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Electrokinetic property of ZrO_2/cordierite composite MF membrane and its influence on the permeate flux

Xiaozhen Zhang *

Key Laboratory of Jiangxi Universities for Inorganic Membranes, Jingdezhen Ceramic Institute 333001, Jiangxi Province, PR China

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ABSTRACT

ZrO_2/cordierite composite microfiltration (MF) membrane was prepared by the combination of extrusion and slip casting techniques. The electrokinetic properties of as-prepared membrane were characterized by streaming potential measurements operated in tangential microfiltration mode. The influences of pH, electrolyte species and concentrations of filtered solutions on the electrokinetic properties and permeate flux were investigated. Results show that the streaming potentials are dependent on the pH, types of the electrolyte and concentrations of filtered solutions. The isoelectric point (IEP) of membranes moved from 4.2 to 5.4 with different types of 10^{-3} M electrolyte solutions. The change of ionic concentration of NaCl solution does not alter the IEP of the membranes, but does make the streaming potential tend to be zero at high salt concentration. The specific adsorption of Ca^{2+} and SO_4^{2-} ions in $CaCl_2$ and Na_2SO_4 solutions onto the pore wall can alter the IEP and the net charge sign of the membrane. The as-prepared ZrO_2/cordierite membrane shows a maximal permeate volume flux near the IEP.

1. Introduction

Ceramic membranes with their various advantages, such as better thermal, chemical and mechanical resistance, controllable microstructure and little pollution to our environment, have been applied for water treatment such as drinking and waste water, separation in organic media such as filtration in CO_2 media, purification of used oil and the application at high temperature [1–3]. However, inorganic membranes commercially manufactured are microfiltration (MF) and ultrafiltration (UF) membranes, while nanofiltration (NF) and reverse osmosis (RO) membranes are under investigation and development [2], and their largest market share is in the microfiltration area. Microfiltration in combination with ultrafiltration can solve almost any separation problems involving particulate materials and macromolecules.

For the case of water treatment by MF membranes, surface charge can play a very important role in determining membrane fouling and flux based on electrokinetic effects [4]. Surface charge and the related distribution of ionic species near pore surface of the membrane can have a significant effect on the permeability and adsorptive fouling of the membrane [5]. In the filtration of solutions containing particles such as silica, kaolin and protein macromolecules, electric force between a membrane and the solutes whose sign of charge is opposite to that of the membrane, causes fouling, which would result in a decrease in permeate flux of the membrane [6]. The pH and ionic concentration may also change the stability and conformation of colloidal species in the feed solutions with important implications for membrane–foulant interactions. The tendency for natural organic matter to sorb, the permeability of cake or gel layers deposited on membranes, and the potential for aggregation of colloids are all expected to be affected by pH and ionic concentration. Numerous observations of the effect of pH and ionic concentration on permeate flux of MF and UF membranes have been reported in the literature [6–8]. Moosemiller et al. [9] reported that the permeation of particle-free electrolyte solutions through Al_2O_3 and TiO_2 membranes reached the greatest value near the isoelectric points of these membranes, since electroviscous effect can be neglected because of no surface charge. However, to the best of our knowledge, few reports have discussed the effect of surface charge on the performance of ZrO_2 MF membranes.

As described in other publications [8,10], the most convenient method to determine the membrane surface charge linked to the zeta potential is the streaming potential measurements. When an electrolyte solution passes through a porous material by means of hydraulic pressure, a streaming potential is created: it depends on the pressure difference ΔP. It was measured when the equilibrium of the potential difference ΔE was reached. Streaming potential is the slope of the straight line given by $\Delta E = f(\Delta P)$ curves [11].

In this work, zirconia, which has a superior stability in acidic and basic solutions, was chosen as the material for the preparation of MF membranes on low cost cordierite support. The electrokinetic properties of as-prepared ZrO_2 membrane and its influence on the permeate flux were studied by streaming potential measurements and MF experiments with different types of electrolyte solutions at various pH values and concentrations.

* Tel.: +86 798 8499328; fax: +86 798 8491837.
E-mail address: zhangxz05@126.com.

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2. Experimental

2.1. Membrane preparation

2.1.1. Preparation of macroporous support

The tubular support with outer diameter 10 mm and inner diameter 7 mm was prepared by extrusion of the mixture paste of cordierite and organic additives. Cordierite powder (from Artal 23 argile et minéraux A.G.S.) with a mean particle size of about 31 μm and organic additives in proper proportion were used to prepare the paste as follows: a) mixing of cordierite 82 wt.%, amidon 10 wt.% (Amidon de maïs RG03408, Cerestar), Methocel 4 wt.% (The Dow Chemical Company), Amijel 4 wt.% (Cplus 12072, Cerestar); b) adding the water (38 wt.% of mixed powder); c) pugging for 30 min; d) aging of the paste in a closed box for 24 h under high humidity to avoid premature drying and to ensure complete interdiffusion of the water and organic additives. The tubular cordierite supports were obtained by extrusion of the paste with good rheological property, and then dried at room temperature. The wet supports were set on rollers during drying to ensure homogenous drying and to avoid twisting and bending. Finally, the samples were heated up to 350 °C for 1 h at a rate of 2 °C/min, and then further heated up to 1275 °C for 1 h at a rate of 5 °C/min to obtain the macroporous support.

2.1.2. Preparation of the zirconia MF layer

The zirconia MF layer was deposited on the inner surface of the cordierite support by slip casting of powder suspension. A deflocculated suspension of zirconia was obtained by mixing 10 wt.% of zirconia powder (Cezus Chimie) with a specific surface area of 8 g/cm^2, 30 wt.% of PVA (12 wt.% aqueous solution) as binder and 60 wt.% of Dolapix CE64 (2 wt.% aqueous solution) as dispersing agent. After drying at 25 °C for 12 h, the ZrO_2 membrane was heated to 300 °C for 1 h and then further sintered at 1100 °C for 2 h with a heating up rate of 5 °C/min.

2.2. Characterization methods

The morphology of as-prepared membrane was observed using scanning electron microscopy (SEM, Hitachi, S-4500) with an accelerating voltage of 20 kV. The pore size distribution (PSD) of the composite membrane and porosity of the support were measured by the mercury porosimetry (Micromeritics autopore). The permeate flux and streaming potential measurement experiments were carried out with a homemade laboratory pilot using a 15 cm long membrane (filtration area 26 cm^2), as illustrated in Fig. 1. The membrane cells operated in crossflow mode with a feed velocity of 2.5 m s^{-1}, and the temperature was maintained at 25 °C. The measurements of the streaming potentials were performed through the membrane by means of two silver wires covered with silver chloride used as reference electrodes. One of the electrodes was positioned in the axis of the membrane tube and the second near the opposite side of the tube. Before the measurements of permeate flux and streaming potential, all the membranes were immersed in the corresponding filtration medium for 24 h. All the filtered solutions with different concentrations were prepared with deionized water (conductivity lower than 0.067 μs cm^{-1}) and electrolytes delivered from Merck (analytical grade). The adjustment of the pH was made with either sodium hydroxide or hydrochloric acid by taking care that the addition of base or acid did not significantly modify the initial concentration of the filtered salts. The pH values of the solution were measured with a Radiometer pH meter.

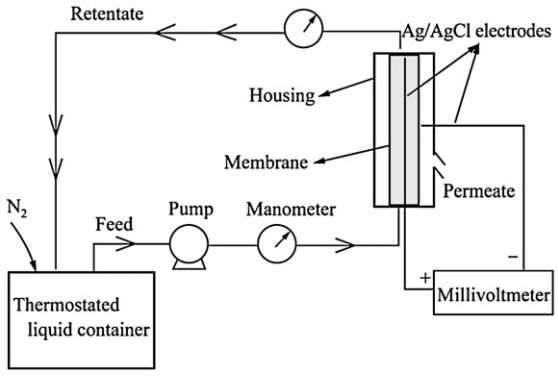

Fig. 1. Homemade laboratory pilot for permeate flux and streaming potential measurements.

3. Results and discussion

3.1. Membrane microstructure

Fig. 2 shows the SEM micrographs of as-prepared ZrO_2/cordierite composite membrane. It can be seen from Fig. 2(a) that ZrO_2 active layer with an average thickness of ca. 20 μm was obtained on cordierite support, and the top membrane shows good adhesion to the support. The infiltration of particles from top layer into support is not found, which is beneficial for reducing the resistance during filtration applications. The surface of as-prepared ZrO_2 membrane is smooth, homogeneous and no microcracks or pinholes are observed as shown in Fig. 2(b). The membranes are mainly composed of 0.3–0.4 μm spherical particles. The cordierite support prepared in this work shows a porosity of 42.3%, and the mean pore size of top layer and support is 0.18 μm and 6.2 μm, respectively.

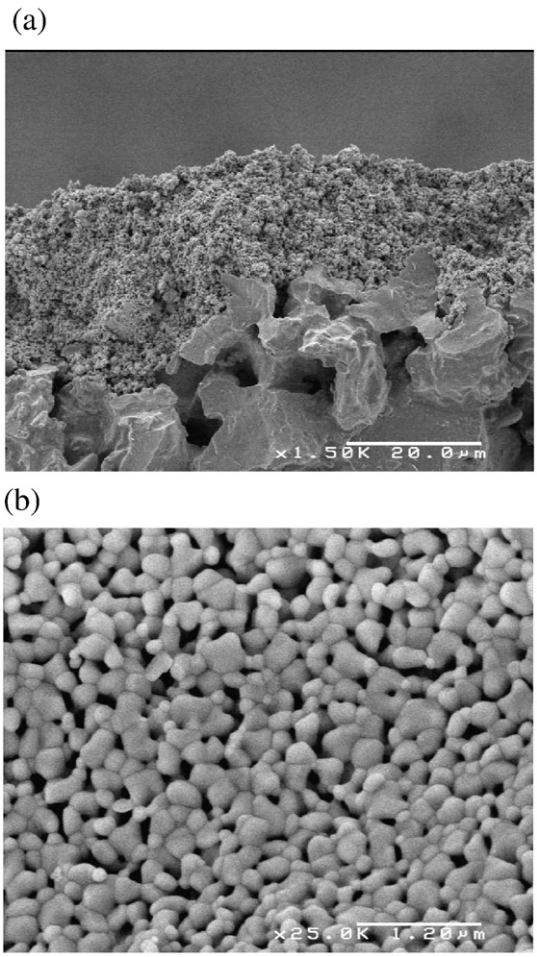

Fig. 2. SEM images of membrane: (a) cross-section; (b) surface of ZrO_2 top layer.