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Preparation of a new ceramic microfiltration membrane with a separation layer of attapulgite nanofibers

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ABSTRACT

To improve the performance of ceramic membranes and reduce their costs, a new ceramic microfiltration membrane with a separation layer made of attapulgite nanofibers was fabricated by dip-coating on the inner surface of α-alumina tubular supports. The membrane has a separation layer of attapulgite nanofibers without evident defects and exhibits excellent interface properties, showing good adherence to the α-alumina substrate. The nanofiber membrane has an average pore size of 0.250 μm, thickness of approximately 6.7 μm, and a pure water flux of 1540 L/(m^2 h bar). The membrane was able to reject all the calcium carbonate particles in suspension, and showed a steady permeate flux of approximately 980 L/(m^2 h bar). In addition, the membrane can be easily regenerated by backwashing without any damage, and therefore used repeatedly.

1. Introduction

The large majority of ceramic membranes are fabricated from particles of ceramic oxides, such as Al_2O_3, TiO_2, ZrO_2, and SiO_2. Recently, novel nanofiber ceramic membranes with high porosity and flux have been fabricated from metal oxide nanofibers [1,2]. Typically, these membranes have a nanofiber separation layer with a distinctive mesh structure. Compared with conventional ceramic membranes fabricated from oxide ceramic particles, nanofibers are able to divide large voids in the separation layer into smaller interconnected pores, without forming dead-end pores. Typically, the porosity of the nanofiber separation layer can exceed 70%, almost twice that of conventional ceramic membranes, and its mesh structure enables the membranes to obtain high flux and selectivity in the filtration process [3–6]. Furthermore, as the randomly oriented nanofibers have large thermal stress resistance and high elastic modulus, the formation of cracks and pinholes decreases during the drying and sintering processes [7,8]. Therefore, the use of ceramic nanofibers instead of oxide ceramic particles represents an effective method to prepare high-performance ceramic membranes.

Attapulgite (palygorskite) is a hydrous layer-ribbon magnesium aluminum silicate mineral with a unique three-dimensional structure [9]. The combination of one-dimensional nanoscale, excellent thermal and mechanical stability, and its natural abundance have made attapulgite a good candidate as inorganic component in many nanotechnology applications, such as inorganic–organic hybrid membranes, polymer nanocomposites, photocatalysis, and adsorption [10–14]. As a raw material in ceramic membranes, attapulgite nanofibers may be more inexpensive and suitable than synthetic nanofibers. The use of low-cost raw materials can increase the competitiveness of ceramic membranes. In this work, we prepared a new ceramic microfiltration membrane with a separation layer made of attapulgite nanofibers.

2. Experimental procedure

Attapulgite nanofibers (98% purity, particle diameter of 20–50 nm, and length of 500–1500 nm) were supplied by Jiangsu Jiuchuan Nano-material Technology Co., Ltd., Jiangsu, China. The outer diameter and wall thickness of the α-alumina tubular supports are 12 mm and 2 mm, respectively (Membrane Science and Technology Research Center, Nanjing, China). The length and mean pore size are equal to 110 mm and 2–3 μm, respectively. The pure water flux is 14,500 L/(m^2 h bar) while the porosity is equal to 35%.

The attapulgite nanofibers were initially dispersed in water to form a suspension. Attapulgite nanofiber membranes were then

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prepared on the internal surface of α-alumina tubular supports by the dip-coating method. The supports were dip-coated with attapulgite nanofibers suspension for 60 s, dried at room temperature for 24 h, at 70 °C for 12 h, and at 110 °C for 12 h, followed by sintering at 600 °C for 3 h in a muffle furnace (with heating and cooling rates of 1 °C/min). The microstructure of the nanofiber membranes was characterized by field emission scanning electron microscopy (FE-SEM, Hitachi, model S-4800). The average pore size distribution was estimated using a Pore-size Distribution Analyzer (PSDA-20, GaoQ Functional Materials Co., Ltd. Nanjing, China). The performance of the attapulgite nanofiber membranes was evaluated by measuring nitrogen and pure water flux at 20 °C. The separation performance was tested via rejection experiment using calcium carbonate ($CaCO_3$) granules with average particle diameter of 1.0 μm, at 20 °C. The concentration of the $CaCO_3$ in feed was 1.0 g/L and remained nearly constant by recycling permeate and retentate back to the feed tank. The operating transmembrane pressure was maintained at 1 bar and the cross-flow velocity at 3.0 m/s. After filtration of the $CaCO_3$ solution for 1 h, the membrane was backwashed with nitrogen at 3 bar for 10 s before being filtered again. Four runs of a filtration test were repeated to examine the stability of the attapulgite nanofiber membrane.

3. Results and discussion

Fig. 1 shows the morphology of the attapulgite nanofiber membrane sintered at 600 °C. As shown by the FE-SEM image in Fig. 1(a), the surface of the α-alumina ceramic substrate was completely covered with attapulgite nanofibers. The surface of the membrane has no obvious cracks or pinholes. Observing the surface of the membrane at a larger magnification (Fig. 1(b)), it can be noted that the attapulgite nanofibers lay randomly on the substrate and a mesh structure was formed. The cross-section image of the membranes in Fig. 1(c) shows a relatively uniform membrane layer of attapulgite nanofiber on the left side. This layer has a thickness of 6.7 μm and exhibits uniform and excellent interface properties with good adherence to the α-alumina substrate and a porosity of about 54%, which is much larger than that of conventional ceramic membranes fabricated from oxide ceramic particles.

The pore size distribution of the attapulgite nanofiber membrane, shown in Fig. 2, appears very narrow, with an average pore size of 0.250 μm. Fig. 3 shows the water and gas permeation properties of the membranes at different operating pressures. The water and nitrogen fluxes increased with the increase of operating pressure, with a measured pure water flux of 1540 L/(m^2 h bar), and a nitrogen flux equal to 15,915 L/(m^2 h bar).

Fig. 4(a) shows the relationship between permeate flux and filter time for a $CaCO_3$ suspension. The permeate flux of the attapulgite nanofiber membrane decreased with time before stabilizing at a steady value of about 980 L/(m^2 h bar). After repeated backwashing, the permeate flux of the membrane was essentially restored to its initial level. Finally, the attapulgite nanofiber membrane was backwashed with nitrogen at 3 bar and then cleaned with dilute hydrochloric acid. Fig. 4(b) shows the surface of the membrane after cleaning. It can be seen that the membrane has no evident defects, even after repeated filtering

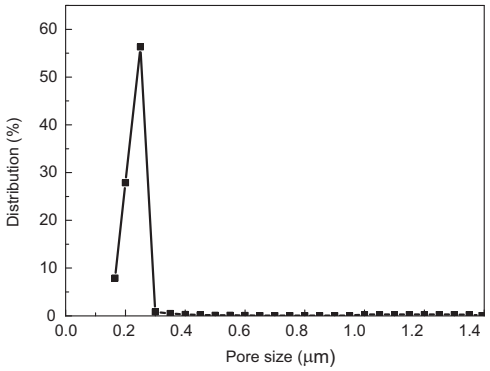

Fig. 2. Pore size distribution of the nanofiber membrane.

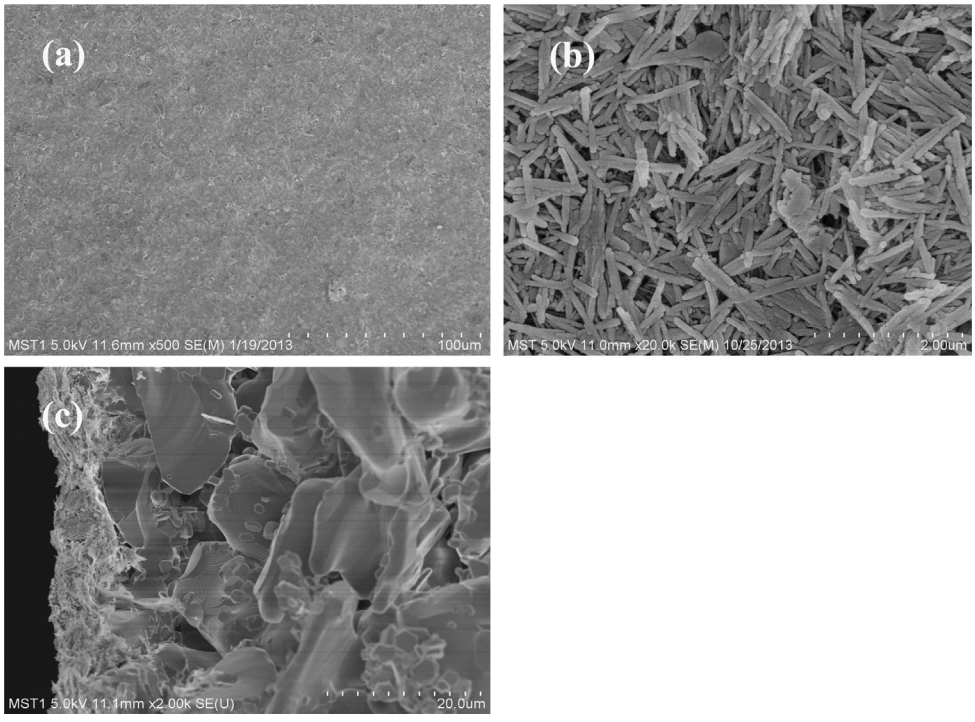

Fig. 1. The morphology of attapulgite nanofiber membrane: (a) surface image 500 × ; (b) surface image 20,000 × ; and (c) cross-section image 2000 × (sintering at 600 °C for 3 h with heating and cooling rates of 1 °C/min).