Antifouling properties of hollow fibre alumina membrane incorporated with graphene oxide frameworks

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\textbf{ABSTRACT}

Membrane fouling takes place due to foulant adsorption on the membrane surface, which leads to the reduction of membrane performance and its durability in application. Hollow fibre alumina membrane incorporated with graphene oxide frameworks (GOFs) could avoid this phenomenon by forming GOFs/alumina composite membranes. Field emission scanning electron microscope (FESEM) structure shows that these composite membranes successfully developed GO and GOFs films with a thickness in the range of ~234 to ~635 nm. Meanwhile, the atomic force microscope (AFM) images show that their average roughness (Ra) becomes smoother, in the range of 30–46 nm, which would enhance antifouling properties. GOF(BDA)/alumina had highest proteins separation for all proteins, which are 98.40, 98.32, 95.82 and 95.65 % for bovine serum albumin (BSA), egg albumin (EA), trypsin (TR) and lysozyme (LSZ), respectively. Furthermore, this composite membrane had high flux recovery rate (FRR) of 94.86 % and 95.21 % at low total fouling ratio (Rt) of 21.70 % and 30.22 % for long-term filtration of LSZ protein and humic acid (HA) solute, respectively. Thus, this composite membrane showed better antifouling properties in proteins separation and HA removal application due to formation GOFs film.

1. Introduction

In biotechnology industries such as fish, dairy, agricultural and pharmaceutical industries were widely discovered for their wastewaters management. The wastewaters from downstream process in these industries contain a high amount of protein [1], they should not be discharged without suitable treatment in order to allow the recovery of high value by-products. The utilisation of by-products is a significant opportunity for the industry, as it can potentially generate additional revenue as well as reduce disposal costs [2]. For example, a plant of 100 ton fish/h capacity generates 10–40 m\textsuperscript{3}/h effluent with protein loads of 0.5–20 g/l [3]. Proteins from this wastewater can be used as an animal feed supplement and serve as a substitute for common sources of protein in soybean meal and commercial fishmeal [2,4]. Thus, these proteins should be recovered as high value by-products in order to prevent the environmental effects induced by their disposal. Membrane technology is an alternative application for protein separation, in particular microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF).

Ceramic membranes have recently occupied a centre stage in the area of research and development due to its properties such as high chemical and thermal stabilities, and experienced accelerated growth over the past decades in proteins separation [5,6]. In the protein separation application, the proteins could bind to membrane surface due to hydrophobic interaction, hydrogen bond and electrostatic attraction [7]. This phenomenon affected membrane durability with the occurrence of fouling. Therefore, improving their durability associated with fouling resistance remains one of the major challenges in the protein separation. Recently, the modification of ceramic surface have become a more prevalent method in order to prevent fouling and improve protein selectivity via surface modification such as coating layer-by-layer [8], chemical grafting [9] and development of new materials [10]. These methods leads to enhancement of membrane performance by reducing pore size and alter membrane surface chemistry, resulting the repulsive interaction between the penetrable solute and membrane surface [11]. Over 50 % of the commercial MF and UF membranes were underwent surface modified and mostly to increase the membrane hydrophilicity character [12].

Generally, surface modification is one of the most efficient approaches owing to its facile processability to form a selective layer on the support membrane. The additional selective layer can enhance the membrane durability [13]. However, the water permeation will usually have an undesired reduction which is followed by an increment in the selectivity performance. In practical, the coating layer also could enhance the antifouling and antibacterial activity by introducing...
promising coating materials. Recently, significant attention has been devoted on carbon-based materials as modified materials due to their availability, good chemical and mechanical properties, and environmentally friendly [14]. Graphene oxide (GO) is known as carbon-based material of graphene derivative which has several distinguished properties, such as high hydrophilicity, good flexibility and mechanical strength [15], making GO a very promising candidate for selective layer formation. In this regard, GO could enhance the performance of membrane selectivity as the GO-layered membranes have many features such as controllable size, high dispersion and easily handle for surface and edge modification, and greater ease of membrane formation; either freestanding or thin-film composite.

GO membrane as free-standing film is strong in dry conditions owing to hydrogen bond and strong van der Waals interaction among the sheets [16]. However, GO film has the potential to crumble and redisperse in wet condition due to the hydrophilic groups on the GO nanosheets which can absorb water molecules [17]. As such, the stability of GO film is required to be improved through cross-linking in order to perform a selective layer on membrane support. For instance, amine groups such as primary, secondary and tertiary have the potential to cross-link with GO nanosheets via electrostatic force. The amine groups simply react with the oxygen functional groups at GO nanosheets and hydroxyl group on alumina surface via covalent bonds. Tiraferri et al. [18] and Xu et al. [19] used amine groups as cross-linker with GO nanosheet to graft on polymeric membrane in order to improve the anti-microbial and anti-biofouling. The application of GO film on polymeric membrane was successfully implemented for gas separation, pervaporation and salt rejection [13,20,21].

Thus, these findings have inspired us to investigate a diamine-modified method to cross-link among GO nanosheets and also between the GO film and ceramic surface in order to improve the grafting technique performance. The diamine-functionalization of GO nanosheets is known as facile GO frameworks (GOFs) to form a selective layer on ceramic support. The GOFs are incorporated with different diamine monomers, which are ethylenediamine (EDA), butylenediamine (BDA) and phenylenediamine (PDA), as selective layers on hollow fibre alumina membrane to form GOFs/alumina composite membrane. To the best of our knowledge, this attempt is a superficial way to form GOFs/alumina composite membranes based on a GOFs film cross-linked by diamine monomers prepared via vacuum deposition (VD) method. Due to the diamine cross-linking, the GOFs film could significantly enhance the stability of selective layer on ceramic support as compared to the use of bare GO film. The resultant composite membranes, GO/alumina and GOFs/alumina were evaluated for their characterizations and performance toward protein separation using four proteins; which are bovine serum albumin, egg albumin, trypsin and lysozyme at different molecular weight as solute model via cross-flow filtration system. In addition, the antifouling performance of these composite membranes was conducted using these proteins and also humic acid removal.

2. Materials and experimental works

2.1. Materials

A commercially available aluminium oxide with three different powder diameters of 1 μm (surface area of 10 m²/g), 0.04–0.05 μm (surface area of 32–40 m²/g), and 0.01 μm (surface area of 100 m²/g), purchased from Alfa Aesar, were used as the ceramic materials. Polyesulfone (PES, 3.5 wt%, Veredel 3000 P, Solvay), Arlacel P135 (Corola, Malaysia), and N-methyl-2-pyrrolidone (NMP, synthesis grade, Merck) were used as binder, dispersant, and solvent, respectively, to prepare the dope suspension. Meanwhile, ethylenediamine (EDA), butylenediamide (BDA) and phenylenediamine (PDA) are used as cross-linkers to form graphene oxide frameworks (GOFs). Bovine serum albumin (BSA, Mw of 66KDa), egg albumin (EA, Mw of 45KDa), trypsin (TR, Mw of 20KDa) and lysozyme (LSZ, Mw of 14.3KDa) are selected as model proteins for proteins separation study. Humic acid (HA) was used in antifouling performance have an approximate molecular weight of 2000 g/mol or 2 kDa.

2.2. Fabrication of hollow fibre alumina membrane

The preparation of alumina membrane in hollow fibre configuration was carried out using extrusion technique-based phase inversion, whereby the parameter employed is presented in Table 1. The composition of alumina dope suspension was prepared at 57 wt.% using three different particle sizes of alumina powders at the ratio of 1:2:7 (0.01 μm:0.05 μm:1 μm). The first step was dissolved 1.5 wt.% of Arlacel P135 as dispersing agent into 35.8 wt.% of NMP as solvent using glass rod and add the alumina powders gradually in the dope suspension. The dope suspension was mixed well by ball milling for 2 days and the mixing is continued for another 2 days after the addition of a polymer binder which is PES. The rotation rate was fixed at speed of 182 rpm using two sizes of milling balls (20 mm and 10 mm) in a planetary ball milling machine (NQM-2 Planetary Ball Mill). The obtained alumina dope was degassed for 1 h, and then transferred to 200 mL Harvard stainless steel syringes using a tube-in orifice (OD = 3 mm, ID = 2.8 mm). The dope was then extruded into a coagulation bath that contains tap water at the extrusion rates of 10 mL/min, bore fluid rate of 10 mL/min and air gap of 15 cm to an external coagulant bath.

The extrude alumina precursors were immersed in the external coagulant bath overnight for the solvent/non-solvent process. This process is also called the spinning-phase based phase inversion technique in order to prepare the hollow fibre configuration of precursor as demonstrated in Fig. 1. Next, the alumina precursors (OD = 1.38 mm, ID = 1.02 mm) were cut into 35 cm in length and complete-dried in room temperature for another 24 h. The last step is to sinter the alumina precursors using two-step profile via a tubular furnace (XL-1700, Magna Value). The first heating was set at 600 °C for 2 h at a heating rate of 5 °C min⁻¹ and the second heating at 1500 °C for 4 h at a heating rate of 2 °C min⁻¹. After completing the two-step heating, the temperature was cooled down to room temperature at a rate of 5 °C min⁻¹. Then, the prepared hollow fibre alumina membrane was ready to be used to incorporated with GO and GOFs via vacuum deposition method.

2.3. Fabrication of GOFs/alumina composite membrane

The hollow fibre alumina membrane was incorporated with GOFs via vacuum deposition (VD) method in order to fabricate the GOFs/alumina composite membranes. For the preparation of GOFs, GO was first synthesized using the simplified Hummers method; [23] its detailed description has been provided in a previous research. The GO gel was diluted in deionized water and dispersed through ultrasonication to form a 10 ppm of GO suspension. Next, 5 mL of diamine monomer (EDA, BDA, or PPD) was dissolved in the suspension and subjected to ultrasonication for 1 h at 60 °C. Three GO-diamine suspensions, known

<table>
<thead>
<tr>
<th>Fabrication parameter of hollow fibre alumina membrane.</th>
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<tbody>
<tr>
<td><strong>Dope formulation</strong></td>
<td></td>
</tr>
<tr>
<td>Alumina (wt.%)</td>
<td>57</td>
</tr>
<tr>
<td>PES (wt.%)</td>
<td>5.7</td>
</tr>
<tr>
<td>NMP (wt.%)</td>
<td>35.8</td>
</tr>
<tr>
<td>Arlacel P135 (wt.%)</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Spinning parameters</strong></td>
<td></td>
</tr>
<tr>
<td>Extrusion rate (mL/min)</td>
<td>10</td>
</tr>
<tr>
<td>Bore fluid rate (mL/min)</td>
<td>10</td>
</tr>
<tr>
<td>Air gap (cm)</td>
<td>15</td>
</tr>
<tr>
<td>Internal &amp; External coagulant</td>
<td>Tap water</td>
</tr>
<tr>
<td>Temperature of coagulant</td>
<td>Room temperature (25 °C)</td>
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<tr>
<td><strong>Sintering parameters</strong></td>
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</tr>
<tr>
<td>Sintering temperature</td>
<td>1500 °C</td>
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<tr>
<td>Heating rate (°C/min)</td>
<td>5</td>
</tr>
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</table>
as GOFs, were then designated as GOF(EDA), GOF(BDA), and GOF (PDA) suspension. Each of this suspension was incorporated with the support membrane via VD method as shown in Fig. 2. One end of the support membrane was first potted into ¼ inch national pipe thread (NPT) male connector and other one end was sealed with epoxy resin, and then connected to the vacuum pump. Then, the vacuum pump was operated at constant pressure of 2 bar for 1 h to attach the GOFs film at the outer layer of the support membrane. These composite membranes were dried in an oven at 80 °C for 24 h to promote cross-linking between the incorporated GOFs film and the support membrane, which is also known as GOFs/alumina composite membranes. Meanwhile, the GO suspension without diamines-functionalization was also prepared to form GO/alumina and presented as a control sample.

2.4. Characterization and performance of membrane

The support membrane and composite membranes consisting of GO/alumina, GOF(EDA)/alumina, GOF(BDA)/alumina, and GOF (PDA)/alumina were characterized for their morphology, surface roughness, wettability and flexure strength properties. The membrane morphology was captured using field emission scanning electron microscope (FESEM) to view the surface and cross-section structure. The samples were coated with platinum under vacuum for 30 s at 20Ma (QUORUM). The pore size distribution of the support membrane was measured via mercury intrusion porosimetry (MIP) (Micromeritics Autopore IV). The MIP data was collected at absolute pressures of between 1.38 × 103 Pa and 2.28 × 108 Pa with an equilibrium time of 10 s. Surface roughness of the membranes was characterized using an atomic force microscope (AFM) (PARK XE-100, SCHAEFER Technology GmbH), obtained by tip scanning with a scanning size of 5 μm × 5 μm.

For wettability property and flexure strength were measured using contact angle measurement and three-point bending test, respectively. Contact angle measurements was investigated using sessile drop method [24], which is a drop of 5 μL water was drop on a membrane surface, and the contact angle between droplet and the membrane surface was measured. Values of at least five measurements were averaged. The flexure strength was measured by three-point bending test using universal testing machine (Instron Model 4469, USA) provided with a load cell for 10 kN and calculated using Eq (1). Where the α is flexure strength (MPa), F is load applied (N), L is length of support span (mm), D and d are outer and inner diameter, respectively of the membrane.

\[ \sigma = \frac{8FLD}{\pi(D^4 - d^4)} \] (1)

Meanwhile, for the performance of membranes, the pure water flux (PWF) and proteins separation were determined for all samples. All these performance tests used a cross-flow filtration system. The PWF is determined by Eq (2), where J is the PWF (L/m²h), Q is the volume of water permeated (L), A is the effective membrane area (m²), and t is the sampling time (h). Further, protein separation was carried out using different proteins with specific molecular weight and radius size, as shown in Table 2. The measurement of protein separation was calculated using Eq (3), where the C₁ and C₂ are proteins concentration at feed and permeate, respectively.

\[ J = \frac{Q}{A \times t} \] (2)

Protein separation percentage (%) = \[ \frac{C_1 - C_2}{C_1} \times 100 \] (3)

For humic acid (HA) rejection, the humic acid with molecular weight of 2 kDa was used as a solute. The concentration of humic acid solution at feed was prepared at 1 gL⁻¹. The LSZ protein and HA were used as solutes for long-term filtration to performed the antifouling performance. The performance test was collected on a digital balance, and the cumulative mass of permeate was recorded in a computer every

Table 2

<table>
<thead>
<tr>
<th>Protein</th>
<th>Molecular weight (kDa)</th>
<th>Average solute radius (nm)</th>
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<tbody>
<tr>
<td>Bovine serum albumin (BSA)</td>
<td>69</td>
<td>4.5</td>
</tr>
<tr>
<td>Egg albumin (EA)</td>
<td>45</td>
<td>3.3</td>
</tr>
<tr>
<td>Trypsin (TR)</td>
<td>20</td>
<td>2.15</td>
</tr>
<tr>
<td>Lysozyme (LSZ)</td>
<td>14.3</td>
<td>1.9</td>
</tr>
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</table>
3600 s via a RS-232 connection in order to calculate the flux for 24 h duration for each permeation, starting firstly with water flux, \( J_1 \) (L/m² h) and followed by solute flux, \( J_2 \) (L/m² h) and secondly with water flux, \( J_3 \) (L/m² h) which is carried out after washing with deionized water. In order to evaluate the antifouling property of membranes, the flux separation ratio (FRR) and the total fouling ratio (Rt) were calculated as follow:

\[
\text{FRR} (%) = \frac{J_2}{J_1} \times 100
\]

(4)

\[
\text{Rt} (%) = 1 - \frac{J_2}{J_1} \times 100
\]

(5)

where the Rt is the sum of reversible fouling ratio (Rr) and irreversible fouling ratio (Rir). The Rr defines the fouling produced by concentration polarization, meanwhile the Rir designates the fouling caused by adsorption or deposition of protein molecules on the membrane surface. Rt and Rir can be calculated using the following equations, respectively:

\[
\text{Rr} = \left( \frac{J_2 - J_p}{J_2} \right) \times 100\%
\]

(6)

\[
\text{Rir} = \left( \frac{J_1 - J_2}{J_1} \right) \times 100\%
\]

(7)

3. Results and discussion

3.1. Hollow fibre alumina membrane as a support membrane

In order to prepare the composite membrane which content a few layer of membranes that consist of support and selective layer with different component. Usually, porous alumina membrane was prepared as support membrane for deposition of MF and UF membrane. The support membrane provides mechanical strength to the selective layer and must have high permeation [25]. The present study, the characteristic of hollow fibre alumina membrane was examined in detail before amended the selective layer using GOFs. As shown in Fig. 3(a), the hollow fibre alumina membrane has the outer diameter and inner diameter of \( \sim 1.3 \) and \( \sim 0.9 \) mm, respectively, and had a wall thickness of \( \sim 0.2 \) mm. The membrane also has an asymmetric structure as shown in Fig. 3(b), including a sponge-like structure at the centre of the hollow fibre wall, which is nearly sandwiched by the finger-like structure from both the lumen and the shell side. Meanwhile, the surface of the membrane exhibited pores on the surface due to the arrangement of alumina particles during sintering process as shown in Fig. 3(c). These pores referred to the pore size of alumina membrane for its selectivity properties of membrane performance.

In addition, Fig. 4(a) and (b) shows the pore size distribution and surface roughness of hollow fibre alumina membrane via MIP and AFM analysis, respectively. The membrane had one peak diameter of 182 nm as shown in Fig. 4(a), which is in the range of MF process. This peak diameter shown that the pore size of the prepared membrane had homogeneous grain arrangement. Meanwhile, Fig. 4(b) shows the surface texture of the membrane with the average surface roughness (Ra) of 59.69 nm. The texture was depicted with the presence of dark regions (valley) and bright regions (peak) formed in nonuniformly-spaced manner. The displayed surface roughness was almost similar with the Ra of hollow fibre alumina membrane (62.85 nm), as reported by Abdullah et al. (2018) [26]. At this value of surface roughness, the hollow fibre alumina membrane was successfully incorporated with UiO-66 particles. Thus, the characteristic in this present study may also facilitate the selective layer of GO and GOF films onto the surface of the hollow fibre alumina membrane. These characterization of hollow fibre alumina membrane are expected to reduce the pore size and surface roughness after going through surface modification by incorporating new selective layer.

3.2. Properties of composite membranes

3.2.1. Morphology structure

In general, GO and GOF nanosheets were stacked on the outer layer of support membrane through a self-assembly process via force from vacuum pump [27], forming GO and GOFs films with a certain thickness from a few hundred nanometres to a few micrometres. Fig. 5 shows the surface morphology of composite membranes which consists of GO and GOFs film as selective layer on support membrane. The surface of these composite membranes were fully covered with selective layer which are GO, GOF(EDA), GOF(BDA) and GOF(PDA) films as shown in Fig. 5(a), (b), (c) and (d), respectively. Among the composite membranes, the GOF(PDA) film formed high agglomeration of GOF particles (yellow circled) on the surface as compared to others composite membranes. Meanwhile, the GOF(BDA) had excellent surface morphology with fully covered and no excess of GOF particles. Overall, the selective layers successfully covered on the support membrane through theVD method for a duration of 1 h of deposition time.

In addition, Fig. 6 shows the FESEM images of the cross-section for GO and GOFs alumina composite membranes. The GO and GOF films were observed on the top of the support membranes. The thickness of GO film was \( \sim 363 \) nm, while the GOF films were \( \sim 234 \) nm, \( \sim 260 \) nm and \( \sim 635 \)nm for GOF(EDA), GOF(BDA) and GOF(PDA), respectively. The GOF(EDA) film was the thinnest film as it has the shortest chain of diamine monomer. Different chain lengths of diamine offered different cross-linking reaction of GO-functionalization [28]. Meanwhile, the GO/alumina and GOF(PDA)/alumina composite membrane exhibited delamination which is due to the shrinkage process. On the other hand, the GO(EDA) and GOF(BDA) composite membranes did not form delamination and has better adhesion effect on the support membrane. The absence of delamination between selective layer and support membrane was significantly affecting the performance of composite membranes, specifically their stability for long term application. This can be due to the lack of interfacial contact between the selective layer and the alumina membrane [29].

3.2.2. Surface topology

Surface topology of the composite membranes was illustrated in Fig. 7 using AFM. It can be clearly seen from the AFM images, the surface texture of these composite membranes are smoother than the support membrane. Thus, the surface roughness of all the composite membranes was relatively lower than the roughness of the support membrane. The GO and GOF films on the support membrane was significantly smoothened by filling the valley regions of the rough support surface. As for the composite membranes, the valleys and peaks structure were spaced more closely together. Among these composite membranes, GOF(BDA)/alumina composite membrane had valleys and peaks on the surface with almost uniform and closely spaced together, as illustrated in Fig. 7(c). The spacing between adjacent valleys and peaks was too small, and therefore, protein molecules could not accumulate on the surface of composite membrane. Thus, the performance of the composite membrane is expected to remain stable over the filtration time.

The AFM image was also used to measure the average roughness (Ra), mean square roughness (Rq) and maximum roughness (Rmax), as shown in Table 3. From the table, the Ra for the composite membranes are in the range of \( \sim 20 \) to \( \sim 45 \) nm. It was found that the highest surface roughness among these composite membranes is GO/alumina due to high level of GO film coverage on the support membrane. Meanwhile, GOF(BDA)/alumina exhibited smoothest surface of \( \sim 20.76 \) nm, whereby smoother membrane surface has higher hydrophilicity. The surface texture significantly avoids the membrane fouling due to high hydrophilicity and lower surface roughness [30].
3.2.3. Hydrophilicity and flexure strength

Hydrophilicity is an important surface property that is highly significant to the membrane performances especially antifouling properties. The presence of the antifouling feature is due to the strong hydration layer of the hydrophilic surface, which opposes the adsorption of any molecules and particles to the membrane surface [31]. Table 4 shows contact angle and flexure strength of composite membranes. The composite membranes exhibited a remarkably higher contact angle than the support membrane (θ = 29.4 ± 6°). The composite membranes which exhibited the GO and GOF films changed the wettability properties of the support membrane and reducing its hydrophilicity, possibly due to less pore size distribution on these films. Among the composite membranes, the GOF(BDA)/alumina composite membrane has the lowest value for contact angle of ~57.8 ± 2°. The low contact angle value leads to high hydrophilicity of composite membrane surface. Whereas, the GO/alumina composite membrane had highest value of 93.0 ± 6 for contact angle which refer to lowest hydrophilicity of GO as selective layer.

The hydrophilicity of membrane surface also related into the membrane surface charge that could provide electrostatic repulsion to prevent the solute deposited on the membrane and resulting better antifouling [32]. Previous study by Chisca et al. was showed that zwitterionic structures are promising membrane surface to be used as antifouling materials due to the presence of positively and negatively charged moieties which lead to high hydrophilicity and reduce the adsorption of solute on the membrane surface [33]. In this study the alumina membrane incorporated with GOF as modify agent are favorable compared to GO due to the zwitterionic structure of GOF, which consist of negative charge from GO structure and positive charge amine group. Thus, modifying the GO with diamine-functionalization to form GOF structure should result in enhancement of hydrophilicity, biocompatibility as well as flux performance.

The table also shows the flexure strength of all the composite membranes. The flexure strength of composite membranes was higher compared to support membrane, which was 156.2 ± 25 MPa. The composite membranes exhibited higher value of flexure strength due to the formation of selective layer to strengthen the composite membranes with the percentage of increment in the range of 5–26 %. This
phenomenon was due to the incorporated GO and GOFs as modifying agent on the surface of hollow fibre alumina. The GO and GOFs were consists of nanoparticles that provide high mechanical strength into the formation of selective layer on composite membrane [34]. Among the composite membrane, the GOF(BDA)/alumina has the highest value of flexure strength of 197.6 ± 12 MPa, which represented the highest percentage of increment at 26% from the support membrane. As a conclusion, from the overall characterization of the composite membrane, GOF(BDA)/alumina composite membrane has an excellent morphology structure with better properties as an effective selective layer compared to other films. More hydrophilicity and smoother surface of the GOF(BDA)/alumina composite membrane is expected to yield better antifouling property for protein separation process.

Fig. 5. Surface morphology for composite membranes of (a) GO/alumina, (b) GOF(EDA)/alumina, (c) GOF(BDA)/alumina and (d) GOF(PDA)/alumina.

Fig. 6. FESEM cross-section for composite membranes of (a) GO/alumina, (b) GOF(EDA)/alumina, (c) GOF(BDA)/alumina and (d) GOF(PDA)/alumina.
3.3. Performance of membranes

3.3.1. The pure water flux (PWF)

Table 5 presents the PWF of the support and composite membranes. The PWF value of support membrane drastically dropped from $242.63 \pm 24$ L/m$^2$.h to values in the range of $3.10 \pm 0.14$ – $10.00 \pm 0.6$ L/m$^2$.h for composite membranes. This phenomenon occurred due to the addition of extra thickness of the overall composite membranes, as observed at the cross-section image of FESEM structure for GO and GOFs composite membranes. The GO and GOF films decreased the PWF by increasing hydrodynamic resistance and also by reducing the effective contact area resulting from the smoothened surface [13]. In this matter, the observation in our study suggests that increasing the surface hydrophilicity and reducing the surface roughness via diamine functionalization of GO to form GOFs, possibly slightly reduced the flux loss by hydrodynamic resistance.

Among composite membranes, the GOF(BDA)/alumina composite membrane has the highest PWF, while the lowest PWF is the GOF(PDA)/alumina composite membrane. The highest PWF of the GOF(BDA)/alumina composite membrane is due to its excellent surface properties of the smoothest surface and high hydrophilicity character as aforementioned previously. Meanwhile, the lowest PWF of GOF(PDA)/alumina composite membrane due to its poor stability of GOF(PDA) film as selective layer, as observed at cross-section FESEM image with an air gap formation In addition, GO and GOF(EDA) films exhibited almost the same value for the PWF, which might be due to their surface properties (hydrophilicity and roughness) being almost the same. Overall, the morphology and surface character of membrane has significantly affected the performance of the PWF.

3.3.2. Proteins separation

The membrane performance was evaluated using proteins separation for support and composite membranes as illustrated in Fig. 8. The figure shows that all these protein recoveries had less than 5% of error bar value for three reading measurement. The support membrane
exhibited lower protein separation for BSA, EA, TR and LSZ, which were recorded to be 63.58, 53.99, 40.91 and 29.56 %, respectively. Interestingly, it was found that the PWF for composite membranes of GO and GOFs films decreased almost 80 % measurement regardless of these films due to the decreasing pore size on composite membrane’s surface. The decrement in pores size significantly enhanced the selectivity of the composite membrane by increasing proteins separation. For example, the PWF of the GO/alumina composite membrane was $5.50 \pm 0.26 \text{ L/m}^2\text{h}$ and exhibited protein separation at 85.15, 75.34, 66.55 and 60.38 % for BSA, EA, TR and LSZ, respectively.

Generally, the decrease in pore size leads to the decrease in water permeability and an increase in the separation rate. The support membrane had higher PWF compared to all the composite membranes, probably due to higher pore size of membrane. Thus, the support membrane could recover less molecules as compared to the composite membranes, which is less than 65 % for all the selected model proteins at a high value of PWF. Practically, the GO film enhances the water permeation due to the GO nanosized that formed a mesh-like structure. The GO is naturally an amphiphilic nanomaterial whereby initially water molecules are adsorbed at the hydrophilic terminal (hydroxides), then quickly diffused among the hydrophobic carbon core by developing a water channel that improves water permeation [35]. Once water molecules infiltrate the GO film, they create a single-layer configuration that drives the consecutive layers apart, resulting in the increase of the interlayer spacing. Meanwhile, the introduction of diamine monomers as a linker agent on the GO structure probably affects the interlayer spacing which acts as a facile molecule pathway. Thus, different diamine monomers with different structure could produce different GO film with specific length of interlayer spacing. Among the composite membranes, the GOF(BDA)/alumina composite membrane has the highest protein separation for all proteins, which are 98.40, 98.32, 95.82 and 95.65 % for BSA, EA, TR and LSZ, respectively. This might be due to the GOF(BDA) film has less interlayer spacing with more well-ordered structure which does not only yield higher PWF, but also exhibit better proteins separation. The well-ordered of GOF interlayer spacing structure leads to low friction flow and thus increase the water permeability [36].

3.3.3. Antifouling properties

For antifouling properties, only GOF(BDA)/alumina composite was performed using long-term filtration using two type of solute which are LSZ protein and humic acid (HA) due to its highest protein separation. The long-term filtration consists of 3 continuous cycles, which are first PWF, solute (1 g/L) and second PWF as shown in Figs. 9 and 10 for LSZ protein and HA, respectively. Every cycle ran for 24 h at the room temperature and using the cross-flow system. From the Fig. 9 at the support membrane, the first PWF decreased rapidly in the early period of the filtration, and then decreased monotonically (almost linearly) with the increasing time up to 24 h. Thus, the flux decline at the first PWF was ~35 % for 24 h operating time. In contrast, for the LSZ, the flux reading decreased gradually, and then reached a plateau for an overall 24 h operating time by resulting only ~6 % of flux decline. Then, second PWF exhibited almost the same trend to the first PWF, with ~10 % of flux decline due to unstable flux measurement at constant pressure. The GOF(BDA)/alumina composite membrane also exhibited same trend of flux decline with support membrane. The flux decline for first PWF, LSZ and second PWF are ~16 %, ~11 % and ~15 % after the filtration for 24 h, respectively. Overall, both membranes had lower flux decline at LSZ protein filtration due to stability of membrane surface with almost constant fouling phenomena.

The LSZ flux for 24 h duration described the fouling behaviour of both the support and GOF(BDA)/alumina composite membranes. Overall, the trend of flux decline for LSZ flux was more stable as compared to the first and second PWF. When the flux is constant, the transmission is the highest for protein separation, due to its self-rejecting effect occurring between the protein in the bulk and the fouled membrane covered by adsorbed proteins [37]. However, it can be seen that the support membrane has less flux decline for LSZ protein as compared to the GOF(BDA)/alumina composite membranes. In general, during the cross-flow process, the LSZ proteins were absorbed on the membrane surface and consequently formed a fouling layer and completely covered the membrane surface. This phenomenon happened to the GOF(BDA)/alumina composite membrane but for support membrane as it has less separation of LSZ protein, leading to its lowest flux decline. Consequently, membranes were less fouled, leading to a lower flux decline.

In addition, Fig. 10 illustrated the long-term filtration for the three cycle filtrations of first PWF, HA and second PWF for both support and GOF(BDA)/alumina composite membrane. At the support membrane, flux decline for first PWF, HA and second PWF are ~40 %, ~50 % and ~75 % after 24 h filtration, respectively. Meanwhile, the GOF(BDA)/alumina composite membrane had flux decline of PWF, HA and second PWF are ~40 %, ~20 % and ~22 % after 24 h filtration, respectively. Both membranes had same value for flux decline of first PWF (~40 %) due to compaction process of membrane. For the HA flux, the support membrane had higher flux decline than GOF(BDA)/alumina composite membrane that expected due to fouling phenomenon of HA solute on the support membrane surface.

On the other hand, the antifouling properties was measured in terms of Rt, Rr, Rir, FRR and separation rate of LSZ and rejection rate of HA for both support and GOF(BDA)/alumina composite membrane as presented in Tables 6 and 7. The LSZ protein separation rate for support and GOF(BDA)/alumina composite membrane are 25.41 % and 98.90 %, respectively. For HA rejection rate of the support and GOF(BDA)/alumina composite membrane are 91.25 % and 97.57 %, respectively. The support membrane had LSZ flux of 138 L/m².h with only 25.41 % LSZ separation, while HA flux of 82 L/m².h with 91.25 % HA removal. This HA removal value was higher than LSZ separation due to fouling phenomenon of HA solute on the support membrane surface. Meanwhile, for the GOF(BDA)/alumina composite membrane had LSZ flux of 7.6 L/m².h with 98.90 % LSZ separation and HA flux of 7.4 L/m².h with 98.75 % HA removal. Both solute fluxes were almost same with high rejection value probably due to repulsion effect of GOF(BDA) film on the composite surface. Thus, the incorporation of GOFs on the alumina as support membrane contributed to higher proteins separation and HA removal process.

The FRR value was obtained to evaluate the extent of flux separation after solute fouling. From the both figures, the FRR of the support membrane for LSZ protein and HA are 63.37 % and 62.42 %, respectively. The GOF(BDA)/alumina composite membrane regained the FRR at 94.86 % and 95.21 % for LSZ protein and HA, respectively. It could be deduced that the GOF(BDA)/alumina composite membrane had a better FRR value for both solutes compared to the support membrane. These results suggested the composite membrane displayed better antifouling properties than the support membrane during both solutes fouling test, which is due to the adhesion of solutes fouling layers on the composite membrane surface is weaker than the support membrane. Therefore, fouling layer was more reversible. On the other hand, pore size of membranes is also related to the membrane fouling phenomena, where solutes size is smaller than the pore size of the membrane, which could cause pore narrowing. When the solutes and the membrane pore are of the same size, it leads to pore blocking. Whereas, when solutes is larger than the membrane pore, it will cause cake layer formation on the membrane surface [38]. The lower LSZ protein separation rate and the lower FRR value for the support membrane are probably due to higher pore size property that could not totally reject LSZ protein at molecular weight size of 14.3 KDa. Meanwhile, the higher HA rejection rate at lower FRR value for the support membrane due to the adsorption of HA solute with molecular weight size of only 2 KDa. This phenomenon probably due to the less antifouling properties of the support membrane which the adsorption of HA solute still occurred on its surface even though its pore size is higher than HA solute.
Antifouling properties of membranes could also be evaluated by the ratio of solute flux and first PWF, which is referred as the Rt value. As shown in both Tables 6 and 7, the support membrane had the Rt value of $\sim 59\%$ and $\sim 69\%$ for LSZ protein and HA solute, respectively. Meanwhile, the GOF(BDA)/alumina composite membrane exhibited $\sim 22\%$ and $\sim 30\%$ of Rt value for LSZ protein and HA solute, respectively. The other series resistance ratios investigated were reversible and irreversible which are Rr and Rir, respectively. In order to perform better antifouling properties, the used membrane required to have high FRR value with low Rt value. Thus, the GOF(BDA)/alumina composite membrane was performed a better antifouling with higher FRR and lower Rt for both solutes. The increment of the FRR value for composite membrane was indicated by the enhancement of smoothen surface roughness that could minimize the preferential attraction between the solute molecule and the membrane surface and the possibility of the solute molecule being stuck at the membrane surface [39].

### Table 6

<table>
<thead>
<tr>
<th>Rate (%)</th>
<th>Support</th>
<th>GOF(BDA)/alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSZ protein separation</td>
<td>25.41</td>
<td>98.90</td>
</tr>
<tr>
<td>FRR</td>
<td>63.37</td>
<td>94.86</td>
</tr>
<tr>
<td>Rt</td>
<td>58.63</td>
<td>21.70</td>
</tr>
<tr>
<td>Rr</td>
<td>22.00</td>
<td>16.56</td>
</tr>
<tr>
<td>Rir</td>
<td>36.63</td>
<td>5.14</td>
</tr>
</tbody>
</table>

![Fig. 9. Long-term filtration of three cycle filtrations](image)

![Fig. 10. Long-term filtration of three cycle filtrations](image)
Table 7

<table>
<thead>
<tr>
<th>Rate (%)</th>
<th>Support</th>
<th>GOF(EDA)/alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA Removal</td>
<td>91.25</td>
<td>98.75</td>
</tr>
<tr>
<td>FRR</td>
<td>62.42</td>
<td>95.21</td>
</tr>
<tr>
<td>Rt</td>
<td>69.10</td>
<td>30.22</td>
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<tr>
<td>Rr</td>
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<tr>
<td>Rrr</td>
<td>37.58</td>
<td>4.79</td>
</tr>
</tbody>
</table>

4. Conclusion

The GOFs/alumina composite membranes have been fabricated by implementing diamine monomers into GO nanosheets which could improve the antifouling properties. These composite membranes were prepared via VD method using three GOFs suspension at different diamine monomers (EDA, BDA and PDA) as cross-linker agent. The cross-linking was essential to provide the GOFs film as selective layer of composite membrane with high stability in PWF. The improvement was combined effects of hydrophilicity, surface roughness, and membrane morphology with favourable thickness of selective layer form. Among the composite membranes, the GOF(BDA)/alumina composite membrane possessed the better properties and performance toward the antifouling study. It delivered a high PWF of 10 L/m².h with a separation rate of all proteins of > 95 %. The composite membrane maintained its stability during a long-term operation at 5 bar for 24 h for two different solutes which are LSZ protein and HA solute. As a conclusion, we found that the performance of composite membranes was a function not only by the variation in the GOFs structure but also by the surface properties of the composite membrane that altered their hydrophilicity and surface roughness. This improvement enhanced the antifouling properties toward protein separation and HA removal applications in the downstream of biotechnology and wastewater industries, respectively.

CRediT authorship contribution statement

Noor Fauziyah Ishak: Methodology, Formal analysis, Investigation, Writing - original draft. N. Awanis Hashim: Conceptualization, Writing - review & editing, Supervision. Mohd. Hafiz Dzarfani Othman: Validation, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


