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Application of ceramic microfiltration membrane modified by nano-TiO_2 coating in separation of a stable oil-in-water emulsion

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ABSTRACT

Hydrophilic modification of the commercial ceramic microfiltration membranes is processed by the nano-TiO_2 coating. The nano-coating does not form a separation layer but increases the hydrophilic character of membrane surface. The modified microfiltration membranes are used to treat stable oil-in-water emulsions. The results show that the ceramic membrane modified by 2 mol/L $Ti(SO_4)_2$ solution is the more suitable in the MF process. Under the following operation conditions: cross-flow velocity of 5 m/s, trans-membrane pressure of 0.16 MPa, feed temperature of 40 °C, the modified membrane has the better stable flux, which is higher than that of the unmodified one. The oil concentration of the filtrate is no more than 10 mg/L if the oil concentration of the feed is not higher than 4 g/L due to the existence of the hydrophilic nano-TiO_2 coating, indicating the modified ceramic microfiltration membrane can be directly applied in the treatment of a stable oil–water emulsion.

1. Introduction

Generally, the stable oil-in-water emulsion is preferred to the emulsion with particles size of oil droplets not bigger than 20 μm. Even though the interface between oil phase and water phase still exists, the oil phase cannot be separated by gravity only. Therefore, this kind of emulsion is seriously harmful in the long-time to environment, and requires to be treated before discharge. The common method is to destroy the emulsion state of the oil droplets [1], such as adding chemical reagent. This results in the formation of sludge that may further pollute the environment. Membrane separation technology represents the economic and environmental-friendly advantages because the treatment cost is low and water or oil can be re-used [2]. Ultrafiltration membranes (UF) are usually chosen because their small membrane pores contribute to the rejection of the oil droplets [3]. However, the treatment cost can be further lowered by choosing microfiltration membranes (MF) since they do not require so high trans-membrane pressures and have higher flux than UF's [4,5]. However, MF is more inclined to membrane fouling than UF because the oil droplets easily block the MF membrane pores due to its high viscosity and distortion. To weaken membrane fouling, the hydrophilic modification of MF is a good choice, which provides an enhanced hydrophilic character to the membrane surface [6,7]. This surface repels oil droplets from adhering on the membrane surface, thus weakening the membrane fouling. Nano-scale ZrO_2 [8], TiO_2/Al_2O_3 [9], Al_2O_3 [10,11] and SiO_2 [12] had been used to enhance the hydrophilic character of commercial membranes. TiO_2 was added to the ceramic membrane support to get a high rejection rate of oil [13]. To ceramic membranes, the difficulty of the modification leads in the way of adding the nano-particles uniformly into the porous ceramic membrane without blocking the membrane pores. The modification of nano-particle must follow the preparation of ceramic membrane. Otherwise, the calcination of ceramic membrane (above 1600 °C) would lead to great particle growth of modification oxide coating. Our team had prepared the modified membrane by nano-ZrO_2 [8] and nano-Al_2O_3 [14], however, the contact angle was only 20°, which had to be improved.

In the present work, commercial ceramic microfiltration membranes were modified by nano-TiO_2 coating by an in-situ precipitation method. $Ti(SO_4)_2$ reacts with urea using the membrane pore channels as the reaction vessel. The precipitation reaction of the titania particles occurs and distributes uniformly onto the surface of alumina grains of the microfiltration membrane, and thus does not form a new separation layer. The modified

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membrane shows an enhanced hydrophilic surface due to the nano-scale effect of TiO_2 coating. The preparation conditions and the operation parameters of the modified membrane applied in the separation of the stable oil-in-water emulsion are discussed.

2. Experimental

2.1. Preparation of modified membranes

The used tubular Al_2O_3 microfiltration membranes, purchased from Nanjing Jiusi High-Tech Co. Ltd., have a 19-channels configuration. The main parameters are as follows: outer diameter of 31 mm, porosity of 40%, and nominal pore diameter of 0.2 μm.

$Ti(SO_4)_2$ and urea (purchased from Sino Chemical Reagent Co. Ltd, China) were used without further treatment. $Ti(SO_4)_2$ and urea (mol ratio of $Ti(SO_4)_2$/urea of 1:2) were dissolved into distilled water, and then mixed directly at room temperature. The concentration of Ti^{4+} in the three tested solutions is 0.1 mol/L, 0.2 mol/L and 0.3 mol/L. The ceramic microfiltration membranes were saturated with the mixed solution. The wet ceramic membranes were sealed with food wrappers, and then put into an oven at 85 °C for 3 h. The ceramic membranes were washed ultrasonically 2 times using distilled water, and then dried at 110 °C overnight. The above process was repeated twice. The dried ceramic membranes were calcined at 950 °C for 2 h at a heating rate of 3 °C min^{-1}.

2.2. Characterization of modified membranes

To avoid the effect of the membrane pores on the measurement of contact angle, the nano-sized TiO_2 coating was prepared onto dense Al_2O_3 disks, as described in Section 2.1. The contact angle was tested using a contact angle meter (SL-200B) by the sessile drop method.

The cross-sectional microstructure of the modified membrane was observed by a scanning electron microscopy (SEM) (JSM-6700F, JEOL).

The kinematic viscosity of the oil-in-water emulsion was measured by the countercurrent method.

2.3. Cross-flow of modified membrane

The oil–water emulsion consisted of hydraulic oil 32 (kinematic viscosity is 32 mm^2/s at 40 °C), Tween-80, Span-80 and distilled water. The mass ratio of hydraulic oil 32/Tween-80/Span-80 is 8/1/1. After weighting, oil and surfactants (Tween and Span) were added to the distilled water. The emulsion was generated using a blender (Fluko Equipment Shanghai Co., Ltd) by mixing for 2 min at a mediate speed. This method allowed the production of a stable emulsion, with an average droplet size of 6 μm with 90% of the oil droplets being in the range of 0.7–20 μm as measured using a Malvern Mastersizer Particle size analyzer (Nano ZS, Malvern). The kinematic viscosity of the oil-in-water emulsion was measured by the countercurrent method.

The membrane equipment was purchased from Nanjing Jiusi High-Tech Co. Ltd. The schematic diagram of the cross-flow filtration system had shown in reference [8]. The new MF membranes modified by nano-TiO_2 coating were chosen in every filtration process. However to study the effect of the feed temperature on the flux, the same ceramic membrane was used when the feed temperature changed from 20 °C to 60 °C without washing, just changing the temperature of the feed.

The oil concentrations of the feed and the filtrate were analyzed using an ultraviolet spectrophotometer (UV-1601).

3. Results and discussion

3.1. Hydrophilic modification of ceramic membrane with nano-TiO_2 coating

Fig. 1 shows the SEM images of the cross-section of the unmodified and the modified membrane with nano-TiO_2 coating. As can be seen, nano-TiO_2 coating distributes uniformly on the surface of alumina particles. The particle size of nano-TiO_2 particles is about 30 nm. The TiO_2 coating does not form a new separation layer but changes the surface character between the emulsion and the membrane surface. It can be deduced the nano-TiO_2 coating distributes on the surface of membrane and membrane pore channels. The TiO_2 coating does not form a new separation layer but changes the feed/membrane interface. Therefore, nano-TiO_2 coating changes the interaction between oil droplets and the membrane surface, and thus has an effect on the membrane fouling. Therefore, nano-TiO_2 coating changes the interaction between oil droplets with membrane surface, and thus may have an effect on the membrane fouling.

Fig. 2 shows the contact angle of water on the nano-TiO_2 coating. The contact angle of the nano-TiO_2 coating is about 8°, which is far smaller than that of the dense alumina disc, indicating the TiO_2 coating is very hydrophilic. This result is also applicable for the modified membrane because the nano-TiO_2 coating distributes directly on the alumina particles of the membrane. The hydrophilic membrane surface contributes to repel oil droplets from adhering to membrane surfaces, thus to weaken membrane fouling.

Fig. 3 shows the flux declines of the modified membranes prepared by $Ti(SO_4)_2$ solutions with different concentrations. The fluxes of all the modified membranes are higher than that of the

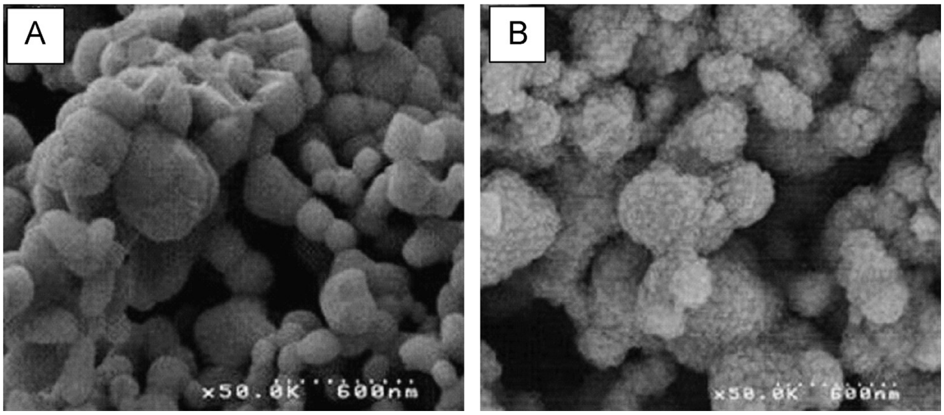

Fig. 1. SEM images of the cross-section of (A) the unmodified membrane and (B) the membrane modified with nano-TiO_2 (0.2 mol/L $Ti(SO_4)_2$).