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Elaboration of novel tubular ceramic membrane from inexpensive raw materials by extrusion method and its performance in microfiltration of synthetic oily wastewater treatment

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ABSTRACT

A tubular ceramic microfiltration membrane was prepared by an extrusion technique using inexpensive clay mixtures namely, ball clay, kaolin, feldspar, quartz, pyrophyllite and calcium carbonate. The mixture of clay powders extruded to form a porous tubular membrane without the addition of any organic additives. The dimensions, such as outer and inner diameters, wall thickness and length of the tube are 11.5, 5.5, 3 and 100 mm, respectively. The sintered membrane possesses the porosity of 53%, water permeability of 5.93×10^{-7} m/s kPa, an average pore size of 0.309 μm and mechanical strength of 12 MPa with very good corrosion resistance in acidic and basic conditions. The fabricated membrane is expected to have potential applications in the pretreatment and also can be used as support for ultrafiltration membranes. With this intention, the membrane is subjected to microfiltration of synthetic oily wastewater emulsion experiments at various combinations of applied pressures (69–345 kPa), feed concentrations (50–200 ppm) and cross flow rates (5.55×10^{-7}–1.66×10^{-6} m^3/s). An increase in the applied pressure and flow rate of oily wastewater emulsion result a decreased oil rejection while, an increase in the oil concentration results in enhanced rejection. The applied pressure of 69 kPa offers the highest rejection of oily wastewater (99.98%) with permeate flux of 3.16×10^{-5} m/s. Additionally, the membrane fouling mechanisms are investigated using diverse pore blocking models (complete, standard, intermediate pore blocking and cake filtration model) with obtained experimental data. It is found that the experimental results are well described by the cake filtration model. Finally, the rejection potential of the membrane is compared with other membranes reported in the literature.

1. Introduction

In recent years, the potential utilization of ceramic membranes has greatly improved, especially in a broad range of industrial processes and pollution treatment technologies. Ceramic membranes can be applied in extreme aggressive environments due to their distinct advantages, including good thermal stability, mechanical strength, chemical resistance, long lifetime and defouling properties. While organic polymer membranes cannot be applied owing to their restricted stability [1–3]. In general, most of the commercialized ceramic membranes available in the market are produced from alumina, silica, zirconia and titania materials. However, these ceramic membranes are severely restricted in large scale application due to the higher cost of starting materials and sintering processes [4–5]. Therefore, the preparation of ceramic membranes with lower cost and excellent characteristics are the challenging tasks for the upcoming development of ceramic membranes for treatment of a large volume of waste matters contaminated liquids. Tubular ceramic membranes are especially suitable in applications where the feed stream contains a relatively high proportion of large particles, and where the membranes are exposed to extreme pH and temperature conditions. In general, the size of the feed flow channels in tubular ceramic membranes is larger than other membrane modules. This type of open channel geometry reduces the risk of the blockage of the feed channels and also the requirement of costly pretreatment before microfiltration [6]. Generally, ceramic membranes comprise of multi-layer formation with the substrate (support), intermediate layer and skin layer (separating layer). The substrate of membranes can be produced by various techniques, including isostatic pressing, extrusion, slip casting, etc., [7,8]. The fabrication of porous ceramic membrane with the tubular configuration needs the expertise on choosing appropriate starting materials and methods. Shaping by extrusion is achievable only if the paste created from starting materials has rheological characteristics similar to those of clays [9]. As a consequence, currently many researches targeted on the development of ceramic membranes

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with utilization of less expensive materials such as apatite powder, dolomite, pyrophylite, Moroccan clay and kaolin, etc,. [10–13]. Talidi et al. [10] prepared the tubular macroporous membrane using pyrophylite clay via extrusion and followed by a sintering process. The properties of the porous pyrophyllite membrane were discussed as a function of sintering temperature in order to optimize the preparation conditions. Saffaj et al. [11] prepared membrane support using Moroccan clay as a raw material by extrusion of the clay paste. The structural and mechanical properties of fabricated low cost membrane support were found suitable for membrane applications. Masmoudi et al. [12] produced tubular porous support using natural apatite powder and suggested for ultrafiltration (UF) and microfiltration (MF) applications. Bouzerara et al. [13] constructed membrane support from mixtures of doloma and kaolin. They strongly recommended that prepared support can be utilized for MF and UF processes.

A huge volume of oily wastewater was created from different process industries, including petrochemical, petroleum refineries, transportation and metallurgical industries [14]. Discharging of this effluent causes environmental pollution as well as decreases the yield of oil. Therefore, the treatment of oily wastewater is compulsorily required before discharging. As per environment (protection) rules (1986, India), the central pollution control board framed the discharge limit of oil into surface water as 10 (mg/L), public sewers as 20 (mg/L), irrigation water as 10 (mg/L) and coastal water as 20 (mg/L) from various industries [15]. Several conventional techniques have been used for oily wastewater treatment that includes electrostatic coalesce, heating treatment, filter coalesce, centrifugal settling, gravity settling, pH adjustment and chemical emulsification. All of these methods have some advantages and disadvantages [16,17]. Hence, membrane technology comes into sight as a best competent technique for treatment of oily wastewater amongst the various conventional techniques. In addition, it is very attractive due to the advantages, such as compact design, lower energy requirement and higher separation efficiency as compared to other existing treatment processes [18]. However, the treatment cost can be further lowered by choosing microfiltration (MF) membranes since they do not require so high trans-membrane pressures and have higher flux than ultrafiltration membranes [19]. Numerous authors have evaluated the potential aspects of ceramic membranes in oily wastewater treatment. Mohammadi et al. [20] formulated a kaolin based tubular ceramic membrane with a pore diameter of 10 μm for the treatment of oily wastewater emulsions. The prepared membrane provided a good separation performance on various operating conditions. Zhong et al. [21] examined the efficiency of ZrO_2 ceramic membrane (average pore diameter of 0.2 μm) in oily wastewater treatment. The prepared zirconia membrane displayed the oil removal of 99.4–99.9%. Yang et al. [22] attained 99.8% of oil rejection utilizing the commercial tubular (ZrO_2/α-alumina) membrane with an average pore diameter of 0.2 μm. In another study, Cui et al. [17] obtained 99% of oil rejection employing the zeolite membrane having the pore size of 1.2 μm in microfiltration of oily wastewater. Amongst many research perceptions, the development and employment of the ceramic membranes derived from inexpensive raw materials for oily wastewater treatment are getting interest in recent days.

Considering such research trends, the study presented here focuses on the preparation of the novel tubular ceramic membrane by an extrusion method and evaluation of separation performance in treatment of oily wastewater emulsion. Contemplation on reducing the price of the membrane and to assess our natural resources, the local clay materials: kaolin, quartz, ball clay, pyrophyllite, feldspar and calcium carbonate are utilized as raw materials. The performance of the membrane is investigated through microfiltration of synthetic oily wastewater emulsions on various operating parameters, such as applied pressure, feed concentration and cross flow rate with respect to rejection and permeate flux. The fouling mechanisms are examined using obtained flux data during the microfiltration.

2. Materials and methods

The starting materials utilized for elaboration of the membrane (kaolin, quartz, ball clay, pyrophyllite, and feldspar) were of mineral grade and obtained in the vicinity (Kanpur). Crude oil was procured from Guwahati Refinery, IOCL (Assam). Calcium carbonate, hydrochloric acid and sodium hydroxide were supplied by Merck (I) Ltd, Mumbai.

2.1. Elaboration of tubular ceramic membrane

Tubular ceramic membrane was fabricated with length, inner and outer diameters of 100, 5.5, and 11.5 mm, respectively. The composition of clays taken for the fabrication of tubular membrane is as follows: Ball clay – 18 wt%, Feldsper – 6 wt%, Kaolin – 15 wt%, Pyrophyllite – 15 wt%, Quartz – 28 wt%, Calcium carbonate – 18 wt%. Clay powders were accurately weighed according to the composition and mixed with the determined volume of Millipore water to make the paste for extrusion. No organic additives were used for the preparation of paste. The obtained paste was fed into the extrusion cylinder. Then, evacuation piston forced the paste through a die in a tabletop extruder to form a tubular shape membrane. The tubular membrane was extruded in the horizontal direction with the forwarding velocity of ~0.007 m/s at room temperature. When the tube reached the length of around 120 mm, the process extruder stopped and the tube was cut with sharp blades. Then, the obtained tubular membrane was subjected to natural drying at room temperature for 12 h. After which, the membrane was dried at 100 °C for 12 h and 200 °C for 12 h in a hot air oven. Subsequently, the membrane was taken to the sintering process with a heating rate of 2 °C/min and sintered at 950 °C for 6 h in a box furnace. These restrained thermal treatment steps were followed to avoid the formation of micro cracks and bends in the membrane. Finally, the elaborated membrane was washed with water and dried at 100 °C for further characterization.

2.2. Characterization of raw materials and tubular ceramic membrane

The XRD study was carried out to identify the phase transformation behavior of the membrane before and after sintering. The profiles measured in a Bruker AXS instrument using Cu Kα radiation source. The profiles were recorded in the 2θ range of 5–75° with a scan rate of $0.05^\circ\ s^{-1}$. Thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis were performed to evaluate the thermal stability and the minimum sintering temperature required for membrane fabrication. The thermal behaviors of mixed raw materials were analyzed by Mettler Toledo TGA/SDTA 851® instrument in an air atmosphere from 30 to 1000 °C in 150 μL platinum crucible with a heating rate of 10 °C/min. The tubular membrane was characterized using a field emission scanning electron microscope (FESEM, JEOL JSM-5600LV) to analyze the presence of possible defects on the surfaces. A small size of the membrane sample was fixed on top of the stub and layered with gold using an auto fine coating instrument (JEOL JFC-1300) preceding to morphology assessment. The porosity of the membrane was measured by utilizing water as a soaking agent. The mechanical strength was measured using a standard three-point bending test by Computerized Universal Tester (DUTT-101, India). Four tubular ceramic membranes (length of 100 mm) were tested with the bending