Synthesis and Characterization of Fly Ash-based Geopolymer Membrane for Methylene Blue Dye Removal

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Abstract. Utilization of fly ash-based geopolymer membranes for the removal of environmentally hazardous materials has become an attractive route due to its cheaper processing cost and prolonged use. This paper reports the preparation of geopolymer composite membranes and the filtration performance of the prepared geopolymer membranes for the removal of methylene blue (MB) contaminant. The geopolymer membrane was prepared by the dissolution of raw material, i.e., fly ash in alkaline activator i.e., sodium hydroxide solution. Various proportions of foaming agents as a mixture of hydrogen peroxide and egg white were added to investigate their impacts on the prepared membrane pore structures and morphology. The morphology, pore structure and functional groups of geopolymeric composite membranes were characterized using field-emission scanning electron microscopy (FESEM), Brunauer-Emmett-Teller (BET) analysis and Fourier Transform Infrared spectroscopy (FTIR) respectively. The performance of the membranes was evaluated for the removal of MB in aqueous solution using a lab-scale membrane filtration setup. The performance tests revealed a promising result with all the rejection was above R>90% for membranes GE0, GE1, GE2.5 and GE5, meanwhile the best permeation obtained was 15 L/m².h when GE5 was used. The results were correlated to BET and FESEM results which showed that the pore structures of GE5 were homogeneous and uniform while having the highest pore size which is 19.60 nm.

1. Introduction
The effluent from textile factories carries various types of hazardous chemicals through a few stages of manufacturing processes and also known to contain highly coloured species [1]. Not only colours, the break down products are toxic and harmful to human and living organisms, raising attention to the world
on the importance of removing the dyes from the wastewater [2]. The regions where the water resources are vital for keeping the maintenance of ecosystem must be protected and freed from the harmful effects of the dye effluents. There are various methods have been made available to remove the pollutants from water which to name a few are biodegradation [3], flocculation-coagulation [4], oxidation [5] and adsorption [6]. Recently, membrane separation techniques which used polymeric and inorganic materials have also been introduced for dye removal, but having facing major disadvantages such as declining in permeate flux [1], low resistance of organic solvent, while inorganic membranes suffer from high fabrication costs primarily due to the expensive powder processing and sintering at high temperature has led to this study of Geopolymer membrane for methylene blue (MB) removal. Methylene blue is a cationic dye which is widely used in various applications such as in biology, chemistry, medical science, and dyeing industry. However, the long-term exposure to MB can cause adverse health effects such as vomiting, nausea, anemia and hypertension [7].

Geopolymers by definition are chains of networks of mineral molecules linked with covalent bonds and have basic characteristics such as non-crystalline (amorphous) networks and they can be distinguished by two synthesis routes which are in alkaline medium and acidic medium. Geopolymer is the most stable material as some geopolymeric materials are durable as they possess unique geopolymeric structure known as three-dimensional crosslink [8]. The synthesis of Geopolymer involves raw material and an alkaline activator. Previous studies reported that Geopolymer has a faster dissolution and gelation, and also cure rapidly as it can gain high strength of Geopolymer as early as 24 hours [9]. The development of Geopolymer synthesis consist of a few steps which are (i) Dissolution of Si and Al from the solid aluminosilicate materials in the strongly alkaline aqueous solution (ii) Formation of Si and/or Si-Al oligomers in the aqueous phase (iii) Polycondensation of the oligomers to form a three-dimensional aluminosilicate framework (iv) Bonding of the solid particles into the geopolymeric framework and hardening of the whole system into a final solid polymeric structure [10]. In this study, fly ash is used as the raw material because it is high in Si and Al content. The high silica and alumina contents is a prime prerequisite for the development of geopolymeric material. Furthermore, fly ash is considered as low-cost and sustainable material because it is an industrial waste that is produced abundantly from a coal power plant [11].

Geopolymer is known for its good properties which made them as a great potential material membrane applications. Due to easy, energy efficient, eco-friendly processing and excellent mechanical properties, Geopolymer is fast emerging material for construction and building materials, fire resistance ceramics, composites, matrix for immobilization of toxic wastes and many others [12]. Other than the typical application for building materials, limited studies have been done for Geopolymer membrane. Geopolymer membrane is gaining interest because of the issues suffered by polymeric membranes which are low durability and low mechanical strength. The properties of Geopolymer which are high in strength and very porous are the main advantages for Geopolymer membrane. Previous study reported that Geopolymer has been used as an adsorbent for water treatment due to its porous nature.

In this present study, the porosity of Geopolymer needs to be tailored to fit the properties needed for a membrane to be able to efficiently remove the MB. Although Geopolymer is porous, the porosity has yet to be further studied as the pores are not homogenous and can affect the performance of the membrane. Current methods to enhance pores are by heat treatment, addition of sodium silicate, varying alkaline activator concentration, addition of pore foaming agents and many more [13]. However, none are reliable enough to create uniform pore sizes with homogeneous distribution within geopolymer matrices. Combining pore foaming agents in 2-stages during geopolymerization could further improve the pore sizes and distribution, but there is a lack of literature available on this subject matter. The Si/Al ratio and pore foaming agents are said to be crucial parameters for producing homogeneous pores. The combination of peroxide route with organic additives is one attractive method that proved that more % of porosity can be achieved [14]. However, the effects of the created foams have not been studied on any applications. Thus, the study on peroxide route combined with organic additive is an interesting method for producing homogenous high porosity geopolymer membrane.
2. Methodology

2.1 Materials

Methylene blue (MB) powder was purchased from R&M Chemicals Co. The raw material, i.e., fly ash, was collected from a coal-fired power plant located at the suburb of Manjung, Perak, Malaysia. Analytical grade sodium hydroxide pellets (NaOH; Merck; 99%), hydrogen peroxide (H$_2$O$_2$, R&M Chemicals, 30%), and distilled water were used to prepare an alkaline solution. Egg white was used as a pore-forming agent in the preparation of geopolymer composite material.

The chosen fly ash raw material was first characterized using X-ray fluorescence (XRF, Bruker, S8 Tiger series), and determined to be class F type fly ash due to its high silica (SiO$_2$) and alumina (Al$_2$O$_3$) contents as shown in Table 1 below. The chemical compositions present in the fly ash that led to the determination of class F fly-ash are tabulated as follows.

| Component | Chemical Composition (wt%) |
|-----------|-----------------------------|
| SiO$_2$   | 44.52                       |
| Al$_2$O$_3$ | 22.48                     |
| Fe$_2$O$_3$ | 11.58                     |
| CaO       | 9.84                        |
| MgO       | 3.92                        |
| C         | 2.54                        |
| K$_2$O    | 1.73                        |
| SO$_3$    | 1.35                        |
| Others    | 2.05                        |

2.2 Fly Ash-based Geopolymer Synthesis

The schematic diagram for Geopolymer synthesis is shown in Figure 1. The standard formulation of Geopolymer paste is prepared by 3:1 of fly ash to alkaline activator which is Sodium Hydroxide solution (NaOH) at room temperature. The ratio of fly ash and alkaline activator as well as the Sodium Hydroxide concentration remain constant throughout the experiment. The preparation of Geopolymer was done by mixing the starting raw material which is fly ash and Sodium Hydroxide by stirring using overhead mixer at 600 rpm for about 9 minutes which is enough to make the solution uniformly mixed. Finally, the egg white was added to the mixture in measure of 1 wt%, 2.5 wt%, and 5 wt% on total mass of the slurry followed by 10 minutes of mixing at 1000 rpm. The Geopolymer paste was poured into a mould and then cured for 24 hours at 60°C. The cured samples were then demoulded for testing and analysis purposes.

![Figure 1. Schematic diagram for the geopolymer composite membrane sample preparation.](image-url)
Egg white as a pore-forming agent was added to the mixture at various percentage weights of 0, 1.0, 2.5, and 5 wt.% based on the total weight of the slurry, followed by the addition of 0.6 wt% of hydrogen peroxide. The composite slurry mixture was then mixed at 1000 rpm for about 10 minutes until it forms a geopolymer paste[14]. The geopolymer paste was poured into a mold of predetermined dimensions of (5 cm diameter and 2 mm thickness) for the preparation and fabrication of geopolymeric membrane. The cast paste was then cured at 60°C for 24 h. Finally, the cured samples were demolded, characterized, and tested for their performance as described in the section 3. The parameters used for the development of the composite geopolymer membrane is shown in Table 2.

| Samples | Dosage of Egg White (wt%) | Dosage of Hydrogen Peroxide (wt%) | Sodium Hydroxide (NaOH) Concentration, (M) | Si/Al Ratio |
|---------|--------------------------|----------------------------------|------------------------------------------|------------|
| GE0     | 0                        | 0.6                              | 10                                       | 3:1        |
| GE1     | 1.0                      | 0.6                              | 10                                       | 3:1        |
| GE2.5   | 2.5                      | 0.6                              | 10                                       | 3:1        |
| GE5     | 5.0                      | 0.6                              | 10                                       | 3:1        |

2.3 Characterization

2.3.1 FESEM analysis

The morphological properties of starting materials and geopolymer composite membranes were analyzed using Field-Emission Scanning Electron Microscope (FESEM, Model: Zeiss Supra 55 VP). FESEM was preferred because of its higher resolution, brightness, and small sized probe size. Before analysis, sample was mounted to the aluminium stub with a carbon tap and the sample was then analysed using secondary electron technique at different magnifications [15].

2.3.2 BET Analysis

The pore diameter distribution was measured by Brunauer-Emmett-Teller (BET) method using the Surface Area Analyzer and Porosimetry System (BET, Model: Micromeritics ASAP 2020). Prior to analysis, samples were placed in a tube and subjected to degassing in a vacuum chamber at 100°C for 10 hours. The measurement of its specific surface area is performed by using BET method on N₂ adsorption desorption isotherm [16].

2.3.3 Performance Evaluation

The prepared composite geopolymer membrane performance was evaluated for the removal of methylene blue from aqueous solution with initial concentrations of 300 ppm, 400 ppm and 500 ppm [17]. Another performance testing was done by investigating filtration efficiency [1] in removing the dye from the feed solution was evaluated through the dye rejection, which was calculated using the classical rejection coefficient [14]:

\[
\text{Removal Efficiency, } R (\%) = \left(1 - \frac{c_f}{c_o}\right) \times 100
\]  

(1)
Where:
\( C_0 \) = Initial concentration of the dye in the feed
\( C_p \) = Dye concentration in the permeate

The fabricated membranes were tested for the flux by using equations (2) with an effective membrane area of 0.0007014 m\(^2\) and with no variations of pressure and flow meter.

\[
\text{Flux,} J (\text{L/m}^2\cdot\text{h}) = \frac{aQ}{A\cdot dt}
\]  
(2)

Where;
\( J \) = Permeate flux (L/m\(^2\)h)
\( Q \) = Quantity of the permeation water filtered (L)
\( A \) = Effective surface area of the membrane (m\(^2\))
\( t \) = Time interval (h)

3. Results and Discussion
3.1 Effect of egg white on morphological structure of FAGP
3.1.1 FESEM Analysis.

![FESEM images](image)

**Figure 2.** FESEM images of sample (a) GE0, (b) GE1 (egg white 1.0 wt%, \( \text{H}_2\text{O}_2 \) 0.6 wt%), (c) GE2.5 (egg white 2.5 wt%, \( \text{H}_2\text{O}_2 \) 0.6 wt%), and (d) GE5 (egg white 5.0 wt%, \( \text{H}_2\text{O}_2 \) 0.6 wt%)

The morphology structures of the synthesized membranes were investigated using FESEM analysis. The FESEM images of the cross-sectional part of the samples GE0, GE1, GE2.5, and GE5 were shown in
Figure 2. The differences of the pore structures between GE0, GE1, GE2.5, and GE5 can be seen as the result of the different amounts of egg white added into the geopolymer solution. Obvious pore structures could be seen through the inner part of all geopolymer membranes, which serve as good passages for methylene blue dye permeation [16]. The pore sizes of these membranes fall into mesoporous type having sizes of between 11.49-19.60 nm, which are larger than the methylene blue with the approximate dimensions of the monomer molecule are 1.25 to 1.60 nm long by 0.57 to 0.84 nm wide with a thickness of about 0.5 nm [18]. These membranes however, were able to filter the MB because of the existing pores on the geopolymer membrane piled and stratified one another therefore the large pore sizes covered each other [19]. For sample GE0, the figure shows very little existence of pores, and there is still more unreacted fly ash caused by incomplete geopolymerization [15]. Meanwhile, for GE1, the pores are formed and appear to be uniform and bigger in sizes, but with some unreacted fly ash due to incomplete chemical reaction during geopolymerization process [15]. The morphology of sample GE2.5 is almost similar to GE1, but with more distributed and interconnected pores. Peroxide routes enable the expansion of gas bubbles [14] during the curing process while the egg white retains the bubbles in time that the expansion will not rupture the pores formed. Meanwhile, sample GE5 showed the desired morphology with homogenous porosity, and almost all of the pores are interconnected. This shows that more addition of egg white facilitated the pore formation as well as the homogeneity of pores, which is very important for membrane filtration study.

3.2 Effect of egg white on porosity structures of FAGP

3.2.1 BET Analysis.

| Membrane Samples | Pore Size (nm) | Percentage of Porosity (%) |
|------------------|---------------|---------------------------|
| GE0              | 11.49         | 25                        |
| GE1              | 13.88         | 31.21                     |
| GE2.5            | 14.53         | 38.19                     |
| GE5              | 19.60         | 54.55                     |

Table 3 summarized total porosities and pore sizes as the result of different percentage of egg white addition in geopolymer matrices. As shown, the average sizes of pores increase when higher amount of egg white is added for samples GE0, GE1, GE2.5 and GE5. This is correlated to the total percentage of porosity where the % of porosity increases from 25 % to 31.21 %, 38.19 % and 54.55 % for samples GE0, GE1, GE2.5 and GE5 respectively. This could be observed by the increase of viscosity in geopolymer’s slurry [14]. When the viscosity is high, the sample will be able to retain the gas bubbles during expansion, thus producing geopolymer foams [14]. However, excessive amount of viscous slurries may hinder the expansion of gas contained in them which is responsible for pore generation at the end of the process [14]. Thus, appropriate amount of egg white addition is vital for parameter study.
3.3 Effects of pore foaming agents on permeability of fly ash-based geopolymer membrane

![Graph](image)

**Figure 3.** Effect of egg white on pore size and permeability of geopolymer membranes.

![Graph](image)

**Figure 4.** Relationship between pore size and removal efficiency with different amount of egg white

The effects of addition of egg white and hydrogen peroxide as pore foaming agents on permeability of fly ash-based geopolymer membranes were investigated and the results were shown in Figure 3. Based
on the figure, the permeability of membranes increases when more egg white with constant amount of hydrogen peroxide was added. At addition of 5 wt% of egg white, (GE5), the permeability of the methylene blue is the highest at 15 L/m²·h, while the lowest permeability recorded is when no egg white is added (GE0) which is only 2 L/m²·h. The larger pore sizes could be the result of higher amount of egg white added that was able to produce more viscous slurries which are in fact, well suited for retaining the formed gas bubbles and produced foams [14]. Other than large pore sizes, uniformity of pores could be of great cause for the increase of membrane’s permeability. As shown in FESEM results, the pore structures for membrane GE5 was the most uniform among other membranes GE0, GE1 and GE2.5. Larger pore sizes were undeniably able to create passages for the methylene blue particles to pass through, but homogeneity and interconnectivity of the membranes also play significant part in enabling the methylene blue to continuously flow under and any around pore blockage [20].

On the other hand, the removal efficiency decreases when the pore sizes increase following the increase in the amount of egg white added as shown in Figure 4. The highest removal is about 94% when 0 wt% of egg white is added and the lowest is when 5 wt% of egg white is added which is 90%. This is due to the solution concentration which decreased the filtering process. The flocculants in the membrane could affect the membrane performance. The increase in membrane resistance by the presence of particles which blocked the pores could lead to the decline of flux [19]. Although the efficiency decreases, it is still significant as the removal of 90% is considered high. The reason for the drop in efficiency when more egg white is added is because the formation of larger pore sizes (19 nm) make the methylene blue removed low in efficiency. In contrast, the permeability is the highest at 5 wt% of egg white which is 15 L/m²·h. Thus, the GE5 sample depicted the best permeability result with a considerably high removal efficiency.

4. Conclusion
Based on the results obtained, the addition of egg white and hydrogen peroxide at certain composition labeled as GE1, GE2.5, and GE5 have successfully enhanced the pore formation in the geopolymer membranes structures. The BET results showed that the pore size of geopolymer membrane samples increased from 11.49 nm when no pore foaming agents were added to 13.88 nm, 14.53 nm, and 19.60 nm when 1 wt%, 2.5 wt% and 5 wt% of egg white was added respectively. Higher amount of egg white addition leads to increase in foamability of geopolymer slurry, and thus larger pore sizes and more pore volumes are produced. In conclusion, fly ash-based geopolymer membrane has shown great potential as a green alternative for wastewater filtration using methylene blue dye as the model dye for this application. This was supported with the homogeneity and interconnectivity of porosity obtained as shown in FESEM results and how it positively affects the removal efficiency and permeability of the methylene blue.

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