Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2019.23895

152 (2019) 11–15
June

Porosity control of self-supported geopolymeric membrane through hydrogen peroxide and starch additives

Amir Naveed[a], Fazli Saeed[a], Majeda Khraisheh[b], Mustafa Al Bakri[c], Noor-ul-Amin[d], Saeed Gul[a,*]

[a]*Department of Chemical Engineering, University of Engineering & Technology Peshawar 25120, Pakistan, emails: saeed.gul@uetpeshawar.edu.pk (S. Gul), amirkhattak@uetpeshawar.edu.pk (A. Naveed), fazli.saeed@yahoo.com (F. Saeed)*
[b]*Department of Chemical Engineering, Qatar University, Qatar, email: m.khraisheh@qu.edu.qa*
[c]*Center of Excellence Geopolymer and Green Technology, School of Material Engineering, University of Malaysia, Perlis, Malaysia, email: mustafa_albakri@unimap.edu.my*
[d]*Department of Chemistry, Abdul Wali Khan University, Mardan, 23200 Pakistan, email: noorulamin_xyz@yahoo.com*

Received 2 July 2018; Accepted 1 February 2019

ABSTRACT

Geopolymerization is a green innovative technique for the synthesis of self-supporting inorganic membranes using fly ash as a raw material. This paper focuses on the preparation of geopolymeric membranes of different porosities of 5%, 10%, and 15% v/v of hydrogen peroxide (H_2O_2) and starch $(C_6H_{10}O_5)_n$ which were used as foaming agents. Sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) activated grinded fly ash were used in the preparation of the geopolymeric slurry with and without any additives. No additives in the preparation of geopolymeric membranes resulted in a total porosity of 29% by volume with compressive strength of 18.41 MPa. Geopolymeric membranes prepared with hydrogen peroxide (5%, 10%, and 15% v/v) additives resulted in a total porosity of 36.12%, 41.23%, and 53.21% and compressive strength of 13.05, 9.85, and 5.22 MPa, respectively. Similarly, total porosity of starch additives 31.76%, 37.33%, and 51.09% was obtained with compressive strength of 14.90, 11.53, and 7.37 MPa, respectively. Increase in the pore size after evaporation of hydrogen peroxide was 1.04, 3.4, and 6.6 μm, while for starch 1.05, 1.77, and 3.45 μm, respectively. The prepared membrane was tested for household wastewater through dead-end filtration.

Keywords: Geopolymerization; Porosity; Hydrogen peroxide, Starch; Membrane household wastewater treatment

1. Introduction

Geopolymerization is a novel technique for the synthesis of inorganic membrane prepared from waste fly ash [1,2]. Geopolymerization is a heterogeneous chemical reaction of aluminosilicate with high alkalis which forms semi-crystalline material of tetrahedral network of silica and alumina and may be used as an alternative to inorganic membranes [3,4]. They are semi-crystalline materials and possess as molecular sieves after chemical activation and hydrothermal treatment [5]. Oxides of silica and alumina are considered the basic ingredients of the geopolymeric materials and are known as source materials [6]. Fly ash from thermal power plant and agriculture wastes contains silica and alumina in appropriate ratio rendering it valuable for the preparation of such membranes [7]. Physical properties such as compressive strength and porosity of geopolymeric materials are controlled by altering the ratio of Si/Al in the source material. Transformation of aluminosilicate of the fly ash into porous geopolymeric membrane is achieved after chemical activation and hydrothermal treatment [8]. Naveed et al., [9] previously

* Corresponding author.

reported that ash of thermal power plants, agriculture waste and bagasse may be used as source material for the synthesis of geopolymeric membrane.

Fly ash from coal generated thermal power plants and agricultural waste has a negative impact on the environment. About 1 tonne of fly ash waste is produced per 3 MW of electricity production in coal thermal power plant [10]. Complete utilization of waste ash to new structural porous products becomes possible through geopolymerization technique [8].

The advantage of using fly ash over other source materials such as kaolin, red mud, and ceramic cake is that it does not need further calcination [11]. Saeed et al. [12] utilized ash of rice husk as a source material for geopolymeric membrane synthesis and achieved average pore diameters of 1.0–3.03 μm.

Separation efficiency of a membrane depends upon the flux and rejection which are regulated through pore size, porosity and surface attraction for the fluid [13]. Ceramic membranes have high thickness and low porosity as compared with organic membranes which result in low flux [14]. Porosity and pore size of resulting geopolymeric membrane are dependent on the composition of the source material, ratio of source material to chemical activators, particle size of source material, molarity of solutions and ratio of the foaming agents [2]. Furthermore, foaming agents are added through different approaches used for the fabrication of porous geopolymeric materials such as direct forming, replica method, sacrificial filler method and additives manufacturing [3]. Bai et al. [15] found that porosity, compressive strength and thermal conductivity of geopolymeric materials can be altered with the ratio of foaming agents and achieved total porosity of ~74.29% upon the use of 5% v/v hydrogen peroxide as a foaming agent. Similarly, Cantarel et al. [16] prepared clay base sintering-free porous geopolymeric inorganic membrane with high compressive strength of 52 MPa and total porosity of ~22.81%, which is comparatively low for reasonable flux.

In addition to hydrogen peroxide, starch was used for enhancing the porosity of geopolymeric materials; however to the best of our knowledge utilization of hydrogen peroxide, starch in fly ash as additives for regulating the porosity of geopolymeric membrane is rarely used. In this study, power plant fly ash was chemically activated through NaOH/Na_2SiO_3 with different additives such as hydrogen peroxide and starch in various ratios (5%, 10%, and 15% v/v) in order to study the impact on the porosity of the resultant inorganic geopolymeric membranes.

2. Materials and methods

Fly ash obtained from Lakhra power plant (Sindh Province, Pakistan) was used as a source material for the synthesis of geopolymeric membrane as shown in Fig. 1. Lakhra coal power plant produces 150 MW electricity per day since 1995 with the release of 50 tonnes fly ash [10]. The percentage composition of fly ash was analyzed through XRF (Model: XRF-1800, Shimadzu) and results are detailed in Table 1. Particle size was reduced to 8.5 μm through wet grinding as shown in Fig. 3.

Geopolymeric slurry was obtained by mixing sodium silicate and sodium hydroxide (Nobel Chemical Limited, Pakistan) solutions with fly ash (fly ash/chemical activators = 2.5) for 30 min at 120 rpm [17]. The ratio of chemical activators (Na_2SiO_3/NaOH = 2.5, 15 M) of sodium hydroxide and sodium silicate solutions were kept constant during formation of geopolymeric paste. Hydrogen peroxide and starch additives were added separately in the volume ratio of 5%, 10%, and 15% at 100 rpm. Poly-condensation was carried out after filling geopolymeric slurry in the mould (50 mm diameter and 5 mm thickness) at 70°C for 12 h as depicted in Fig. 2.

After curing and hydrothermal treatment, the prepared membrane was placed in muffle furnace at 600°C for 1 h (furnace model: L5C6, Nabertherm; temperature: 1,200°C) for evaporation of hydrogen peroxide and starch (Nobel Chemical Limited, Pakistan). Prepared geopolymeric membranes of different additives were tested for household wastewater treatment in stirrer cell having capacity of 2 L. Prepared membranes were characterized for pore size, pore size distribution, and porosity. Scanning electron microscope (SEM) was used for this purpose. Compressive strength of the membranes was tested using Universal testing machine (UTM model: 100–500 KN, Testometric Inc.). Total porosity of geopolymeric membrane was calculated through Archimedes method using distilled water as an immersion medium. Sugawara and Yoshizawa [22] reported that

Fig. 1. Fly ashes of Lakhra coal power station, Sindh, Pakistan.

Table 1
Compositional analysis (mass, %) of Lakhra coal power plant fly ash

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

Fig. 2. Synthesis and additives addition for porosity of geopolymeric membrane.

thermal conductivity and porosity are inversely related. Farhana et al. [23] found that thermal conductivity is dependent on total porosity and compressive strength of geopolymeric materials. Therefore, the thermal conductance of the synthesized membrane was also utilized to analyze the porosity of prepared geopolymeric membrane. Thermal conductivity meter (QINSUN Inc., model GB/T1081.2) was used to measure the thermal conductivity of the synthesized membrane. The synthesized geopolymeric membranes were tested for household wastewater treatment at pressure of 2 bar using locally fabricated dead-end stirred membrane filtration cell.

3. Results and discussion

3.1. XRF analysis.

The percentage composition of silica and alumina in fly ash during chemical activation [20,21] of the collected fly ash was conducted. Wang et al. [7] reported that high ratio of aluminosilicate gives enhanced compressive strength in the resulting products. For the prepared membranes in this study, aggregated percentage of silica and alumina was found to be in the ratio of 2.86 as presented in Table 1. The results indicate that the collected fly ash form thermal power plant exhibits excellent source material ratios rendering it as a potential candidate for the synthesis of the geopolymeric membrane.

3.2. Particle size distribution

The average particle size of fly ash from the Lakhra power plant was in the range of 100–150 μm, which was reduced to 7–10 μm through grinding by using ball mill. Jedidi et al. [13] reported that the pore size and uniform porosity of a geopolymeric membrane depend on particle size and particle size distribution of source materials used in geopolymeric material. Particle size and particle size distribution of grinded fly ash were measured through Coulter counter (model; 41113903, range 0.1–1,500 μm) as shown in Fig. 3. Small particle sizes provide a large surface area which increases the dissolution and reactivity, hence results in high mechanical strength [22]. A uniform particle size distribution with average particle size of 8.5 μm was mixed with chemical activator. Furthermore, porosity and permeability of inorganic membrane can be controlled by sorting, packing and shape of particle [2].

3.3. Porosity and compressive strength

Table 2 shows the effect of two different additives and their proportions on porosity, compressive strength, and thermal conductivity. Force evaporation of hydrogen peroxide at 150°C and starch additives at 450°C produced high porosity geopolymeric membrane. It was observed that the increase in the additives percentage increases the porosity

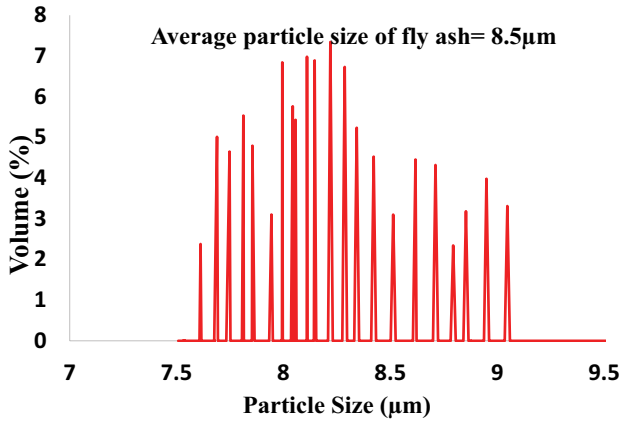

Fig. 3. Uniform particle size distribution of fly ashes.

Table 2
Effects of foaming agents (hydrogen peroxide and starch) on the porosity, compressive strength and thermal conductivity of geopolymeric membrane

Foaming agent	Total porosity		Compressive strength		Thermal conductivity	
(% Volume)	(% Volume)		(MPa)		(W mK^{-1})	
Additives	H_2O_2	Starch	H_2O_2	Starch	H_2O_2	Starch
0%	29	29	18.41	18.41	0.02131	0.02131
5%	36.12	31.76	13.05	14.9	0.01926	0.0201
10%	41.23	37.33	9.85	11.53	0.01439	0.01849
15%	53.21	51.09	5.22	7.37	0.01022	0.01496

for both foaming agents; however; higher values of porosity has been observed for hydrogen peroxide compared with starch. This is attributed to the high volatility of hydrogen peroxide as compared with the starch, which also resulted in the decrease of compressive strength. The least compressive strength of 5.22 MPa has been observed for 15% addition of hydrogen peroxide, which is still reasonable as the prepared membrane is intended to be used as microfiltration membrane. The typical operating pressure for microfiltration is in the range of 0.05–0.2 MPa. The increase in the porosity was confirmed through the decrease in the thermal conductivity for all prepared membranes.

3.4. SEM analysis

Both the additives based geopolymeric membranes were assessed through SEM. Morphological studies of hydrogen peroxide and starch additives-based geopolymeric membrane were conducted at magnifications of 2,000 and 1,000, respectively. Fig. 4 highlights that as the proportions of hydrogen peroxide increases, the porosity also increases. From the SEM analysis, average pore size was estimated to be 0.8 μm without additives. The value significantly increased to 1.04, 3.4, and 6.6 μm upon addition of 5%, 10%, and 15% hydrogen peroxide, respectively. Hydrogen peroxide evaporates at 150°C leaving well-structured pores behind. Fig. 5 shows the SEM analyses of starch additive membrane. Pore size increase of 1.05, 1.77, and 3.45 μm with addition of starch with ratio of 5%, 10%, and 15% were observed, respectively. Force evaporation of starch additives at 450°C left dense porous surface. Furthermore, pin hole and cracks were not observed on the surface of all the prepared geopolymeric membranes. The pore sizes obtained for both additives recommend microfiltration application of prepared membrane. Total porosity of prepared geopolymeric membrane has significantly increased by the release of H_2O_2 and starch additives in this process.

3.5. Wastewater treatment through the prepared membrane

Microfiltration of household wastewater was conducted using a variety of prepared geopolymeric membranes

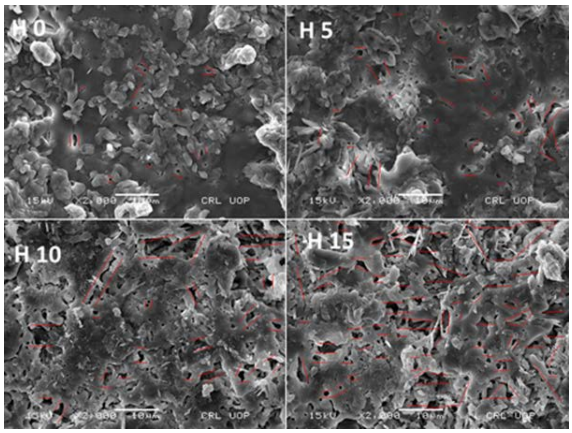

Fig. 4. SEM of inorganic geopolymeric membrane: (H 0) without additive, (H 5) with 5% H_2O_2 additive, (H 10) with 10% H_2O_2 additive (H 15) with 15% H_2O_2 additive.

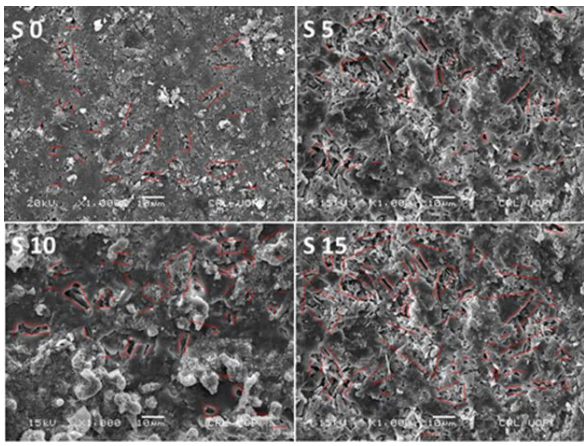

Fig. 5. SEM images of inorganic geopolymeric membrane: (S 0) without starch additives, (S 5) with 5% starch additives, (S 10) with 10% starch additives (S 15) with 15% starch additives.

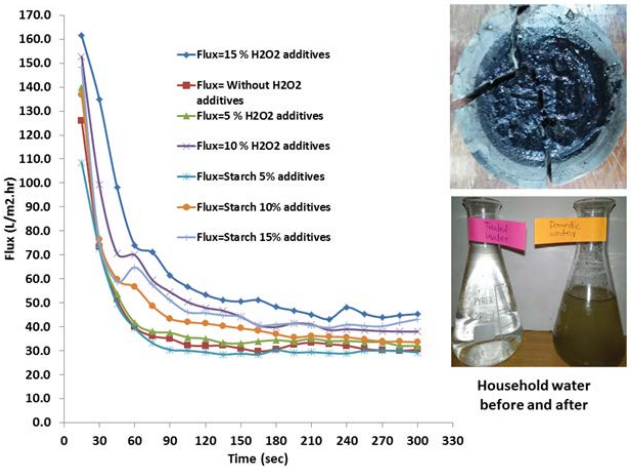

Fig. 6. Household wastewater treatment through inorganic geopolymeric membrane.

under constant pressure of 2 bar. The membranes cells were locally fabricated dead-end stirred cells of 2 L capacity. Household wastewater was collected from the general drainage of kitchens. Main ingredients of household wastewater are detergents, fats, oil, grease, and suspended particles. Membranes of 15% hydrogen peroxide and starch additives give flux in the range of 66 and 43.1 L m^{-2} h^{-1}, respectively. A clear and transparent permeate, as shown in Fig. 6, was collected for all membranes. The permeate flux of the membrane was calculated by Eq. (1):

$$J_P = \frac{W_P}{\Delta t \times A_{\text{mem}}} \tag{1}$$

where J_P is the permeate flux, Δt is the time interval, and A_{mem} is the active membrane area. Similarly, flux through 5% and 10% additives of hydrogen peroxide and starch were also investigated as shown in Fig. 6. Significant change in flux was observed as ratios of foaming additives were increased. It was also observed that liquid additives (H_2O_2) created high

porosity and flux than solid starch additives which evaporate at high temperature. Flux decline was observed in first 90 s due to cake formation on the surface of geopolymeric membrane as shown in Fig. 6.

4. Conclusions

Geopolymerization is sintering-free synthesis techniques of inorganic membranes having many advantages and potential of waste ash utilization as a source material. Successful transformation of fly ash to porous geopolymeric membrane with rational compressive strength and enhanced flux was done with the mixing of hydrogen peroxide and starch additives. Results show that additives of hydrogen peroxide provide high porosity then same ratio of starch additives. Therefore, additions of 15% hydrogen peroxide show high flux with transparent permeate for household wastewater as compared with starch with rational compressive strength. Inorganic geopolymeric membrane is one of the promising cost-effective technologies for household wastewater treatment.

References

[1] S.A. Bernal, E.D. Rodríguez, R. Mejía de Gutiérrez, M. Gordillo, J.L. Provis, Mechanical and thermal characterisation of geopolymers based on silicate-activated metakaolin/slag blends, J. Mater. Sci., 46 (2011) 5477.

[2] C. Bai, T. Ni, Q. Wang, H. Li, P. Colombo, Porosity, mechanical and insulating properties of geopolymer foams using vegetable oil as the stabilizing agent, J. Eur. Ceram. Soc., 38 (2018) 799–805.

[3] C. Bai, P. Colombo, High-porosity geopolymer membrane supports by peroxide route with the addition of egg white as surfactant, Ceram. Int., 43 (2017) 2267–2273.

[4] M.M.A.B. Abdullah, K. Hussin, M. Bnhussain, K.N. Ismail, Z. Yahya, R. Abdul Razak, Fly ash-based geopolymer lightweight concrete using foaming agent, Int. J. Mol. Sci., 13 (2012) 7186.

[5] E. Kishar, D. Ahmed, N. Nabil, Geopolymer cement based on alkali activated slag, J. Scient. Res. Sci., 34 (2017) 538–552.

[6] M.-x. Xu, Y. He, C.-q. Wang, X.-f. He, X.-q. He, J. Liu, X.-m. Cui, Preparation and characterization of a self-supporting inorganic membrane based on metakaolin-based geopolymers, Appl. Clay Sci., 115 (2015) 254–259.

[7] H. Wang, C. Yan, D. Li, F. Zhou, Y. Liu, C. Zhou, S. Komarneni, In situ transformation of geopolymer gels to self-supporting NaX zeolite monoliths with excellent compressive strength, Microporous Mesoporous Mater., 261 (2018) 164–169.

[8] N. Singh, Fly ash-based geopolymer binder: a future construction material, Minerals, 8 (2018) 299.

[9] A. Naveeda, S. Gula, N.U. Aminb, M. Younasa, N. Ullaha, Synthesis and characterization of inorganic microfiltration membrane through geopolymerization, Desal. Wat. Treat., 66 (2017) 203–209.

[10] Lakhra Coal Development Company (LCDC).

[11] J.L. Provis, S.A. Bernal, Geopolymers and related alkali-activated materials, (2014).

[12] F. Saeed, A.N. Khattak, S. Hassan, Geopolymerization: A Green & Sustainable Approach for Inorganic Membrane Synthesis, ICSP-Proceedings, 2017, pp. 19–21.

[13] I. Jedidi, S. Saïdi, S. Khmakem, A. Larbot, N. Elloumi-Ammar, A. Fourati, A. Charfi, R.B. Amar, New ceramic microfiltration membranes from mineral coal fly ash, Arabian J. Chem.,2 (2009) 31–39.

[14] D. Shah, K. Kissick, A. Ghorpade, R. Hannah, D. Bhattacharyya, Pervaporation of alcohol–water and dimethylformamide–water mixtures using hydrophilic zeolite NaA membranes: mechanisms and experimental results, J. Membr. Sci., 179 (2000) 185–205.

[15] I. Jedidi, S. Saïdi, S. Khemakhem, A. Larbot, N. Elloumi-Ammar, A. Fourati, A. Charfi, A.B. Salah, R.B. Amar, Elaboration of new ceramic microfiltration membranes from mineral coal fly ash applied to waste water treatment, J. Hazard. Mater., 172 (2009) 152–158.

[16] V. Cantarel, F. Nouaille, A. Rooses, D. Lambertin, A. Poulesquen, F. Frizon, Solidification/stabilisation of liquid oil waste in metakaolin-based geopolymer, J. Nucl. Mater., 464 (2015) 16–19.

[17] C. Bai, P. Colombo, Processing, properties and applications of highly porous geopolymers: a review, Ceram. Int., 44 (2018) 16103–16118.

[18] A.N.F. Saeed, S. Gul, Synthesis of Geopolymeric Membrane using Locally Available Rice Husk Ash as a Source Material, ICSP-Proceedings, 2017, pp. 19–21.

[19] A.M. Mustafa, M.M.A.B. Abdullah, H. Kamarudin, M. Binhussain, I.K. Nizar, A.R. Rafiza, Y. Zarina, The processing, characterization, and properties of fly ash based geopolymer concrete, Rev. Adv. Mater. Sci., 30 (2012) 90–97.

[20] P. He, M. Wang, S. Fu, D. Jia, S. Yan, J. Yuan, J. Xu, P. Wang, Y. Zhou, Effects of Si/Al ratio on the structure and properties of metakaolin based geopolymer, Ceram. Int., 42 (2016) 14416–14422.

[21] A. Antoni, D. Wiyono, A. Vianthi, P. Putra, G. Kartadinata, D. Hardjito, Effect of particle size on properties of sidoarjo mud-based geopolymer, Mater. Sci. Forum, 803 (2015) 44–48.

[22] A. Sugawara, Y. Yoshizawa, An experimental investigation on the thermal conductivity of consolidated porous materials, J. Appl. Phys, 33 (1962) 31–35.

[23] F. Farhana, H. Kamarudin, A. Rahmat, M.M.A.B. Abdullah, A Study on relationship between porosity and compressive strength for geopolymer paste, Key Eng. Mater., 594 (2013) 1112–1116.