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Study on the pollution mechanism of drinking water source water to ultrafiltration membrane

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ABSTRACT

The effects of particulate matter (represented by humic acid, kaolin and algae) on ultrafiltration membranes in micro-polluted water sources were investigated, and the mechanism of ultrafiltration membranes was further understood with the change of membrane flux and transmembrane pressure difference. The results showed that the removal rate of kaolin and algae by UF membrane was over 99%, while the removal rate of humic acid was only about 72%. Moreover, the extent of UF membrane fouling caused by humic acid was larger than that caused by kaolin and algae. The higher the concentration of humic acid, the more serious the membrane fouling was. Ultrafiltration membranes contaminated by humic acid were washed by 0.05mol/L NaOH alkali and 0.05mol/L HCL acid. The permeability of the membranes was restored to 91.24% of the cleaned surface, which was better than that of pure water, sodium hypochlorite and sodium hydroxide. It can provide better guidance for choosing appropriate cleaning agents for ultrafiltration membrane fouling.

Key words: Ultrafiltration membrane; Humic acid; Kaolin; Algae

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Introduction

At present, the drinking water source of residents in mountainous rural areas in China mainly comes from river water, river water, well water and reservoir water. The water treatment method is relatively simple, mainly based on faucet filter and direct heating. Very few residents adopt more professional and effective. The water treatment process treats drinking water. By the end of 2010, more than 400 million rural residents in China have used direct water to draw water. Nearly 100 million rural residents have not used any water treatment facilities and direct drinking water. At the same time, with the improvement of people's living standards, the drinking water safety standards have been continuously improved, and the traditional water treatment process cannot meet the requirements of safe drinking water standards. Therefore, it is very urgent to seek a new water treatment process. Ultrafiltration membrane can effectively retain water particles in water, and it is widely used in industrial wastewater reuse and urban drinking water, with its advantages of good filtration performance, small footprint, short process, energy saving, low cost and no secondary pollution. However, the problem of water pollution is also becoming more and more serious, and the main substance causing water pollution is derived from water particles in water bodies.^[1]

The composition of water particles can be divided into three parts: organic matter, minerals and biological materials. In this experiment, humus, kaolin and algae were used to replace organic substances, mineral substances and biological substances in natural water bodies. Humus in natural water is generally derived directly from the decomposition of plants and animals in water, especially lignin, by microorganisms, or a relatively stable product formed by the condensation

of smaller molecules such as triglycerides, sugars and amino acids. As a disinfectant in China's traditional water treatment process, chlorine gas has the advantages of high efficiency and economy, and is widely used in the field of water treatment in China. Humic acid in water can react with chlorine disinfectants to form organic disinfection by-products (DBPs)^[2,3], which are extremely harmful to human health. At the same time, humic acid is also a major precursor to the production of "three" substances in the chlorination process. Clay minerals are one of the most important colloids in natural waters and constitute the core skeleton of water particles. As the most common clay mineral in nature, kaolin combines with hydrated oxides and humus to form the most active components in the particles, which affects the geochemical behavior of surface elements and the migration, transformation and migration of various pollutants in water. Home. Membrane fouling caused by particulate matter in water has been a major problem that restricts the further promotion of ultrafiltration membranes, especially in summer, algal blooms exacerbate membrane fouling^[4]. Accordingly, it is necessary to conduct further research on the removal of particulate matter in water.

1. Materials and methods

The removal of humus and kaolin is in the experimental stage in China, and less engineering practice is carried out, mainly in the laboratory water distribution research; summer ultrafiltration algae can ensure the stable operation of water plants and water quality, but the water production rate caused by membrane pollution The decline is in contradiction with the high-load operation of the summer water plant, so the development of the experiment has certain engineering value.

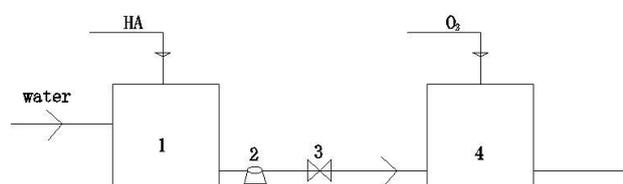
1.1 Test reagent

Humic acid, kaolin, potassium permanganate and ferric chloride are all excellent grade; 1% hydrochloric acid, 0.05mol/L NaOH solution.

1.2 Preparation of water samples

The experiment was carried out in the laboratory of Suzhou Membrane Separation Technology Co., Ltd. The experimental water samples were prepared by artificial simulation. The tap water was pumped into the 70L water distribution tank, and then humic acid and kaolin were added to the water distribution tank to obtain experimental water.

1.3 Experimental device



1, water tank 2, water pump 3, valve 4, ultrafiltration equipment

1.4 Method for measuring humic acid concentration

Take 250mL of known concentration of humic acid solution in the evaporating dish, add 1mL of 0.05mol/L ethylenediaminetetraacetic acid (EDTA solution), evaporate and cool, add 25mL of mixed extract (0.1mol/L pyrophosphate sodium solution is mixed with 0.1% LL/L sodium hydroxide solution by volume 1:1. After the mix-

In order to understand the membrane fouling situation more accurately and intuitively, the experiment used a monolithic membrane module and conducted a small-scale experiment in the laboratory of Suzhou Membrane Separation Technology Co., Ltd. The membrane module is supplied by Minard, Germany, and is made of polyether-sulfone resin (PES), which is capable of separating particles with a molecular weight of more than 1500 Daltons and an effective area of 0.33 m². It uses an external pressure mode of operation and runs flux. It is about 35L/h. The experimental setup is shown in Figure 1.

ed extract is fully contacted with the dried product, it is transferred to a centrifuge tube, allowed to stand for 24 hours, and then centrifuged at 25 °C, 400 r / min. 20min. The supernatant was taken and the absorbance of the supernatant at 340 nm and 440 nm was measured and recorded as E3 and E4 [5]. The corresponding absorbance is shown in Table 1.

Absroance(Abs)	Humic acid concentration (mg/L)	Wavelength (nm)						
		2	4	5	6	8	10	15
340		0.027	0.074	0.10	0.13	0.22	0.29	0.43
440		0.007	0.009	0.01	0.02	0.06	0.10	0.13

	4	9	9	1	2
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Table 1 UV spectrum of different concentrations of humic acid in water samples

Taking (E3-E4) as the abscissa and the humic acid concentration as the ordinate C (mg/L), the equation of the standard curve and the correlation coefficient R2 are:

$$Y=45.695(E3-E4)+1.0532$$

$$R2=0.997$$

Measure the humic acid solution of unknown concentration and determine the concentration of humic acid at an unknown concentration by measuring E3 and E4 according to the above

Steps degree.

2. results and talk

2.1 Membrane flux in the presence of humic acid (HA) and kaolin alone

In this experiment, the effects of humic acid and kaolin on the membrane flux and the removal rate of the membrane were investigated. The acidity and alkalinity of the membrane flux when humic acid and kaolin were present alone are shown in Fig. 2

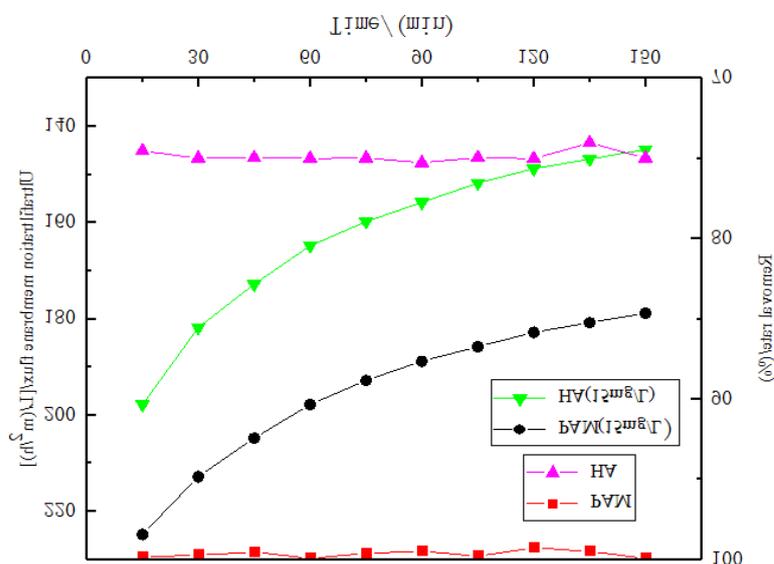


Figure 2 Membrane flux decay in the presence of kaolin and humic acid alone

The removal rate of kaolin by PES ultrafiltration membrane can reach 100%, because the particle size of kaolin is almost more than 1µm, which is much larger than the pore size of ultrafiltration membrane, that is, almost all kaolin is trapped on the surface of ultrafiltration membrane to form dense filtration. Cake layer. The ultrafiltration membrane has a low removal rate of humic acid of only 72%. This is because the molecular weight and chemical structure of humus vary greatly with the degree of humification. Humic acid (HA) and fulvic acid (FA) constitute the most reactive component of humus, and its molecular weight

is also large. The difference. It is generally believed that the average molecular weight of humic acid ranges from 50 000 to 100 000 and that there are few molecules exceeding 250 000. The molecular weight of fulvic acid is much smaller than that of humic acid, and the molecular weight of typical fulvic acid is usually in the range of 500-2 000. The ultrafiltration membrane was unable to retain the fulvic acid in the humus, resulting in a removal rate of humus by the ultrafiltration membrane of 72%. It can be seen from Fig. 2 that the membrane flux attenuation rate caused by humic acid in the two pollutants is higher

than that of the ridge. The removal rate of the two can be explained as follows: the kaolin particle diameter is much larger than the ultrafiltration membrane pore size, and the membrane is completely trapped. The surface, while the humic acid particles are small, it is easy to enter the ultrafiltration membrane pores to cause the membrane pores to block or narrow, which leads to the membrane flux decay rate much greater than the membrane flux decay rate caused by kaolin [6].

2.2 Analysis of membrane flux characteristics when kaolin, Ca²⁺, HA coexist

Because clay minerals, hydrated oxides and humus combine to form the most active components in water particles, hydrated oxides mainly include hydrated oxides such as aluminum, iron, calcium and silicon. In this paper, Ca²⁺ is the research object. Figure 4 shows the change of membrane flux corresponding to the presence of kaolin, Ca²⁺ and HA, and the presence of humic acid alone at a concentration of 15 mg/L.

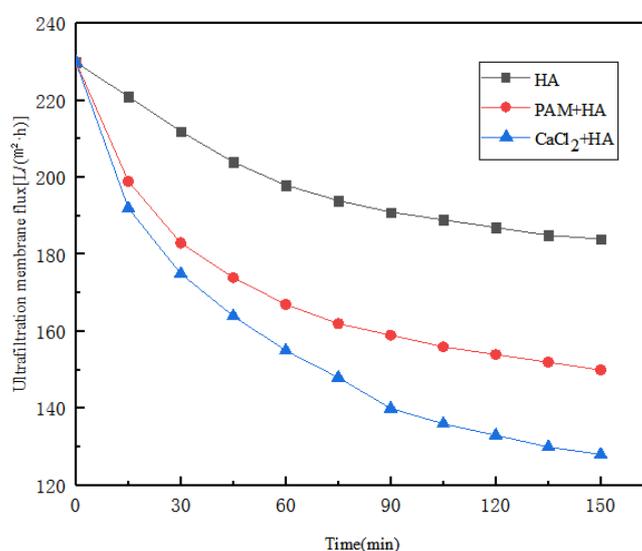


Fig. 3 Membrane flux attenuation diagram of humic acid, kaolin and Ca²⁺ coexisting

It can be seen from Fig. 3 that when the humic acid is present alone, the membrane flux decay rate is lower than that of kaolin, Ca²⁺ and humic acid. When kaolin and humic acid coexist, the membrane flux decay rate is significantly greater than the membrane flux decay rate when humic acid is present alone. The researchers showed that the membrane fouling when kaolin and humic acid coexisted was significantly larger than that of humic acid alone. They believed that humic acid was mixed with kaolin, and humic acid adsorbed on the surface of kaolin particles, which hindered the agglomeration between kaolin particles and formed a dense cake layer, which

increased the rate of membrane fouling [6]. However, studies by Zularisam et al. showed that the membrane fouling of kaolin and humic acid was significantly smaller than that of humic acid alone. Some of the humic acid adsorbed on the surface of kaolin due to the coexistence of kaolin and humic acid. It reduces the probability of humic acid entering the pore size of the ultrafiltration membrane, thereby slowing the rate of membrane fouling [7].

As can be seen from Fig. 3, the membrane flux attenuation is increased after the addition of calcium chloride. This is because humic acid is a long chain of molecules, or two- or three-dimensional

ional hinge-like macromolecules whose surface charge is generated by the ionization of acidic groups. Due to the mutual repulsive force of surface charge (for example, COO⁻), the molecule is in a state of micro-expansion. When Ca²⁺ is present, the molecule is compressed to form a larger polymer due to charge neutralization [8], making HA easier. It is adsorbed on the surface of the membrane and within the pore size of the membrane to form a dense oxide film, resulting in a sharp decrease in membrane flux. However, some researchers believe that in the absence of Ca²⁺, as the concentration of humic acid increases, the more humic acid adsorbed on the surface of the membrane, due to the negative

charge of humic acid, the presence of Ca²⁺, the surface of the membrane The potential of Zate moves to the square, which strengthens the shielding between molecules, reduces the charge intensity, weakens the electrostatic repulsion between the membrane surface and the humic acid molecules, and causes the humic acid to adsorb more to the surface of the membrane, forming a dense Filter cake layer, which increases the rate of membrane fouling [7]

2.3 Ultrafiltration membrane removal of algae

The experiment was carried out in the Maoshan River in the lower reaches of Taihu Lake. The conventional water quality indicators during the test period are shown in Table 2.

Table 2 Raw water quality analysis table

Water temperature (°C)	pH value	Turbidity	Number of algae cell (105/L)	CODMn (mg/L)	DOC (mg/L)	UV254 (cm-1)
20-25	7.2-7.4	11.8-14.9	600-800	3.52-4.23	2.79-3.56	0.035-0.039

The experimental process is shown in Figure 1. The river water enters the original water tank after pre-oxidation and coagulation sedimentation in the water distribution tank, and then enters the ultrafiltration equipment through the raw water tank. In this experiment, polyaluminum chloride

was used as a coagulant, and the dosage was 25 mg/L. Potassium permanganate was used as a pre-oxidant to study the effect of different dosages of potassium permanganate on the removal rate of algae cells and turbidity.

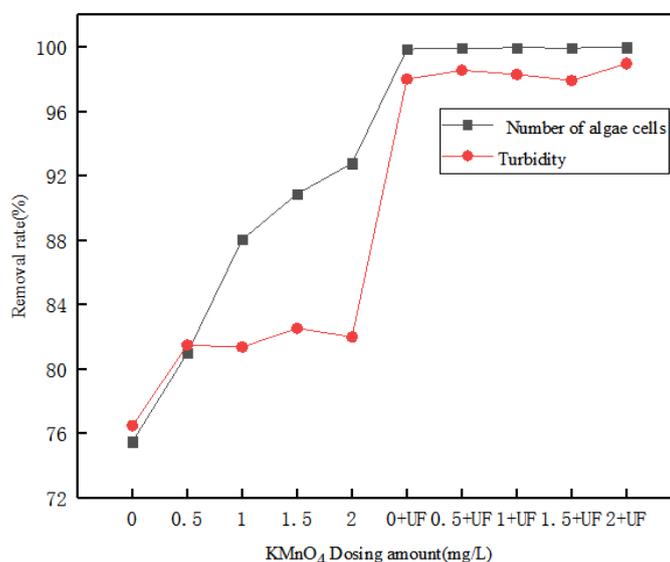


Figure 4 Removal rate of algae cells and turbidity by KMnO₄ dosage

The removal rate of algae cells and turbidity is shown in Figure 4 after KMnO₄ is filtered by coagulation sedimentation and ultrafiltration membrane at different dosages. It can be seen from Fig. 4 that the removal rates of algae cells and turbidity by coagulation and sedimentation were 75.32% and 76.36, respectively, without KMnO₄ pretreatment and ultrafiltration membrane filtration. When the dosage of KMnO₄ is small, the removal rate of turbidity is higher than that of algae cells. With the increase of KMnO₄ dosage, the removal rate of algae cells is higher than turbidity, because KMnO₄ can oxidize organic The gelatinous layer further destroys the algae enzyme activity and causes it to die. In addition, the hydrated manganese dioxide formed by the reaction of KMnO₄ with water adsorbs on the surface of the algae cells, increasing the specific gravity of the cells and making them easily removed by coagulation precipitation. On the other hand, regardless of the influent conditions, the ultrafiltration membrane has a removal rate of 100% for algae cells and a turbidity removal rate of 99%. Since the ultrafiltration membrane has an average pore diameter of 0.04 μm and the algae cell diameter is much larger than its pore diameter, it is theoretically possible to completely

retain the algae cells. However, the ultrafiltration membrane directly treating high algae water will cause serious membrane fouling problems, so it is especially important to reduce the algae content in the membrane water.

2.4 Membrane fouling and cleaning

Since the advent of the film, the problem of ultrafiltration membrane pollution has been one of the key and difficult issues for research staff. For a long time, people have been working on the law of membrane fouling and membrane fouling in order to find suitable backwashing intervals, backwashing methods and membrane cleaning agents, and even to find a cleaning agent that has no effect on membrane life. Membrane pollution brings a series of problems that need to be solved urgently. Therefore, it is necessary to conduct further research on the problem of membrane fouling in order to find a more efficient membrane cleaning agent.

Considering that the humic acid is weakly acidic, an alkaline cleaning agent is used. The membrane was cleaned by using 0.01 mol/L HCL, 0.01 mol/L NaOH, 0.1 mol/L NaOCL, 0.01 mol/L NaOH and 0.01 mol/L HCL acid and alkali as cleaning agents. The effect of cleaning time on membrane flux recovery is shown in Figure 5.

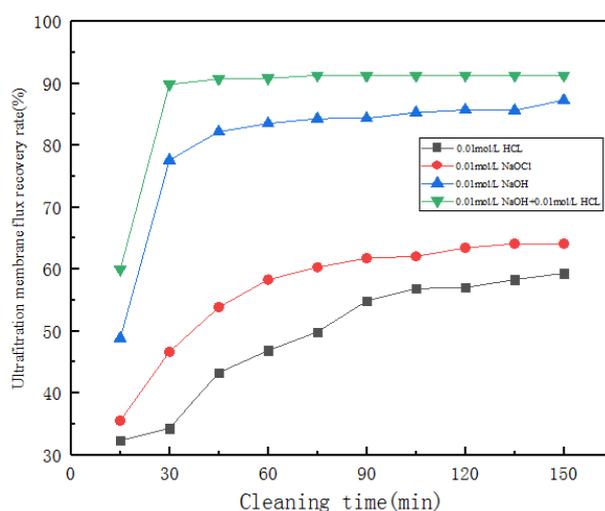


Figure 5 Effect of cleaning time on membrane flux recovery rate

It can be seen from Fig. 5 that the membrane flux recovery rate is 91.24%, which is the highest recovery rate of the ultrafiltration membrane after the alkali washing and pickling treatment, indicating that the acid-base composition has contamination of the membrane surface caused by humic acid. Very good removal effect. The membrane flux after cleaning with 0.01mol/L HCL can only recover to 59.37% of the clean membrane surface, the membrane flux after NaOCL cleaning is restored to 65.95% of the clean membrane surface, and the membrane flux after NaOH cleaning is restored. To 85.69% of the clean film surface. The effect of washing with sodium hydroxide and sodium hydroxide combined with hydrochloric acid solution is better, and the cleaning time is shorter.

3. Conclusion

(1) The degree of contamination of ultrafiltration membrane by kaolin and the contamination of ultrafiltration membrane by humic acid, and the higher the concentration of humic acid, the more serious the membrane fouling. Mainly because: the interaction between humic acid molecules is small, and its agglomeration ability is smaller than that of kaolin, which makes humic acid easy to enter the pores of the membrane, which causes membrane clogging, resulting in a sharp decrease in membrane flux.

(2) Compared with the humic acid-contaminated membrane, the membrane fouling caused by the coexistence of kaolin and humic acid is more serious. The humic acid adsorbs on the surface of the kaolin particles, hindering the agglomeration behavior of the kaolin and forming a dense The filter cake layer, which increases the degree of membrane fouling.

(3) In the coexistence system of humic acid and Ca^{2+} , Ca^{2+} neutralizes the negative charge carried by the humic acid adsorbed on the surface of the membrane, which reduces the surface charge intensity and weakens the electrostatic repulsion between humic acid molecules. The effect accelerates the rate at which humic acid

adsorbs on the surface of the membrane and aggravates membrane fouling.

(4) The degree of membrane fouling when humic acid and Ca^{2+} coexist is higher than that of humic acid and kaolin. This is because Ca^{2+} not only reacts with humic acid to form a complex, but also increases the shielding effect between molecules. And the negative charge adsorbed on the surface of the membrane. The adsorption of humic acid on the surface of the membrane causes a decrease in membrane flux and aggravates membrane fouling.

(5) Pickling with hydrochloric acid can not effectively remove the pollutants on the surface of the membrane. Sodium hydroxide or 0.05mol/L hydrochloric acid washed with 0.05mol/L sodium hydroxide has good cleaning effect. The membrane flux can be Restored to the original cleaning membrane surface 85.69%, 91.24%, providing guidance for membrane cleaning.

(6) Pretreatment of KMnO_4 can effectively increase the removal rate of algae cells by coagulation and sedimentation, up to 18.32%, but the removal of turbidity is not obvious, only about 7%.

(7) Pre-oxidation of KMnO_4 can effectively reduce membrane fouling, so that algae removal in summer can improve the water production rate to some extent and the high-load operation in summer water plants.

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