Research Paper

Enhancement of Antifouling of Ultrafiltration Polyethersulfone Membrane with Hybrid Mg(OH)$_2$/Chitosan by Polymer Blending

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Article info

Keywords

Highlights

- A hydrophilic hybrid additives chitosan-Mg(OH)$_2$ were added into the PES membrane.
- These additives causes significant improvement of the PES membrane hydrophilicity
- Water contact angle of the membrane decreased from 84.2° to 68°.
- The additives also brings notable effects on the enhanced water permeability.

Graphical abstract

Abstract

One of the most straight-forward approaches to improve the membrane performance is by imposing the hydrophilic property. This paper discusses the fabrication of polyethersulfone (PES)-based membranes using chitosan and Mg(OH)$_2$ as organic and inorganic additives with the specific aim of increasing membrane hydrophilicity, respectively. Three variants of dope solutions were prepared with the addition of 1 wt% chitosan, 1 wt% Mg(OH)$_2$ and a combination of chitosan/Mg(OH)$_2$ into three different PES polymer solutions. The effects of additives on the resulting membranes were evaluated in terms of chemical functional groups by ATR-FTIR, morphological changes by SEM, and hydrophilicity degree of membrane surface based on the water contact angle (WCA), as well as the filtration profile, and antifouling properties. SEM images shows that the presence of additives altered the morphological structure of the membrane. It also enhanced the hydrophilicity significantly as shown by decreasing WCA from 84.2° to 68°. The modification also brings notable effects on the membrane performance as proven by the enhanced permeability of both pure water and humic acid (HA) solution as well as acceptable rejection of the HA solute. Overall, the Mg(OH)$_2$-modified PES membrane produces much greater permeability and antifouling property compared to the rest thanks to its good hydrophilicity.

1. Introduction

In the membrane separation and technology field, researchers have been continuously making progressive attempts in developing the best-characteristic and high-performing membranes. However, membrane fouling still remains a main culprit in performance deterioration. Fouling on the membrane can occur due to the interaction of organic (mostly) hydrophobic compounds with the membrane surface. During the filtration process, polymer as the main building-block of the membrane tends to be hydrophobic allowing particles of foulant adsorbed on its surface, which causing the blockage of pores, thereby, leading to the decline of water flux [1].

Membrane fouling resistance can be inhanced by by altering the hydrophobic polymer surface into hydrophilic. This endeavour can be done in many ways; for instances, by mixing the polymer with another polymer (via
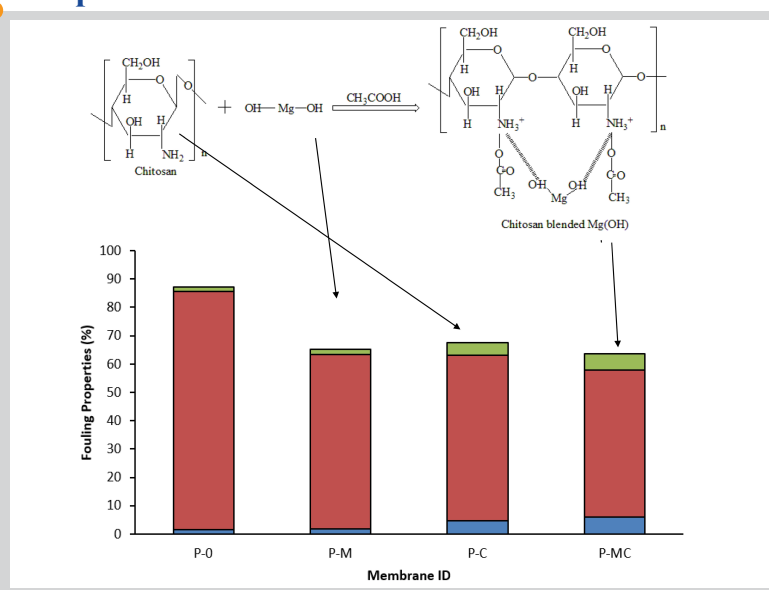
polymer blending) [2], chemical grafting [3,4] and surface modification [5]. Among these methods, polymer blending is known as one of the simplest yet effective. It not only enhances the hydrophilicity, but also resuts in membrane with excellent pore characteristics, high-flux, and good antifouling. Previous studies reported that the addition of hydrophilic additives to the casting solutions such as polyethylene glycol (PEG) [6], pluronic F127 [7], polydopamine [8–10] and chitosan [11,12], all have been proves to enhance the anti-fouling property of the resulting membranes.

In recent years, modification through bio-polymer mixing has attracted a lot of attention thanks to its positive influence on the membrane properties [13]. Chitosan is one of the most used as additive. It is considered as low-cost, harmless and environmentally friendly material, and often can be found in the industrial waste [14]. Chitosan is a straight-chained polysaccharide composed of NH and OH groups allowing further modifications. The NH and OH groups facilitate the binding mechanism between chitosan and metal ions [15]. Chitosan has a high density of positive charge in acidic solutions which can be linked to the glucosamine group in its molecular chain [16]. Chitosan is a biopolymer that occurs naturally from renewable natural resources with high hydrophilicity and good biocompatibility [12,14].

Chitosan has been used to modify hydrophobic membranes such as PES [17], PVDF [12], PAN [18] to increase its hydrophilicity. The use of chitosan as PVDF additive has been proven to reduce protein fouling by increasing surface hydrophilicity [12].

The use of nano size inorganic particles as additive in membrane preparation is also quite widespread [19]. A number of inorganic materials such as silica [20,21], TiO$_2$ [22], and Mg(OH)$_2$ [23] have been successfully added to PES-based polymeric membranes to enhance the resulting membrane hydrophilicity. Accordingly, the hydroxyl-carrying particles such as Mg(OH)$_2$ has also been used to modify membrane morphology with the aim to increase hydraulic performance [24–26]. Mg(OH)$_2$ is an inorganic compound that can be easily obtained, as it is affordable, non-toxic, and often used as an additive in drugs and food sectors [27,28]. Several studies regarding antibacterial and antifouling properties in the membrane mentioned that Mg(OH)$_2$ poses an outstanding antibacterial performance against *E. Coli* and at the same time can improve the hydrophilicity of PVDF membranes [23,24]. In another study, Mg(OH)$_2$ nanoplatelet as the PES additive enhanced the resulting membrane pore properties as well as surface hydrophilicity, leading to enhanced water permeability [24].

Considering the positive impact of chitosan and Mg(OH)$_2$ as additives, it is hypothesized in this study that combination of both would further offer enhanced performance. Combination of the two material is simple as chitosan has a good biocompatibility as well as functionality with Mg(OH)$_2$ particles due to the enriched presence of -OH and NH$_2$ groups. Moreover, chitosan and Mg(OH)$_2$ are nontoxic and are very safe to use. Based on search of the literature, no research regarding the antifouling propensity of PES membranes modified with hybrid Mg(OH)$_2$/chitosan-PES has been found. To unravel the effect of dual additive, the effect of both additives when added as a single component was also investigated.

2. Material and methods

2.1. Materials

Polyethersulfone (PES, Ultrason E6020, Mw 65000, BASF, Ludwigshafen, Germany) was the main polymer used for preparing the membranes. N-methylpyrrolidone (NMP, Merck, Hohenbrun, Germany) was used as a solvent. Mg(OH)$_2$ (Xinglu Chemical Tech Co., China) and chitosan (Sigma Aldrich, Germany) were used as additives. Humic acid as a mimic foulant was purchased from Sigma Aldrich (Germany). DI (Deionized) water was used as a non-solvent for membrane fabrication and the feed during membrane filtration process for clean water flux characterization.

2.2. Preparation of chitosan

A certain amount of chitosan was milled for 20 hours. Subsequently, the chitosan was sifted using a vibrator screen of 325 mesh. Chitosan solution was made by dissolving 1 gram of chitosan in 100 mL of acetic acid 1 wt% [17]. Furthermore, the solution was left to homogeneity for 24 hours with agitation. The ready solution was then stored at room temperature to be used as one of additives for membrane preparation.

2.3. Preparation of Mg(OH)$_2$/chitosan solution

The hybrid Mg(OH)$_2$/chitosan solution was prepared by referring to earlier work of Munnawar et al. [17]. Chitosan (1%) and Mg(OH)$_2$ (1%) were dissolved in 100 ml of 1% acetic acid solution. Following that, the mixture was stirred while heated at 50°C until a homogeneous solution was obtained.

2.4. Preparation of membrane

Four types of flat sheet membranes were prepared. There were the pristine PES (18wt%) and three modified membranes using additive of Mg(OH)$_2$, chitosan and Mg(OH)$_2$/chitosan into the PES-NMP system. Complete information of the membrane compositions is shown in Table 1. The polymers, additives and solvent (dope solution) were mixed altogether in a vial bottle by stirring. Once the homogeneous condition was obtained, the dope solution was poured on a glass flate and was flattened by a casting knife. Subsequently, the glass plate was immersed in a bath containing the non-solvent. Following that, the membrane sheet was kept in a water-containing container until further use.

Table 1
Composition of membrane dope solution.

Membrane	PES (%)	Mg(OH$_2$) (%)	Chitosan (%)	Mg(OH$_2$)/ Chitosan	NMP (%)
P-0	18	0	-	-	82
P-M	18	1	-	-	81
P-C	18	-	1	-	81
P-MC	18	-	-	1	81

2.5. Membranes characterization

Several instrumental analysis were used for membrane characterization , namely the Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) analysis was carried out using a FTIR-8100A (Shimadzu Co., Kyoto, Japan) for analysis of chemical functional groups existing in the membranes. Scanning electron microscoe (FE-SEM, JSF-7500F, JEOL Co., Ltd., Japan) was used to observe changes in membrane morphology. The hydrophilic nature of the membrane was evaluated through water contact angle (WCA) analysis using a contact angle meter (Drop Master 300, Kyowa Interface Science Co., Japan). In addition, Gravimetric method (Eq. (1)) was used to calculate the porosity (ε) of the membrane was determined by the gravimetric method [29]:

$$\varepsilon(\%) = \frac{(\omega_w - \omega_d)}{\rho x A x l} x 100 \tag{1}$$

ω_w and ω_d are the respective weights of the membrane sample in the wet and dried state (kg), ρ is the density of water, A and l represent the surface area (m^2) and thickness (m) of the membrane sample, respectively.

2.6. Dead-end ultrafiltration set-up

The filtration test was performed using a dead-end ultrafiltration cell illustrated in Figure 1. It could accommodate 300 mL of feed for each filtration. The membrane performances were evaluated in terms of permeability of pure water and rejection of humic acid solution. Prior filtration test, the membrane sample was compacted until the constant flux rate was met.

For the pure water permeability (PWP), the test was conducted by using the DI water as the feed. The permeate was collected every 10 minutes and weighed using a digital balance. The data were then used to calculate the PWP (L/m^2.h.bar) using Eq. (2):

$$PWP = \frac{Q}{A \times \Delta t \times \Delta P} \tag{2}$$

where Q is the amount of permeate produced (L) at a certain filtration time, Δt, (h), A represents area of membrane surface (m^2) and ΔP is the pressure used during filtration (bar).

For evaluation of membrane selectivity, a filtration experiment was carried out using a 50 ppm humic acid solution as the feed. The feed solution was prepared by dissolving 0.05 grams of humic acid into 1 liter DI water. The separation performance of the membrane was evaluated from the rejection coefficient (R), calculated using Eq. (3):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) x\ 100 \tag{3}$$

where C_p and C_f are the concentration of humic acid in the permeate and the

feed, respectively.

2.7. Antifouling performance of fabricated membranes

Antifouling performance of the membranes was evaluated through the following procedures. Initially, pure water flux (J_{w1}) was obtained for 1 hour at ΔP of 1 bar. It was followed by replacing the feed with humic acid (J_{HA}), conducted under similar condition. The membrane sample was then flipped to allow back-flushing using the DI water as the feed. After that, the membrane was reversed again for PWP test to obtain (J_{w2}). By obtaining these data, the water flux recovery ratio (FRw) can be calculated using Eq. (4) [30]:

$$FRw(\%) = \left(\frac{J_{w2}}{J_{w1}}\right) \times 100 \qquad (4)$$

Those data were also used to evaluate the membrane fouling propensity of the prepared membranes using few other parameters, namely. Recoverable fouling (R_r, Eq 5), irrecoverable fouling (R_{ir}, Eq. 6) and fouling total (R_t, Eq. 7).

$$R_r(\%) = \left(\frac{J_{w2} - J_{HA}}{J_{w1}}\right) \times 100 \qquad (5)$$

$$R_{ir}(\%) = \left(\frac{J_{w1} - J_{w2}}{J_{w1}}\right) \times 100 \qquad (6)$$

$$R_r(\%) = \left(\frac{J_{w2} - J_{HA}}{J_{w1}}\right) \times 100 \qquad (7)$$

3. Results and discussion

3.1. Chemical structure

The IR spectra of P-0, PM, PC and P-MC membranes in Figure 2 shows an interesting transformation of the chemical structures. Generally, all the membranes (P-0, PM, PC, P-MC) have aromatic ring functional group (C = C) which appears at wavenumbers of 1483 and 1580 cm^{-1}. Moreover, sulfonate group (O = S = O) is detected with appearance of a peak at 1137 cm^{-1}. The C-O-C group from aromatic ether is detected at a wavenumber of 1237 cm^{-1} and aromatic C-H at a wavenumber of 834 cm^{-1}. The appearance of these groups and peaks distinguish the molecule vibration in the polymer PES [31].

For the P-M membrane, a small peak is visible at a wavelength of 3697 cm^{-1} as a result from stretching vibration of the hydroxyl group (-OH) of Mg(OH)$_2$ water crystal. Whereas, the broad peak appears at a wavelength of 3362 cm^{-2} on the P-C membrane is associated to the stretching vibration of the hydroxyl group (O-H) and the primary amine group (N-H) (asymmetrical strain) for the chitosan. In addition, the appearance of peak with weak intensity at 1640 cm^{-1} indicates the N-H group of the secondary amine group (symmetrical strain) [3, 33].

For the P-MC membrane, the emergence of a broad peak at a wavelength of 3358 cm^{-1} appears at greater intensity ascribed to immobilization of OH-group of Mg(OH)$_2$ to O-H and N-H groups. The frequency absorbed at 1640 cm^{-1} which is the N-H bend of the secondary amine (symmetrical stretching) is transformed into a smaller bend at 1635 cm^{-1} due to NH deformation [32]. Mixing different components triggers the interaction among the substances, chemically and physically, which generally exhibited from the behaviour of IR spectrum [34]. The existence of a shift in the stretching of OH and NH groups on the P-MC membrane confirms the successful interaction of chitosan and Mg(OH)$_2$ residing in the membrane matrix.

The schematic representation of the interaction between chitosan and Mg(OH)$_2$ is shown in Figure 3. When Chitosan and Mg(OH)$_2$ are dispersed in diluted acetic acid solution, the NH group of chitosan is protonated to NH^{3+}. The enriched presence of NH molecules in the chitosan chain forms hydrogen bonds with OH groups from the Mg(OH)$_2$ chains. This bonding indicates the interactivity between chitosan and Mg(OH)$_2$. Similar findings were also reported by other research groups in which chitosan reacted well with starch in acetic acid system through the hydrogen bonding formation between NH

and OH molecules [35]. The proposed of possible bonding reaction between chitosan and Mg(OH)$_2$ in PES is presented in Figure 4.

3.2. Membrane morphology

The cross-sectional SEM images in Figure 5 show all the membranes (P-0, PM, PC, P-MC) pose an asymmetric structural with denser top-layer supported by a sublayer having pores resembling the structure of fingers or macrovoid morphologies. The asymmetric morphology is very common for membranes prepared by NIPS method. The original PES membrane (P-0) is observed to have a dense structure in the upper layer, supported by fingers and macrovoid morphologies (Figure 5a). However, slight change in the morphology appears for membranes loaded with additive(s). For instance on the P-M membrane, a significant change is seen in the sublayer part in which the macrovoid-like pores appear to increase in number and size, meanwhile the finger-like morphologies become lesser and shorter (Figure 5b).
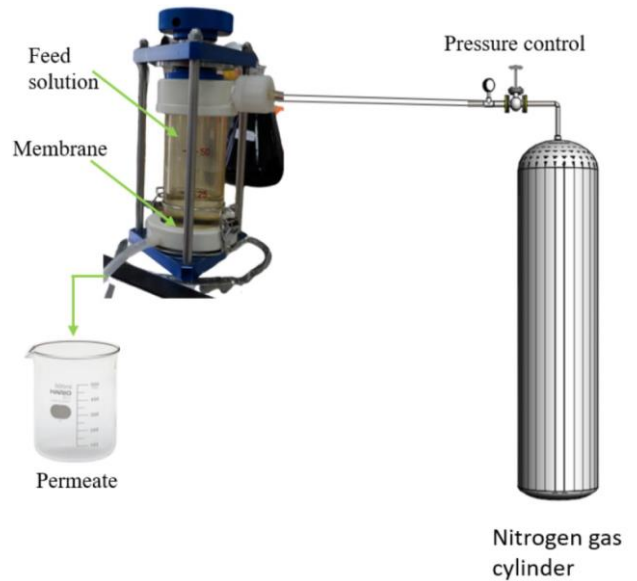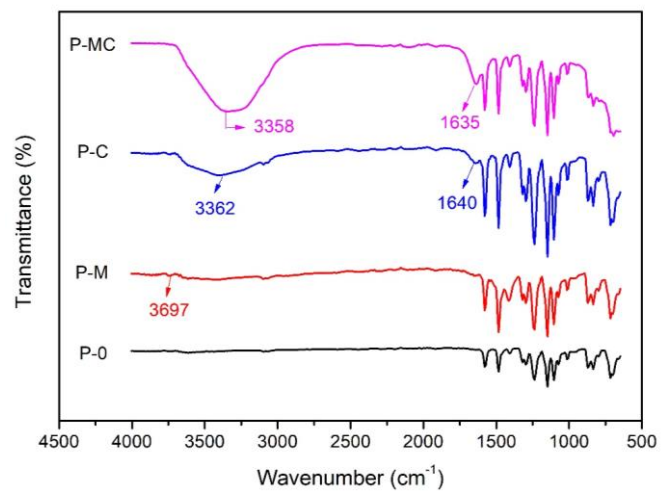

Fig. 1. Dead-end ultrafiltration cell.

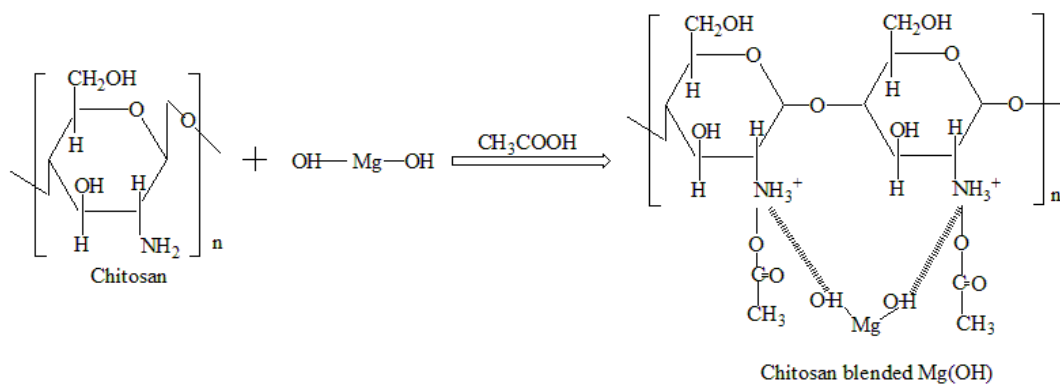**Fig. 2.** FTIR spektra of the four membrane samples.

Fig. 3. The proposed scheme of interaction between chitosan and Mg(OH)$_2$.
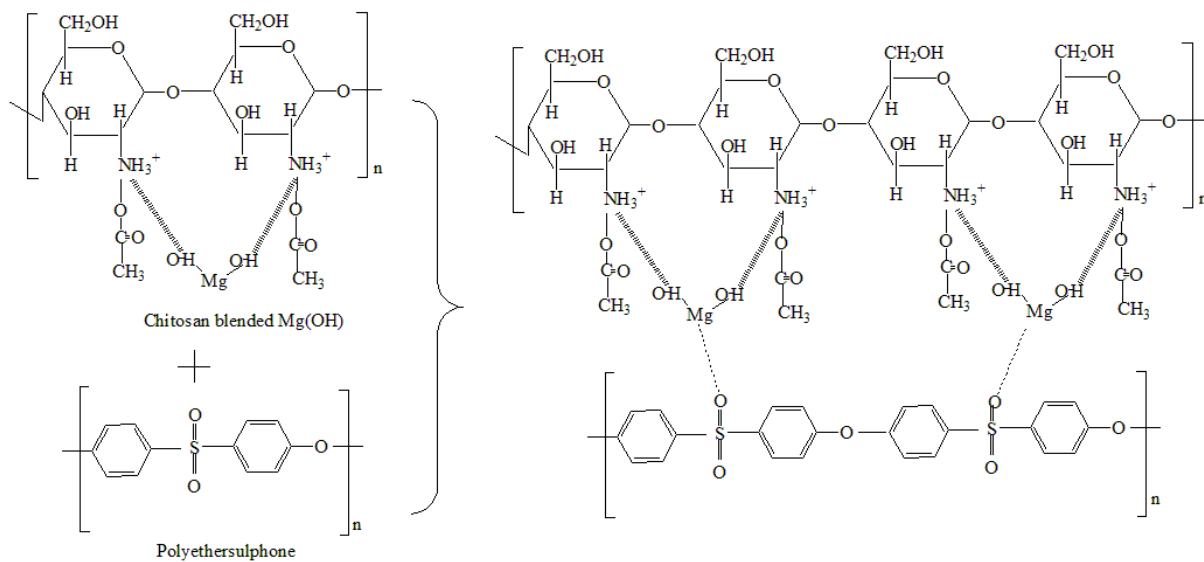

Fig. 4. The proposed scheme of interaction between PES and hybrid Mg(OH)$_2$/chitosan.
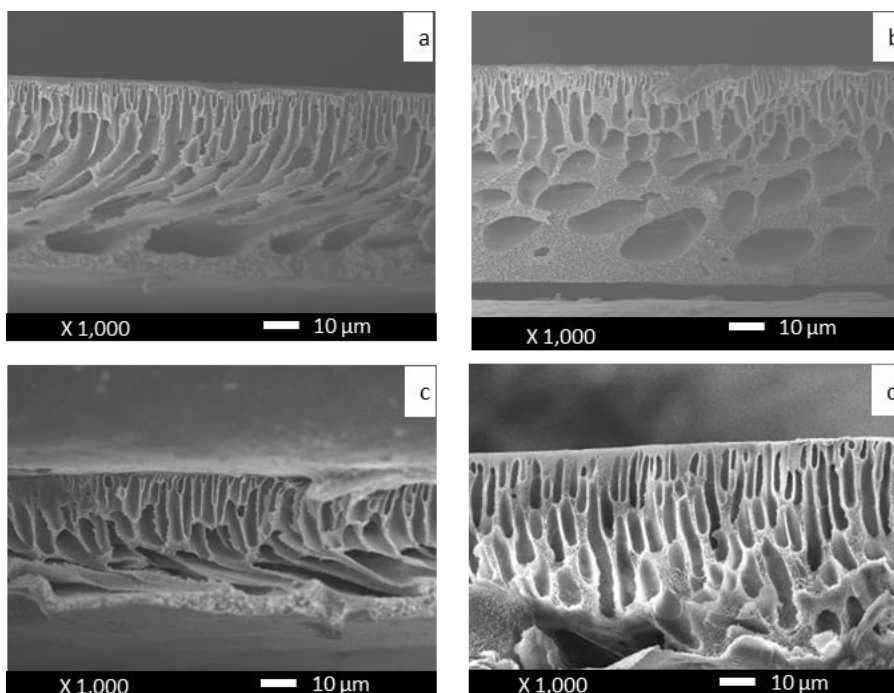

Fig. 5. Cross-sectional morphology of fabricated membranes; (a) Pure PES, (b) P-M membrane, (c) P-C membrane, (d) P-MC membrane.

During membrane formation in the coagulation bath, several factors such as the thermodynamic instability of polymer solution and the solvent-nonsolvent exchange rate greatly influence the morphology of the resulting membrane. Addition of hydroxyl-bearing inorganic particles like $Mg(OH)_2$ to the dope solution can reduce the thermodynamics stability of the system [36]. Not only that, the hydrophilic nature of this additive also accelerates the transfer of the water inflows during the membrane formation [37]. Thus, with the reduction of thermodynamic stability and an increase in the flow rate of non-solvent (water) into the system, the phase inversion undergoes the instantaneous demixing, which results in the formation of large macrovoid. Changes in void structure in the bottom layer with the addition of hydrophilic additives were also reported by others [1,19].

In the case of chitosan, its presence in the dope solution does not significantly affect the pore structure of the resulting membrane, hence the P-C membrane shares almost identical morphology with the pristine PES membrane. However, if observed closely, the P-C membrane has a matrix structure with shorter finger-like voids than the pristine PES membrane (Figure 5c). This result can be attributed to the increasing viscosity of dope solution with addition of the chitosan [38], which increases the kinetic resistance in the phase separation process, thus, the solvent and the non-solvent exchange rate is reduced and brings about the formation of smaller size macrovoid on the P-C membrane.

On the contrary, when $Mg(OH)_2$ and chitosan are combined as a hybrid additive, they contribute to the formation of membrane with thicker active layer and sublayer with bigger and longer finger-like pore structures than the rests. Like the P-C membrane, P-MC membrane also has a denser and more compact matrix structure. This is presumably owing to the decline of the kinetic barrier due to an increase in the viscosity of the dope solution with an increasing amount of additives used [39]. Overall, it can be concluded that the presence of hydrophilic additive in the casting solution increases the solvent-non-solvent rate of exchange during the process of membrane formation by NIPS method. It affects the structure of pore as well as the thickness of the upper layer of the membrane.

3.3. Membrane porosity

Figure 6 shows the effect of modification using $Mg(OH)_2$ and chitosan on the surface pore characteristics and porosity of the resulting membranes. It appears that although the P-M, P-C and P-MC have a higher porosity than the P-0, the improvement tendency of surface porosity varies for each membrane of different additives. For example, a single additive of $Mg(OH)_2$ or chitosan does not result in membranes with notable difference in porosity compared to the hybrid additive.

As shown in the SEM results in Figure 5, the P-M membrane has a void with larger size but small in quantity. This is because chitosan does not function effectively as a pore former. Whereas, the resulting P-C membrane has pores in smaller numbers and sizes which are not far different from the pristine PES. When both additives are combined, its addition causes the hydrodynamic state of the casting solution to become more unstable. $Mg(OH)_2$ particles which are supposed to form large pores are disturbed by the presence of chitosan which increases the dope solution viscosity and at the same time inhibits formation of pores. Although it is not yet can be explained in a complex and profound manner, we suggest that this event is the ultimate reason that causes the P-MC membrane to have more number of pores, though, not as large in size as those on the membrane modified using $Mg(OH)_2$ alone.

3.4. Membranes hydrophilicity

The WCA data in Figure 7 shows that unmodified PES membrane has a hydrophobic characteristic with contact angle of 84.2°. Blending of either $Mg(OH)_2$ or chitosan or combination of both into the membrane system brings about the reduction of WCA in P-M, P-C and P-MC membranes to 69°, 71.1° and 68°, respectively. The addition of $Mg(OH)_2$ enriches the membrane system with hydroxyl group. Therefore, the hydrophilicity of the P-M membrane is promoted. Similar results were also mentioned by some researchers in their published works that the decrease in the contact angle of the PES and PVDF membranes were contributed by the -OH group from the $Mg(OH)_2$ matrix [23, 25].

The enhancement of membrane hydrophilicity is also seen in the P-C promoted by the existence of highly hydrophilic groups of hydroxyl and amino in the chitosan. Similar finding was also reported by Ghaemi et al, by blending 0.8%wt of chitosan. They successfully lowered the WCA of the membrane to 57° [11]. In this work, by only adding chitosan, the WCA of P-C was lowered to 71.1°, slightly higher than that of P-M which is due to the better pore properties of P-C. However, when chitosan is added together with chitosan, the generated contact angle of the water droplet declines further to

68° Thanks to the hydroxyl groups presence in $Mg(OH)_2$ and chitosan. The existence of two hydrophilic group additives in a casting solution enriches the hydroxyl content of the P-MC. This result was also confirmed by FTIR analysis where the P-MC membrane showed a higher hydroxyl group intensity (Figure 2).

3.5. Pure water permeability

Figure 8 shows the effect of adding $Mg(OH)_2$, chitosan, and combination of both on the membrane PWP. All the modified membranes have higher PWP that the pristine membrane. The P-0 membrane has the lowest PWP of 4.123 $L/m^2.h.bar$. By adding either $Mg(OH)_2$ or chitosan to the casting solution, the PWPs improve up to 30.6 $L/m^2.h.bar$ and 11.226 $L/m^2.h.bar$ for P-M and P-C, respectively. This enhancement is closely linked to the hydrophilicity degree of membrane as evidenced by results of WCA measurement (Figure 7). It is clear that the WCAs of the P-M and P-C are lower than that of the P-0 membrane, suggesting an increase degree in hydrophilicity, which enhances the interactivity of water molecules with membrane surface during the filtration process. Besides that, the increment of PWP is also directly correspondent to the morphology of the film (Figure 5). The macrovoid structure is more advantageous in facilitating water to penetrate through the membrane than the finger-like, thus the PWP of the P-M membrane is greater than that of the P-C membrane.

Figure 8 shows that the P-MC membrane poses the highest PWP value of 39.74 $L/m^2.h.bar$. It can be ascribed by the hydrophilicity property, which in this case, the P-MC has the lowest WCA. The membrane morphology of this membrane pores poses macrovoid structure with large size and longer finger-like parts, this trait facilitates the permeation of water during the filtration process. The increasing amount of macrovoid from the supporting layer of P-MC membrane is caused by the presence of hydrophilic moieties in the polymer solution thereby increasing demixing speed during the phase inversion process. In addition, the aligned and straight macrovoid shape in the P-MC membrane helps to increase membrane permeability [40].
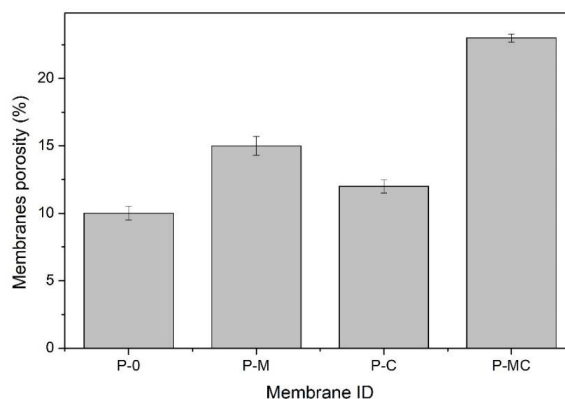
Fig. 6. Effects of the addition of $Mg(OH)_2$ additives and chitosan to the porosity of PES membrane.
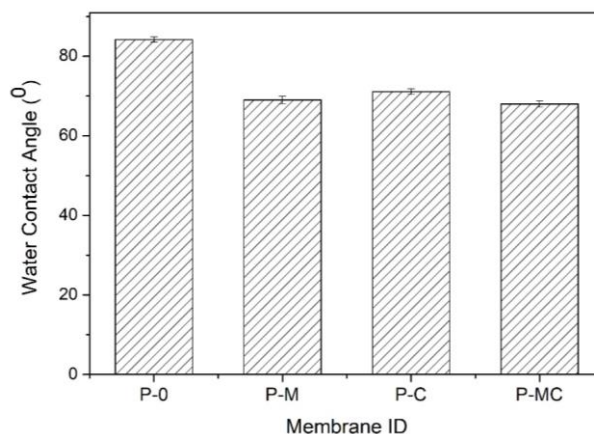
Fig. 7. Effect of additives on the water contact angles of the prepared membranes.

3.6. Rejection performance

The influence of Mg(OH)$_2$ and chitosan as additives on the selectivity performance of the membranes was investigated and results are presented in Figure 9. The pristine membrane (P-0) produces permeate with the highest rejection of 77.6% due to the dense and hydrophobic structure of the PES. After modification, the rejection of the P-M, P-C and P-MC membranes decrease to 68.8, 70.3, and 72%, respectively. This is due to the formation of pores and/or enhancement of pore size after the modification using Mg(OH)$_2$ and chitosan. The P-M membrane experiences the biggest decline of rejection because of the introduction of Mg(OH)$_2$ to the dope solution results in a membrane with a larger pore structure compared to the P-0, P-C, and P-MC membranes. For the P-C membrane, the rejection obtained is slightly higher than the P-M membrane because the chitosan is less effective pore former than the Mg(OH)$_2$, which is also seen from the decrease in the value of water flux (Figure 8). Modification of the membrane with the combination of Mg(OH)$_2$ and chitosan increases both humic acid rejection and water flux because when the combined additive lead to higher pore sizes shown by the results of SEM (Figure 4) and porosity (Figure 5). Such properties allow the P-MC membrane to have the highest permeability with moderate humic acid particles rejection. Moreover, the addition of hybrid Mg(OH)$_2$/chitosan enhances membrane surface hydrophilicity that reduces the bonding interaction between membrane surface and foulant particles. As reported by Zhao et. al (2015), hydrophilic layers helped increase the rejection by acting as an obstacle for humic acid particles [6].

3.7. Antifouling properties

Figure 10 shows that blending of PES polymer with hydrophilic additives is an effective method for producing membranes with better antifouling propensities. It is observed that all modified membranes have higher FRw than that of the pristine PES membrane with FRw of 14%, while the P-M and P-C membranes have FRwS of more than twice higher, and the P-MC membrane has the highest FRw value of 42% almost threefold higher than the P-0 membrane. Higher FRw indicates the high antifouling properties of membranes. During filtration of humic acid, the flux of all membranes decreases, which is due to the formation of cake from the accumulated humic acid particles attached on the membrane surface. After a 20-minute backwash, the flux of pure water can be recovered back with different values on each membrane.

The interaction between hydrophobic membrane surfaces and contaminant particles plays a major role in the occurrence of membrane fouling. The presence of Mg(OH)$_2$ or/and chitosan as additives can increase the hydrophilicity of the resulting membranes, thus, reducing the hydrophobic membrane-foulant interaction. The low WCA of the P-MC (68° in Figure 7) suggest that the Mg(OH)$_2$ and chitosan can form a water hydration layer on the membrane surface that prevents foulant from sticking to the membrane surface [41]. Therefore, the humic acid particles that fouled the membrane could be washed off easily just by backwashing and resulting a higher second (post-membrane cleaning) water flux.

During the filtration process, the total flux-loss due to fouling is caused by reversible and irreversible fouling. The flux loss due to reversible fouling can be recovered by membrane cleaning meanwhile irreversible fouling is a permanent loss of flux that cannot be recovered through the cleaning mechanism. To look into this further, each of this type of fouling was evaluated through mathematical calculation, and results are shown in Figure 11.

Figure 11 shows that the total fouling value of 87.26%, 65.23%, 67.59%, and 63.62% with a reversible fouling value of 1.6%, 1.82%, 4.5%, and 5.87% for the membrane P0, PM, PC, and P-MC, respectively. As PES is revealed to have the most hydrophobic trait amongst the other membranes, it is obvious that the fouling occurred in high intensity on the P-0 membrane. As shown in Figure 10, P-0 membrane has the smallest ratio of FRw as shows in Figure 11 attributed to a very low rate of the reversible fouling. On the contrary, the irreversible fouling that occurred on the P-0 membrane is 85.66%, which means most HA particles cannot be cleaned off the membrane surface due to strong hydrophobic-hydrophobic interaction with the membrane surface.

The improved hydrophilicity of the P-M and P-C membranes results in the less severe occurrence of fouling as seen from the lower percentage of F$_T$ and higher percentage of F$_R$. Considering the results in Figure 10 and Figure 11, it can be concluded that the membrane which was modified with hybrid Mg(OH)$_2$/chitosan showcased more favourable antifouling behaviour.

The attempt of modifying membrane using chitosan and Mg(OH)$_2$ in this research has been proven to be successful in enhancing the characteristics and performances of the PES membranes. Especially, when both additives combined as a hybrid particle. It promotes the water flux performance up to ~40 L/m2.h. With this level of performance, the membrane

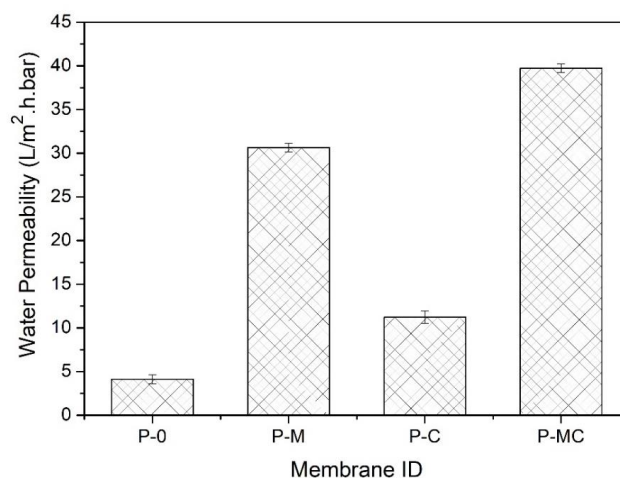is considered feasible to be used, at least for small-scale practical applications.

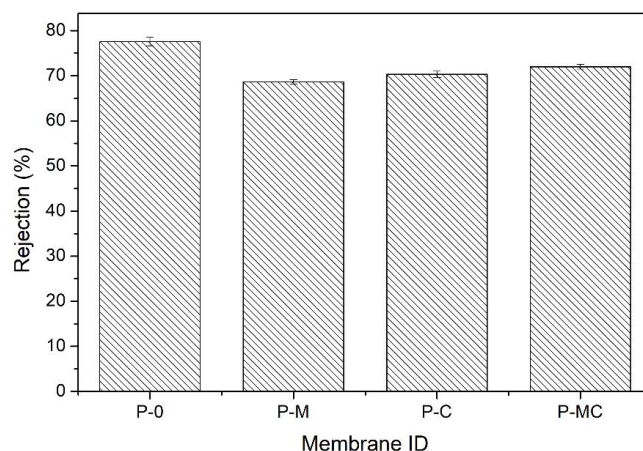**Fig. 8.** Pure Water Permeability of fabricated membranes.

Fig. 9. Effect of additives on the humic acid rejection of the prepared membranes.
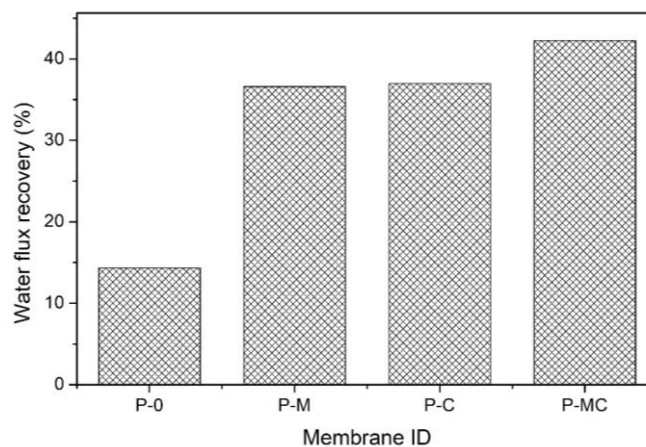

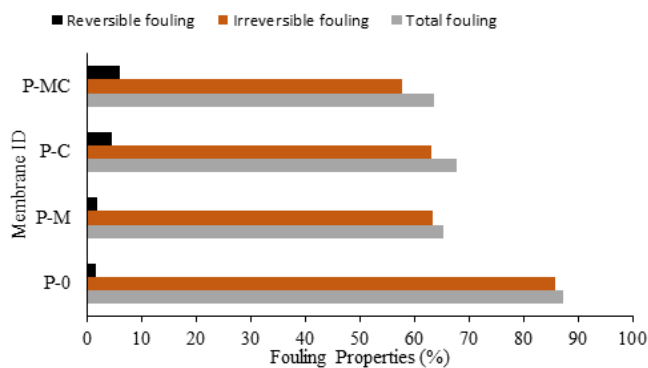**Fig. 10.** Water flux recovery of fabricated membranes.

Fig. 11. Antifouling properties of fabricated membranes.

4. Conclusions

Modification of PES membrane using additives Mg(OH)$_2$ and chitosan and hybrid Mg(OH)$_2$/chitosan have been successfully carried out. The result of SEM observation reveals that the additives alter the membrane morphology when introduced solely and when combined. Chemical interactions of blended Mg(OH)$_2$ and chitosan in the P-MC membrane was confirmed by FTIR analysis. Hybrid Mg(OH)$_2$/chitosan additive augmented the hydrophilicity as evidenced by declining WCA from 84° to 68°. It enhances the permeability of PES membrane almost 10-fold higher with humic acid rejection of 72%. The hybrid additive also enhances the fouling resistance of the resulting membrane due to improved surface hydrophilicity. Further investigations regarding the effects of additive concentration, and stability of membrane in long-term use need to be studied.

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