

Effect of Sodium Hydroxide and Mould Shape in Geopolymer Fabrication Made With Synthesised Local Clay for Water Filtration

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ABSTRACT

The preparation and testing of geopolymer ceramic membranes for water separation is presented. Geopolymers are typically used in refractories and as precursors to ceramic formation, allowing the production of ceramic-like materials with low temperature processes. A new geopolymer material was synthesized using local clay from Sabah, Malaysia and its filtration performance was compared to a commercial clay fabrication. The synthesized formulation of geopolymer ceramic paste was made by mixing local metakaolin clay as a source of aluminosilicate with alkaline solution, and then curing in a sealed environment. The amorphous paste was crushed and moulded prior to firing at an elevated temperature up to 700°C. The feasibility of this laboratory-fabricated geopolymer for water filtration applications was studied by evaluating its performance at different thicknesses and mould shapes of fabricated membrane using 8 to 16 Molar sodium hydroxide (NaOH) as the alkali activator in the synthesis of the geopolymer. The result found that increased molarity of sodium hydroxide results higher compressive strength and affect filtration rate. Improved filtration performance (subject to the shape and width of the geopolymer membrane) was found by analysis and separation rates of 47% for blue dye colour and 88% for turbidity were achieved when operated without pressure or pump.

Keywords: Geopolymer ceramic membrane, Water Filtration Performance, Geopolymerisation, Alkali Activator, compressive strength

1.0 INTRODUCTION

Water purification using membrane technology has received considerable interest in recent years due to increasingly stringent water supply standards and requirements for effluent discharge. Membrane technology also provides a number of attractive properties: compactness, modular construction, no moving parts with low maintenance requirements, no chemical addition requirements, minimal chemical sludge disposal, absolute barriers to particles and pathogens, constant filtered water

quality irrespective of feed water quality, easy system upgrading, and suitability for small systems and distributed locations [1, 2]. There are many types of water filter material derived from either organic or inorganic materials.

Ceramic is an inorganic membrane and is usually made from alumina, titania, zirconia, and silica, which are usually monoliths of tubular capillaries with channel sizes in the millimeter range [3-4]. Compared to organic (polymeric) membranes, ceramic membranes have high chemical, mechanical, and thermal resistance, as

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well as high permeability rates. The remarkable physical and chemical stability of ceramic membranes gives them reproducible performance over long service lifetimes [5]. However, the major factor limiting the use of ceramic membranes is cost [6]. Capital costs are usually higher than those for polymeric membranes primarily due to high energy and temperature processes [7].

Geopolymers are members of the inorganic polymers family, allows production of ceramic like materials by using low temperature processes [8]. They are used in refractories as a precursor to ceramic formation [9] and are aluminosilicate binders formed by alkali silicate activation of aluminosilicates materials [10]. Geopolymers consist of metakaolin clay composite and alkali-activator solution that produces ceramic-like materials. Alkali-activator is required to initiate the geopolymerisation reaction and the most commonly used hydroxide activator is sodium hydroxide (NaOH) due to its cheapness and wide availability [11].

The use of metakaolin eliminates the issues associated with highly inhomogeneous aluminosilicate sources by providing a purer, more readily characterized starting material, thereby greatly enhancing the microstructure [12]. This composition is mixed and cured at a fixed temperature and the hardened composition is fired at up to 1000°C for thermal treatment [13-14].

The properties and uses of geopolymers are being explored in many scientific and industrial disciplines: modern inorganic chemistry, physical chemistry, colloid chemistry, mineralogy, geology, and in other types of engineering process technologies. Geopolymer ceramic membranes are easy to produce since their main material is kaolin clay that

exists naturally. Clay minerals and phosphates are a well-known class of natural inorganic materials, but the application of kaolin clay to membrane filtration is still new. Geopolymer ceramic membranes can be improved by adding alkali activator at a different ratio [15], calcination temperature [16] or even curing temperature [17].

Hence, the objective of this work is to produce and evaluate geopolymer membranes using synthesized Sabah local clay as aluminosilicate material, and a mixture of sodium hydroxide and sodium silicate as alkali activator. The effects of different molarities (M) of sodium hydroxide (8M, 10M, and 16M) on geopolymer membrane strength were explored and correlated to membrane permeability filtration. The permeation characteristics and efficiency of the geopolymer membrane will then be compared with commercial clay by conducting a pure water permeation test and a colour separation removal in synthetic water sample.

2.0 METHODS

2.1 Clay Synthesis and Geopolymerisation

Two types of kaolin clay were used: 1) local Sabah clay and 2) commercial clay (Starcast GH 95% purity) as pictured in Figure 1. The commercial clay was used after being sieved at 25 μm and calcined, whereas the local clay was prepared by synthesizing raw kaolin clay taken from Papar, (6°12'15"N 116°14'55"E) Sabah, Malaysia. The raw local clay was initially air-dried and further synthesized via flocculation to produce metakaolin through a calcination process at 110°C for 24 hours. It was then manually crushed by mortar and pestle and sieved at 25 μm size. The

sieve product of powdered clay was then purified and cleaned from impurities by flocculation.



Figure 1 Raw kaolin clay material at 25µm sieved

In the flocculation process, 200 g of powdered clay sieve product was mixed and stirred with 400 mL of distilled water in a 1L beaker. After that, sodium hexametaphosphate (NaPO_3)₆ was added to the mixture in a 0.5 wt% portion of distilled water. Mixtures were stirred for approximately 5 to 10 minutes and then allowed to settle for 5 minutes. The accumulated sediment was then discarded and liquid product was added with 2.0 wt% of (NaPO_3)₆ going through the sedimentation process for about 2 to 5 minutes. Mixtures with sodium solution were allowed for flocculation, which was repeated 5 times to ensure reaction between impurities. Then, sedimentation without sodium was repeated 5 times to allow the separation of pure clay solution.

In the formation of geopolymers, metakaolination is an important process. The metakaolinite was the most reactive in alkaline conditions among the aluminosilicate raw powder [13]. In the metakaolination process, pure powdered clay was fired and calcined in a furnace at a temperature of 800°C for 1.5 hours. This temperature was adapted from previous work which had used the same source of clay, confirming the most suitable temperature to ensure the

best evolution of kaolinite to metakaolinite [18].

An alkali activator is required to initiate the geopolymerisation reaction. The concentrations of the alkali-activator used in this study are 8M, 10M, and 16M of sodium hydroxide (NaOH) solution. The alkali activator solution was dissolved with 8M of sodium silicate (Na_2SiO_3) solution, similar to previous work [19].

Geopolymerisation was conducted by mixing the metakaolinite produced by calcination of pure kaolinite with the alkaline activator. The homogeneous mixture was obtained by stirring metakaolinite and alkaline activator for 5 minutes in a heat mixer. The geopolymer paste was then moulded and cured in an oven at 70°C for 24 hours. Next, the moulded geopolymer was fired in a furnace at 700°C for 90 minutes to enable microstructure reconstruction and thermal treatment. Suitable heat treatment temperatures that enable the geopolymer to be more compact are between 600 to 800°C [6]. This work used a temperature of 700°C as such a value would reorganize the geopolymer composition structure without cracking it. The geopolymer ceramic membrane fabrication and synthesis is illustrated in Figure 2 and the prepared geopolymer casting and compositions are summarised in Table 1.

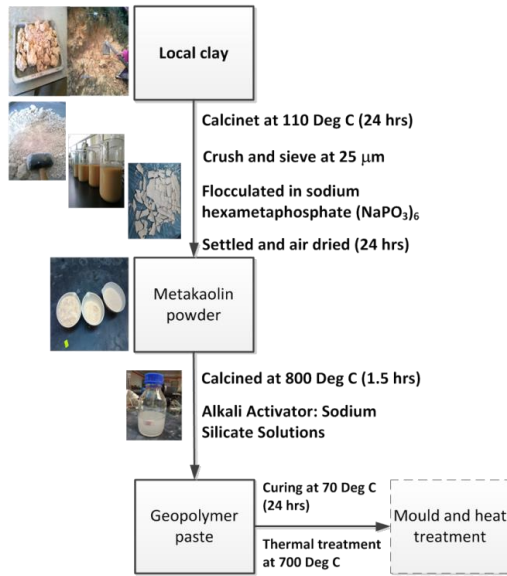


Figure 2 Process and synthesis of geopolymer ceramic fabrication

Table 1 Geopolymer membrane process formation and composition

Membrane ID	Geopolymer ceramic fabrication parameter			
	alkali activator: Sodium hydroxide (NaOH) molarity	Kaolin clay	Mould type	
			Shape	Thickness
CG-t1	10M	Commercial clay (Starcast GH)	Rectangular	1 cm
CG-t0.5	10M	Commercial clay (Starcast GH)	Rectangular	0.5 cm
G1-t1	10M	Purified Local clay	Rectangular	1 cm
G1-t0.5	10M	Purified Local clay	Rectangular	0.5 cm
G2-8M	8M	Purified Local clay	Circular	0.5 cm
G2-10M	10M	Purified Local clay	Circular	0.5 cm
G2-16M	16M	Purified Local clay	Circular	0.5 cm

2.2 Geopolymer Strength Test

The compressive strength of the geopolymer ceramic membranes was measured using a Universal Testing Machine (Instron 8801). The geopolymer was prepared in a 50 mm x 50 mm x 50 mm square metal mould and was heat treated. Samples were tested in two conditions: 1) dry condition, which was directly tested after being de-moulded at room temperature, and 2) wet condition which, after 24 hours of water immersion, demonstrated a weight increase of approximately 30%. The test cubes were subjected to a compressive force at the rate of 6.5 kN/s until failure.

2.3 Water Sample Preparation and Filtration Protocol

The filtration rate of the fabricated ceramic geopolymer was analyzed and measured using distilled or blue dye solute sample water in a gravity filtration setup. Prior to each filtration, 2 L of distilled water was used to flush and soft scrub at the surface to remove any impurities in the geopolymer. The water filtration rate was measured and recorded by filtering a 200 mL water sample three times to increase result reproducibility. The permeation flux (J) and solute separation ($R\%$) was computed calculated using the equation:

$$J = \frac{V}{At} \quad (1)$$

$$R\% = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (2)$$

where V as volume of filtrate (Liter), A as area in m^2 , and t as time (hours) and solute concentrations in the feed, c_f , and permeate, c_p .

The solutes were synthetic coloured water samples prepared in the range of

1000-3000 ppm of Ujala Brand (Jyothy Laboratories Limited, India) blue dye colour, consisting of fine blue powder pigments.

The filtrate was evaluated in terms of total suspended solid (TSS) (standard procedure APHA 2540 D), dissolved oxygen measured using DO meter (HI 9142-Hanna DO Meter, USA), temperature (standard thermometer), pH, colour (DR-6000 UV spectrophotometer, HACH), and turbidity (2100AN-Hach Turbidimeter, USA).

3.0 RESULTS AND DISCUSSIONS

3.1 Geopolymer Product Strength Test

Figure 3 shows the compressive strength of the geopolymer using three different molarities of NaOH alkali activator mixed with local clay at increased stress/strain loads. Higher molar of sodium hydroxide solution results in higher compressive strength, except for dry 16M NaOH. The mechanical strength of microstructural geopolymers is related to its composition, which is correlated with reaction of the microstructure binder [12]. It was observed here that compressive strength increased almost twice after 24 hours of immersion in water, reflecting the advantageous application of a water environment such as water filtration and distillation processes. Water immersion or curing improved compressive strength as a result of water hydration in the formation of geopolymer. The 24 hours water curing of geopolymer 8M to 16M sodium hydroxide has improved its compressive strength. It is due to better dissolving ability of the metakaolin and higher levels of sodium hydroxide produce increased reaction during dissolution process, thus

increasing the bonding of solid particles and increased strength [20].

3.2 Geopolymer Filtration Performance

Figure 4 shows geopolymer membranes (G1 and G2) made from local Sabah clay that fabricated using different mould thickness and alkali activator. Only two out of six were shown here because the fabricated membranes either rectangular or circular in shape have a similar surface area and surface roughness when touched by hand. From physical observation, membrane colour became lighter orange when thickness was reduced, which could be attributed to lower alkali activator volume in the geopolymer when moulded at a lower width or shape. It is also worth noting here that thickness may not be exact due to slight expansion or contraction during the geopolymerisation reaction process.

Prior filtration test, an initial cleansing/flushing by distilled water was conducted before the filtration rate was recorded. The filtration rate of distilled water for each membrane is shown in Figure 5.

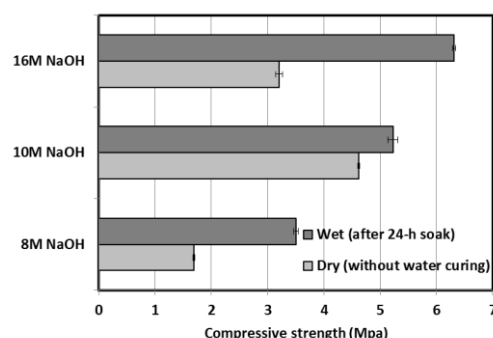


Figure 3 The effect of sodium molarity on geopolymer with and without immersion (24 hours water)

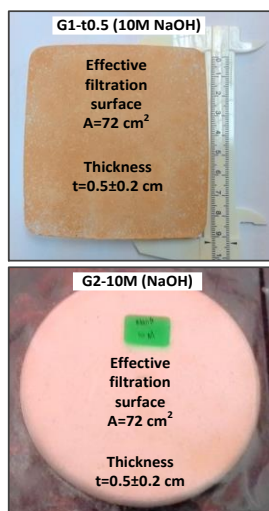


Figure 4 Fabricated geopolymer membranes using Sabah clay at 10 M NaOH

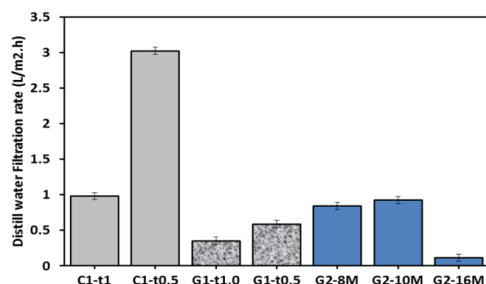


Figure 5 The effect of clay type, shape and NaOH molarity on the filtration rate of geopolymer membranes

The filtration rates for local clay geopolymer membranes were lower than the commercial clay membrane (ID C1) due to their low permeability and denser geopolymer compound as shown in Figure 5. This can be seen by comparing the large increase in the filtration rate of commercial clay when its thickness was reduced by half, to the minimal change shown by the highly compact local clay membranes, even at thinner dimensions. However, between the local clay geopolymer membranes (G1 and G2), 0.5 cm difference in thickness did influence the filtration rate slightly and, as expected, greater widths gave a lower

rate of water permeation due to longer distance and resistance.

Additionally, the circular-shaped membrane G2 with 0.5cm width shows an improvement in filtration rate twice that of the rectangular shape. This could be related to the loose geopolymerisation arrangement which is scattered in the circular mould than the rectangular shape. Inter-particle attraction during sintering and shape moulding such as circular may result in homogenous packing and lead to higher permeability as studied similarly by [21] Biesheuvel and Verweij, (1999).

Furthermore, between the circular shape membranes at increasing molarity, it was observed that an optimum filtration rate was produced when using the 10M NaOH alkali activator, suggesting that a reaction binder of 16M was too condensed and thus had low water permeability.

The temperature, pH, and dissolved oxygen were measured and no significant changes on the filtrate were observed, implying a negative biochemical reaction of geopolymer to the water. The temperature of the water sample before and after filtration by both geopolymers was recorded and observed maintained at 25.0°C (room temperature). This confirms the non-existence of NaOH in the geopolymer membrane which had completely reacted during the geopolymerisation process. The exothermic reaction of NaOH and water will produce heat in the water and may increase the water sample's temperature. Then, the recorded pH was also monitored and it was found that the geopolymer membrane filtrate did not impose any chemical contamination nor acidification on the filtrate. This is because the entire acidic chemical, which is the alkali activator, has fully reacted with the metakaolin.

Figure 6 shows the filtration result for the rectangular geopolymer membrane on a 2000ppm coloured synthetic water sample. The flowrate of the synthetic water was higher for commercial clay (CG) than for the local clay geopolymer membrane (G1) and thus removal was expected to be inversely proportional due to the physical size exclusion and compact arrangement of the geopolymer material. The geopolymer membranes using local clay demonstrated higher percentages of removal than the commercial clay membranes. Both turbidity and colour were significantly removed and separated when using local clay (84-88% and 45-47% respectively), whereas only 15-36% turbidity and 18-24% colour were removed by the commercial clay membrane.

Figure 6 shows that the thicker geopolymer was able to filter more colour particles because of the physical separation of the membrane thickness and packing arrangement. The local clay (G1) shows a more stable packing arrangement even at half thickness due to its high removal capability and slight change in permeation rate.

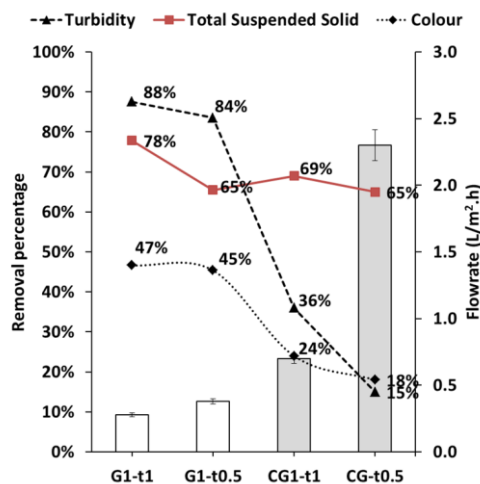


Figure 6 The effect of geopolymer thickness and clay material on the removal of a synthetic coloured 2000 ppm water sample

However, removal of total suspended solid (TSS) showed only a very slight difference between the two geopolymers (65-78% by local clay and 65-69% by commercial clay). This might be due to the large size of the suspended solid (compared to colour pigment) that can be easily separated via physical sieving. Additionally, the influence of existing clay or remainder which is not fully reacted inside the geopolymer may also cause the similar results found for local and commercial clay. Although the membranes were initially flushed with 2 L distilled water to remove any unreacted material and suspended solid, the leaching of clay or suspended solid from the membrane may still exist, typically when using the commercial clay.

The total suspended solid (TSS) of the synthetic water sample was attributed to suspended particles such as clay, which may contribute to the raw material of the geopolymer itself. These clay particles were the remainder in the geopolymer as the alkali activator has been fully reacted and thus percolated after a series of water permeations. TSS is also related to the turbidity value of the water sample: the higher the suspended solid amount, the higher the turbidity reading of the water sample [22] (Lakrets *et al.*, 2014). However, turbidity was more significantly removed by the local clay geopolymer (G1) than the commercial clay geopolymer (CG) due to the better geopolymerisation binding network which was able to separate particles that are generally visible, thus improving the translucent water quality.

Further tests to evaluate the efficiency of the local geopolymer membranes were carried out using different dye concentrations. The samples were prepared using a dye

concentration range of 1000ppm to 3000ppm and the filtration results are shown in Figure 7. It can be seen that the thicker G1-t1 geopolymer removed 10% higher amounts of colour pigment and suspended solids from both water samples than the G1-t0.5 geopolymer. This implies that the thicker geopolymer provides a greater infiltration surface to separate colour in water.

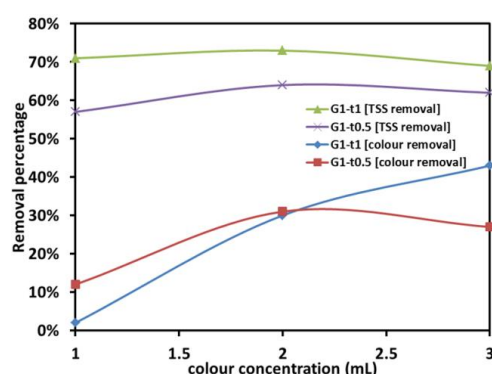


Figure 7 Thickness influence by local geopolymer membrane on the removal of colour at 1 to 3 mL dye concentration

Figure 7 also shows that higher removal was observed as the dye concentration in the water samples increased. However, it was found that the concentration removal percentage was less for 3000ppm of dye than for 1000ppm and 2000ppm. This is related to the fouling phenomenon of saturation and clogging at the geopolymer membrane surface. Suspended solid and colour particles that were filtered eventually formed a layer at the surface of the membrane, thus making more difficult for water particles to pass through the membrane. Separation and flux enhancement using cleaning agent and mechanical action to reduce feed accumulation on geopolymer membrane surface is recommended.

4.0 CONCLUSION

Geopolymers have outstanding technical properties such as high strength, high acid resistance, temperature, and high hydraulic resistance which make them suitable as durable membranes for water filtration. An attempt to fabricate a sodium geopolymer membrane for water separation from in-situ synthesised local Sabah clay was successfully made. This study explored the ability of geopolymer to filter water and concluded that: Although water separation is possible, the fabricated local geopolymer is very compact and has very low filtration flux but good colour removal even at simple gravity filtration. Additives to increase permeability and porosity to improve the flux are highly recommended in future work. The unchanged pH, temperature, and dissolved oxygen show that the alkali activator has successfully reacted during geopolymer fabrication. However the remaining clay residue contributes to increased turbidity and suspended solid during filtration subject to clay variation. Membrane compressive strength increased with sodium hydroxide molarity, leading to a denser geopolymer matrix, which is in proportion to the membrane filtration rate. The experimental results indicate that a circular shape has better filtration rate than rectangular shape although at the same thickness and a thicker geopolymer membrane can achieve higher colour removal due to the larger infiltration surface sites and geopolymerisation inter-particle arrangement.

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