Preparation and application of low-cost ceramic membranes for separation of oil-water emulsion

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Abstract. This work presents the impact of fabricating pressure on the performance of ceramic membranes during the dead-end microfiltration of an oil-water emulsion. The membranes used in this study were fabricated at a pressure of 40 kN and 100 kN using the dry compaction method. The membrane characterization was done using XRD and FTIR analysis. The membrane performance was evaluated by carrying dead-end microfiltration experiments using synthetic oil-water emulsion as a feed at a trans-membrane pressure of 30 psi. The experimental results confirmed that the membrane fabricated at higher fabricating pressure (100 kN) gives better performance in terms of maximum oil rejection of 95.7% with the maximum flux of 2.04x10⁻³ m³/m².s.

Keywords: ceramic, membrane, oil, flux, rejection

1. Introduction
The oily water discharged from the petroleum, and petrochemical industries not only affect the environment but also human health [1]. The typical concentration of oil in the effluent produced from the petroleum refineries is in the range of 100-300 ppm [2]. According to the Environmental regulations, the maximum tolerable concentration of oil in the effluent is not more than 10–15 ppm [3]. Thus, to recover the oil from discharged effluent many conventional treatment techniques like gravity separation, skimming, coagulation, flocculation, biodegradation, de-emulsification, and membrane filtration have been in use [4]. Amongst all, membrane filtration is considered as suitable candidature because of its simplicity, low cost, high permeability, and oil rejection [5, 6]. In the literature, few researchers fabricated ceramic membranes composed of Al₂O₃, ZrO₂, TiO₂, and zeolite for oil-water emulsion separation and achieved a greater oil rejection [7, 8, 9]. Though they achieved the highest oil rejection one of the major drawbacks reported by the authors was the high cost of fabrication. Due to this reason lately, there has been substantial importance towards the development of low-cost ceramic membranes using inexpensive ceramic precursors [10]. Low-cost ceramic precursors have become a renewed interest among researchers due to their increased durability and chemical stability. Sriharsha et al. [11] synthesized low-cost ceramic membranes of average pore size and porosity in the range of 30.1-37.4% and 3.06-2.16 µm, respectively at different fabricating pressure using inexpensive ceramic precursors (kaolin, quartz, sodium carbonate, calcium carbonate, sodium metasilicate, and boric acid). The authors reported that the membranes exhibited the highest oil rejection of 98.5% for the trans-membrane pressure maintained at 207 KPa and concluded that a high rejection was achieved at a very low cost of fabrication. Therefore, to engineer decent ceramic membranes, it is necessary to choose...
suitable membrane precursors by taking into consideration their cost and properties followed by optimizing the fabrication pressure. Considering this as an objective, this work aims to investigate the impact of fabricating pressure on the removal efficacy of oil from the synthetic solution of oil-water emulsion using dead-end microfiltration.

2. Experimental

2.1. Preparation of membrane

The membranes (36 mm OD and 4 mm thickness) used in this work were made from inexpensive ceramic precursors like kaolin, feldspar, quartz, sodium carbonate, sodium metasilicate, pyrophyllite, and boric acid whose wt% and significance are given in Table 1. The preparation of the membrane consists of the sequential steps of mixing and grinding the ceramic precursors, casting, sintering followed by cooling to room temperature, polishing, and cleaning the membrane in an ultrasonic bath. The casting is done by the uniaxial dry compaction method at fabrication pressure of 40 kN and 100 kN. The sintering process comprise drying the membrane at 100°C for 24 hrs followed by raising the temperature to 800°C at a heating rate of 1.6°C/min and maintaining it at 800°C for 4 hours.

| Material             | Composition (wt% on dry basis) | Properties                                      |
|----------------------|--------------------------------|-------------------------------------------------|
| Kaolin               | 40                             | Low plasticity and high refractoriness           |
| Feldspar             | 15                             | Improves hardness, durability                    |
| Quartz               | 15                             | Thermal and mechanical stability                 |
| Sodium carbonate     | 10                             | Improve dispersion properties and act as colloidal agent |
| Pyrophyllite         | 10                             | Thermal stability                                |
| Boric acid           | 5                              | Increase mechanical strength by creating metabolates during sintering |
| Sodium metasilicate  | 5                              | Increase mechanical strength by creating silicate bonds |

2.2. Characterization of Membrane

X-ray diffraction (XRD) was used to determine the elemental composition of both raw materials and the membrane. Fourier Infrared Transform Spectroscopy (FTIR) was used to identify the functional group existing in the raw material and in the membrane.

2.3. Oil-water emulsion preparation

The synthetic oil-water emulsion of 400 ppm was prepared by dissolving 200 mg of crude oil (Ankleshwar crude) in 500 ml of water. For efficient dispersion of oil in water, the mixture was then placed in an ultrasonic bath for 5 hours.

2.4. Microfiltration of oil-water emulsion

Microfiltration of synthetic oil-water emulsions was performed at a trans-membrane pressure of 30 psi using a dead-end microfiltration setup shown in Fig. 1. In order to obtain the permeate flux and percentage of oil rejection, the permeate sample was collected at different time intervals by placing an electronic weighing balance at the bottom of the permeate cell. The concentration of oil in the feed and in the permeate samples was determined using UV-spectrophotometer at a wavelength of 235 nm. The permeate flux ($m^3/m^2.s$), and % oil rejection (R) were determined using the Eq. 1 and Eq. 2.
\[ J = \frac{V}{A\Delta t} \]  

(1)

\[ R = 100(1- (C_p/C)) \]  

(2)

Where \( V \) is permeate volume (\( m^3 \)), \( A \) is the active surface area of membrane (\( m^2 \)), \( \Delta t \) is the sampling time (\( s \)), \( C \) and \( C_p \) are respectively, the concentration of oil in the feed and in the permeate (\( mg/L \)).

3. Results and Discussion

3.1. Membrane Characterization

Fig. 2 depict the XRD pattern of the raw material and the sintered membrane. It can be viewed that the peaks appearing in the raw material are corresponding to kaolin and quartz. The increase of intensity of quartz peak reflecting at 26.75° in ceramic membrane is an indication of an increase of crystallinity of the quartz. Similarly, the disappearance of kaolinite peaks in ceramic membrane is an indication of the transformation of kaolin into metakaolinite. Fig. 3 depict the Fourier transform infrared spectra (FTIR)

![Figure 1. Experimental setup for dead end microfiltration](image)

![Figure 2. X-ray diffraction for raw material and ceramic membrane](image)
of raw material and the sintered membrane. The kaolin characteristic peak observed at 3674 cm\(^{-1}\) is due to the stretching vibration of OH\(^{-}\). After sintering, the decrease of vibration peak to 3348 cm\(^{-1}\) is suggesting incomplete calcination of kaolin to calcined kaolin. The peak at 2922 cm\(^{-1}\) was ascribed to C-H bonds which were visible after sintering. Bands 1031 cm\(^{-1}\) and 948 cm\(^{-1}\) are consigned to Si-O bonds and absorption at 484.83 cm\(^{-1}\) is assigned to Si-O-Al bonds. The peak appearing at 1660 cm\(^{-1}\) is due to stretching H\(_2\)O present in the raw materials and is disappeared after sintering. Similarly, a C=C bond peak was found at 1660 cm\(^{-1}\). The peaks in the region between 1420 cm\(^{-1}\)-1460 cm\(^{-1}\) denoted the presence of carbonate minerals. The Si-O bonds are the strongest and they are readily recognized by the infrared spectra. Feldspar, on the other hand, has three different structures with the same molecular formula (monoclinic, triclinic, and tetrahedral). The peak range between 580-583 cm\(^{-1}\) persisted due to bending vibrations of O-Si(Al)-O in triclinic feldspar and the range pertaining between 640 cm\(^{-1}\) and 1748-1775 cm\(^{-1}\) are due to Al-O coordination vibration pointed out the presence of monoclinic feldspar [12].

![FTIR spectral for raw material and ceramic membrane](image)

**Figure 3.** FTIR spectral for raw material and ceramic membrane

![Variation of flux with time at 30 psi TMP](image)

**Figure 4.** Variation of flux with time at 30 psi TMP
3.2. Microfiltration of oil-water emulsion

Fig. 4 depicts the time dependent permeate flux profiles for the membranes fabricated at 40 and 100 kN. From the figure, it can be observed that for both membranes, at a trans-membrane pressure of 30 psi the permeate flux declination was rapid in the first 3 min and thereafter it becomes gradual. The flux declination could be due to either the membrane pore blocking or the formation of oil film over the membrane surface which further offers additional resistance for the permeate to flow. For the membrane fabricated at 40 kN, the flux declined from $3.1 \times 10^{-3}$ to $8.9 \times 10^{-5} \text{ m}^3/\text{m}^2\cdot\text{s}$ within the first 24 min. On the other hand, for the membrane fabricated at 100 kN within the same time period, the flux is declining from $2.05 \times 10^{-3}$ to $2.33 \times 10^{-5} \text{ m}^3/\text{m}^2\cdot\text{s}$. Higher the flux for the membrane fabricated at 40 kN is due to the presence of wider pore distribution as compared to the membrane fabricated at 100 kN.

Fig. 5 shows the percentage of oil rejection with respect to time for the membrane fabricated at 40 kN and 100 kN. From the figure, it can be seen that for the membrane fabricated 40 kN at a trans-membrane pressure of 30 psi the percent of oil rejection is increasing from 84.4% to 89.6% with filtration time. Similar trends were observed for the membrane fabricated at 100 kN. The increase of percent of oil rejection with the time is due to the reduction of the pore size caused by the plugging of pore or deposition of oil layer over the membrane surface.

4. Conclusion

This work aimed at preparing low-cost ceramic membranes, followed by characterization, and industrial application using oily wastewater. The prepared membranes possessed properties for the treatment of oily wastewater. The major conclusions obtained from the study are reviewed below:

- On increasing the fabrication pressure, the pore size of the membrane decreased. This eventually led to decrease in permeate flux with increase in the rejection rate of the membrane.
- The cake formation on the membrane surface acted as second filter, which increased the rejection rate.
- The overall rejection percentage of 100 kN membrane was 95.7%, whereas the overall
rejection % of 40 kN was 89.6%. This clearly indicated that, as the pore size increased, the purity of permeate decreased.

- In case of 100 kN membrane, the steady state permeate flux was reached after 30 minutes and the value was noted to be $2.33 \times 10^{-5} \text{m}^3/\text{m}^2 \cdot \text{s}$. On the other hand, 40 kN ceramic membranes exhibited steady state behavior of permeate flux in 24 minutes and the value was noted to be $8.9 \times 10^{-5} \text{m}^3/\text{m}^2 \cdot \text{s}$.

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