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Hydrophobic modification of PP membrane coated by $Al(OH)_3$ colloids

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Abstract. By using the hydrolysis of Al^{3+} salt under near-neutral conditions, $Al(OH)_3$ colloidal solution has been prepared. The polypropylene based ultrafiltration (UF) membrane materials were uniformly coated with $Al(OH)_3$ colloid via hydraulic spin coating technique. It was indicated that the degree of hydrophobicity of membrane increases with the extension of coating time. The surface of polypropylene membrane with colloidal structure was analyzed by scanning electron microscopy, infrared spectroscopy and field emission scanning electron microscope. Samples characterization with the aid of Fourier transform infrared spectroscopy (FTIR) found that the interaction between colloidal coating and PP membrane is due to the physical force. It was shown that nano-particles are formed on the surface, which increases the surface area and thereby increases the hydrophobicity behavior of the samples.

Introduction

A growing concern has drawn to reduce water pollution by using eco-technology water-processing method. However, membrane fouling which results in frequent cleaning, shorter membrane life and high cost of treatment have been technological problems to be solved for membrane biological reactor (MBR) [1,2]. There are plenty of sticky substances, such as soluble organics, colloids, microorganisms and their secretions in sewage. During the process of water treatment, ultrafiltration membranes would be contaminated with the sewage. The underling mechanisms of membrane fouling are concentration polarization, remaining contamination and membrane pore blockage. All these factors would lead to the decreasing flux and water quality, and the increasing of treatment costs. Thus, reducing the membrane lifetime.

The surface properties of the membrane determine the interaction between sewage and the UF membranes, therefore it would influence the operating conditions and the reflux activity of the concentrated liquid in the MBR. It is revealed that the surface of hydrophobic membrane is more easily to cause the accumulation of contaminants than hydrophilic one. Thus, more and more researchers have paid much attention on the surface treatment technology. Among them, the surface coating is the most simple and effective method. Using sulfonation reaction, Bai [3] had fabricated a TiO_2 sol coating on a membrane, by which the surface contact angle was decreased about 30%. The anti-pollution performance of polyvinylidene fluoride hollow fiber membranes has significantly improved when using the ferric pre-film method [4]. It is also found that the PVDF hollow fiber ultrafiltration membrane coated with $Fe(OH)_3$ colloid [5] has effectively improved the stain resistance of membrane and makes it easier to clean.

This research focuses on the surface structure and hydrophobic properties of polypropylene (PP) membrane coated with amphoteric $Al(OH)_3$, to improve its hydrophilicity and fouling resistance.

Experimental procedures

The hollow fiber UF PP membrane has been selected as test objective. The colloid solution was prepared with the chemical solution reaction method. Sodium hydroxide (analysis purity) and aluminum chloride (analysis purity) are used to fabricate aluminum hydroxide colloid. The concentration of $Al(OH)_3$ colloid is 0.025 $molL^{-1}$. During the spin coating experiments, pH value and temperature are held around 6.5±0.1 and 40°C, respectively. The flux of colloid solution is 0.5 $Lmin^{-1}$ during hydraulic spin coating. Different coating times of 5 min, 10 min, 15 min, 20 min, and 30 min is performed. The deposition velocity of about 0.2μm/min has been obtained. After cleaning with absolute alcohol, the coated membranes are naturally dried in air. Then, the surface morphology and cross section quenched by liquid nitrogen are observed by scanning electron microscope. The interaction between colloid coating and membrane molecules was studied by Fourier transform infrared spectrometer. The hydrophilic property of colloid coating was tested by a water drop angle measuring instrument.

Results

Surface Morphology

The surface morphology and microstructure of colloid coating of 5 min, 15 min and 30 min are shown in Figure 1. Under a coating time of 5 min, the filter holes and the particles of coating are clearly visible. In the magnification of microstructure images, the coated colloid is observed. And some big grains of sub-micrometer scale are obtained, which are attributed to the rapid growth of colloid particles on the surface of the membrane. As shown in Fig 1(b), most of the filter holes are visible and partly coated. It indicates that the colloids are preferred to be deposited on the skeleton of the UF membrane. This indicates the effectiveness of $Al(OH)_3$ colloid coating in protecting the filter holes rather than blocking them.

As the coating time increases, the colloids become thicker and more uniform surface is obtained. This similar scenario can be seen even when the grains grow up further to around the size of one micron. In addition, the magnifications of microstructures exhibit the increase of the colloid thickness therefore fewer holes are visible due to the prolonged coating time. The structure of nano-scale grains and particles are still loose, which is helpful to increase hydrophilic and high flux properties of the coated membranes.

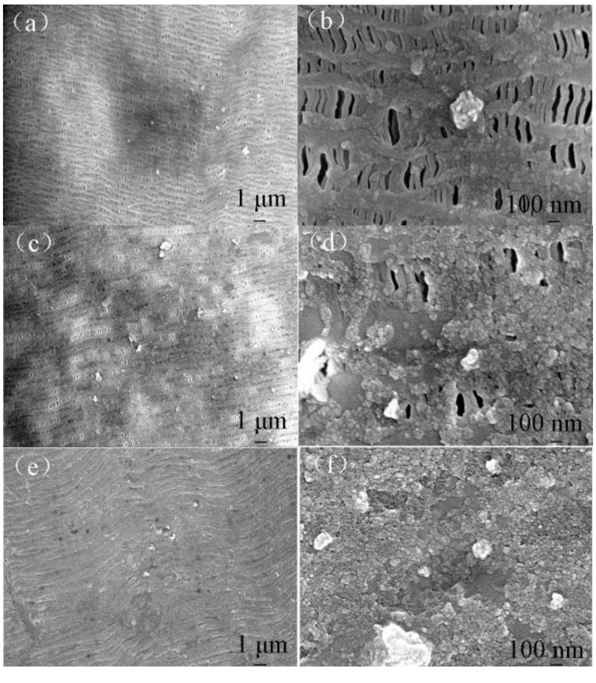

Fig. 1 Surface morphology and microstructures.

The colloids become much thicker and the surface exhibits a morphology of undulating waves, with an interval of about 1 μm, when the coating time was increased to 30 min. No holes could be observed both in Fig 1(e) and Fig 1(f). The surface of coating with loose structure is observed. The thick colloid coating would protect the deposition of contaminants from suppressing the membrane fouling.

Cross Section

The cross section morphology of colloid coated membrane is shown in Fig 2. The PP hollow fiber is quenched by liquid nitrogen, however it is a little inclined due to its thin wall. As shown in Fig 2(b), the thickness of the colloid coating is about 6 μm.

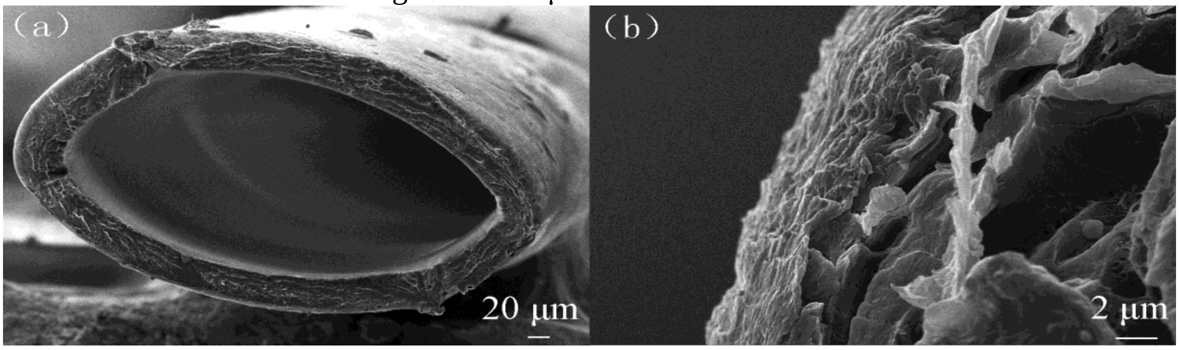

Fig. 2 Morphology of the cross section of the coated membrane at coating time of 15 min.

FTIR

The FTIR of PP membrane and colloid coated membrane are shown in Figure 3.The characteristic peaks of PP are obvious, including four sharp peaks in the range from 2988 to 2855 cm^{-1}, three single peaks around 1459, 1375 and 1163 cm^{-1} and double peaks around 993 and 973 cm^{-1}. When it is coated with colloids, the peak around 1163 strengthens besides a slight motion in position of peak around 2868. The latter indicates that the O-H stretch due to the coating of $Al(OH)_3$, while the former is related to the slight twisting of C-H bonds. These facts imply that the interaction between $Al(OH)_3$ colloids and PP membrane is mainly physical interaction. This would be feasible to clean the membrane fouling when the membrane maintains are needed, since the $Al(OH)_3$ colloids are amphoteric.

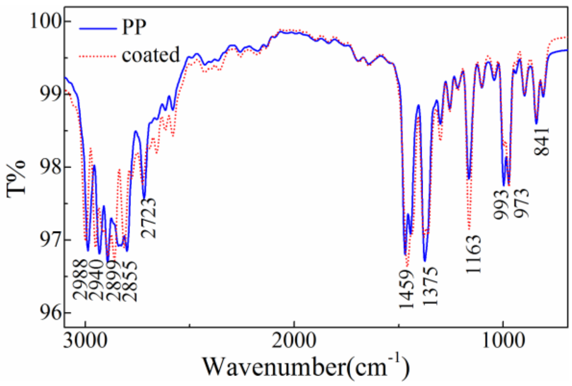

Fig. 3 FTIR of PP and coated PP membrane.

Contact Angle

The hydrophilic property of coated membrane is studied by using the contact angle measurement, as shown in Figure 4. Obviously, the contact angles between the water drops and membrane decrease with the increase of the coating time and the coating thickness. The contact angle rapidly decreases when the coating time is not more than 15 min.

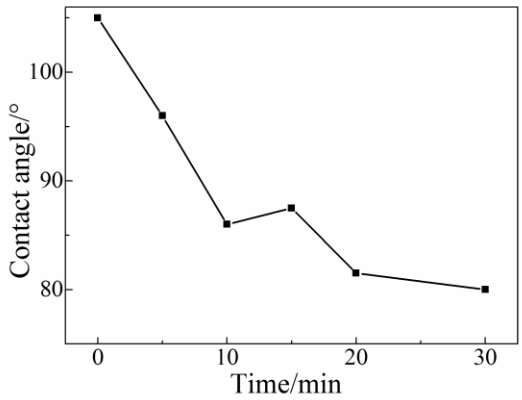

Fig. 4 Contact angle behavior with coating time.

The effect of coating time on contact angle weakens with the further increase of the colloid thickness. The contact angle decreases about 23.8% from 105 ° to 80 ° when the coating time was increased to 30 min. This is attributed to the existence of hydroxyl (-OH) in the colloid coating. The present wetting angle is much larger than that of Al_2O_3 nono-particle co-mixed Polyvinylidene Fluoride (PVDF) membrane [6].

Discussion

The present study indicates that the $Al(OH)_3$ colloid coating is effective to improve the hydrophilic property for nano-scale surface structure and hydroxyl groups. The contact angle decreases from 105 ° to 80 ° when the coating time is 30 min. This is a great improve in the hydrophilic property. The present contact angle of the coated PP membrane is larger if compared to that of Al_2O_3 nanoparticles co-mixed PVDF [6]. This could be attributed to the high addition of Al_2O_3 nanoparticle and its segregation in the surface, which results in a compact surface structure. Not to mention the facts that PVDF membrane is hydrophilic with a contact angle of 83.64 ° [6]. As shown in Fig 4, the slope in contact angle behavior with coating time decreases with increasing coating time. This implies that the modification effect on hydrophilic property has a limit by colloid coating under present experimental condition. On the other hand, the thickness increases with coating time which will lead to a decrease in the flux of membrane. So, a balance must be obtained between antifouling and membrane flux during colloid coating. Also, the high spin velocity, high colloid concentration and pH value should be improved to get a more compact surface and high hydrophilic property.

Conclusions

A loose surface structure is obtained in the present study of colloid coating on PP membrane, which provides hydroxyl and obviously improves its hydrophilic property. The slope in the behavior of the contact angle with the coating time was proven to be decreased with the increasing of the coating time. The Al(OH)3 colloid coating could be used to improve the anti-fouling performance of PP membrane, although a balance between coating thickness and membrane flux should be achieved in the colloid coating technology.

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