Recent Research in Science and Technology 2014, 6(1): 14-17
ISSN: 2076-5061
Available Online: http://recent-science.com/

Synthesize and characterization of clay based low-cost membrane for solid-liquid separation

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Abstract
In this work, locally available clay material was mixed with inorganic materials to synthesize the low-cost ceramic membrane in microfiltration range. Membrane was sintered at different temperatures (800-950°C) and the effect of sintered temperature on membrane preparation was studied in detail. The membrane porosity was found to decrease (44-30%) with membrane sintering temperatures (800-950°C). The corrosion resistance of the prepared ceramic membranes at different sintering temperatures was analyzed using N-methyl-2-pyrrolidone (NMP), NaOH and HCl. It was observed that the elemental composition by EDX analysis and porosity measurement of the synthesized membrane was found almost invariant. Finally, the synthesized membranes were characterized by scanning electron microscope (SEM) and Fourier transform infrared (FT-IR) spectra analysis to study their morphological properties and porosity measurement, and functional group analysis, respectively. The abrupt morphological changes on the membrane surface and micro porosity formation at 800°C sintering temperature suggest that the synthesized clay based ceramic membrane could be used for various solid-liquid separations.

Keywords: Ceramic membrane; Solid-liquid separation; Membrane characterization; Microfiltration

INTRODUCTION

Many industrial processes use different synthetic chemicals for various purposes. Effluents coming out from these industries are highly polluted, resulting in major environmental problems. So these chemical wastes need to be treated before disposal. Many methods are available for the removal of pollutants from water, the most important of which are adsorption, biodegradation, flocculation-coagulation and oxidation (Sulaymon et al. 2011). Recently membrane separation technologies have been used for the separation of many dissolved chemicals and suspended solids from the waste stream. Membrane techniques have several additional advantages as (i) the non-requirement of any chemical addition, (ii) the capability of generating permeate of acceptable quantity and (iii) low energy requirement relative to conventional separation technologies (Burggraaf and Cot, 1996). Research in this area primarily aims at the development of functional materials to achieve low-cost processing of industrial separation schemes. Compared to organic membranes, inorganic membranes offer several beneficial options (Emani et al. 2013). In inorganic membrane, ceramic membranes are gaining a lot of interest nowadays due to their higher selectivity, permeation rate, and chemical and thermal stability that enable them to possess long life in solid-liquid separation (Yoshino et al. 2005). Microfiltration of oil–water emulsions, dye and heavy metal solutions are regarded to be an important avenue for the application of ceramic membrane technology in industrial processing schemes (Benito et al. 2005). It has been reported that some of the inorganic films and membranes composed of carbon, silica, or a zeolite displayed higher permeabilities and selectivities than organic ones. These membranes were not tried industrially due to the high cost of the support. Hence, there is a necessity to look for alternative low-cost materials for preparing the ceramic support so as to make the prepared membrane commercially competitive. In order to reduce the cost of the membrane, recently, low-cost clays are utilized for the fabrication of membrane. These include raw clay, Algerian clay, dolomite, Moroccan clay, sepiolite clay, Tunisian clay and kaolin (Saffaj et al. 2006; Khemakhem et al. 2006; Emani et al. 2013).

In the present work, low-cost ceramic membrane was fabricated at different sintering temperatures using locally available clay material with inorganic materials. The structural characteristics and chemical stability of the membrane was investigated for various sintering temperatures. Porosity and structural density were also evaluated to optimize the sintering temperature to get high porous low-cost ceramic membrane for solid-liquid separation.

MATERIALS AND METHODS

Raw materials

Kaolinite ($Al_2Si_2O_5(OH)_4$), sodium meta silicate (Na_2SiO_3), sodium carbonate (Na_2CO_3) boric acid (H_3BO_3) and 125 µm size locally available clay were used for the fabrication of ceramic membrane. Chemicals were procured from Loba Chemie Pvt. Ltd, Mumbai, India and used without further purification.

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Table 1 Composition of the ceramic membrane

Components	Weight%	
	Dry basis	Wet basis
Clay	60	47.36
Kaolinite	29	22.89
Sodium carbonate	5	3.94
Sodium meta silicate	3	2.37
Boric acid	3	2.37
Water	-	21.06

Membrane preparation

Initially, raw materials were kept in a hot air oven for 5-6 hr at 105°C. Then certain compositions (Table. 1) of dried raw materials were mixed properly in ball mill. The membrane disk was prepared by paste casting method. In paste method, raw materials were mixed properly with adequate amount of millipore water to make paste. The paste was then cast over gypsum in the shape of a circular compact disk (55 mm diameter and 5 mm thickness) using a stainless steel ring of 55 mm inner diameter and 5 mm thickness. Subsequently, the ring was carefully removed and the paste was kept under distributed pressure of 2-3 kg for 24 hours to prevent the propagation deformation and drive homogeneity in the inorganic matrix. The paste was then subjected to four different sequential heat treatment steps. The first step involved drying at ambient temperature for 24 hours. During the second heat treatment step, the membrane was dried at 100°C for 12 hours in a hot air oven. The third heat treatment step consists of drying at 250°C for 24 hours. During the transition from 100□250°C, low heating rate was maintained in order to eliminate the induction of thermal stresses generated due to loss of moisture. The final heat treatment step involved heating of the membrane from 250°C to desired sintering temperature at a heating rate of 2°C per minute. Finally, the membrane was kept for 5 hours for sintering. The membranes were sintered at different temperatures (800, 850, 900 and 950°C) based on the literature information. Subsequent cooling of the membrane was carried out by atmospheric cooling procedure adopted by switching off the muffle furnace that was previously maintained at the desired sintering temperature. After sintering, membrane achieved hard, rigid and porous texture. Finally, the prepared membrane was polished with silicon carbide abrasive paper (C-220) to obtain a smooth, flat membrane of diameter 50 mm and thickness 5 mm.

Membrane characterization

Membrane morphological studies were carried out using SEM to analyze the presence of possible defects and estimate the membrane pore size. (ii) Membrane porosity and structural density was estimated to find the optimum of sintering temperature. (iii) Membranes were tested for their corrosion resistance using NMP, NaOH and HCl solution. (iv) FTIR analysis was performed to find the functional groups of the fabricated membrane. (v) Energy Dispersive X-ray (EDX) analysis of the membrane before and after corrosion resistance test was carried out to verify any change in elemental composition.

RESULTS AND DISCUSSION

Surface morphology

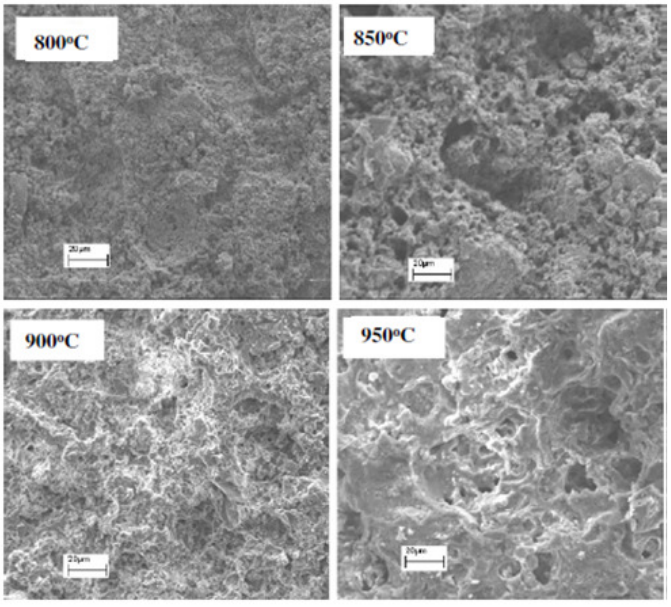

Fig 1. SEM micrographs of ceramic membrane at different sintering temperature

Morphological study of prepared ceramic membrane was done by scanning electron microscope (SEM, LEO 1430VP, Oxford) to analyze the presence of possible defects in membrane. Image software (version 1.37) was used to measure the pore size and the pore size distribution of membrane (Chakrabarty et al. 2008). SEM images were taken from various parts of the prepared membrane and magnified using software. SEM pictures of the sintered membranes at four different temperatures are shown in Fig. 1. All membranes showed a rough surface structure. The ceramic membranes sintered at lower temperature (800 and 850°C) possessed highly porous structure. The membranes sintered at 900 and 950°C were more consolidated due to the fact that sintering temperatures over 900°C enabled greater agglomeration of particles to yield more dense structure. Due to this reason, the porosity of the membrane reduced with an increase in sintering temperature. An overall observation of the images shows that, for all the membranes maximum number of pores was within the range of 0.35-0.7 μm and the average pore size was 0.58 μm.

Porosity and Structural density

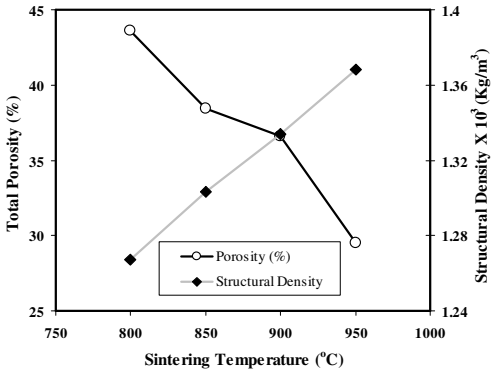

Fig 2. Effect of sintering temperature on porosity and structural density

The total porosity of the synthesized membrane was calculated by Archimedes principle. The experimental procedure involved in the measurement of the volume of the wetting liquid that displaced air in a dry membrane after equilibrating the membrane with water for 12 hours. Total porosity (ε_m) and structural density (ρ_{mem}) of the membrane were calculated using the following equations (Mulder, 1991):

$$\varepsilon_m\ (\%) = \left(\frac{w_1 - w_2}{\rho_{water}}\right) \times \frac{100}{v_{mem}} \quad (1)$$

$$\rho_{mem} = \frac{w_2}{v_{mem}} \quad (2)$$

where, v_{mem} is volume of the membrane in wet state (m^3), w_1 is weight of membranes in wet condition (kg) and w_2 is weight of membranes in dry condition (kg).

The variation of membrane porosity and structural density of membrane with varying sintering temperature are shown in Fig. 2. It can be seen from the Fig. 2 that structural density of the membrane increased with an increase in sintering temperature. However, the total porosity reduced with increasing sintering temperature. When the sintering temperature was increased from 800 to 950°C, porosity of the membrane decreased 43.6 to 29.5% where as structural density increased 1267 to1368 kg/m^3. This was due to the reason that higher sintering temperatures enable densification of the porous structure to enhance structural density and reduce membrane porosity. This was also reasoned with the fact that with increasing sintering temperature, the number of pores representing small pore sizes reduced and hence the overall pore volume and porosity decreased.

Chemical stability

The corrosion resistance and chemical stability of the prepared ceramic membranes at different sintering temperatures was analyzed using NaOH (pH = 12), HCl (pH = 2) and pure NMP solutions. The membranes were subjected at different pH solutions for porosity and weight loss measurement, and EDX analysis after 7 consecutive days at atmospheric conditions. It was observed that the membrane porosity and elemental compositions of the prepared ceramic membranes were found almost invariant with NaOH, HCl and NMP. Similarly, the weight loss of membranes during chemical stability tests was not significant and was less than 4% for all membranes at different sintering temperatures. Therefore, the ceramic membranes had good corrosion resistance and suitable for different microfiltration applications.

Fourier transform infrared (FT-IR) spectroscopy analysis

Fourier transform infrared spectroscopy (FTIR) analysis was performed to observe the presence of functional groups in the synthesized membrane after sintering. Diffuse reflectance spectra were recorded in the range of 4000–400 cm^{-1}. Membrane sample was mixed separately with KBr in 5:100 (wt/wt) to make a pellet of less than 20 µm size. The pellet was prepared under an infrared light to prevent possible absorption of water. In FTIR analysis, broad bands observed around 3443 cm^{-1} and 1647 cm^{-1} are due to the water absorbed during pelletization. The peak at 594 cm^{-1} is assigned to AlO_6 and the shoulder observed at 865 cm^{-1} is assigned to AlO_4. The peak observed at 464 cm^{-1} is due to the kaolinite mineral group. From these results, it may be concluded that Al_2O_3 (calcined samples) contain tetrahedral and octahedral Al–O (Cross, 1964).

CONCLUSIONS

A membrane based technique was proposed to improve the economy for solid-liquid separations. The work summarized fabrication of a defect free ceramic microfiltration membrane with average pore diameter of around 0.58 µm. Membrane characterization was performed and porosity was measured as 43.6% to 29.5% within sintering temperature range of 800–950°C. The prepared ceramic membrane had good chemical stability with highly acidic and basic pH solutions. FTIR analysis showed the broad bands of OH^- functional group which is responsible for many minerals separations. Therefore, this low-cost membrane based technology will definitely reduce the overall fabrication cost compared to the existing commercial membranes.

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