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Synthesis and characterization of fly ash based geopolymeric membrane for produced water treatment

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ABSTRACT

Geopolymerization is a green innovative technique for the synthesis of inorganic membrane using fly ash as a raw material. In this work, fly ashes from thermal power plant were used as a source material for the synthesis of sintering-free, self-supported geopolymeric membrane. Geopolymeric slurry was obtained by chemical activation (Na_2SiO_3/NaOH = 2.5 and 15 M) of fly ashes (Si/Al = 2.8) after mixing of 30 min with 120 rpm. Compressive strength of 18.5 MPa was achieved after curing and hydrothermal treatment at 90°C for 24 h with the average pore size of 0.4–0.3 μm. Flux of different range 10, 14, 20, 26, and 29 L h^{-1} m^{-2} was obtained at driving pressure of 2, 3, 4, 5, and 6 bar respectively. Flux decline for produced water through prepared membrane were investigated after 60 s. Parametric studies of produced water from oil and gas production facility were also investigated before and after treatment.

Keywords: Fly ash; Chemical activators; Geopolymeric membrane; Produced water treatment

1. Introduction

Thermal power plants have global share of 75% in the electricity generation which produced fly ashes as waste products during coal combustion [1,2]. Besides, problematic environmental pollutants these waste ashes occupy a lot of land and attract the focus of environmental protection agencies, which are the additional tasks for the management, while, there is no such disposal units and effective utilization policy for the transformation of waste ashes to meaningful products [3]. Utilization of ashes from coal thermal power plants to produce membranes is the prime objective of this research work. Bakri et al. [4] used fly ashes for the synthesis of cementitious products for construction purpose through geopolymerization technique. Ashes are used as a source material in geopolymerization reaction because these ashes have silica to alumina in the ratio of 2.0 to 3.0 , which is considered the optimum ratio for synthesis of geopolymeric materials [5,6]. This involves a heterogeneous chemical reaction between alumina-silicate materials with high alkali silicates. Hydroxides and silicates of sodium or potassium are used as chemical activators for dissolution of silica and alumina oxides of fly ashes [7]. Aleem et al. [8] investigated that alkaline activators attack

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on the silica and alumina oxide of source materials and form strong tetrahedral network.

The term "geopolymer" was first devised by Davidovits in St. Quentin, France in 1970s [9]. Yan et al. [10] reported that geopolymeric materials are economical due to sintering-free temperature and less emission of CO_2 during cement manufacturing which make them eco-friendly. These inorganic polymeric materials are chemically inert and have strong physical properties such as high compressive strength, durability and long operational life. Adak et al. [11] used geopolymeric techniques for the synthesis of porous inorganic membrane for the waste water treatment.

In the last two decades, separation through membranes has replaced the heat intensive conventional techniques of separation such as distillation and evaporation because membrane technology offer eco-friendly, economical an less utility cost which considered membrane as a best available technology [12]. The strong physical properties such as its resistance to harsh environments, long term stability and inertness to biological degradation of inorganic membranes have attracted the attention of researchers [13]. On the other hand, inorganic membrane are costly than polymeric membrane because of its expensive raw materials such as alumina, mullite, silica, titania and zirconia along with the complex manufacturing process with heat intensive steps such as calcination and sintering [14]. These difficulties are overcome by sintering-free geopolymerization techniques using waste ashes as a source material [10]. Cui et al. [15] synthesized inorganic self-supported membrane by using geopolymerization technique for the separation of ethanol from water. Similarly, other researchers, used metakaolin and red mud as a source material for synthesis of inorganic geopolymeric membrane which need high calcination temperature up to 800°C for 2 h [12]. Furthermore, conventional techniques need high sintering temperature which made the synthesis process of inorganic membrane heat intensive and less economical. On the other hand, geopolymerization technique provides a road to sintering-free preparation of ceramic membrane. The intensive nature of sintering techniques is replaced by the chemical reaction between alkali activators and fly ashes [16]. Geopolymerization is a two steps processes of inorganic membrane synthesis i.e. attack of chemical activators and hydrothermal treatment of membrane while other conventional techniques have complex nature and multi-steps synthesis processes [17].

In this research work, geopolymeric membrane was synthesised through geopolymerization technique using fly ashes of Lakhra coal power plant, Sindh, Pakistan as a source materials. The fabricated membranes were characterized for surface morphology, pore size and compressive strength, the self-supported geopolymeric membrane was then tested for treatment of produced water of oil and gas production facilities (MOL, Pakistan).

2. Materials

2.1. Fly ashes from power plant

Fly ash used in the present study was taken from the power plant at Lakhra, Sindh Pakistan, which generate electricity of 150 MW since 1995 with the release of 50 tons fly ash per day [2]. Ratio of silica and alumina oxides was the prime factor for selecting source material which must be in the range of 2.5–3.0. It was observed that after moisture evaporation at 105°C for 2 h, black colour changed to white grey. Naveed et al. [13] used kaolinite as a source material having a ratio of Si/Al is 3.0 for synthesis of inorganic membrane. Selmani et al. [18] found that compressive strength of prepared materials was dependent on the ratio of Si_2O_3/Al_2O_3.

2.2. Chemical activators

Chemical activators were required for silica and alumina oxide dissolution in the fly ashes. Concentrated sodium hydroxide solution (Nobel chemical limited, Pakistan) of 15 M was prepared in deionized water (98% purity). Sodium silicate (Nobel Chemical Limited, Pakistan) of 15.8% of Na_2O = 55.0%, SiO2 = 30.4%, and 60.0% of water by mass were mixed with sodium hydroxide solution. Separate mixing of fly ashes and chemical activators were done in light duty mixer (Sammic BM-5, 120 V, 1/3 hp). Bai et al. [19] reported that porosity and compressive strength of membrane depends on the molarity of sodium hydroxide solution.

3. Methodology

Geopolymerization techniques involve sintering-free, two-step process such as grinding of source material and mixing with chemical activators as shown in Fig. 1. Fly ashes were grinded in ball mill for 1 h at 180 rpm. Particle size distributions of fly ashes were measured through coulter counter and were found in the range of 5.4–8.5 μm by volume %. In Coulter counter fly ash particles are pulled through an orifice, concurrent with an electric current, produce a change in impedance that is proportional to the volume of the particle traversing the orifice. This pulse in impedance originates from the displacement of electrolyte caused by the particle. Coulter counter give reading in the form of size distribution ranges (Size distribution vs Intensity). Separate mixing of fly ashes was carried out with chemical activators in the ratio of 2.5 for 30 min. Geopolymeric paste was placed in closed vessel for 24 h at ambient temperature. Flat sheet circular membranes were obtained by filling the geopolymeric paste in the mould of 50 mm and thickness of 10 mm. Hydrothermal and curing treatment was done in muffle furnace at 90°C for 9 h to achieve compact structure and strength of 18.5 MPa with appropriate porosity for microfiltration. The prepared membrane was placed in a universal testing machine and specific load were applied until the sample was breakdown. This procedure was applied on all the prepared membrane and their respective breakage point of 18.5 MPa was recorded. Synthesized membrane was washed in the sonicator for 10 min to remove loose particles from the membrane and dried at 120°C. Produced water was treated through prepared membrane in dead end stirred cell as shown in Fig. 1. Produced water is the undesirable product of hydrocarbon production facilities which contains chemical contaminants [20].

Fig. 1. Synthesis of geopolymeric membrane for produced water treatment.

4. Results and discussions

4.1. XRF analysis

X-ray fluorescence (XRF) analysis shows that fly ashes collected form Lakhra coal power plant contain silica and alumina oxides in amount which is suitable for geopolymerization. The aggregate percentage of silica and alumina oxide in fly ashes were 85% and considered an optimum ratio for the development of geopolymeric material as shown in Table 1. XRF analysis (Model: XRF-1800, Shimadzu, Japan) shows that fly ash have SiO_2 and Al_2O_3 with 63% and 22% respectively. Fly ashes from thermal power plant need no additives for silica and alumina oxide for ratio adjustment. Finally, SiO_2/Al_2O_3 was recorded 2.8 after XRF analysis. Percent composition of silica and alumina in the fly ashes play important role in resulting compressive strength of prepared membrane [21].

Table 1
Compositional analysis of fly ash (mass %)

Oxides	Composition
Al_2O_3	22
SiO_2	63
CaO	3.80
Fe_2O_3	7.22
MgO	0.7
K_2O	1.3
Na_2O	0.2
TiO_2	1.3

4.2. XRD analysis

Diffraction pattern of fly ash and prepared geopolymeric membrane were obtained through X-ray diffraction (XRD) technique. XRD pattern of fly ash collected from Lakhara power plant shows aggregative finger prints of mullite ($Al_4Si_2O_{10}$), quartz (SiO_2) and ferric oxide (Fe_2O_3). Peaks show amorphous nature of ashes; however there are some peaks of semi crystalline nature in between 20°–27° at 2θ. Furthermore, the obtained fly ash has a very similar mineralogical composition to metakolin, rice husk ashes and red mud [3]. After chemical activation and hydrothermal treatment the prepared geopolymeric membrane was characterized. XRD pattern of fly ash shifted to crystalline phase after chemical activation. The shift in XRD profile of geopolymeric membrane show the formation of hardens alkaline aluminosilicate products [22]. Amorphous and crystalline phases present in fly ashes and geopolymeric membrane were compared respectively with the powder diffraction file of International centre for diffraction data as shown in Fig. 2.

4.3. Fourier-transform infrared spectroscopy analysis

Fly ashes are mainly composed of silica, alumina and ferric oxide [1]. The presence of silica and alumina induced different linkages which have different vibration modes for identification. High intensity of Si–O–Si and Si–O–Al

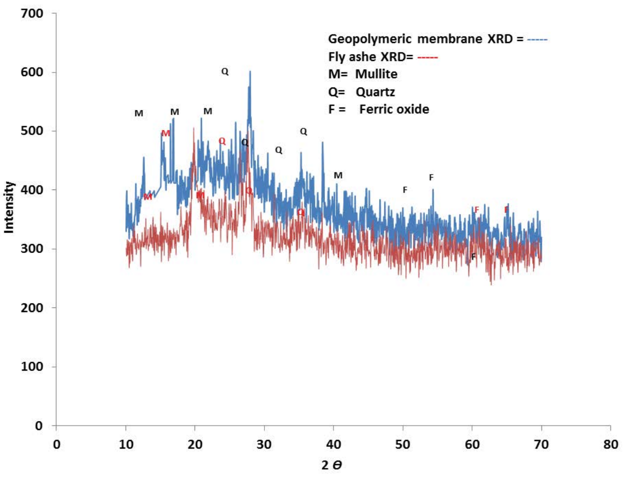

Fig. 2. XRD spectrum of fly ash and prepared geopolymeric membrane.

in fly ash show more reactivity for chemical activators in geopolymeric materials. The bonding environments of Si–O–Al, Si–O–Si and H–O–H in the fly ash were investigated through Fourier-transform infrared spectroscopy (FTIR). Spectral analysis of fly ash was done over in the range of 4,000–450 cm^{-1} at a resolution of 1 cm^{-1} as shown in Fig. 3. The central band at 1,445 and 846 cm^{-1} caused the asymmetric stretching mode which shows high reactivity toward chemical activators. It was found that relative intensities of Si–O–Si and Si–O–Al for geopolymerization reaction were found the in the range of 1,500 to 650 cm^{-1}. FTIR spectrum of fly ash show minor quantity of hydroxyl group at 3,451 cm^{-1} which is due to presences of bounded moisture contents [4]. Functional groups, particle size distribution and particle size of fly ash predict the rate of reaction and physical properties of geopolymeric materials [13].

4.4. Surface morphology of synthesized membrane

Surface morphology, porosity, pore size, pore size distribution and pine hole cracks of synthesized membrane were investigated through visualization of scanning electron microscopy (SEM) with the magnification of 20 kV, 3,000 and 5 μm. The average pore diameter of 0.3–0.4 μm was measured from SEM analysis by plotting the standard scale on pores of membrane. Average of the pore size was taken on a specific selected area during pore size calculation. It was observed that prepared ceramic membrane surface had no major and minor cracks and had uniform pore size distribution as shown in Fig. 4. The pore size of prepared geopolymeric membrane is suitable to be used for produced water treatment. Naveed et al. [13] used metakolin based geopolymeric membrane for pre-treatment of car washing stations water.

4.5. Separation efficiency

Synthesized fly ash based geopolymeric membrane was test in stirrer cell of 4 litres for the treatment of produced water. Experimental analysis show that flux of produced water through geopolymeric membrane varies with permeation pressure under a fixed thickness of 5 mm. Produced water flux increase in the ranges of 10, 14, 20, 26, and 29 L h^{-1} m^{-2} at 2, 3, 4, 5, and 6 bar respectively. Liner water flux with permeation pressure developed during microfiltration of self-supporting geopolymeric membrane under the same thickness of 5 mm as shown in Fig. 5. Increases in transmembrane pressure increase the passage of produced water through the micro pores and provide

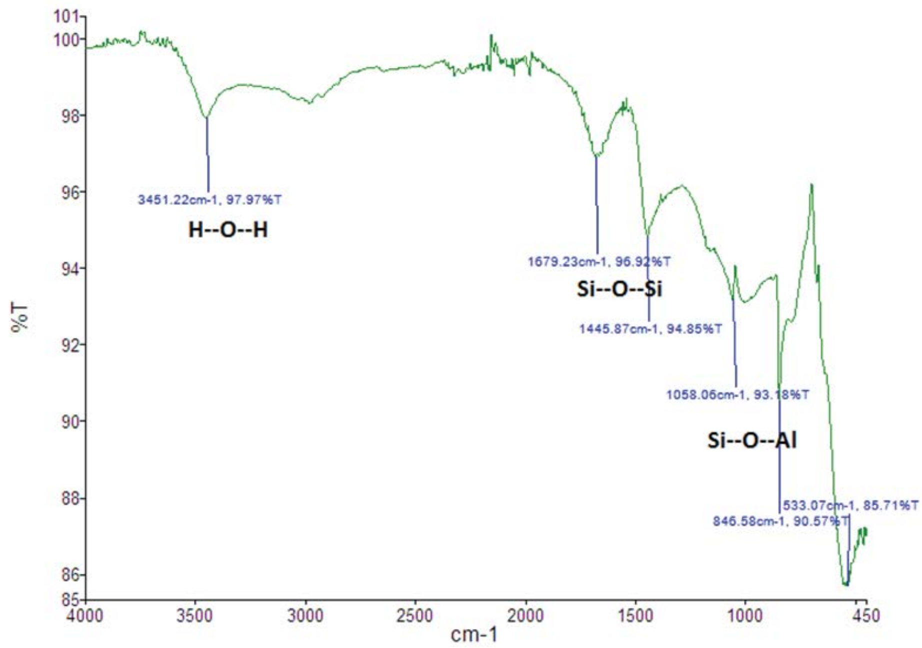

Fig. 3. Fourier transform infrared (FTIR) spectrum of fly ash.

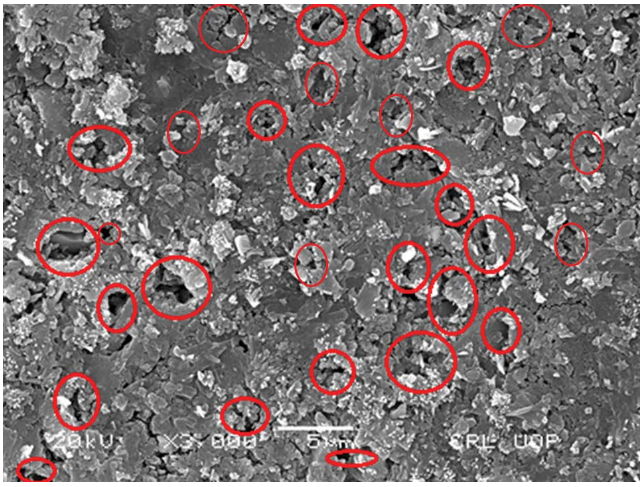

Fig. 4. SEM of fly ash based geopolymer membrane.

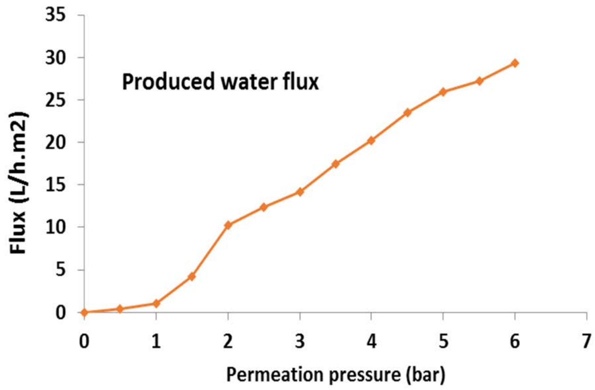

Fig. 5. Variation of Transmembrane flux with permeation pressure.

clarified permeate. Linear relationship of transmembrane pressure with the flux show that membrane is good for microfiltration produced water treatment. Produced water of hydrocarbon production facilities contains major contaminants of oil, suspended solids and naturally occurring mineral materials. Separation performance of geopolymeric membrane was checked by produced water treatment flux, total dissolved solid, turbidity, conductivity and pH of produced water after membrane permeation at 3 bar. Separation results of turbidity (NTN), total dissolved solid (TDS), total suspended solid (TSS), conductivity and pH are shown in Table 2. Total dissolved solid and turbidity of produced water was reduced from 22,300 to 1,681 mg ml^{-1} and

Table 2
Fly ash based geopolymeric membrane performance for produced water separation

S.No.	Constituent	Produced water	Treated water
1	TDS (mg L^{-1})	22,300	1,681
2	Turbidity (NTU)	6.8	1.4
3	Conductivity (s cm^{-1})	2,500	2,170
4	TSS (mg L^{-1})	660	375
5	pH	6.1	6.5
6	Total oil (mg L^{-1})	597	128
7	COD	2,600	1,210
8	Silica (mg L^{-1})	1,234	12

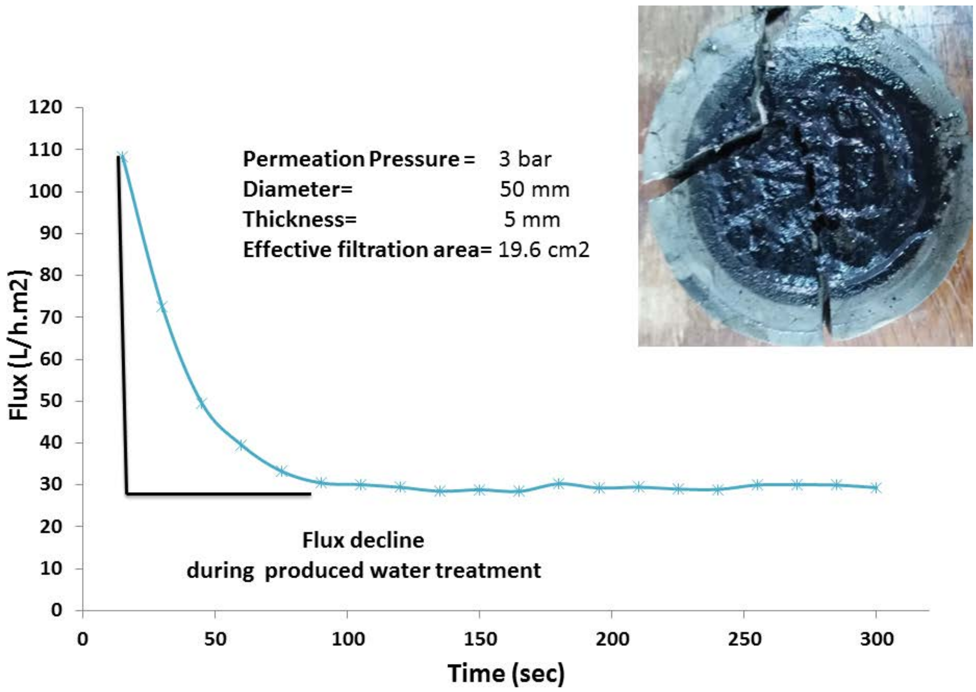

Fig. 6. Flux decline of geopolymeric membrane.

6.8 to 1.4 NTU respectively. Silica was removed from 1,234 to 12 mg ml^{-1} which recommends fly ash base geopolymeric membrane as a good candidate for pre-treatment processes of produced water. At constant permeation pressure of 3 bar microfiltration, produced water has been investigated in a dead end filtration without stirring. Variation in the flux rate with time from 110 to 35 L h^{-1} m^{-2} was observed due formation of cake on membrane surface. Furthermore, flux decline was observed from 15 to 100 sec due to cake formation on the surface of membrane as shown in Fig. 6. Large particles accumulate the surface of geopolymeric membrane and formed cake layer, which decrease the permeate flux.

5. Conclusions

Fly ash based geopolymeric membrane was successfully synthesized and microfiltration process was applied for produced water treatment in this study. Results show that geopolymerization is a promising sintering-free technique for synthesis of inorganic membrane by utilization of fly ashes for the treatment of produced water. Geopolymerization reaction conform the transformation of thermal intensive synthesis (high sintering temperature) of inorganic membranes to sintering-free one step reaction. The prepared geopolymeric membrane possesses compressive strength of 18.5 MPa and can survive in harsh corrosive environment such as high produced water treatment. In addition, the higher chemical oxygen demand, total dissolved solid, TSS, turbidity and conductivity of produced water were reduced along with high removal efficiency were obtained through geopolymeric membrane. 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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