Special Issue Published in International Journal of Trend in Research and Development (IJTRD), ISSN: 2394-9333, www.ijtrd.com

Fabrication and characterization of Circular Disc Membrane (CDM) using Cheaper Ceramic Precursors for Hemofiltration Application

[1]Roshni. M, [2]Mohit. C, [3]D. Vasanth and [4]R. Periyasamy,
[1,2,3]Department of Biotechnology, National Institute of Technology Raipur, Raipur, Chhattisgarh – 492010, India
[4]Department of Biomedical Engineering, National Institute of Technology Raipur, Raipur, Chhattisgarh – 492010, India

***Abstract*—** In recent years, the ceramic membrane has received significant attention in biotechnological and medical applications. Due to their excellent chemical resistance, reusability and longer shelf life, ceramic membranes could be subjected to steam sterilization and rigorous cleaning procedures. In addition, ceramic membranes could be also deployed in process scenarios that involve higher shear rates, vibratory systems and oscillatory flow conditions. In this work, the circular disc membrane (CDM) was fabricated using cheaper ceramic precursors such as natural white clay, quartz and calcium carbonate. The membrane was sintered at 900^{o}C to obtain consolidated ceramic substrate. The characterization of membrane was carried out on various parameters such as morphology (Scanning electron microscopic analysis), porosity, water flux, pore size, water permeability, chemical resistance and biocompatibility. SEM result shows that the membrane doesn't have any crack and pin holes. The porosity, water permeability and pore size is found to be 42%, 2.88×10^{-4} L/m^{2}.h.Pa and 127 nm, respectively. The membrane displays good corrosion resistance in acidic and alkali solutions. The biocompatibility tests affirm that the prepared membrane is more suitable for hemo-filtration applications.

***Keywords*—** *Natural white clay, porosity, pore size, water permeability, biocompatibility*

I. INTRODUCTION

The research in the field of membrane technology is targeted towards the synthesis of membrane for medical applications. Nowadays, the preparation of membrane for hemo-dialysis and hemo-filtration is intensified. For instance, Fissell et al. [1] prepared the silicon/PEG nanopore hemofiltration membranes using MEMS technology. The prepared membranes posses pore size in the range of 9.7–10.9nm. Similarly, the hollow fiber polyethersulfone membrane was prepared for hemofiltration by yang et al. [2]. The results show that the polyethersulfone membrane clears toxic waste from blood. Dukhin et al. [3] used hollow fiber polymeric membrane for hemofiltration application and achieved continuous and consistent operation for more than 100h. Recently, kaleekkal et al. [4] fabricated the polymeric membrane for hemodialysis. The membranes were prepared using polysulfone and polyethersulfone polymeric materials. The results show that the prepared membranes possess excellent biocompatibility.

A critical review of above literatures conveys that the polymeric membranes are primarily used for the hemo-filtration applications. However, the polymeric membranes have poor blood and cell compatibility, lower mechanical and chemical stability and more swelling property. In this context, the application of ceramic membrane for blood purification application is very important. Compare to polymeric membranes, ceramic membranes have good blood compatibility, excellent chemical resistance, reusability and longer shelf life. To best of our knowledge, the applicability of ceramic membrane for hemo-filtration application has not yet been studied. Considering this issue, this work reports the preparation of disc ceramic membrane for blood purification application. Using inexpensive raw materials such as natural white clay, quartz and calcium carbonate, the ceramic membrane was fabricated with newly identified composition of raw materials. Morphological analysis of the membrane was performed to identify the general membrane characteristics. Water permeation test was carried out to evaluate the membrane performance. Corrosion resistance test was conducted to identify suitable cleaning procedures and its stability in highly corrosive medium. Biocompatibility experiment was performed to verify its suitability for blood purification application. Finally, the cost estimation was carried out to compare the cost of other reported membrane in literatures.

II. EXPERIMENTAL

A. Raw Materials

Three different ceramic raw materials namely natural white clay, quartz and calcium carbonate were used to fabricate the ceramic membrane (Table 1). The natural white clay and quartz were procured from Royalty minerals, Mumbai, India. Calcium carbonate was purchased from Loba Chemie, Ltd. All materials were used as received without purification.

TABLE I. COMPOSTION OF RAW MATERIALS

S. No	Composition of raw materials		
	Materials	***Quantity (gm)***	***Function***
1	Natural white clay	50	Refractory properties
2	Quartz	25	Increases the mechanical strength
3	Calcium carbonate	25	Porosifier and sintering aid

Amongst these raw materials, natural white clay provides high refractory property, quartz increases the mechanical and thermal stability and calcium carbonate acts as pore forming agent as well as sintering aid.

B. Membrane preparation

Using trial and error based approach, a new composition of raw materials was identified and employed for preparation of disc membrane. The identified composition of raw materials is

presented in Table 1. The membrane was fabricated by uni-axial compaction method and involves different sequential steps (Fig.1). Initially, the raw materials were thoroughly mixed with the 4ml of 2% polyvinyl alcohol (binder) using pestle and mortar. The necessary amount of powder was then pressed at higher pressure (50 MPa) using hydraulic press (Guru Ramdas Machine Works, Raipur, India) and stainless steel mold to obtain disc type of membrane (51 mm diameter and 5 mm thickness). Next, the obtained disc membrane was dried at 100°C for 24 h in hot air oven to remove the moisture present in the membrane. Subsequently, the membrane was sintered at 900°C in a muffle furnace (Nanotec, Chennai, India) with heating rate of 2°C per min for 5 h. The cooling of membrane was done by natural cooling process by switching off the muffle furnace. After sintering, the membrane was polished both sides using abrasive sheet (No. 220) and washed using ultrasonicator (PCI Analytics, India) to remove the loose particles present in the pore path. Finally, the membrane was dried at 100°C for 24 h. Fig.2. shows the image of prepared disc membrane. It is visible that the membrane is exactly circular in shape with uniform thickness.

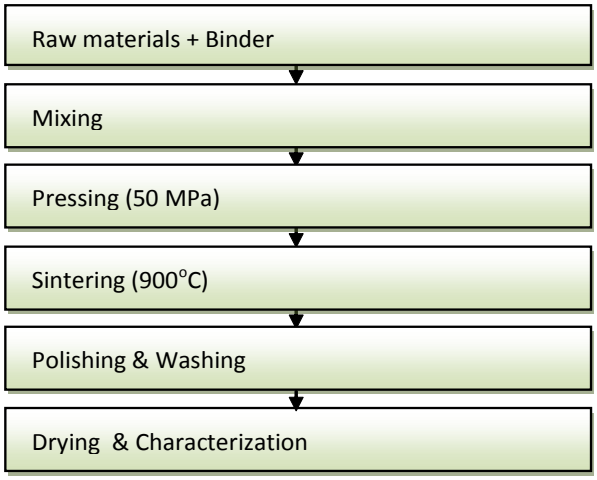

Fig. 1. Schematic representation of membrane preparation

C. *Characterization techniques*

The characterization techniques of membrane includes scanning electron microscopy analysis (SEM), porosity, water flux and water permeability, pore size and chemical stability were conducted. The morphological study of membrane was performed using scanning electron microscope (ZEISS – EVO18). The primary objective of the SEM analysis was to identify the morphology of the membrane surface. The EDX analysis was performed to confirm the elements present in the prepared membranes and their dependence with respect the variations in compositions of the precursors. The average membrane porosity was determined using Archimedes' principle, in which the membrane was first dried in hot air oven at 110 °C for 6 h to remove moisture and its dry weight (W_1) was determined. It was then immersed and kept in water for 24 h. After that, the membranes were taken out from water and water on the outer surface was removed using tissue paper. Finally the wet weight of the membrane (W_2) was measured. The porosity of the membranes were determined using the expression

$$\varepsilon(\%) = \left[\frac{W_2 - W_1}{\rho_{water}}\right] \times \frac{100}{v_{mem}} \quad (1)$$

where W_2 & W_1 are the wet and dry weight of membranes, ρ_{water} is the density of water and ν_{mem} is the volume of the membranes.

Corrosion resistance (chemical stability) of membrane was analyzed at different pH ranging from (1-14) using HCl and NaOH solutions. To determine the chemical stability, firstly, the weight of the membrane before leaving them in contact with acid and base solutions was measured. Then the membrane was left in contact with acid and base solutions for seven consecutive days under atmospheric condition. Thereafter, the wet membrane was taken out and dried. Eventually, the weight of dried membrane after acid and base treatment was taken. The difference in the weights of membrane characterizes the chemical stability of membrane. The water flux (J, L/m^{2}h) of membrane was evaluated at different applied pressure (69-345 kPa) using a indigenous continuous dead-end filtration setup (Fig. 3).

Fig. 2. Image of prepared membrane

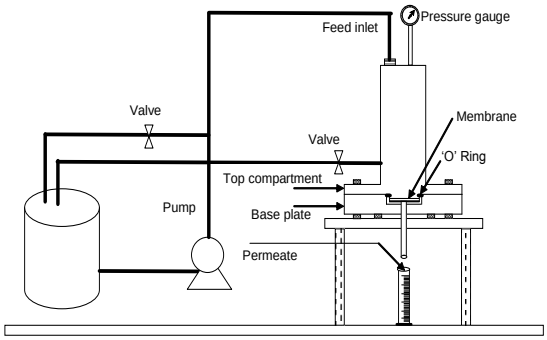

Fig. 3. Experimental setup for water flux

The flux measurement was conducted at room temperature (25°C) that involves the measurement of permeate volume at an interval of 10 min during the total run time of 60 min. The flux was evaluated using the relation.

$$J = Q/A \times t. \quad (2)$$

Where, Q is the volume of permeate collected (l), t is the time and A is effective membrane area (m^2) for permeation.

The water permeability (L_h) and average pore radius (r_l) of the membranes were determined from water flux data according to the following expression

$$J_v = \frac{\varepsilon r^2 \Delta P}{8\mu l} = L_h \Delta P \quad (3)$$

where J_v (L/m^{2}h) is the liquid flux through the membrane, ΔP (kPa) is the trans-membrane pressure drop across the membrane, μ is the viscosity of water, l is pore length, ε is the porosity of the membrane. The reported water flux values were average of three different readings and the time

dependent flux data was regressed as a straight line to obtain hydraulic permeability.

In order to identify the biocompatibility of prepared membrane, the protein adsorption test was conducted using bovine serum albumin (BSA) and phosphate buffer saline (PBS) solution. Initially, the protein solution was prepared at a concentration of 4.5 mg/mL using PBS as buffer. Next, the membrane sample (1 × 1 x 0.5 cm) was immersed in protein solution for 2 h at room temperature. After that, the membrane was rinsed in PBS solution for several times to remove unbound protein in membrane surface. The adsorbed protein was removed by immersing the membrane into 1wt% sodium dodecyl sulfate (SDS) solution for 1h at room temperature. Eventually, the concentration of adsorbed protein present in the SDS solution was quantified by Bradford method.

III. Results and Discussion

A. Scanning electron microscope analysis

Fig. 4 illustrates the SEM image obtained from prepared ceramic membrane. It is apparent that the membrane posses rough and porous morphological structure. Further, it is observed that the membrane doesn't have any crack and pinholes. Using Image J software, the surface pore size of membrane is found to be about 300 nm.

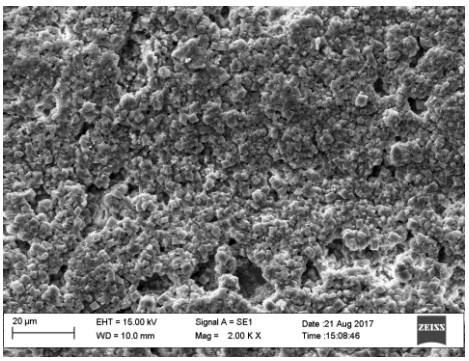

Fig. 4. SEM image of prepared membrane

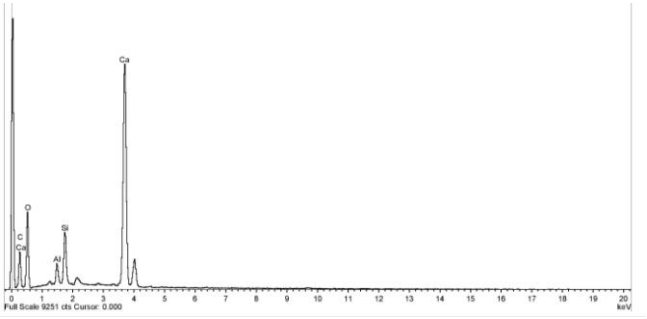

Fig. 5. EDX analysis of membrane

Fig. 5 illustrates the EDX analysis of membrane. The EDX graph was obtained to identify the elemental composition of membrane. It is analyzed that the main elements that are present in the membrane are carbon, oxygen, aluminum, silicon and calcium and their relevant compositions are present in Table 2.

B. Porosity

Porosity is an important parameter that determines the pore size and number of pores present in the membrane. The porosity was determined by Archimedes principle using water as wetting liquid. The porosity of membrane was found to be 42%. In this regard, it can be analyzed from porosity data presented by various researchers [5,6] that the membrane prepared with cordierite and kaolin posses porosity of 36.2% and 40.9 %, respectively. Thus it is apparent that the formulated composition of raw material provides higher porosity.

C. Water flux and permeability

The pure water flux was measured at different trans-membrane pressure (69-345 kPa) for total run time of 60 min at time interval of 10 min (thickness of membrane is 3.5 mm). The time dependent flux of at different applied pressure is presented in Fig. 6. It can be observed that the flux is constant over entire time range studied. It indicates that there is no any resistance for pure water flow. Further, it is noted that water flux increases linearly with increasing pressure (Fig. 7). Thus it obeys Darcy's law. Using the water flux data, water permeability of membrane is determined to be 2.88×10^{-4} (L/m^2hPa).

TABLE II. EDX analysis of membrane sintered at 900 ^{o}C

S. No	Elemental composition	
	Elements	*Weight (%)*
1	Carbon	16.99
2	Oxygen	48.57
3	Aluminum	1.67
4	Silicon	4.12
5	Calcium	28.68

D. Average pore size

Using the water flux data, the average pore diameter of membrane is evaluated to be 127 nm. In this context, it can be pointed out that the reported pore size (127nm) is significantly lesser than the average pore size obtained with different precursors namely apatite (5 µm), cordierite (8.66 µm), and Moroccan clay (10.75 µm) [5,7]. Henceforth, it can be concluded that the membrane is suitable for blood purification application.

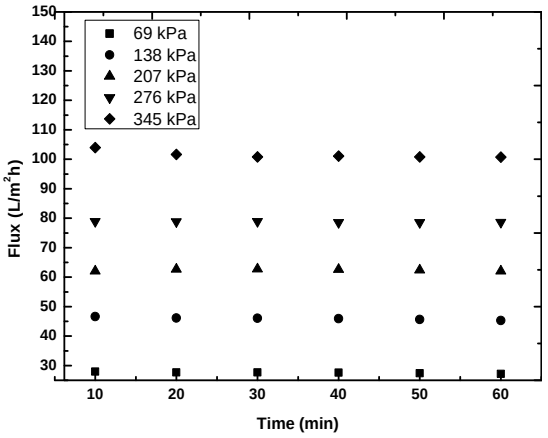

Fig. 6. Time Vs flux

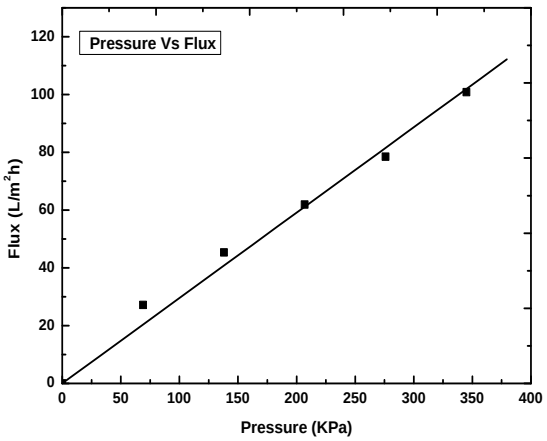

Fig. 7. Applied pressure Vs flux

E. Corrosion resistance

Corrosion resistance test was conducted to identify the suitable pH range for membrane cleaning and process application. In view of this, the membrane was subjected to treat with acid and alkali solutions at different pH range (1-14). Fig. 8, presents the weight loss of membrane evaluated after treatment with acid and alkali solutions. It can be observed that the major weight loss occurred at pH 1 (15 %) and 1% weight loss also observed at pH 2. This indicates the membrane is not suitable for any process application with feed streams of pH range (1-2). Also, the membrane is not suitable for cleaning at pH range of (1-2). However, no weight loss was observed at pH range of (3-14) which indicates the membrane have good chemical stability at pH range of (3-14). From this test, it can be concluded that the membrane is very suitable for cleaning as well as process application at pH ranges of 3-14.

F. Biocompatibility

Static protein adsorption is the primary technique to evaluate the antifouling and hemocompatibility of membrane surface. Protein adsorption can be influenced by various factors such as membrane surface chemistry, protein shape and size, charge and isoelectric point. The amount of protein adsorbed on the membrane surface is found to be 4µg/cm^2. The value is significantly less which indicates the suitability of membrane for hemofiltration application. Further, this result is in accordance with the result of kaleekkal et al [4]. The summary of characterization results is presented in Table 3.

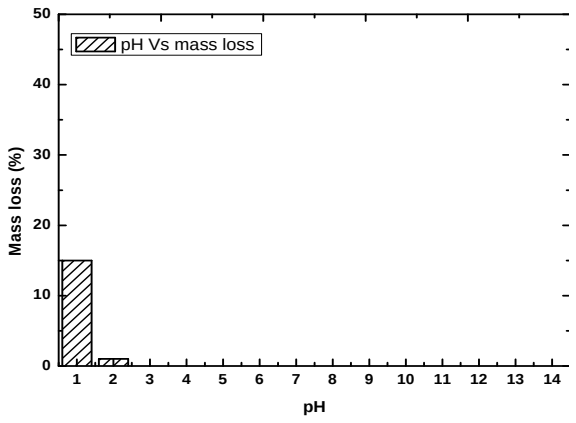

Fig. 8. Chemical stability analysis of membrane

TABLE III. SUMMARY OF CHARACTERIZTION RESULTS

S. No	Characterization results	
	Properties	***Values***
1	Porosity (%)	42
2	Water permeability (L/m^2 h Pa)	2.88×10^{-4}
3	Pore size (nm)	127

TABLE IV. COST ESTIMATION OF PREPARED MEMBRANE

S. No	Cost Estimation			
	Raw materials	***Unit price/kg (Rs.)***	***Raw materials used for preparation of one membrane (gm)***	***Cost of one membrane (Rs)***
1	Natural white clay	11.40	10	0.11
2	Quartz	11.40	5	0.06
3	Calcium carbonate	252	5	1.26
			Total	1.43

G. Cost Analysis

In general, the cost of ceramic membrane is high as compared to polymeric membrane. Therefore, the research in the preparation of low cost ceramic membrane is intensified worldwide. Further, the cost of membrane is primarily depending upon the raw material cost and fabrication method. Therefore, the selection of raw materials is vital for preparation of any membrane. Based on the raw material cost, the cost of membrane is estimated to be Rs. 1.43 (5mm thickness and 51 mm diameter). The details of cost estimation are presented in Table 4

IV. CONCLUSIONS

A new ceramic raw material composition was identified for the preparation of ceramic disc membrane. In addition, the identified ceramic formulation can be provided defect-free membrane. SEM result shows that the membrane doesn't have any crack and pin holes. The porosity, water permeability and pore size is evaluated to be 42%, 2.88×10^{-4} L/m^2.h.Pa and 127 nm, respectively. The membrane exhibits better corrosion resistance in acidic and alkali solutions. The biocompatibility tests affirm that the prepared membrane is more suitable for hemo-filtration applications.

Acknowledgment

The authors would like to express their sincere thanks to Department of Science and Technology, India (DST-SERB) for the financial support.

References

[1] W. H. Fissell, A. Dubnisheva, A. N. Eldridge, A. J. Fleischman, A. L. Zydney and S. Roy, High-performance silicon nanopore hemofiltration membranes, J. Membr. Sci., vol. 326, pp. 58–63, 2009.

[2] Q. Yang, T.S. Chunga and M. Weber, Microscopic behavior of polyvinylpyrrolidone hydrophilizing agents on phase inversion polyethersulfone hollow fiber membranes for hemofiltration, J. Membr. Sci., vol. 326, pp. 322–331, 2009.

[3] S.S.Dukhin, Y. Tabani, R. Lai, O.A. Labib, A.L. Zydney and M.E. Labib, Outside-in hemofiltration for prolonged operation without clogging, J. Membr. Sci. vol.464, pp.173–178, 2014.

[4] N.J. Kaleekkal, A.Thanigaivelan, M. Tarun and D. Mohan, A functional PES membrane for hemodialysis – Preparation, characterization and Biocompatibility, Chin. Jr. Chem. Eng., vol. 23, pp 1236 – 1244, 2015.

[5] Y. Dong, X. Feng, D. Dong, S. Wang, J. Yang, J. Gao, X. Liu and G. Meng, Elaboration and chemical corrosion resistance of tubular macro-porous cordierite ceramic membrane supports, J. Membr. Sci., vol.304, pp. 65 –75, 2007.

[6] F. Bouzerara, A. Harabi, S. Achour and A. Larbot, Porous ceramic supports for membranes prepared from kaolin and doloma Mixtures, Jr. Euro. Ceram. Soci., vol. 26, pp.1663 – 1671, 2006.

[7] N. Saffaj, M. Persin, S.A. Younsi, A. Albizane, M. Cretin and A. Larbot, Elaboration and characterization of microfiltration and ultrafiltration membranes deposited on raw support prepared from natural moroccan clay: application to filtration of solution containing dyes and salts, App. Clay. Sci., vol. 31, pp. 110 – 119, 2006.