Dynamic experiment on de-fluoridation of Manganese-loaded Activated Alumina

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Abstract. This work used Manganese-loaded Activated Alumina (MAA) as the adsorbent to analyze the effect of column height and filtration rate on the removal of fluoride and iron ions, and clarified the fluoride removal mechanism by using dynamic experiments when the fluoride and iron in drinking water exceed the standard at the same time. The results showed that the height of the column and the filtration rate have a significant impact on the operation of the system. It was the best operating condition for the system that the filtration rate was 1m/h and the column height was 300mm. After the system run for 102 hours, the fluoride ion effluent concentration exceeded the standard, which was 1.02mg/L; the concentration of iron ions in the effluent reached the standard stably after the system run for 1 hour, and the concentration was not more than 0.18mg/L. When the filtration rate was 1m/h and the column height was 150mm, the stable running time of fluoride removal of MAA column was 2.5 times that of ordinary activated alumina (AA); the start-up time of MAA to remove iron ions was one-twelfth of AA. The effect of removing fluoride and iron by MAA was significantly better than AA.

1. Introduction
Fluoride is widely present in groundwater systems [1]. The low concentration of fluoride ions plays an important role in the development of human bones and dental health[2]. However, excessive fluoride ions in drinking water can cause serious problems such as skeletal fluorosis[3]. There are over 60 million people in more than 20 provinces who drink excessive fluoride in China, especially in the countryside [4]. The content of fluorine and iron in groundwater both exceeds the standard in parts of the Northeast China, the northeastern part of Inner Mongolia and other regions[5]. Therefore, how to remove excess fluoride from groundwater becomes an urgent problem when the iron ions are excessive.

Adsorption is the most common method of fluoride removal. AA is widely used as an adsorbent for groundwater treatment due to its unique physical, chemical and structural characteristics [6]. But the defects of activated alumina are slow diffusion in the particles in the solution, poor adsorption rate, and a small available pH range, which limits its application in the treatment of large amounts of water[7]. Therefore, in this paper, MnOOH, which can effectively remove anions in the aquatic environment[8], was coated on AA to make the adsorbent MAA, and MAA was used as the adsorbent in the dynamic experiment to analyze its fluoride and iron reduction efficiency. It provided reference to simultaneously remove fluoride and iron from drinking water sources in northern China.
2. Materials and methods

2.1. Preparation of MAA
Sulfate type AA was prepared by adding Al2(SO4)3 solution to AA particles, and then was added to MnSO4 solution to prepare MAA for experiment by heating, stirring, washing and cooling.

2.2. Column studies
Sodium fluoride and ferrous ammonium sulfate were added to distilled water to prepare a simulated water sample with fluoride concentration of 5±0.5 mg/L and iron concentration of 2 mg/L.

The test device uses a glass column with a height of 60 cm and an inner diameter of 5 cm. The bottom of the column is equipped with 1~2 cm ordinary quartz sand as a supporting layer. According to research needs, AA or MAA particles of different heights are filled, and water intake is set every 150mm.

The device entered water from the upper end, and output water from the lower end, using continuous operation. The concentrations of fluoride and iron ions in the water were measured and analyzed regularly when the filtration rate was 1m/h and 2m/h, and the height of the filter column was 150mm and 300mm. Explore the effect of MAA in removing fluoride and iron.

2.3. The detection index
The main water quality indicators are tested and analyzed in accordance with the limits and methods required by "Standards for drinking water quality" (GB5749-2006). Fluoride (F-) adopted fluorine reagent spectrophotometry, and total iron adopted phenanthroline spectrophotometry. The drinking water standard limits for fluoride (F-) and total iron are 1.0 mg/L and 0.3 mg/L, respectively.

3. Results and discussion

3.1. The effect of filter height on fluoride and iron removal in MAA

3.1.1. Influence of column height on the effect of fluoride removal
The results of the MAA dynamic test are shown in Figure 1. The 150mm and 300mm columns have the same effluent fluoride ion concentration change trend with the same filtration rate.

Figure 1(a)(b) shows that when the filtration rates are 1m/h and 2m/h, the fluoride ion concentration in the effluent of the 150mm column after 120h operation has increased from the initial 0.77mg/L and 0.85mg/L to 2.04mg/L and 3.5mg/L, respectively. The fluoride ion removal rate is reduced from 84.6% and 83% to 59.2% and 30%. When the system was operated for 27h and 8h, the fluoride ion effluent concentration exceeded the standard, which was 1.03mg/L and 1.02mg/L, respectively. The fluoride ion effluent concentration exceeded the standard, which was 1.03mg/L and 1.02mg/L. In comparison, the concentration of fluoride ion in the effluent of the 300mm column increased from 0.35mg/L and 0.38mg/L to 1.11mg/L and 2.26mg/L after 120h of operation. The fluoride ion removal rate decreased from 93% and 92.4% to 77.8% and 54.8%, respectively. When the filter column was operated for 102h and 28h, the fluoride ion effluent concentration exceeded the standard, which was 1.02mg/L and 1.04mg/L, and the removal rate dropped to 79.6% and 79.2%, respectively. When the filtration rate is 1m/h, the effluent fluoride ion exceeded the standard after the 150mm and 300mm columns run for 27h and 102h, respectively. The stable running time of the 300mm MAA column is 3.8 times that of the 150mm column. When the filtration rate was 2m/h, the effluent fluoride ion exceeded the standard after the 150mm and 300mm columns were operated for 8h and 28h, respectively, and the 300mm MAA column was 3.5 times longer than the 150mm column.
It can be seen that the height of the column has a significant impact on fluoride removal when the filtration rate was constant. As the height of the column increases, the fluoride ions removal effect is better. This is due to the increased number of active sites provided by the MAA column. The fluoride ions first contact the upper layer of the adsorbent, and part of it is intercepted that its concentration decreases. As the influent flows from top to bottom, the remaining fluoride ions in the water contact the lower layer of MAA for ion exchange [9]. The solution is in full contact with the MAA, and the stable operation time of the system is extended.

3.1.2. Influence of column height on iron removal efficiency

The change trend of the iron ions concentration of the 150mm and 300mm column water is basically the same with the same filtration rate. The higher the filter column, the better the iron ion removal effect.

Figure 2(a)(b) shows that the iron ion concentration of the system effluent is not more than 0.28mg/L and 0.22mg/L after continuous operation of the 150mm column for 5h and 10h respectively when the filtration rate is 1m/h and 2m/h, and the removal rate is more than 86% and 89%. In the later stage, the iron ion concentration has always reached the standard stably. The iron ion concentration in the later period is always stable and up to the standard. The iron ion concentration reached the standard stably after the 300mm column was operated for 1h and 4h at the filtration rate of 1m/h and 2m/h. Under the two filtration rate conditions, the 150mm filter column needs to run 5 times and 2.5 times longer than the 300mm column, respectively.

The reason is that the higher the column, the longer the contact time between the raw water and the MAA in the filter column, and the more fully the iron ions are oxidized in the adsorbent. With the increase of running time, the iron active filter membrane gradually matures, the iron removal effect is gradually stable, and the dynamic iron removal effect is better.
3.2. The effect of filtration rate on defluorination and iron reduction in MAA

3.2.1. Effect of filtration rate on the effect of fluoride removal

The filtration rate also has a great influence. The change trend of the fluoride ion concentration in the effluent of the filter column with filtration rate of 1m/h and 2m/h is basically the same with the same height of the column.

(a) The height of the filter column is 150mm (b) The height of the filter column is 300mm

Figure 3. Effect of filtration speed on fluoride removal by MAA

Figure 3(a)(b) shows that the filtration rate increased from 1m/h to 2m/h, and the time for a 150mm column to stably reach the standard was reduced from 27h to 8h; for the same 300mm column, the time for the column to stably reach the standard was reduced from 102h to 28h.

The reason is that the higher the filtration rate, the shorter the residence time of the raw water in the column, which leads to insufficient adsorption time of MAA for fluoride ions and the concentration of fluoride ions in the effluent increases; under the condition of low rate, MAA can fully contact with fluoride ions that the removal effect of fluoride ions is better and the running time of the filter column stable up to standard is extended. It is consistent with the study of Ghorai et al. [10].

3.2.2. Effect of filtration rate on iron removal efficiency

At the same height, the change trend of iron ion concentration in the effluent is basically the same when the filtration rate is 1m/h and 2m/h.

(a) The height of the filter column is 150mm (b) The height of the filter column is 300mm

Figure 4. Effect of filtration rate on iron reduction effect of MAA

Figure 4(a)(b) shows that when the filtration rate has been increased from 1m/h to 2m/h, the time to produce iron ions to reach the standard for the 150mm column from 5h to 10h and from 1h to 4h for 300mm. The principle is that when the filtration rate is faster, the contact time between iron ions and the adsorbent is shorter, so the time for the formation of an iron active filter membrane on the surface of the adsorbent is slower. When the filtration rate is slow, the iron active filter membrane matures quickly, the iron ion effluent concentration gradually decreases and the effect is stable.
3.3 Comparison of fluoride and iron reduction effects between MAA and AA.
When the filtration rate was 1m/h and the column height was 150mm, the experiment compared and analyzed the effects of MAA and AA in removing fluoride and iron. The results are shown in Figure 6.

![Figure 5. Comparison of fluoride and iron removal effects of MAA and AA](image)

In Figure 5, the trends of MAA and AA's fluoride ion removal effect are basically the same. The stable up-to-standard running time is 11h and 27h respectively, and the MAA column is 2.5 times longer than the AA column. This result is because AA modified by MnOOH increases the adsorption sites of fluoride ions, and manganese ions increase the adsorption capacity of AA.

At the same time, it can be seen from Figure 5 that the AA and MAA columns need to run for 60h and 5h respectively, and the iron ion concentration can reach the target. The starting time for iron removal required for AA is 12 times that of MAA. Since there is no substance on the surface of AA that can promote the formation of high-valent iron oxides, it takes longer time to form an iron membrane.

4.Conclusions
The effect of removing fluoride and iron by MAA is significantly better than that of AA. Under the conditions of influent fluoride ion concentration of 5mg/L, iron ion concentration of 2mg/L, filtration rate of 1m/h, and column height of 150mm, AA column and MAA column's fluoride removal stable up-to-standard running time are 11h and 27h respectively, and MAA's fluoride removal stable running time is 2.5 times that of AA; the time for iron ions to steadily reach the standard was 60h for AA and reduced to 5h for MAA.

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