

The Effect of Humic Acid on Ultrafiltration Membrane Fouling

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Abstract. To investigate the fouling phenomena of ultrafiltration membrane caused by humic acid solution, four important parameters such as time, pressure, pH value and calcium ion concentration were considered in the experiment. The changes of various membrane fouling resistances and humic acid retention rates were also analyzed. Moreover, the surface and cross section of the clean and fouled ultrafiltration membranes was observed by emission scanning electron microscope. The results show that a rapid fouling takes place due to internal pore adsorption, pore blocking and a fouling gel developed on the membranes. Concentration polarization plays a main role in initial period. The pH value as the important parameter decided what kind of fouling playing the main role. As pH value ranges between 6 and 9, the membrane fouling is relatively light. Both acid and alkali can aggravate humic acid fouling: acid promotes the formation of the gel layer, while alkali accelerates the blockage of membrane hole. The existence of calcium ion will aggravate the fouling of ultrafiltration membrane and reduce the rejection rate of humic acid.

Keywords: Humic acid, Ultrafiltration, Membrane fouling

1. Introduction

Membrane separation technology is an advanced technology, which is applied to further waste water treatment. However, humic acid (HA) is a major component of organic matter in waste water. It can cause serious fouling problems during membrane filtration processes for water treatment [1-2]. The pollutant caused by humic acid on the membrane surface and within membrane pores lead to flux decline, and restrict the wide application of membrane separation technology.

In recent years, more and more scholars are concerned about the effect of humic acid on the membrane system performance [3-5]. The purpose of this pilot study is to observe the complex phenomena and understand the mechanism of membrane fouling caused by humic acid, particularly the impact of pH value and calcium ion concentration in the formation of membrane fouling. The changes of membrane fouling resistance in the filtration process were also studied.

2. Materials and Methods

2.1. Membranes and Equipments

The experimental studies were performed in a lab-scale apparatus developed in the laboratory, which is schematically shown in Fig. 1. The apparatus consists of a single UF hollow fiber membrane module, which simulates the hydrodynamic and operational characteristics of large scale units. The membrane is made of polysulfone (PS) with MWCO 50 kDa.

2.2. Feed Solution

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Take a certain amount of humic acid and make it dissolved in sodium hydroxide solution. After the insoluble substance was filtered by millipore filter membrane then dissolved original liquid was ready, which must be saved in a sealed brown container for later usage. Fresh humic acid solutions at a concentration of 50 mg/L were prepared for each experiment using original liquid and deionized water. The experiments operated at pressure 0.2 MPa. The solution pH value was adjusted using a few drops of HCl or NaOH. Experiments were carried out in the pH value range between 5 and 10. The duration of the dead-end filtration experiment was 1 h. Finally, in order to study the effect of calcium ions, all types of experiments were performed at calcium ion concentrations of 0, 0.5, 1, 2, 4 and 6 mmol/L, by adding appropriate amount of CaCl₂ to the feed solutions.

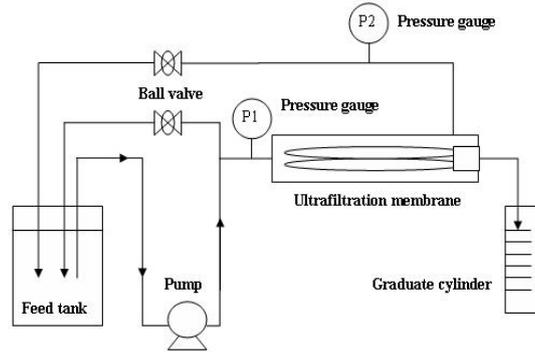


Fig.1: Schematic diagrams of membrane fouling test unit

2.3. Analysis Methods

Humic acid solution has a characteristic absorption peak at 254 nm wavelength. According to the linear relationship between absorbency and concentration, the penetrant humic acid concentration can be measured. And the humic acid retention rate of ultrafiltration membrane can be figured out. Pictures of fouled membranes were taken by emission scanning electron microscope (TECNAIG2F20, USA).

Before the experiment, clean membrane fibers must be soaked in ethanol for 6 h and in deionized water for 24 h respectively. Then preload for 1 h to make sure the flux stable before the trial.

The membranes fouling was established in terms of J_t/J_0 , where J_0 is the filtration flux of new membrane, L/(m²·h); J_t is the membrane flux at time t, L/(m²·h).

J_t can be calculated in terms of

$$J_t = \frac{V}{A \cdot t} \quad (1)$$

where V denotes volume of permeate sample collected within time t, L; A indicates the effective membrane surface, m².

$$J_t = \frac{\Delta P}{\mu R_t} \quad (2)$$

where ΔP is transmembrane pressure, MPa; μ is solution viscosity, Pa·s; R_t is total resistance, m⁻¹. It can be obtained after the filtration experiment with water sample; $R_t = R_m + R_{cp} + R_c + R_p$ where R_m is resistance of clean membrane, m⁻¹. It can be obtained after the filtration experiment with deionized water; R_c is cake resistance; R_p is pore blocking resistance, m⁻¹; R_{cp} is concentration polarization resistance, m⁻¹ [6-7].

Fouling resistance R_f was defined as

$$R_f = R_{cp} + R_c + R_p$$

$R_m + R_c + R_p$ can be obtained after the filtration experiment of fouled membrane with deionized water; $R_m + R_p$ can be obtained after the filtration experiment of the washed membrane with deionized water; In summary, R_m , R_{cp} , R_c and R_p can be obtained.

3. Results and Analysis

3.1. Effect of Operating Time

Fig. 2(a) shows that membrane flux decreased with a steep curve and reached a stable state after a long time. While membrane flux decreased significantly within 25 minutes, and decreased to 65% of the starting flux 5 hours later. The rejection of humic acid declined sharply within 25 minutes. Then it changed little later. As Fig. 2(b) shows, membrane fouling resistances changed quickly. In a short term, concentration polarization phenomenon was significant, it played a major role first and then gradually replaced by the membrane pore blockage resistance and gel resistance. Membrane fouling resistances continued to grow higher by turns. Fig. 3(a) shows that humic acid adsorbed strongly onto PS ultrafiltration membrane surface. This is because humic acid has a high active surface and two gender characteristics: one is the hydrophilicity of $-COOH$ and $-OH$ functional groups; another is the hydrophobicity of central aromatic and fat molecules groups [8-9]. In solution, humic acids exist in the shape of loose micellar aggregates which show the characteristics of colloidal particles. Since humic acid can be easily absorbed onto membrane surface and into membrane pores, the hydrophobicity of polysulfone membrane made the interaction of membrane and humic acid trend great, resulting in heavy absorption pollution and flux decline significantly.

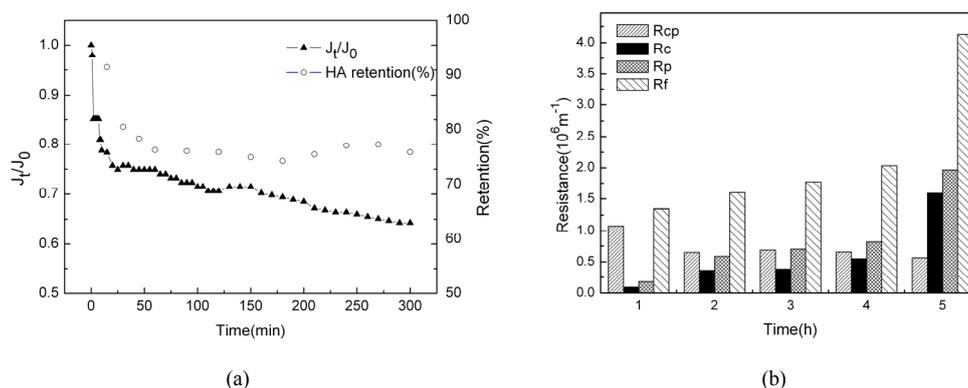


Fig. 2: Effect of operating time on membrane fouling: (a) effect of time on the flux and retention; (b) effect of time on resistances

3.2. Effect of Operating Pressure

As shown in Fig. 3(a), with time, membrane flux declined quickly under different pressure. The higher the operating pressure was, the bigger the rate of flux declined. Under low pressure membrane flux declined relatively flat. Fig. 3(b) shows that concentration polarization played a major role at low pressure, while membrane pore was blocked lightly, and no cake layer formed. At high pressure increased the concentration polarization made humic acid precipitated on the film surface and formed gel layer. With the increase of pressure, the cake resistance, which played a major role in blocking, increased significantly. Humic acid micelles rapidly absorbed onto membrane surface with bridge-type blockage under high pressure. Then the surface and inner of the membrane both were blocked, resulted in sharp decline of flux and seriously pollution.

3.3. Effect of pH Value

The experiment reviewed membrane fouling process at various pH values. As Fig. 4 shows, in acidic conditions, the decline rate of membrane flux increased with the decrease of pH value, while in alkaline conditions, the rate increased as the pH value increased. In Fig. 5 cake resistance played a major role under

acidic conditions, and its size decreased with the increase of pH value. Membrane pore blocking resistance played a major role under alkaline conditions, and its size increased with the increase of pH value. As Fig.6 shows, with the increase of the pH value the retention rate of humic acid decreased. Such a phenomenon is due to the change of pH value, it not only affects the state and capacity of humic acid molecules electric charge, but also changes the properties of membrane surface, causing the interaction between membrane surface and solution. This phenomenon is related with the complex structure of humic acid molecules. Humic acid is reticulate macromolecule polymer which is linked by hydrogen bonds of functional groups. The basic unit of humic acid is aromatic nucleus. Among them, more active functional groups are carboxyl and phenolic hydroxyl groups. Whether hydrogen ion of Carboxyl and phenolic hydroxyl groups can be dissociated or not, is related to the pH value of solution. When the pH value is low, the existing forms of carboxyl and phenolic hydroxyl groups are -COOH and -OH respectively. When the pH value is high, the existing forms are -COO- and -O- [10]. Since the dissociation degree of carboxyl group in humic acid molecules increases at high pH, the molecules take more negative charges. Spatial exclusion that engendered by functional groups of humic acid make the molecules existed in a more stretched state in solution. While the pH value is higher, because membrane surface has absorbed more OH-, it takes more obvious negative electrical charges. Owing to the increase of the electrostatic repulsion between membrane surface and the organic molecules, the absorption and precipitation of humic acid in the membrane weakened, Thus membrane fouling phenomena are light when pH value is low.

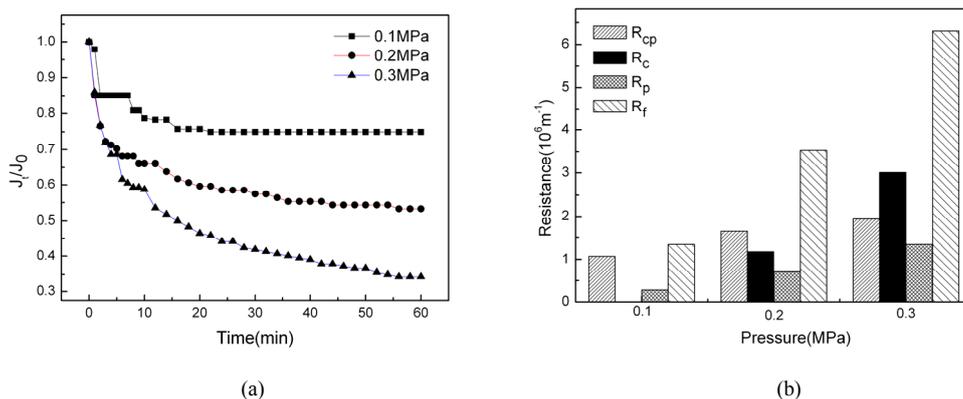


Fig.3: Effect of pressure on membrane fouling: (a) effect of pressure on the flux; (b)effect of pressure on resistances

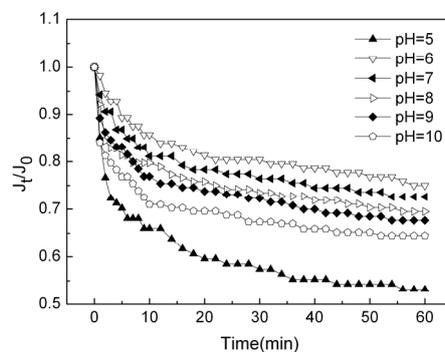


Fig.4: Effect of pH on membrane flux

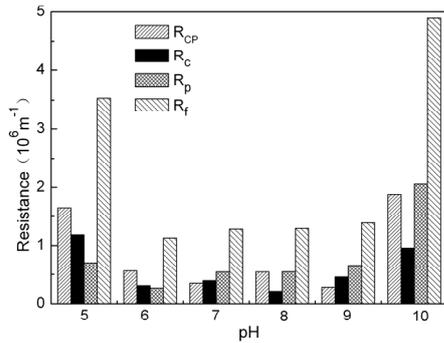


Fig. 5: Effect of pH on fouling resistances

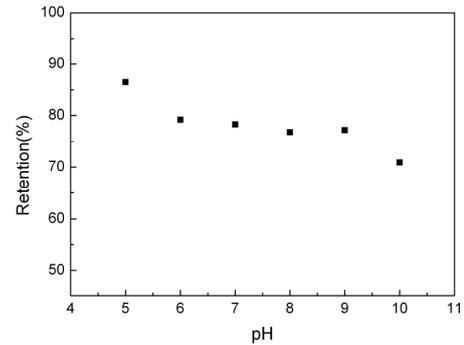


Fig. 6: Effect of pH on humic acid retention

3.4. Effect of Calcium Ion Concentration

In real wastewater, the ubiquitous calcium ion increases the hardness and deposition tendency of water. Since there are many oxygen-containing functional groups in the humic acid molecular chain such as carboxyl and phenolic hydroxyl, while the hydrogen of the carboxyl and phenolic hydroxyl can exchange each other in reaction. Owing to the existence of these functional groups, humic acid that possesses acidity and capacity of exchange can exchange ion and complex with metal ions [10]. Combination of calcium ions and humic acid molecules can reduce the deposition and decline filtrate flux.

As Fig.7 shows, with the increase of calcium ion concentration in the feed solution, the membrane fouling aggravated. Although the final membrane flux basically stabilized, the flux decline rates were higher and the time to achieve a stable state was longer in high calcium ion concentration case. So in solution that contains calcium ion and humic acid, calcium ion combines with the humic acid molecules, which could reduce the deposition and decline the membrane flux.

In Fig.8, with the increase of calcium ion concentration, the concentration polarization resistance changed little. But the cake resistance increased significantly. And the membrane pore blocking resistance increased. The phenomena can be explained as follows: PS membrane itself is uncharged. In solution without calcium ion, the membrane surface takes on negative charge due to the absorption of organic micelle with negative charge on it. With the addition of calcium ion, some calcium ions react with humic acid and neutralize the negative charge carried by functional groups of humic acid molecules. Meanwhile, free calcium ion which did not react with humic acid neutralized part of negative charge that membranes have adsorbed. It makes the charge polarity and intensity of the membrane surface change, and reduced the electrostatic repulsion between the membrane surface molecules and humic acid molecules. Consequently, the absorption of humic acid increased on the membrane surface. The membrane flux declined accordingly.

As Fig.9 shows, with the calcium ion concentration increased, the rejection rate of humic acid decreased significantly. This is because humic acid and calcium ion reacted and formed complex material. As Fig.10 shows cores can be seen from the cake lay formed by humic acid and calcium ion. It is looser than the compact cake lay formed by humic acid lonely showed in Fig. 3(b). So the rejection rate of humic acid is lower in this case.

4. Conclusions

The experiments have shown that severe fouling occurred in the ultrafiltration membrane filtrate humic acid solution process. The pH value and pressure affect membrane fouling largely. With the correct understanding of fouling mechanism, it is possible to improve the filtration results. Characterization of humic acid is not easy, but combining different methods can give an image of its behavior.

1) With time, contamination of the PS membrane caused by humic acid is significant, Membrane flux decreased significantly within 25 minutes, and decreased to 65% of the starting flux 5 hours later. The rejection of humic acid declined sharply within 25 minutes and changed little later.

2) Operating pressure is directly related to the fouling rate of membrane filtration, especially, the rate of cake layer formation. With the increase of pressure, the cake resistance which played a major role, increased significantly.

3) Feed solution's pH value directly related to the dissociation degree of H⁺ that exists in the groups of humic acid macromolecule chain. Therefore, with the pH value increased or decreased, the membrane flux increased dramatically. As pH value ranged between 6 and 9, the pollution caused by humic acid on the ultrafiltration membrane was relatively light. The retention rate of humic acid is relatively stable within the range of 70%-80%

4) Complex reactions take place between the calcium ion concentration and oxygen-containing functional groups that exist in the humic acid molecules, accelerated the formation of gel layer on the membrane surface. The presence and concentration of calcium ion in feed solution has not only exacerbated the membrane fouling and reduced the flux, but also reduced the retention rate of humic acid.

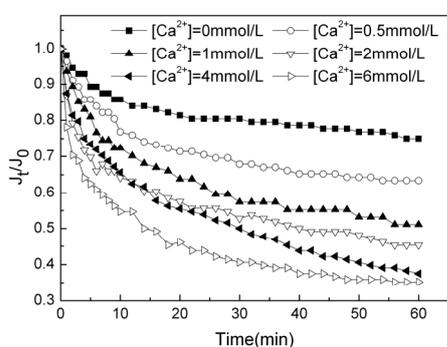


Fig. 7: Effect of calcium ion on membrane flux

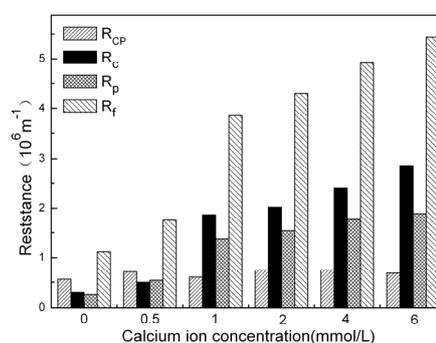


Fig. 8: Effect of calcium ion on fouling resistances

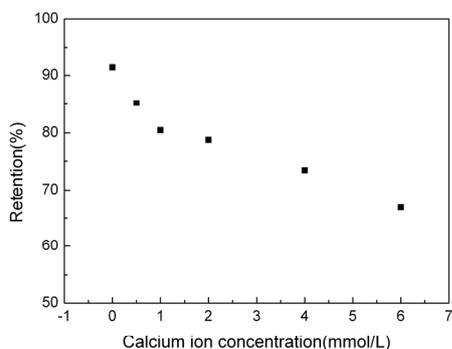


Fig. 9: Effect of calcium ion on humic acid retention

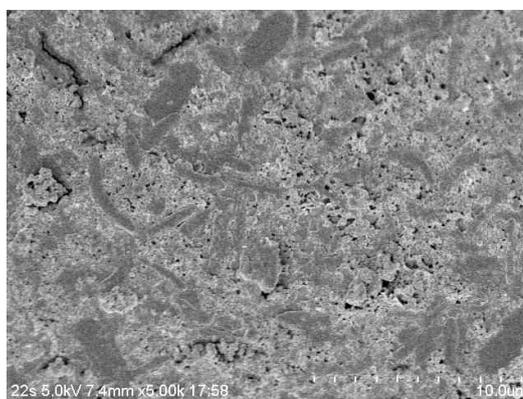


Fig.10: SEM images of PSmembrane fouled by humic acid and calcium ion

5. References

- [1] V. Siyanytsya, V. Kochkodan, and V. Goncharuk, "Natural organic matter removal from water by complexation-ultrafiltration," *Desalination*, vol. 223, 2008, pp. 91–96, doi:10.1016/j.desal.2007.01.220.
- [2] J. Lowe, and Md.M. Hossain, "Application of ultrafiltration membranes for removal of humic acid from drinking water," *Desalination*, vol. 218, 2008, pp. 343–354, doi:10.1016/j.desal.2007.02.030
- [3] K. Katsoufidou, S.G. Yiantsios, and A.J. Karabelas, "A study of ultrafiltration membrane fouling by humic acids and flux recovery by backwashing: Experiments and modeling," *Journal of Membrane Science*, vol. 266, 2005, pp.40-50, doi:10.1016/j.memsci.2005.05.009.

- [4] K. Katsoufidou, S.G. Yiantsios and A.J. Karabelas, "An experimental study of UF membrane fouling by humic acid and sodium alginate solutions: the effect of backwashing on flux recovery," *Desalination*, 2008, vol. 220, pp. 214–227, doi:10.1016/j.desal.2007.02.038
- [5] J. Lowe, and Md.M. Hossain, "Application of ultrafiltration membranes for removal of humic acid from drinking water," *Desalination*, vol. 218, 2008, pp. 343–354, doi:10.1016/j.desal.2007.02.030.
- [6] Wei Yuan, Aleksandra Kocic, and Andrew L. Zydney, "Analysis of humic acid fouling during microfiltration using a pore blockage–cake filtration model," *Journal of Membrane Science*, vol. 198 , 2002, pp. 51–62.
- [7] Eszter Csiszár, Ildikó Galambos, Erika Békássy-Molnár, and Gyula Vatai, "Ultrafiltration of humic acid containing well-water in pilot scale: new mass transfer model for transient flow regime," *Desalination*, vol. 199, 2006, pp. 512–514, doi:10.1016/j.desal.2006.03.115
- [8] Daniella B. Mosqueda-Jimenez, Peter M. Huck, and Onita D. Basu, "Fouling characteristics of an ultrafiltration membrane used in drinking water treatment," *Desalination*, vol. 230, 2008, pp. 79–91, doi:10.1016/j.desal.2007.09.014.
- [9] Hasan A. Mousa, "Investigation of UF membranes fouling by humic acid," *Desalination*, vol. 217, 2007, pp. 38–51, doi:10.1016/j.desal.2007.02.006.
- [10] Yingge Wang, Corine Combe, and Mark M. Clark, "The effects of pH and calcium on the diffusion coefficient of humic acid," *Journal of Membrane Science*, vol. 183, 2001, pp. 49–60.