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Synthesis and characterization of inorganic microfiltration membrane through geopolymerization

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ABSTRACT

An inorganic microfiltration membrane has been synthesized by the hydrothermal method at a curing temperature of 90°C for 15 h through geo-polymerization technique using kaolinite material found in Azakhel Matani, Khyber Pakhtunkhwa, Pakistan. The metakaolin was obtained from the kaolinite material through calcination process at 700°C. XRF analysis of the thermally activated material revealed the presence of Si and Al in the ratio of 2.97. Geopolymer gel $Na_2O–3SiO_2–Al_2O_3$ was prepared by separate mixing of metakaolin with alkaline activator with the molar ratio of 2.5. The higher compressive strength of 62 MPa was achieved with the applied pressure of 46.55 MPa keeping Na_2SiO_3 to NaOH of 4.3 and 18 M concentrations.

Keywords: Geopolymerization; Inorganic membrane; Microfiltration; Kaolin; Metakaolin; Compressive strength; Hydrothermal treatment.

1. Introduction

Membrane separation is one of the most attractive, economical and novel separation processes. Separation through membrane is considered to be sustainable because of its environmentally friendly behaviour and less operational cost as compared to other available conventional processes. The membrane act as a barrier between the phases adjacent to it under a driving force such as pressure difference across the membrane [1]. The membrane process can operate continuously and the separation mechanism is controlled by the size of the particles to be removed. Solutes larger than the membrane pore size will be rejected and termed as retentate [2].

Both organic and inorganic membranes play a vital role in processes such as water treatment, gas separation and in various other applications [3]. Polymeric membranes are susceptible to high temperatures and harsh chemical environment. The inorganic ceramic membranes attracted the attention of scientists because of its long-term stability at high temperature, resistance to harsh environments, inertness to the microbiological degradations, easy to clean-ability and catalytic activation [4]. Ceramic membranes are however costly due to high sintering temperature, therefore, the research has been focused to prepare membranes with low cost. Ceramic membranes prepared by geo-polymerization technique do not need sintering process. Further, these membranes have shown higher compressive strength and other superior structural properties [5].

The concept of geopolymerization was first introduced by Davidovits in 1978 [6], with a three dimensional network of aluminoslilicate by reacting with high alkaline hydroxides and dehydroxylate clay or other materials rich in silica and alumina oxides.

Two major constituents of the geo-polymeric material are the source material and the alkaline activator [7]. The source materials contain silica and alumina oxides. The mechanical properties and reaction time for geo-polymer material is highly dependent on the ratios of these two components. The Si and Al contents can be obtained from different sources i.e

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natural pozzolana, clay, fly ash, silica fume, slag, rice husk ash, red mud and kaolin [8]. Kaolin contains significant amount of Al and Si which can be a suitable source material for geo-polymer production [9]. The other important constituent of geo-polymer material is the alkaline activator i.e. mixtures of sodium or potassium hydroxide and potassium or sodium silicates which reacts with silicon (Si) and aluminium (Al) in a source material to produce geo-polymer material [10]. Geo-polymerization is a stepwise process where first the calcinations is carried out to convert the rich alumina and silica oxide to metakaolin by removing hydroxyl group through thermal activation of the kaolin material at 700 °C to 800 °C [11]. The higher amount of hydroxyl group leads to the high calcinations temperature and subsequently long reaction time having lower compressive strength [12]. Fourier transform infrared spectroscopy and X-ray diffraction are used to analyse the presence of hydroxyl group and amorphous nature of metakaolin respectively. Chemical activation of metakaolin through high alkaline silicate is the second steps in geopolymerization i.e. KOH and K_2SiO_3 or NaOH and Na_2SiO_3 are mixed with the source material forming a three dimensional network [13]. As a result of chemical activation, amorphous geopolymer material is produced which is then processed through curing and hydrothermal treatment to enhance its compressive strength [14].

Cui et al [15] synthesized a self-supported zeolite membrane of 10 mm thickness with compressive strength of 19.6 MPa using alumina and silicon oxide at calcinations and hydrothermal temperature 800°C and 90°C respectively. Duxsona et al. [16] investigated the production of inorganic membrane using metakaolin material with Si to Al ratio of 3.1 and 1.21 respectively. Bouzerara et al [17] found that ceramic membrane characteristic is dependent on the Al and Si composition, particle size of the source material and alkali ratio in chemical activation. They found that a particle size of 9.52 µm is the most suitable for developing inorganic microfiltration membrane.

Zeng et al. [18] investigated the effect of alkali ratio on the compressive strength of membrane and found that the compressive strength increases with increasing ratio of Na_2SiO_3/NaOH. Various inorganic membranes were synthesized using fly ash as source material and found compressive strength of 26 MPa, 70 MPa and 75 MPa with 3.5%, 3.8% and 4.1% of Na_2SiO_3/NaOH ratio respectively.

Geopolymerization is sintering free membrane fabrication technique, which can also utilize waste materials as compared to the other conventional inorganic membrane synthesis techniques [19,20].

In the present work, inorganic micro-filtration membrane has been synthesized by geo-polymerization techniques using the locally available kaolinite materials.

2.1. Material and methods

2.1. Experimental procedure

In the present study, the mineral material was collected from Mattani Aza Khel, 23 km south of Peshawar Pakistan as shown in Fig. 1. Specific gravity of the sample was recorded as 1.28 which is comparatively low as reported in the literature but the material under investigation is fluffy in nature; therefore the specific gravity is low.

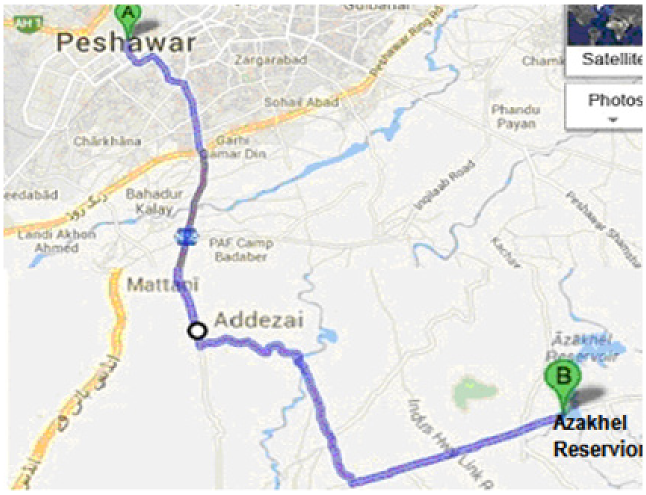

Fig. 1. Google map indicating location of mineral material.

The moisture was removed by placing the sample for 1 h at 105°C in the muffle furnace (model: L5/12/C6, manufacturers: Nabertherm, Germany, max. temperature: 1200°C). The particle size of the source material was reduced to 250 mesh (67.39 µm) for characterization through impact grinder. The composition of the source material was investigated through X-ray fluorescence (Model: XRF-1800, Manufacturer: Shimadzu).The result is shown in Table 1. Geopolymerization is a stepwise process, and chemical activation is carried out after thermal activation [20]. Fig. 2 illustrate the experimental procedure for the development of inorganic microfiltration membrane through geo-polymerization process. The particle size was reduced by wet milling process using a ball mill with zirconia media for 19 h. The particle size of metakaolin was measured by Coulter counter (model: UNSPSC 41113903, analysis range: 0.4 µm to 1200 µm, diameter 0.036 to 904.8 × 106 µm³ volume), which consist of a tube with a small aperture at the bottom. Sample material is dipped into the beaker containing a low concentration electrolyte. The sample material is forced to flow through the apertures of the tube varying in sizes. An electric field is applied across the beaker. Any flow of the sample from tube affect the flow of current which directly proportional to their sizes.

Table 1
XRF results kaolin and metakaolin at 650°C and 700°C

Chemical composition	Kaolin (%)	Metakaolin	
		650°C	700°
SiO_2	54.98	59.55	60.51
Al_2O_3	17.54	19.56	20.33
Fe_2O_3	5.33	4.68	4.75
CaO	5.40	5.17	5.58
MgO	0.20	0.21	0.15
SO_3	0.00	0.00	0.00
Na_2O	0.95	0.07	0.07
K_2O	0.09	0.86	0.86
L.O.I.	14.50	4.18	2.23

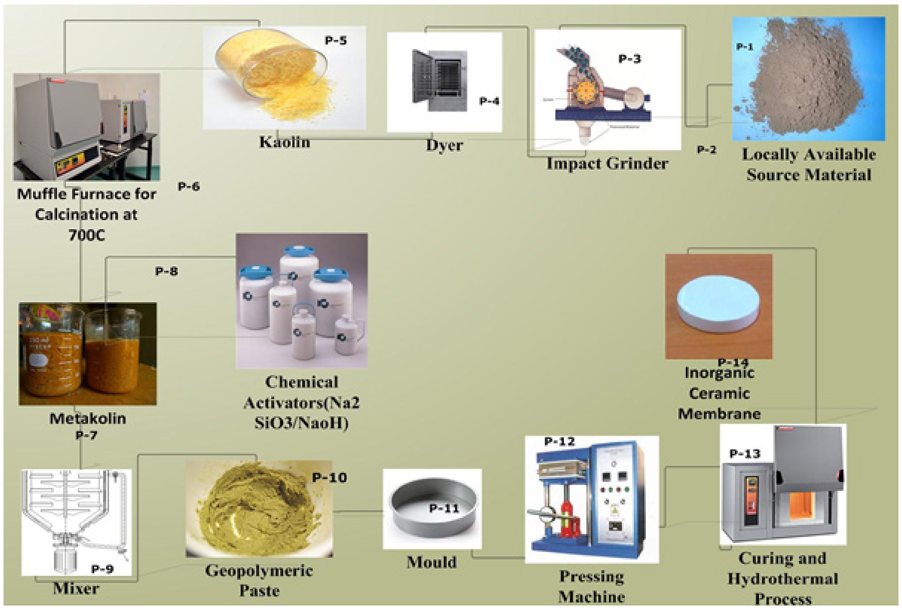

Fig. 2. Processing schematic for synthesis of geo-polymeric inorganic membrane.

TGA analysis (model: TGA 8000, operation range: 20–1200 °C) of the source material was carried out to find out the activation temperature. Thermal activation of material was done in muffle furnace for kaolinite material conversion into metakaolin. Removal of hydroxyl group and amorphous nature of metakaolin was conformed through FTIR (model: FTIR-4000, manufacturer: JASCO) and XRD (machine model: JDX3532, voltage: 20–40 kV, current: 2.5–30 A, X-rays: CuKa (l = 1.54 Å), 2 theta-range: 0 to 160°).Source material used in geopolymerization techniques must have a rich amount of Si and Al oxide. The alkaline activation of Si and Al of the natural source material from three dimensional geopolymeric networks [21]. In this research work, sodium hydroxide (98% Pure) and sodium silicate (Na_2O = 14.7%, SiO_2 = 29.4% and water = 55.9% by mass) were used as a chemical activator. Metakaolin material were then chemically activated through separate mixing in a ratio of 2.5 by an alkaline activator such as Na_2SiO_3/NaOH (4.4 molar ratio of Na_2SiO_3:NaOH with 18 M concentration of NaOH solution) [22]. The resulting geo-polymer pastes were then moulded and pressed in a load machine to obtain the rigid pellets of geopolymeric membrane.

To overcome the partial crystalline nature of the geopolymer membrane, the samples were subjected to curing process at 50°C for 6 h followed by the hydrothermal treatment at 90°C for 14 h in muffle furnace. The structural and surface characterization of the developed membrane were performed by scanning electron microscope (model JSM5910: manufacturer: JEOL, Japan, magnification max: 300,000X). The pore size was measured from SEM analysis by plotting the standard scale on pore of membrane. As the membrane was containing pores of different dimension, the average was taken. The compressive strength of the synthesized membrane was checked through the universal testing machine (model: 100-500KN, make: testometricinc). Each membrane sample was placed in a testing machine and a specific pressure was applied until the sample breakdown. This procedure was applied for all the specimens and their respective breakage point were recorded as shown in Table 3.

3. Results and discussion

3.1. Characterization of material

3.1.1. Mineral and activated materials characterisation

Table 1, shows the XRF results of source material i.e. kaolinite and metakaolinite. The aggregate percentage of SiO_2 and Al_2O_3 in the source material is more than 70%, which shows an optimum ratio for the development of geopolymeric material with no need of any additive for composition adjustment [16]. Fig. 3 shows the thermal gravimetric analysis of the source material. Calcinations temperature is observed around 650°C–700°C as no weight losses is seen beyond these temperatures. For confirmation, further characterization was done through XRD and FTIR, as shown

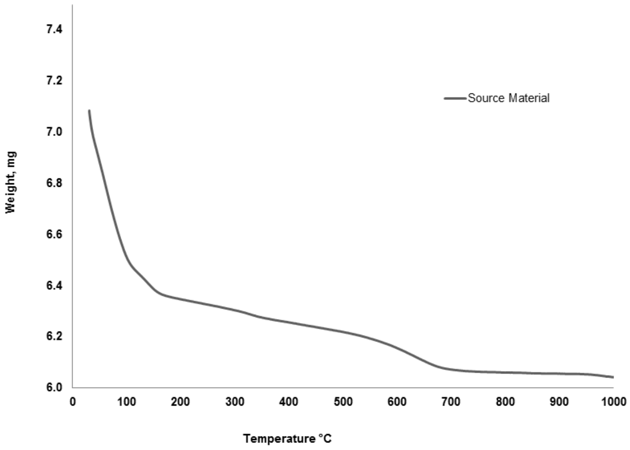

Fig. 3. TGA analysis of source sample.

in Figs. 4 and 5 respectively. Fig. 4 shows semi crystalline structure at 650°C while show amorphous nature at 700°C. Fig. 4A–C show XRD patterns of as received sample, activated at 650°C and 700°C respectively. Fig. 5 confirms the presence of hydroxyl group at 650°C but no hydroxyl group at 700°C. From the results of Figs. 3–5 it was concluded that the final thermal activation temperature is 700°C. Further, the LOI of source material is dropped by about half i.e. from 4.18 to 2.23 when the activation temperature was increased from 650°C to 700°C, which make satisfying ASTM-C595 (5% LOI) for thermal and chemical activation [23]. Percent ratio of Al and Si oxide in source material significantly alter the mechanical properties of geopolymeric material. It was found that material at a temperature of 700°C has the maximum Si to Al ratio of 2.97, which was considered the optimum ratio for high compressive strength [24].

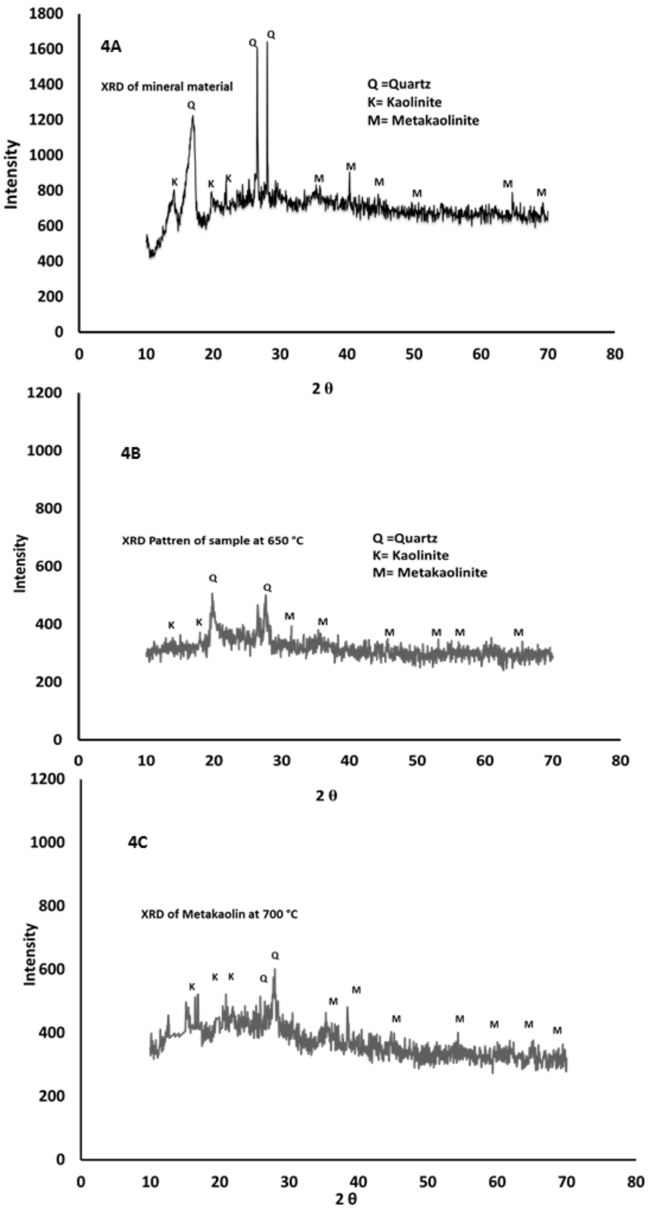

Fig. 4. XRD pattern of activated material at 650°C and 700°C.

XRD is the finger print of crystalline materials [25]. Many researchers [26], reported that conversion of kaolin to metakaolin is in the range of 600–800°C. In the present research work the kaolinite material was converted to metakaolin by thermal activation at 700°C for 2 h in muffle furnace.

3.1.2. Particle size distribution

Fig. 6 shows the relationship between volume percent and particle size of metakaolin. Resulting particle size of the source material (metakaolin) was found in the range of 8.4 to 9.5 micrometres which is a good size distribution for microfiltration [18]. In geopolymerization; the source material undergoes chemical reaction with the alkaline activator to form the geopolymer. However, the initial particle size also contributes to affect the pore size which ultimately affects the filtration capacity of the membrane. Jedidi et al.

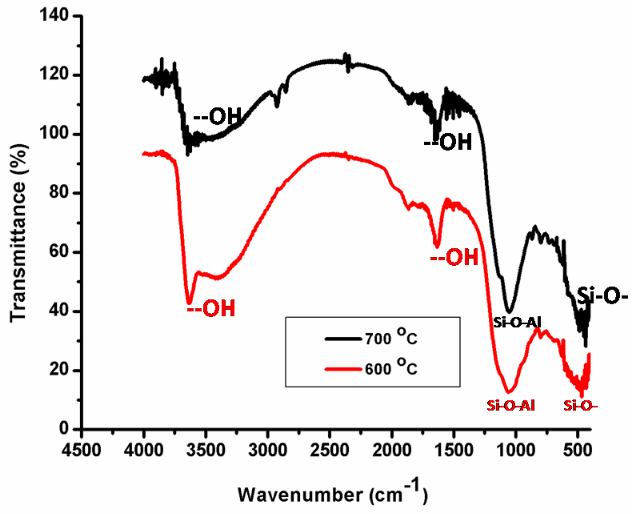

Fig. 5. FTIR pattern of activated material at 650°C and 700°C.

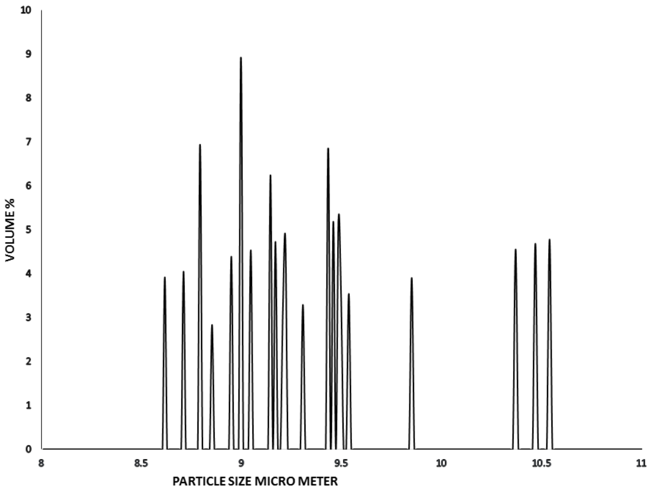

Fig. 6. Relation between metakaolin volume percent and particle size (μm).

[19] also reported that the pore diameter of ceramic microfiltration membrane from coal ash depends on the particle size distributions before mixing with binding solution.

3.2. Characterization of membrane

3.2.1. Influence of Na_2SiO_3/NaOH on compressive strength of inorganic membrane

To examine the effect of alkali solution on compressive strength of inorganic membrane, Na_2SiO_3/NaOH solutions in a percent ratio of 3.3, 3.6, 3.8, 4.0, 4.1, 4.2, 4.3 and 4.4 were mixed with the fixed amount of metakaolin, which was then further treated in mixer having 18 M solution at 100 rpm for 12 min through a separate mixing process. From Fig. 7 it is observed that the maximum compressive strength of 62 MPa is achieved at 4.3% ratio after curing and hydrothermal treatment at 90°C for 14 h.

3.2.2. Effect of applied load on membrane thickness and compressive strength

The membranes of various thicknesses have been prepared by varying applied load as shown in Table 2. Increasing the applied load not only decreases the thickness of the membrane but also increases its compressive strength. Maximum compressive strength has been achieved with applied load of 46.55 MPa which corresponds to membrane thickness of 2.73 mm. The low thickness will results in low resistance to flow and consequently will results in high permeation membrane.

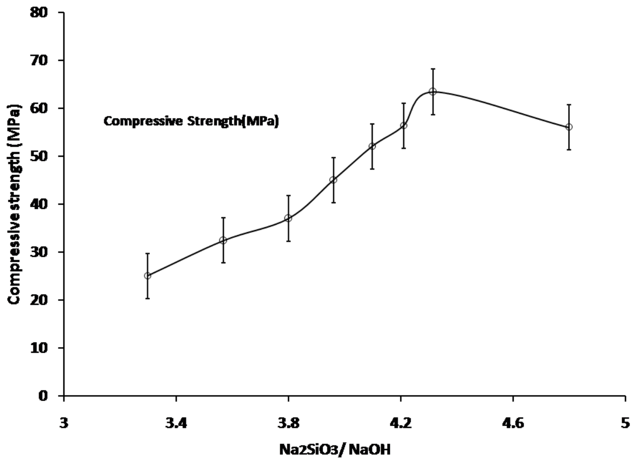

Fig. 7. Effect of chemical activator ratios on compressive strength.

Table 2
Effect of applied load on geo-polymeric paste on compressive strength after 4 days

Load applied (MPa)	Thickness of membrane (mm)	Resulting compressive strength (MPa)
18.38	6.01	25
27.58	4.08	32
36.76	3.98	37
40.17	3.73	39
46.55	2.73	50

3.2.3. Comparison of compressive strength before and after hydrothermal treatment

Compressive strength is an important physical property for the determination of the structural strength. The compressive strength is not only effected by the applied load but curing and hydrothermal treatment also affects the compressive strength. Hydrothermal treatment enhances the crystallinity and compactness of the ceramic membranes [11]. This increase in crystallinity and compactness also increases the compressive strength. Table 3, shows the effect of hydrothermal treatment on compressive strength of the geo-polymeric membrane with a 2.5 metakaolin to alkaline and 4.3 Na_2SiO_3 to NaOH ratios. It was observed that for each sample the compressive strength is higher with hydrothermal treatment and a maximum compressive strength of 62 MPa was achieved after curing and hydrothermal treatment at 90°C for 15 h at applied load of 46.55 MPa.

3.2.4. Morphological characterization of synthesized membrane

Morphological study of membrane was carried out with the help of scanning electron microscopy to analyse the presence of possible defect, pore size and pore size distribution of inorganic ceramic membrane which was synthesized from metakaolinite materials. Narrow pore size distribution can be seen in Fig. 8, which would result in better separations or good rejections efficiencies.

SEM images were taken from cross section and surface of the ceramic membrane with different magnification before and after curing and hydrothermal treatment. Fig. 9A and 9B show the comparative results of pore size before and after curing and hydrothermal treatment respectively. The SEM of Fig. 9A and 9B clearly indicate that the relative surface density and crystallinity have been well developed due to curing and hydrothermal treatment which resulted in high compressive strength.

The average pore diameter of 1.04 µm is obtained before curing and hydrothermal treatment. After curing

Table 3
Effect of hydrothermal treatment on compressive strength of geopolymeric ceramic membrane

S. No	Geo-polymeric sample without hydrothermal treatment (MPa)	Geo-polymeric sample with hydrothermal treatment (MPa)
1	25.0	27.7
2	32.0	33.0
3	37.0	37.1
4	39.0	45.8
5	44.0	53.1
6	47.8	56.0
7	50.1	62.0
8	52.1	53.1

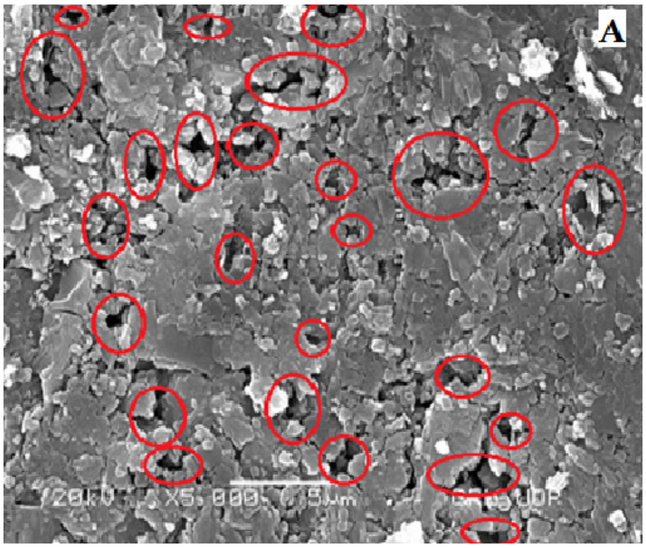

Fig. 8. SEM image of geopolymeric membrane showing pore distribution before hydrothermal treatment.

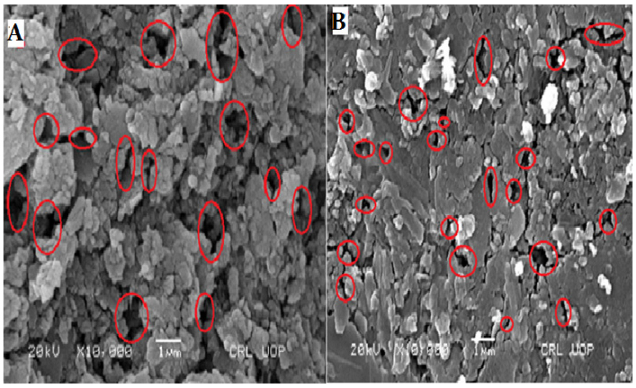

Fig. 9. (A) SEM image of geopolymeric membrane showing the pore size. (B) SEM image of ceramic membrane after curing and hydrothermal treatment.

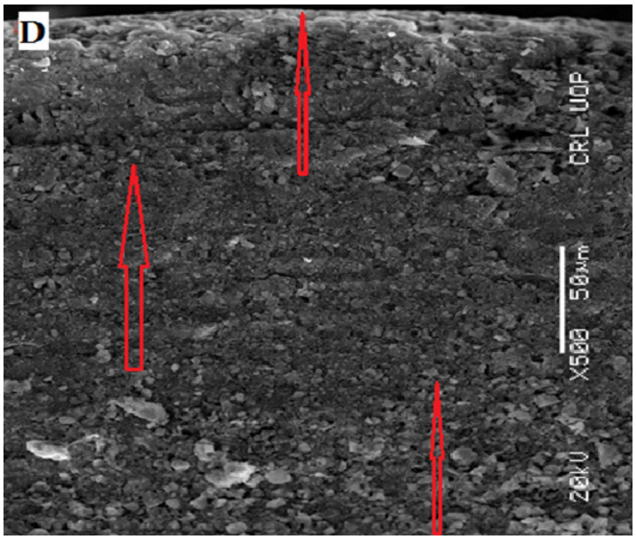

Fig. 10. Cross sectional SEM image of ceramic membrane.

and hydrothermal treatment the average pore size was reduced in the range of 0.6 to 0.8 µm. The SEM shows that membranes can be made dense and compacted after hydrothermal treatment at 90°C for 15 h [27]. Fig. 10 shows the thickness and the asymmetric nature of the membrane.

Apparent observations from the SEM images show that the ceramic membrane does not have any pinhole crack.

The main focus of the study is to utilize the sintering free geopolymerization techniques for the synthesis of ceramic microfiltration membrane. In the present work, the synthesized membrane has average pores size of 0.6 µm to 0.8 µm which can be used for the treatment of waste water from car washing stations and produced water treatment, where inorganic ceramic membrane have already shown good results [28].

4. Conclusions

From this research work, it is concluded that inorganic microfiltration membranes with structurally enhanced pores and high compressive strength of 62 MPa under the applied pressure of 46.55 MPa can be prepared by sintering free geopolymerization technique using locally and readily available kaolinite mineral materials with a calcinations temperature of 700°C. The developed membrane posseses high mechanical strength. The porosity of geopolymeric membrane under a fixed ratio of Si/Al and metakaolin/alkaline can be adjusted by particle size of source materials before chemical activation. Geopolymerization is preferable for synthesis of cost effective and high compressive strength membrane which can survive in demanding, harsh and corrosive environment.

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