was about 150, the adsorption performance changes greatly. When pH=7 and BV was about 200, the adsorption effect changes greatly, and the subsequent adsorption performance did not change much. At pH =8, the adsorption effect gradually became better when BV was about 270. And it can be seen that the adsorption performance at pH=6.5 were much better than that at pH value of 7 and 8. It can be seen that, in the acidic environment, the modified adsorbent had a faster curve growth rate and better adsorption performance when the column ratio was smaller. Therefore, the adsorption effect of adsorbent on fluorine was better at pH=6.5.

Figure 5. Effects of various regenerated liquids on fluoride removal effect.

As shown in figure 5, the line B, D and F were the adsorption curve obtained by using the regenerated liquid for aluminum potassium sulfate, sodium hydroxide and sodium sulfate, respectively. It was obviously seen that the adsorption efficiency of aluminum potassium sulfate was optimum in the range of small column ratio. The

adsorbent regenerated from aluminum potassium sulfate had the best adsorption performance, followed by sodium sulfate and sodium hydroxide. Therefore, aluminum potassium sulfate with a mass ratio of 5% should be selected as the regeneration solution for the regeneration experiment of adsorbent.

4 Conclusions

The adsorption effect of modified activated alumina is much better than that of unmodified activated alumina. In a particular situation, the adsorption performance of modified activated alumina was affected by many factors. Especially, the initial fluorine concentration, the flow rate ratio, the type of regenerant, the concentration of regenerant, pH and so on all had a great effect on its adsorption performance.

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