



Research paper

Preparation and characterization of a self-supporting inorganic membrane based on metakaolin-based geopolymers



Meng-xue Xu, Yan He, Chao-qun Wang, Xue-feng He, Xu-qing He, Jing Liu, Xue-min Cui *

School of Chemistry and Chemical Engineering, Guangxi University, Nanning, 530004, PR China

Guangxi Key Lab of Petrochemical Resource Process and Process Intensification Technology, Guangxi University, Nanning, 530004, PR China

ARTICLE INFO

Article history:

Received 29 January 2015

Received in revised form 18 March 2015

Accepted 20 March 2015

Available online 1 April 2015

Keywords:

Geopolymers

Self-supporting

Ultrafiltration

Inorganic membranes

Water treatment

ABSTRACT

This paper is focused on a new self-supporting inorganic membrane prepared by a one-time cast molding process with geopolymer paste. This new preparation method has the advantages of easy fabrication, free sintering and low cost compared with the conventional inorganic membrane preparation methods. This work explores the influence of the H₂O/Na₂O molar ratio on the strength and porous structure of the inorganic membrane. A linear relationship between the permeated water flux and the membrane thickness or operating pressure was observed after a filtration test. By optimizing processing parameters, this study obtained an inorganic membrane (with the H₂O/Na₂O molar ratio of 18) between the ultrafiltration membrane and the microfiltration membrane with a high compressive strength of 20 MPa, a pore size distribution of 20 to 100 nm, a rejection rate of 100% for nano-Al₂O₃ particles and a permeated water flux of 185 kg/m²h when the operating pressure was 0.3 MPa and the membrane thickness was 5.0 mm. This membrane will be a good choice for the field of water treatment with membranes.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The latest developments in membrane separation processes are likely to replace a step that was part of an existing industrial process and may reduce the total energy consumption. In addition, membrane separation processes generally permit continuous operation and can easily be combined with other separation processes. The separation mechanism was principally based on the size exclusion of matter, i.e., rejected substances with sizes larger than the pores of the membranes. In the past decades, there has been a considerable interest in the fabrication of mesoporous membranes with pore sizes within the range of 2 to 50 nm (Zaman and Chakma, 1994; Armor, 1998). This pore size range is comparable to the size of many organic molecules, and the mesoporous membranes have therefore been proposed for use in water treatment or separation of large organic molecules from aqueous solutions. Most of the mesopore-sized membranes are polymeric and have been used in industry. However, polymeric membranes cannot withstand some organic solvents or high-temperature conditions, etc. (Zaman and Chakma, 1994; Armor, 1998) so the utilization of polymeric membranes was limited in many chemical processes. The polymeric membrane may usually be substituted by porous inorganic membranes that are organic solvent resistant, high-temperature resistant and chemically stable. Inorganic membranes with mesopores were therefore highly desirable and have been studied extensively in

recent years. A great deal of research had been devoted to new types of inorganic membranes, including zeolites (Bein, 1996; Shah et al., 2000; He et al., 2013), carbon (de Lannoy et al., 2013; Ahmad et al., 2014; Li et al., 2014), dense metals (Saracco et al., 1999) and porous ceramics (Roy et al., 2006). However, these methods were economically unacceptable due to their complexity and high fabricating cost. Therefore, developing a low-price and effective inorganic membrane is imperative.

This study fabricated a type of self-supporting inorganic membrane for water treatment, synthesized using geopolymeric gel materials shaped in the mold. The geopolymers were noncrystalline or quasicrystalline gels with a three-dimensional network structure that was first introduced by Joseph Davidovits in 1978 (Davidovits, 1991). Geopolymer products have recently demonstrated very significant commercial and technological potential because of their high strength, free sintering, easy fabrication and low cost, but these properties were rarely reported in membrane materials. Because the traditional inorganic ceramic membrane is usually sintered at high temperature above 1000 °C (Abetz et al., 2006; Landi et al., 2013), but geopolymer membrane can harden at ambient temperature rather than requiring high-temperature sintering. Hence, developing geopolymer membrane has an obvious advantage compared to ceramic membrane.

The geopolymeric aluminosilicate material was one type of cross-linked long-chain inorganic polymeric material between tetrahedral [AlO₄] and [SiO₄] units, with a built-in three-dimensional structure with excellent properties of high strength, anticorrosion, withstanding fire and long life. Geopolymers were amorphous gels with some water

* Corresponding author.

E-mail address: cui-xm@tsinghua.edu.cn (X. Cui).

of hydration that was prepared from natural minerals or solid wastes by the polymerization of silicon–oxygen tetrahedra and aluminum–oxygen tetrahedra at ambient or slightly elevated temperatures (Mo et al., 2014). The representative geopolymerization product was fabricated by alkaline- or alkali-silicate-activated metakaolin, which had a wide range of compositions represented by $M_2O-mAl_2O_3-nSiO_2$, usually with $m \approx 1$ and $2 \leq n \leq 6$, where M represents one or more alkali metals. The geopolymerization mechanism for metakaolin-based geopolymers had been explained by Joseph Davidovits (Davidovits, 1991). The polycondensation of $[AlO_4]$ and $[SiO_4]$ groups occurred to form polymer gels with three basic structure units of $-Si-O-Al-O-$, $-Si-O-Al-O-Si-O-$ and $-Si-O-Al-O-Si-O-Si-O-$ in the hydration layer of hydrated sodium ions in the condensation polymerisation process that were located at the interface between the solid and liquid in the initial gel (Davidovits, 1991). These gels were converted into a three-dimensional network structure (simultaneously forming a porous structure) after dehydration. The pore distribution of geopolymers is usually shown by using electron microscopy and mercury intrusion porosimetry, but the pore distribution has not been discussed in the application of membrane materials and separation processes in prior studies (Liu et al., 2010; Rovnaník, 2010; Okada et al., 2011; Mo et al., 2014).

This paper reports the successful preparation and characterization of a self-supporting inorganic membrane (with most mesopores and a few macropores) that was obtained using a geopolymer gel with a suitable composition and a specifically designed Si/Al/Na/H₂O molar ratio using metakaolin-based geopolymers through a simple one-time molding process.

2. Experimental procedure

Metakaolin was produced by the calcination of kaolin (obtained from Yanzhou Mining Group Company, Beihai, China) at 800 °C for 3 h. The oxide composition of metakaolin is presented in Table 1.

The alkaline activator-sodium silicate solution (named water-glass, the mass composition is Na₂O = 18.55%, SiO₂ = 24.59% and water = 56.85%) was prepared by dissolving solid sodium hydroxide in commercial sodium water-glass.

Fig. 1 is the schematic for the self-supporting geopolymer inorganic membrane preparation process. In this study, the geopolymer paste was prepared using metakaolin and modified sodium silicate solutions and deionized water as the raw materials. The composition of the geopolymer paste was (Na₂O:Al₂O₃ molar ratio = 0.8, SiO₂:Al₂O₃ molar ratio = 2.88–3.12, H₂O:Na₂O molar ratio = 14–19). The geopolymer paste was cast into molds, and the molds were sealed and cured at 60 °C for 24 h. The formation of the geopolymer inorganic membrane is shown in Fig. 1. The geopolymer inorganic membranes were tested for their filtration performance, using the testing membrane device as depicted in Fig. 2. The liquid storage tank and the membrane clamp constituted a water circulating system. A self-supporting inorganic membrane is placed in the clamp. The diaphragm pump provides an operating pressure that can be adjusted to the ideal state by controlling the hand-wheel and observing the pressure gauge readings. With this membrane device, the water flux and rejection performance can be measured better.

The structural characterization of the geopolymer materials was conducted using SEM (Accelerating voltage of 20 kV, Hitachi scanning electron microscope S-340, Japan). The mesopores, macropores and their porosity were measured by a mercury injection apparatus (AutoPore IV 9500, Micromeritics Instrument Corporation, USA). The mechanical properties of the geopolymers and the self-supporting

inorganic membrane were tested by using a universal testing machine (DNS100, Changchun Machinery Research Institute Co., Ltd., China) as follows: The geopolymeric paste was casted into 2.0 × 2.0 × 2.0 cm cubic moulds and cured at 60 °C for 72 h. The cubes were then removed from the mould and tested for compression strengths and replicated 6 samples.

The separation performance or solid particle rejection rate of the self-supporting geopolymer inorganic membrane could first be characterized by the nano-Al₂O₃ rejection test. Next, the turbidity removal test was conducted by the standard turbidity test method (according to China GB/T 13200-1991). Under the conditions of 25 °C, N₂H₄ · H₂SO₄ and C₆H₁₂N₄ can form a high molecular weight polymer, as a turbidity standard solution turbidity (NTU, Nephelometric Turbidity Unit), using an ultraviolet spectrophotometer characterized the feed solution or permeated solution turbidity so as to reflect the separation effect of the geopolymer inorganic membrane on the filtration process.

3. Results and discussion

3.1. The optimal process of geopolymers materials

This work found the compressive strength, pore structure and specific surface area that had an intensive impact on the properties of the geopolymer inorganic membranes based on different H₂O/Na₂O ratios because the self-supporting membrane needed a high strength to ensure the ability to sustain the operating pressure in the filtration process. Therefore, we should first obtain a high strength geopolymer inorganic membrane by adjusting the geopolymeric composition.

The geopolymeric membrane was prepared from geopolymeric slurries with the following molar ratios: Na₂O:Al₂O₃ = 0.8, SiO₂:Al₂O₃ = 2.88–3.12, H₂O:Na₂O = 14–19. After 10 min of mechanical mixing, the geopolymeric paste was casted into 2.0 × 2.0 × 2.0 cm cubic moulds and cured at 60 °C for 72 h, then we obtained samples with different proportions of geopolymer based on different water-glass modulus (SiO₂:Na₂O molar ratio of sodium silicate solutions ranging from 1.1 to 1.4). We determined the optimal geopolymer inorganic membrane composition through the compressive strength test.

The characterization of the membrane is essential for the evaluation of the compressive strength of the synthesized membrane. From Fig. 2, a similar tendency could be observed with different H₂O/Na₂O ratios, and the highest compressive strength was obtained when the modulus of the water-glass was 1.3 because a suitable alkaline environment for the reaction could be provided when the SiO₂:Na₂O molar ratio of water-glass was 1.3. Therefore, the geopolymers produced under these conditions showed the highest compressive strength. Based on this work, the composition of the optimal geopolymer inorganic membrane can be designed according to Na₂O:Al₂O₃ = 0.8, SiO₂:Al₂O₃ = 2.96, H₂O:Na₂O = 14–19 and water-glass modulus (SiO₂:Na₂O molar ratio) = 1.3.

The microstructure of the geopolymer inorganic membrane was characterized using scanning electron microscopy (SEM). The cross-sectional morphologies of the membrane fractures were observed by scanning electron microscopy (SEM) as shown in Fig. 3. During the process of the experiment, this study found that the vacuum defoam technology (vacuum stirring for 20 min in special container) can effect a certain degree of change in the structure of the membrane (Weir et al., 2001; Abetz et al., 2006; Landi et al., 2013; Lee et al., 2013). Fig. 3(a) presents SEM images of the top surface of the geopolymeric inorganic membrane untreated process, and Fig. 3(b) shows SEM images of the top surfaces of the geopolymer inorganic membrane after the vacuum defoam process. By comparing Fig. 3(a) and (b), this study found the vacuum defoam process that could effectively eliminate large holes with diameters in the tens of micrometers in the self-supporting membrane body of Fig. 3(a). Fig. 4(b) showed that the vacuum defoam process could make the geopolymer reaction sufficiently dense, and the

Table 1
Oxide composition of metakaolin.

Component	SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	MgO
Composition(mass %)	52.89	43.50	1.80	1.38	0.44

Download English Version:

<https://daneshyari.com/en/article/1694341>

Download Persian Version:

<https://daneshyari.com/article/1694341>

[Daneshyari.com](https://daneshyari.com)