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# Study on the Mechanism of Humic Acid on Ultrafiltration Membrane

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### ABSTRACT

In view of the problem of clogging of ultrafiltration membrane in ultrafiltration process, the contamination mechanism of humic acid solution on ultrafiltration membrane was studied in depth. Through the ultrafiltration test of different concentrations of humic acid solution, it was found that humic acid can cause pollution to the ultrafiltration membrane, and the higher the humic acid concentration, the more serious the membrane contamination. The introduction of calcium carbonate particles can delay the progress of ultrafiltration membrane fouling in the initial stage of ultrafiltration, but as the ultrafiltration time increases, the membrane fouling rate increases rapidly. The kaolin particles can aggravate the contamination of the ultrafiltration membrane by humic acid, and the contamination can be washed away by the aqueous sodium hydroxide solution. The introduction of calcium ions can significantly aggravate membrane fouling and polymerize humic acid molecular chains. Sodium hydroxide and sodium hypochlorite alkali solution can effectively remove the humic acid pollution on the ultrafiltration membrane, wherein the sodium hydroxide solution has better cleaning effect, and the calcium carbonate-containing pollutant can be washed with a citric acid solution.

**Key words:** Ultrafiltration membrane; Humic acid; Membrane fouling; Calcium ion; Kaolin.

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## 1. INTRODUCTION

In recent years, ultrafiltration membrane technology has developed rapidly in China. The third generation of water purification technology with ultrafiltration technology as the core has been applied to the upgrading of waterworks, or as the core process of water quality safety for new waterworks. However, the ultrafiltration membrane pollution caused by natural organic matter, especially the irreversible pollution caused by the ultrafiltration membrane system after long-term operation, is still a key problem in the actual production of water supply plants [1]. Scholars have studied and reported the mechanism of organic matter causing ultrafiltration membrane contamination, such as membrane pore blockage and formation of filter cake layer [2]. Other scholars have studied the different pretreatment processes of ultrafiltration membranes to enhance the removal efficiency of organic matter, thereby alleviating membrane fouling caused by organic pollutants. In addition, studies have shown that the water chemical environment in the ultrafiltration membrane filtration process is also an important factor affecting the ultrafiltration membrane pollution, such as humic acid.

As the most important component of natural organic matter (NOM), humic substances react with oxidants in the disinfection process of drinking water to produce disinfection by-products with carcinogenic and teratogenic effects [3,4]. Jermann et al. [5] examined the effects of interactions between different NOM components (humic acid and polysaccharides) on the ultrafiltration membrane fouling mechanism and found that the presence of humic acid led to severe irreversible contamination. The separation mechanism of ultrafiltration is mainly mechanical screening and physical adsorption. Membrane pore size and surface properties are considered to be the two dominant factors controlling the separation performance of ultrafiltration membranes [6]. In the water, organic matter and colloidal particles with a particle size larger than the pore size of the membrane are deposited on the surface of the membrane to form a concentration polarization effect, which increases the filtration resistance, and finally forms a dense filter cake layer and causes serious membrane fouling, while the colloid having a particle diameter smaller than the pore diameter of the membrane The particles will adsorb in the pores of the membrane

and block the membrane pores leading to irreversible contamination [7].

Obviously, the pore size and pore size of the ultrafiltration membrane are closely related to the size distribution of colloidal particles and organic matter. The structure of the cake layer on the surface of the ultrafiltration membrane is closely related to the degree of membrane fouling, and the structure of the cake layer on the membrane surface is directly related to the pollutant composition of the membrane [8,9].

To this end, the humic acid-kaolin, humic acid-CaCo<sub>3</sub>, humic acid-CaCl<sub>2</sub> mixed solution was used as the test water, and the pollution of humic acid solution on ultrafiltration membrane at different concentrations was studied. The pollution of humic acid on ultrafiltration membrane under different inorganic substances. And to study the cleaning effect of different reagents on the ultrafiltration membrane after pollution.

## 2. MATERIALS AND METHODS

### 2.1 Test materials

Ultrafiltration Membrane (PES, UP150, Germany, Microdyn-Nadir), Humic Acid, HA, Sigma-Aldrich, St.Louis.Mo, Kaolin, AR, CaCl<sub>2</sub>, AR, CaCo<sub>3</sub>, AR, Sodium hydroxide, Tianjin Komi Chemical Reagent Co., Ltd., Sodium hypochlorite, Tianjin Komi Chemical Reagent Co., Ltd., Citric acid, Tianjin Komi Chemical Reagent Co., Ltd.

The test water was a humic acid solution having concentrations of 5 mg/L, 8 mg/L, 15 mg/L and 20 mg/L, respectively. Under the premise of maintaining the humic acid concentration of 15 mg/L, 1.5 g/L of calcium carbonate, 0.15 g/L of calcium chloride and 0.1 g/L of kaolin mixture were respectively added as test water.

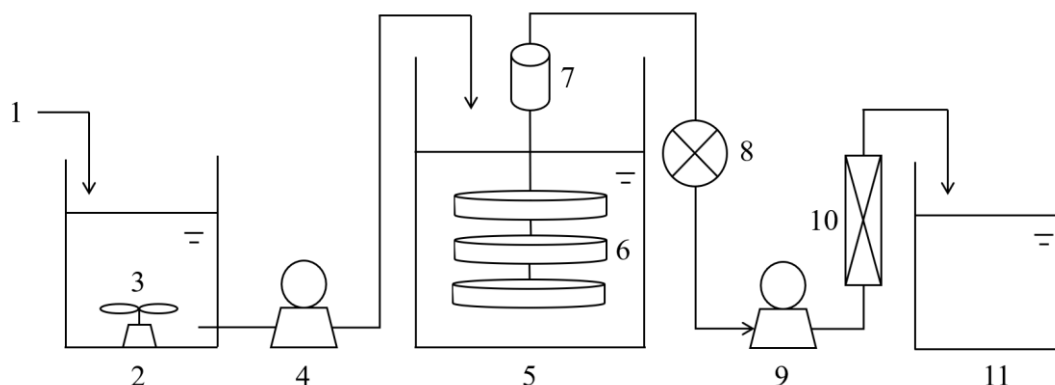
### 2.2 Test device

The test uses the MXU001 rotary cross-flow membrane separation water purifier produced by Suzhou Membrane Separation Technology Co., Ltd. The test flow chart is shown in Figure 1. The sewage treatment capacity of the equipment is 240 L·h<sup>-1</sup>, and the UP150 type PES ultrafiltration membrane produced by Minard Company of Germany has a throttling molecular weight of 150 kDa, an average pore diameter of 0.04 μm and an ultrafiltration membrane area of 2 m<sup>2</sup>. The test procedure was as follows: filtration with pure water for 10 min, the steady water membrane flux and transmembrane pressure difference were recorded after the steady state was reached; then the test water sample was filtered,

and the membrane flux and membrane pressure difference were measured every 15 min.

Rotary cross-flow membrane separation equipment, whose core processing component is an active cross-flow membrane module, realizes active cross-flow filtration through the programmed rotation of the membrane module under the

liquid, eliminates concentration polarization, increases membrane flux, and makes full use of Rotation produces flushing shear and filtrate turbulence, preventing the formation of a filter layer, effectively preventing membrane clogging and retarding membrane fouling without aeration and backwashing.



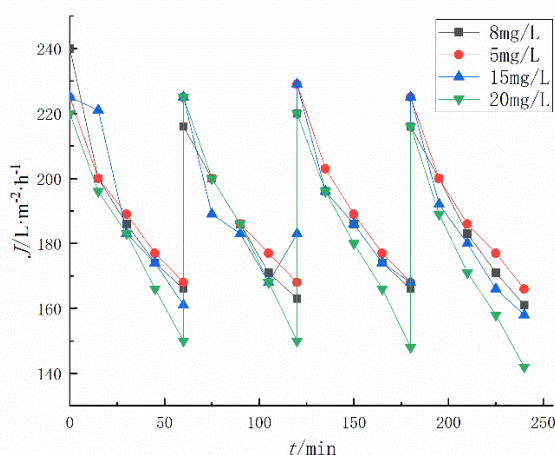
1-dosing; 2-original pool; 3-mixer; 4-feed pump; 5--ultrafiltration membrane tank; 6-active cross-flow membrane turntable; 7-drive motor; 8-pressure gauge; ;10-Rotor flowmeter; 11-outlet  
Figure. 1 Ultrafiltration test flow chart

### 3. RESULTS AND DISCUSSION

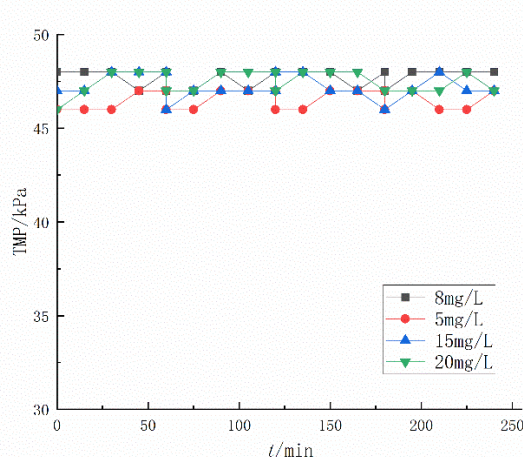
#### 3.1 Influence of different concentrations of humic acid solution on ultrafiltration membrane fouling

The humic acid solution was filtered at a concentration of 5 mg/L, 8 mg/L, 15 mg/L and 20 mg/L with ultrafiltration equipment, and each time the filtration was stopped for 1 hour, using a sodium

hydroxide solution with a mass fraction of 1% (pH= 9~10) Inflation for 1 hour, then repeat the previous test again. The test was performed 4 times in total, and the membrane flux and transmembrane pressure difference were measured every 15 minutes. The test results are shown in Figure 2.



(a) Membrane flux



(b) Transmembrane pressure difference

Figure. 2 Changes in membrane flux and transmembrane pressure difference of different concentrations of humic acid solution

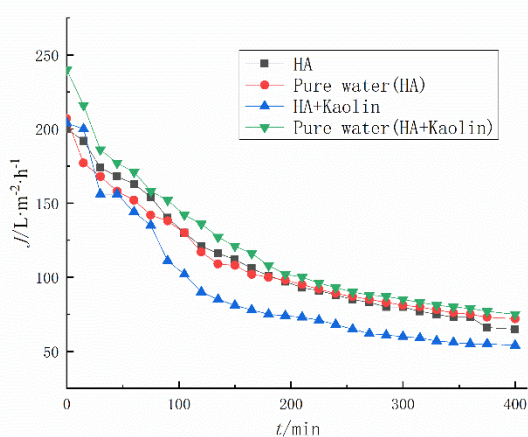
It can be seen from Fig. 2 that as the concentration of the humic acid solution increases, the membrane flux decreases continuously, and the membrane flux of the 20 mg/L humic acid

solution is the lowest, and the transmembrane pressure difference is the highest. Although the humic acid solution of 5mg/L, 8mg/L and 15mg/L satisfies this rule, the membrane flux difference is not large, indicating that the humic acid is equivalent to the ultrafiltration membrane in this concentration range. At the same time, it can be seen that the sodium hydroxide solution with a mass fraction of 1% can effectively remove the contamination of the ultrafiltration membrane by humic acid, the membrane flux can be restored by 90%, and the flux remains at a high level after three cleanings. This is because the humic acid can be dissolved in an alkaline solution which not only removes contaminants from the cake layer, but also removes humic acid that is clogged in the pores of the membrane. It can be seen from Figure (b) that the higher the humic acid concentration is, the higher the transmembrane pressure difference is at different concentrations of

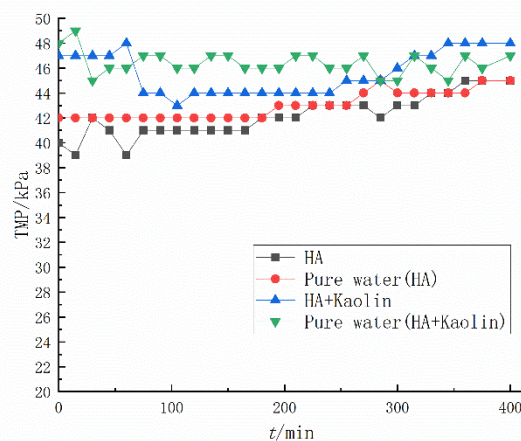
humic acid solution, but they are always maintained between 45 kPa and 50 kPa, after each cleaning. The membrane pressure difference will decrease slightly, but the decline will not be large.

### 3.2 Limit test of humic acid solution for ultrafiltration membrane fouling

In order to study the contamination of the ultrafiltration membrane by humic acid in the case of long-term filtration, and the state of the ultrafiltration membrane after washing. A mixed solution of 8 mg/L humic acid solution, 8 mg/L humic acid and 50 mg/L kaolin was used as the test water, and the membrane flux and the transmembrane pressure difference in the state of continuous uninterrupted filtration for 400 minutes were measured. Thereafter, it was incubated with a sodium hydroxide solution having a mass fraction of 1% for one hour, and then washed with pure water as test water. The other test conditions were the same as before.



(a) Membrane flux



(b) Transmembrane pressure difference

Figure. 3 Changes in membrane flux and transmembrane pressure difference under humic acid limit pollution

It can be seen from Fig. 3(a) that the membrane flux drops rapidly within 150 minutes before the filtration test, and the membrane flux value decreases by 50%. After that, the membrane flux decay rate decreases, and the membrane flux value slowly decreases to 60 L·m<sup>-2</sup>·h<sup>-1</sup>. This is because, in the initial stage of filtration, the contamination of the ultrafiltration membrane by the pollutants is mainly blocked by the membrane pores, and the humic acid is rapidly adsorbed on the pore walls of the membrane and continuously adsorbed and accumulated, so that the pores of the ultrafiltration membrane become small or even blocked. After the filtration was carried out for 150 minutes, the ultrafiltration

membrane was contaminated and entered the plugging stage of the filter cake layer. Contaminants continue to accumulate on the surface of the ultrafiltration. After the surface of the ultrafiltration membrane is completely covered, the interaction between the contaminants causes the contaminant layer to continuously thicken, eventually forming a cake layer. At the same time, it can be seen that the membrane flux of the mixed solution of kaolin and humic acid is lower than that of the humic acid solution, and the rate of membrane flux decline in the early stage of the mixed solution is much larger than that of the humic acid solution. It shows that kaolin can aggravate the contamination of ultrafiltration



membrane by humic acid. This is because the kaolin particles can be combined with humic acid, so that the interaction between the contaminants is enhanced, and the contamination process of the ultrafiltration membrane by the pollutants is accelerated.

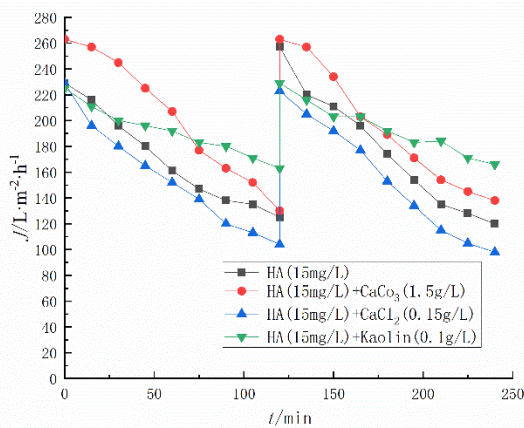
After washing with a 1% sodium hydroxide solution, the membrane flux returned to the original value. It shows that sodium hydroxide can also remove the mixed pollution of humic acid and kaolin. At the same time, it was observed that after cleaning the ultrafiltration membrane contaminated with mixed pollutants, the initial value of the pure water membrane flux was slightly larger than the initial value of the membrane flux of the contaminated solution. This is because the ultrafiltration membrane resistance itself is lower than the membrane resistance when the water is filtered, and the sodium hydroxide solution is more alkaline, which causes certain damage to the surface of the ultrafiltration membrane, and the pore size of the ultrafiltration membrane increases. Naturally, the membrane flux is increased.

It can be seen from Fig. 3(b) that the transmembrane pressure difference between the humic acid and kaolin mixed solution is higher than that of the humic acid solution, indicating that the mixed solution is more polluted to the

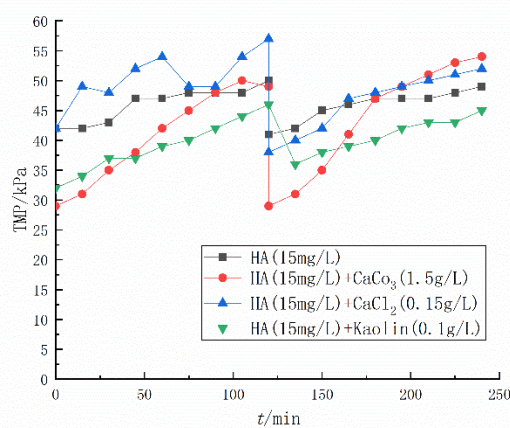
ultrafiltration membrane, and this conclusion is also related to the membrane flux. The phenomenon presented by the curve is consistent. At the same time, it can be seen that the overall change of the transmembrane pressure difference is not large, showing a small increase trend.

### 3.3 Influence of different inorganic substances on the contamination of humic acid ultrafiltration membrane

Configure 15mg/L humic acid, 15mg/L humic acid and 1.5g/L calcium carbonate mixture, 15mg/L humic acid and 0.15g/L calcium chloride mixture, 15mg/L humic acid and An ultrafiltration test was carried out as a test solution of a 0.1 g/L kaolin mixture. After filtering for 2 hours, the ultrafiltration membrane was infested and washed in the cleaning solution for 1 hour, except that the ultrafiltration membrane contaminated with calcium carbonate was washed with a citric acid solution having a mass fraction of 1%, and the remaining membranes were each used with a mass fraction of 1%. The sodium hydroxide solution is incinerated and cleaned. After washing, the ultrafiltration test was repeated in the original test solution, and the membrane flux and the transmembrane pressure difference were measured every 15 minutes, and the change curve is shown in Fig. 4.



(a) Membrane flux



(b) Transmembrane pressure difference

Figure 4 Variations in flux and transmembrane pressure difference of different water samples

It can be seen from Fig. 4(a) that the average flux of the mixed solution containing calcium chloride is the lowest, the membrane flux changes a lot, and the membrane fouling degree is the most serious. The membrane flux value under the simple humic acid solution is the second lowest. This indicates that the synergistic effect of humic acid

and calcium ions has a significant effect on the flux of the ultrafiltration membrane, which aggravates the contamination of the ultrafiltration membrane. This is because the humic acid molecular chain contains easily dissociated functional groups such as -COOH and -OH. The addition of calcium ions acts as a "salt bridge" [10], which can

be complexed with humic acid and with ultrafiltration. The surface of the membrane is electrostatically bonded to form a larger polymer, which is more easily adsorbed onto the surface of the ultrafiltration membrane and the pores of the ultrafiltration membrane, resulting in a sharp decrease in membrane flux. However, as time passes, the gel layer concentration increases, the formed structure becomes dense, the filtration resistance becomes large, and the membrane flux is further lowered.

In the absence of calcium ions, humic acid adsorbs to the surface of the membrane, causing the membrane to carry a strong negative charge. With the addition of calcium ions, some calcium ions react with humic acid to form a complex, enhancing molecular shielding. In addition, another part of the free calcium ions can neutralize the negative charge adsorbed on the surface of the membrane, causing the zeta potential of the membrane surface to move in the positive direction, reducing the charge intensity, thereby weakening the electrostatic repulsion between the ultrafiltration membrane surface and the humic acid molecule. As a result, humic acid is more adsorbed on the surface of the ultrafiltration membrane, causing a decrease in membrane flux and aggravation of membrane fouling.

At the same time, it was found that the initial membrane flux of the calcium carbonate suspension decreased slowly, and the membrane flux decreased rapidly after 1 hour. At the end of the ultrafiltration test, the membrane flux was comparable to that of the pure humic acid solution. This may be because in the initial stage of ultrafiltration, calcium carbonate particles are rapidly adsorbed on the surface of the ultrafiltration membrane to form a filter cake layer, which hinders the humic acid from entering the pores of the ultrafiltration membrane to some extent, so that the membrane pore plugging process is delayed. However, due to the large particle size of the calcium carbonate particles, the pores of the membrane could not be blocked, and the particles on the surface of the ultrafiltration membrane could not form a dense layer. After the ultrafiltration, the humic acid began to block the pores of the membrane, resulting in a rapid decrease in membrane flux.

#### 4. CONCLUSION

Humic acid can cause pollution to the ultrafiltration membrane, and the higher the concentration,

the more serious the pollution. The humic acid solution is equivalent to the ultrafiltration membrane at a concentration of 5 mg/L to 15 mg/L, and the sodium hydroxide solution can effectively remove membrane fouling caused by humic acid. The addition of kaolin can aggravate the contamination of the ultrafiltration membrane by humic acid and enhance the plugging stage of the filter cake layer. The sodium hydroxide alkali solution can remove the mixed pollution of humic acid and kaolin on the ultrafiltration membrane, but cleaning too frequently will damage the surface of the ultrafiltration membrane and damage the membrane pores, so that the initial membrane flux is increased. After mixing with calcium ions, the humic acid solution significantly enhanced the contamination of the ultrafiltration membrane, and the flux decreased significantly. The "salt bridge" effect of calcium ions helps the cleavable functional groups on the humic acid molecular chain to form a polymer and is more easily adsorbed on the surface of the ultrafiltration membrane. The introduction of calcium carbonate particles will delay the membrane fouling process at the beginning of ultrafiltration, but then the ultrafiltration membrane will be accelerated, and the final contamination level will be comparable to that of pure humic acid solution.

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