



Chitosan/chitin whiskers composite membranes with polyethylene glycol for removal of cadmium ions

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ABSTRACT

Biopolymer based membranes have garnered remarkable attention as an alternative to synthetic polymer based membranes due to exceptional properties such as biocompatibility, renewable, biodegradability and environmentally-benign. In this study, a novel porous chitosan/chitin whiskers composite membrane was successfully fabricated with the extraction of polyethylene glycol (PEG) for the removal of cadmium ions. The physicochemical and mechanical properties of selected composite samples were examined by varying the amount of chitin and PEG concentration respectively. Surface morphologies characterization study proves that highly porous structure is induced through the PEG dissolution meanwhile incorporation of chitin whiskers aids to produce a well-dispersed membrane with smaller pore size. Herein, strong interfacial adhesion between chitosan and chitin leads to interconnected network and increase in compactness of the matrix. Furthermore, these composite membranes exhibited high efficiency in cadmium ions removal. Overall, this study provides a framework on understanding the way to control the pore size, physicochemical and mechanical properties of polymer membranes using PEG and chitin whiskers. Thus, these bio-composite membranes have a great potential to be extensively employed in wastewater treatment.

Keywords: Bio-composite membranes; Chitin whiskers; Chitosan; Mechanical properties; Cadmium removal

1. Introduction

A continuous supply of water for daily usage is vital to meet the demand of the expanding population and industrial development. Unfortunately, fresh water resources are depleting due to the pollution caused by the inadequate discharge of industrial effluent. Hence, perpetual efforts are in progress to come up with a highly efficient membrane technology that is cost-effective and environmental benign. Membrane technologies are explored widely in the field of wastewater treatment as it proves to be one of the most

promising techniques to supply clean water [1]. Over the years, membranes are developed with a wide range of material and mostly, polymer-based membranes are fabricated due to its flexibility and low cost factor [2,3]. The common polymers utilized for the development of membranes are polyacrylonitrile [4], poly(vinylidene fluoride) [5], polysulfone [6] and poly(vinyl chloride) [7] which are categorized as petroleum based polymers.

Despite of owing adequate mechanical and chemical stability, synthetic polymers brings concern to the effect on environment as they are derived from fossil fuels which

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may be replenished over time. Moreover, these membranes are required to be replaced after the life span ends and the discarded membranes leads to accumulation of waste in huge amount as they are non-biodegradable [8]. This factor provokes global quest to distinctively exploit natural based polymer membranes to their full potential in order to substitute the synthetic polymers as it paved the path for sustainable development and environmentally benign technology.

Chitosan is the N-deacetylated derivative of chitin, is the second most abundantly available natural polymer in the world. Both chitin and chitosan are known as potential green candidates for wide range of applications due to its biodegradability, non-toxicity and biocompatibility [9–11]. Due to the factor of flexibility, chitosan-based membranes are developed extensively for the use of many applications such as water treatment, biomedicine, wound dressings, packaging and tissue regeneration [12–14]. The presence of high content of chemical functional groups (amino and hydroxyl groups) as well as hydrophilic properties of chitosan favour for the filtration and adsorption technologies. Moreover, chitosan-based membranes are elected over other forms of chitosan adsorbents correspond to easy separation, faster kinetics and requirement of no post-treatment filtration [15].

Nonetheless, the drawbacks of chitosan such as high sensitivity towards pH and poor mechanical properties restrict its further development [15,16]. Thus, researchers discovered few strategies to overcome the shortcomings by coating, incorporating fillers and polymer blending. A number of papers were reported on the work of chitin and chitosan to fabricate composite membranes with superior performances for various applications due to their excellent compatibility [14,17–21]. Although chitin/chitosan composite have a great potential as membrane technology, yet their application on wastewater remediation is not immensely explored.

In this study, a porous bio-composite membrane is developed for the eradication of cadmium ions in wastewater. High porous structure was induced in the chitosan membrane by adding the pore forming agent known as polyethylene glycol (PEG) which is a biodegradable polymer. The effect of blending PEG with chitosan (CS) at different mass ratio was investigated by performing characterization studies to determine the surface morphologies and hydrophilicity of membrane. Since chitosan with highly porous structure are not always preferable to be used as membrane due to low mechanical properties, it is vital to prepare a membrane with mutual benefits in terms of performances and reinforced structure. Thus, different amount of chitin whiskers (CH) was incorporated into CS/PEG membranes to further enhance the mechanical properties. All these aforementioned membranes were prepared through solvent casting followed by selective dissolution technique. Interestingly, the successful preparation of a porous composite membrane based on CS/CH/PEG formulations is considered the novelty of this study.

2. Materials and methods

2.1. Materials

Chitosan powder (medium molecular weight, minimum of 75% deacetylation degree), commercial chitin flakes

(acetylation degree $\geq 95\%$, MW = 100 kDa) produced from shrimp shells, poly(ethylene glycol) (PEG MW = 6,000) and cadmium nitrate tetrahydrate were purchased from Sigma-Aldrich (M) Ltd., (Malaysia). Glacial acetic acid, calcium chloride dihydrate, hydrochloric acid, sodium hydroxide (NaOH) pellets and methanol utilized were obtained from Friendemann Schmidt Chemicals Ltd., (Malaysia).

2.2. Pretreatment and extraction of chitin whiskers

Chitin whiskers were prepared using method reported by [22,23] with minor modifications. Chitin flakes were first was soaked in 7% HCL for 24 h to remove the mineral salts. Afterwards, the samples were boiled and stirred in a 5% of potassium hydroxide (KOH) solution for 6 h to get rid of proteins. Then, this suspension was filtered and washed with distilled water for several times. The suspension was mixed with 50% of ethanol for 12 h and washed with distilled water again. Saturated calcium chloride (CaCl_2)/methanol solvent were prepared by dissolving 680 g CaCl_2 in 800 mL methanol under reflux heating. Next, 12 g of powdered chitin was added to solvent and heated under reflux at 110°C for 24 h while stirring vigorously. Excess water was poured into the suspension and stirred continuously for 1 h. After cooling, the sample was placed in dialysis tube for 5 d. Pure chitin whiskers were homogenized using Warring blender to obtain homogenization.

2.3. Preparation of composite membranes

Chitosan flake was dissolved in 2% of acetic acid to prepare 2% (w/v) of chitosan solution. 0.1% (w/v) of chitin whiskers suspension was prepared by dispersion in water under ultrasonic treatment for 5 min to obtain homogenous suspension. After that, chitosan solution and chitin whiskers suspension were mixed to prepare chitin dispersed (at concentration of 0%, 0.3%, 0.6%, 0.9% and 1.2%) chitosan solution (CS-CH) with a total dry weight of 0.60 g. Then, the mixtures were stirred for 24 h under room temperature until it homogenize. Next, PEG was diluted in water with certain mass (Table 1) and then was mixed with chitin dispersed chitosan solution. The mixtures were stirred thoroughly for 1 h and ultrasonicated for 2 min before they were poured into petri dish and dried at 80°C for 4 h. After drying, they were neutralized with 2% of sodium hydroxide (NaOH) solution for 30 min. The membranes were washed with distilled water to remove the remaining NaOH. After that, the membranes were kept in water at 70°C for 12 h to wash out the PEG component and to generate porous structure. The procedures of membrane fabrication are illustrated in Fig. 1. It is important to note here that the PEG does not contribute to the weight of the composite membrane since it will be removed completely during the dissolution step. Next, excess water on the surface of the membrane was removed with a filter paper and allowed it dry. The thickness of the composite membranes ranged from 50 to 60 μm . The composition of the mixtures is shown in Table 1.

Neat CS, CS-P1 and CS-P2 represent the mass ratio of CS:PEG mixture at 100:0, 80:20 and 75:25 respectively. Preliminary study was conducted by mixing CS:PEG at different mass ratio (100:0, 80:20, 75:25, 70:30 and 65:35).

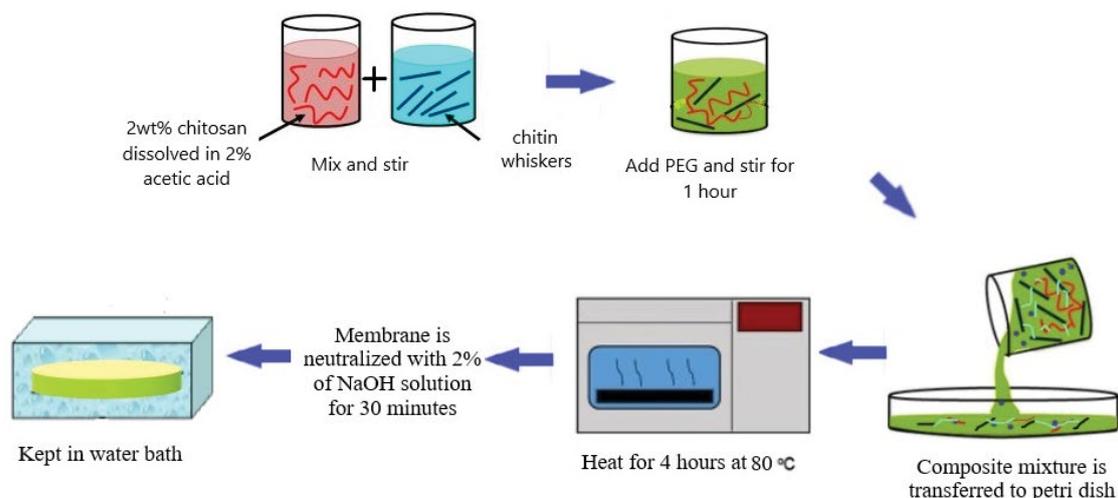


Fig. 1. Preparation of composite membrane.

Table 1
Composition of mixtures

| Sample code | Composition of CS-CH | | Mass of PEG (g) |
|-------------------|----------------------|--------|-----------------|
| | CS (%) | CH (%) | |
| Neat CS (control) | 100 | 0 | 0 |
| CS-P1 | 100 | 0 | 0.15 |
| CS-P2 | 100 | 0 | 0.2 |
| CS/0.3CH-P2 | 99.7 | 0.3 | 0.2 |
| CS/0.6CH-P2 | 99.4 | 0.6 | 0.2 |
| CS/0.9CH-P2 | 99.1 | 0.9 | 0.2 |
| CS/1.2CH-P2 | 98.8 | 1.2 | 0.2 |

It was found that the membranes with mass ratio of 70:30 and 65:35 exhibited bigger voids in the matrix which leads to extremely low mechanical stability. Meanwhile, CS-P1 implied smaller pore size and lower water uptake which is expected to give a very low water flux. However, CS-P1 results were included in this study to provide better understanding on the effect of varying PEG concentration of the CS matrix. All in all, the incorporation of chitin whiskers was employed only for CS-P2 membranes due to desirable pore size and adequate mechanical properties obtained.

2.4. Field-emission scanning electron microscopy

The surface morphologies and microstructure of the composite polymer membranes were examined using field emission scanning electron microscopy field-emission scanning electron microscopy (FESEM) (JEOL JSM-7600F from Japan) after gold coating.

2.5. Fourier-transform infrared spectrophotometry characterization

The Fourier-transform infrared (FTIR) spectra of the samples were measured using Perkin Elmer FTIR spectrometer. The transmittance wavelength for this study was in the

range of 450 to 4,000 cm^{-1} and the scanning was performed at a resolution of 4 cm^{-1} for 32 scans.

2.6. Water uptake

The membranes samples were cut into 2 cm \times 2 cm and soaked in water for 24 h. Then, the membrane was weighed after blotting the excess water on surface. These membranes were weighed again after dried for 24 h. The water uptake was calculated using Eq. (1):

$$\text{Water uptake (\%)} = \left[\frac{W_w - W_d}{W_d} \right] \times 100\% \quad (1)$$

where W_w (g) is the swollen weight of membrane and W_d (g) is the dry weight of the membrane.

2.7. Contact angle measurement

Contact angle measurement were assessed by a Dataphysics OCA 15EC (Germany) equipped with image capturing SCA-20 software. 5 μL of water was dropped on the flat surface of a sample and the value of contact angle was recorded after 10 s. The measurements were repeated 3 times to obtain an average surface contact angle respectively for all the composite membranes. Contact angle study is one of the important parameters to determine the hydrophilicity of composite membranes. The lower the value of water contact angle, the higher the hydrophilicity of the sample.

2.8. Mechanical properties

Mechanical properties which encompasses of tensile strength, Young's modulus and elongation at the break of the composite membranes were identified using the Shimadzu AGS-X series tensile machine (Japan) with a 500 N load cell. Three samples were measured for each sample in accordance with ASTM D882 and the average results were recorded. Meanwhile, the thickness of the

composite membranes was calculated by measuring at three random positions along the sample with a Mitutoyo Digimatic Indicator (Mitutoyo Manufacturing Co. Ltd., Tokyo, Japan).

2.9. Pure water flux

Pure water flux for membranes was determined using a stirred dead-end cell connected with a N₂ gas cylinder. The composite membranes were immersed in water for 24 h before conducting the test. The permeate flux (J) at various operating pressures (1–4 bar) were calculated using Eq. (2):

$$J = \frac{Q}{A \cdot t} \quad (2)$$

where J is the permeate flux (L/h²m²), Q is the amount of permeate (L), t is the time duration and A is the surface area (12.56 cm²).

2.10. Adsorption study of composite membranes

Batch adsorption studies were performed by immersing 20 ± 2 mg of weighed composite membrane in 10 mL of cadmium ions solution with concentration of 10 mg/L and stirred continuously at 200 rpm for 20 h. All the tests were carried out at room temperature and the solutions pH was adjusted at 7.0 using 0.1 M HCl and 0.1 M NaOH solutions [24]. The concentration of heavy metal ions before and after the adsorption is measured using ICP-OES. The rejection efficiency (R) of cadmium ions were determined using following expression:

$$R(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (3)$$

where C_0 and C_e are cadmium ion concentrations (mg/L) before and after adsorption, respectively.

3. Results and discussions

3.1. Surface morphologies

Fig. 2 shows the surface morphologies for different composition of bio-polymer composite membranes. Based on Fig. 2a, neat CS membrane exhibited uniform plain structure, smooth surface and dense polymeric structure with no pores. Meanwhile, the addition of pore forming agent (PEG) successfully induced micropores in the composite membranes where the pore size lies in between the range of microfiltration as shown in Fig. 2b and c. It is notable that the pore size and pore density in CS-P2 membrane are higher than CS-P1 membranes due to higher concentration of PEG added. This is attributed to the poor attractive force between chitosan and PEG eases the PEG to leach out and hence induces the pores [25]. Previous researchers reported similar results for the PEG-blended membrane whereby the higher PEG concentration resulted in bigger pore size in chitosan matrix [26].

On the other hand, Fig. 2d–f show the CS/1.2CH-P2 composite membranes with different magnifications respectively.

Composite membrane with highest concentration of chitin whiskers (1.2%) was chosen for morphology test to determine the smallest pore size that can be obtained and also observed the surface roughness. It is discovered that the composite membrane CS/1.2CH-P2 has higher pore density and their pore sizes are much smaller compared to CS-P2 membrane. Noteworthy, it can be clearly seen that the size of the pores reduces remarkably from micron size to pores less than 100 nm [27]. Interestingly, the reduction in pore size maybe due to the strong interfacial adhesion between the chitosan and chitin whiskers [19]. Since there is no macro voids or large agglomeration observed in CS/1.2CH-P2, it can be concluded that the chitin whiskers dispersed well in chitosan and they are compatible enough.

3.2. FTIR characterization

Fig. 3 represents the FTIR spectra for the composite membranes. FTIR analysis is conducted in this study because it is crucial to identify the presence of PEG after the extraction process in order to generate pores in chitosan membrane [26]. Besides, it also shows the formation of composite membrane with loading of chitin. The peaks of chitosan observed in Fig. 3a has similar spectrum compare to paper reported by [28,29]. The broaden peak at 3,310 cm⁻¹ indicates the O–H and N–H stretching vibrations (3,000–3,600 cm⁻¹). Meanwhile the bands at 2,880 and 2,923 cm⁻¹ are attributed to the symmetric and asymmetric C–H vibrations [30]. The presence of amide I and amide II vibrations are observed at 1,644 and 1,557 cm⁻¹ respectively. Also, the absorption band at 1,026 cm⁻¹ represents the –CO vibration in chitosan.

On the other hand, Fig. 3b shows the absorption peaks in PEG at 1,100 cm⁻¹ that corresponds to C–O band and few other peaks at 1,240 and 1,279 cm⁻¹. Fig. 3c shows the spectra for chitosan membrane after the extraction of PEG. Interestingly, the absence of absorption peaks at 1,100; 1,240 and 1,279 cm⁻¹ simply proves that PEG is extracted effectively during the hot dissolution step. However, previous study stated that minor portion of PEG were not be able to removed due to the existence of strong hydrogen bonding between chitosan and PEG [26]. This statement is in agreement with the water uptake and contact angle results which will be elucidated thereupon. Furthermore, Fig. 3d represents the absorption peaks for chitin whiskers at 3,256; 2,880; 1,552; 1,154; 1,069 and 1,011 cm⁻¹. Meanwhile the chitosan membrane reinforced with 1.2% of chitin whiskers depicted in Fig. 3e has almost the similar spectra as Fig. 3c due to very small amount of chitin whiskers content in chitosan membrane. In fact, the absorption peaks of chitin cannot be observed because of the strong coverage of absorption by chitosan [17].

3.3. Water uptake

Table 2 shows the water uptake for composite membranes with different amounts of PEG and chitin added. Neat CS has the lowest water uptake among others at 103% due to its dense structure. Herein, the hydroxyl and amine groups in CS which have affinity with water molecule are responsible for high water uptake beyond 100% even

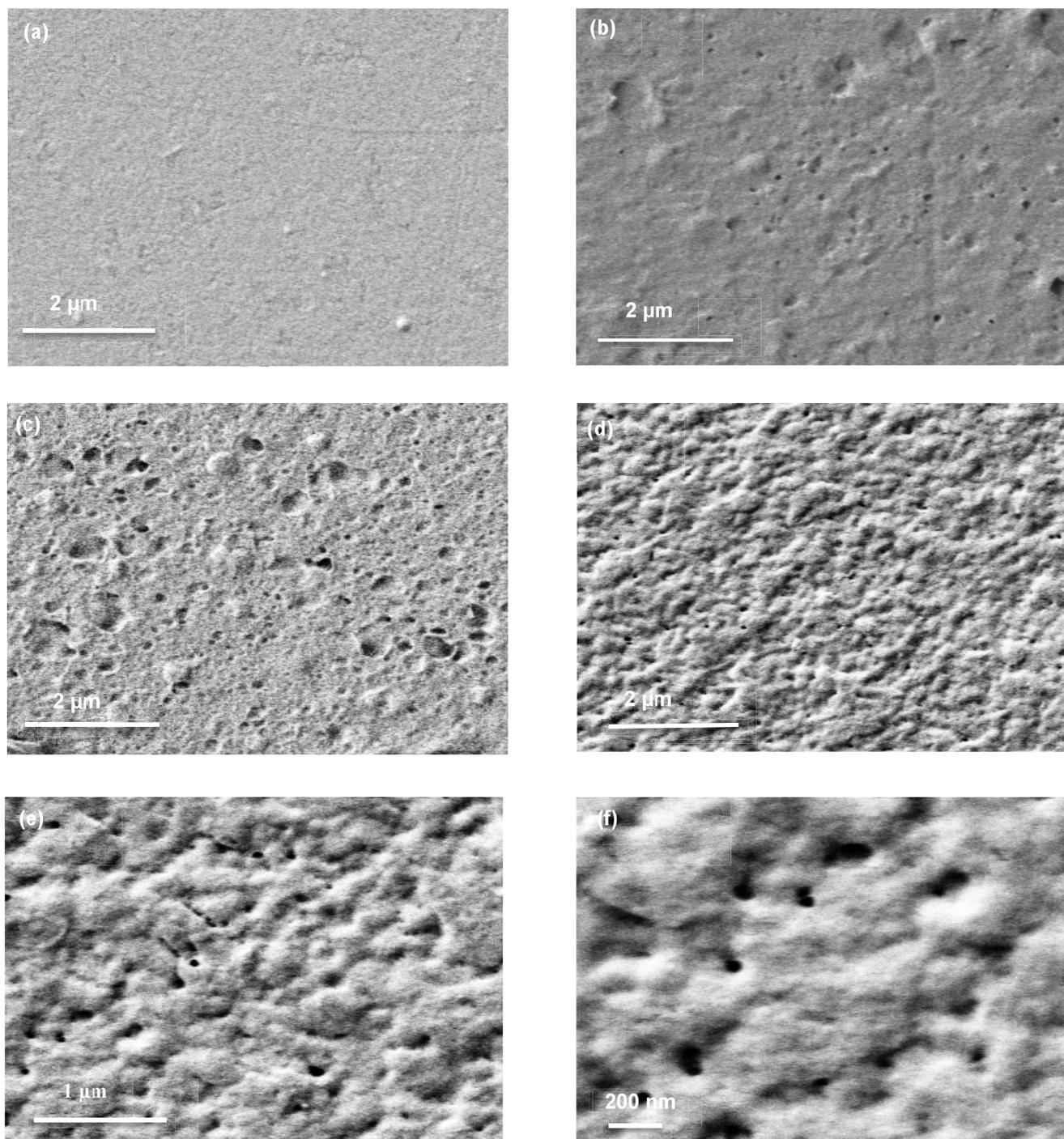


Fig. 2. Surface morphologies of membranes (a) neat CS, (b) CS-P1, (c) CS-P2, (d–f) CS/1.2CH-P2 at different magnifications.

without the addition of pore forming agent. Based on the results, it can be deduced that the water uptake of membranes increases with increasing porogen content, CS-P2 achieved highest water uptake at 215%. The findings are directly in line with previous findings reported by Salehi, Madaeni [25]. This result corresponds to increasing PEG loading that facilitates better interactions between PEG chains and subsequently gave rise to large aggregations that leads to macrovoids formation through extraction of

PEG aggregates from matrix [1,31]. Eventually, the macrovoids which are converted to larger pores are the prime factor for higher water uptake [32]. Moreover, it is notable that there is still a little amount of PEG left in the membranes as mentioned in previous discussion. In this context, PEG which possess ample amount of terminal hydroxyl groups leads to increasing of water affinity that is reflected in the results obtained in this study. This data is in good agreement with paper reported by [31]. Also, enhanced

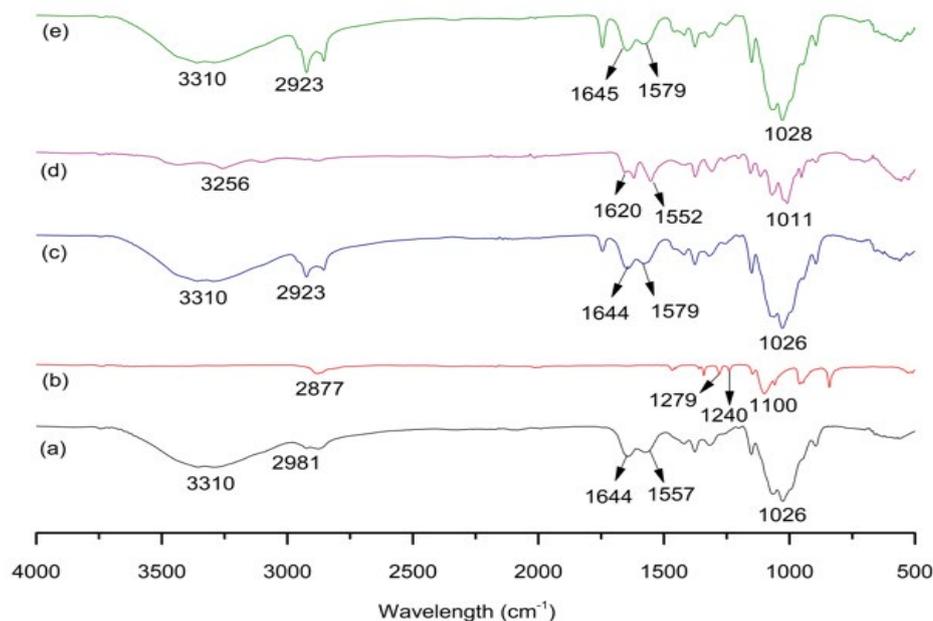


Fig. 3. FTIR spectra of (a) neat CS, (b) PEG, (c) CS-P2, (d) chitin whiskers and (e) CS/1.2CH-P2.

Table 2
Water uptake of membranes

| Sample code | Water uptake (%) |
|-------------|------------------|
| Neat CS | 103 ± 4 |
| CS-P1 | 139 ± 3 |
| CS-P2 | 215 ± 1 |
| CS/0.3CH-P2 | 206 ± 1 |
| CS/0.6CH-P2 | 197 ± 2 |
| CS/0.9CH-P2 | 162 ± 3 |
| CS/1.2CH-P2 | 152 ± 1 |

water uptake may also be attributed due to improved segmental gap between polymer chains [33].

On the other hand, the gradual increase in the amount of chitin whiskers reinforced with chitosan have led to declining trend of water uptake of the composite membranes. This is due to the high crystalline structure of whiskers which inhibits the permeation of water molecules between polymer molecules [28]. Besides, the lower affinity towards water is the effect from the reduction of amino groups available in chitosan matrix due involvement of amino group in electrostatic and hydrogen bonds with chitin whiskers as illustrated in Fig. 4 [17]. However, the water uptake of CS/1.2CH-P2 is still higher compared to neat CS which indicates that more water can permeate through the polymer chain due to the existence of pores.

3.4. Hydrophilicity of composite membranes

Water contact angle (WCA) is the fundamental indicator of surface hydrophilicity of composite membrane as depicted in Fig. 5. Contact angle of water less than 90° is known to be hydrophilic meanwhile greater than 90° is

termed as hydrophobic [34]. This particular characterization is important as it can be correlated with surface morphology and the flux permeability of membranes [35]. The water contact angle obtained for the neat CS is 72.4°, evidencing that it is hydrophilic. This is due to the presence of enormous hydrophilic –OH and –NH₂ groups which has excellent interaction with water molecules [36]. It is revealed that the wettability of CS-P1 and CS-P2 is higher compared to neat CS due to increasing PEG concentration that significantly enhanced the hydrophilicity of the membranes. This is attributed to the accumulation of hydroxyl rich PEG molecules at the membrane surface which forms hydrophilic surface network [1]. Noteworthy, the value of water contact angle reduces upon increasing the PEG concentration for other composite membranes which in accordance with the findings expounded by [37].

On the other hand, the water contact angle obtained for the composite membranes reinforced with 0.3% and 0.6% of chitin is 70° and 84° evidencing that it is hydrophilic. In contrary, composite membranes reinforced with 0.9% and 1.2% of chitin whiskers prevailed to be hydrophobic as the water contact angle observed was 99° and 104° respectively. Hence, it can be deduced that increasing amount of chitin whiskers addition in composite membrane has drastically escalate the values of water contact angle due to reduction of amino groups available to interact with the water molecules. Similar trend of water contact angle were reported for addition of alginate to chitosan membrane [38]. In addition, the enhancement of water contact angle after reinforcement of chitin can be due to increase in surface tension caused by the excellent interfacial adhesion between the functional groups in chitosan and chitin whiskers. The exceptional compatibility between chitin and chitosan was also proved through FESEM and water uptake results previously.

Moreover, surface roughness also is an essential factor that influenced the water contact angle. Incorporation of

PEG proves to induce smoothing effect and thus reduces water contact angle. Meanwhile, the incorporation of chitin imposed a rougher surface noticeably in the case of CS/1.2CH-P2 which can be observed through FESEM. This proves that surface which is rougher will reduce the hydrophilicity which lowers the flux permeability, coincides with finding of [1,39].

3.5. Mechanical properties

The ultimate success of this study is the enhancement of mechanical properties of composite membranes as shown in Fig. 6. It is crucial to note that all these tests were conducted in wet condition (swollen state) to ensure the membrane has adequate strength to work under high pressure.

The tensile strength and Young’s modulus obtained for neat CS (control) is 2.9 and 10.1 MPa respectively as shown in Fig. 6a and b. The value of tensile is slighter higher than the reported value at 1.0 MPa for neat CS (swollen state) probably due to factors such as different CS concentration, membrane preparation method, thickness of membrane and etc. [40]. An inconsiderable reduction in both tensile and Young’s modulus can be observed in CS-P1 and CS-P2 due to the fact that the presence of porous structure and cavities in membrane that subsequently lessens the strength and stiffness of membrane [1,41,37]. Nevertheless, these values are sufficient to be used as microfiltration membrane [42].

On the other hand, increasing of chitin whiskers content drastically enhanced the tensile strength along with Young’s modulus until the threshold. In particular, both the maximum tensile and Young’s modulus are achieved at chitin whiskers loading of 0.9%, the increment of tensile is by 58.2% at 4.3 MPa whereas the enhancement of modulus is by 89.4% at 16.4 Mpa respectively compared to chitin loading at 0%. These results can be attributed due to factors such as; (1) both chitosan and chitin whiskers possess excellent electrostatic attractions and

hydrogen bonds between them as aforementioned, (2) the high crystalline structure of chitin whiskers fosters to escalate the strength of the composite membranes. Nonetheless, declining trend is depicted in the tensile graph when the addition of chitin whiskers are beyond the optimum percentage which is 0.9%, the prime reason may be due to the aggregation of the chitin structure [17,19].

Furthermore, the elongation at break has improved for CS-P2 as shown in Fig. 6c. This can be probably due to the strong hydrogen between CS and PEG which eventually enhanced the ductility of membrane. However, the elongation values reduced gradually upon the increment of chitin whiskers addition. Similar trend were found in paper published by [28]. It is deduced that high crystalline structure of chitin whiskers which substantially causes the membrane to be rigid has contributed to the reduction of elongation at break. In this case, the mechanical properties of

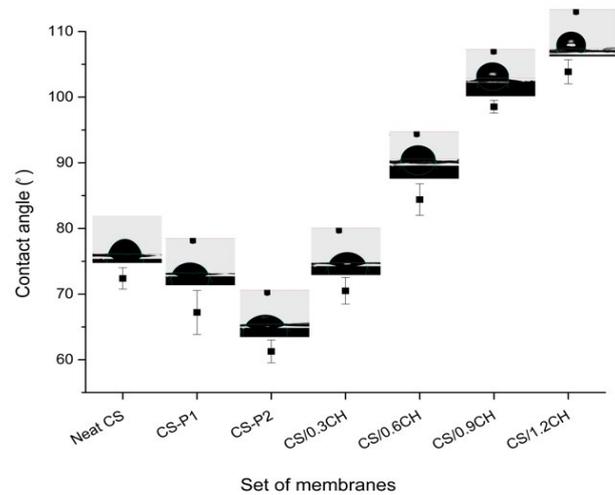


Fig. 5. Wettability of the all samples sets.

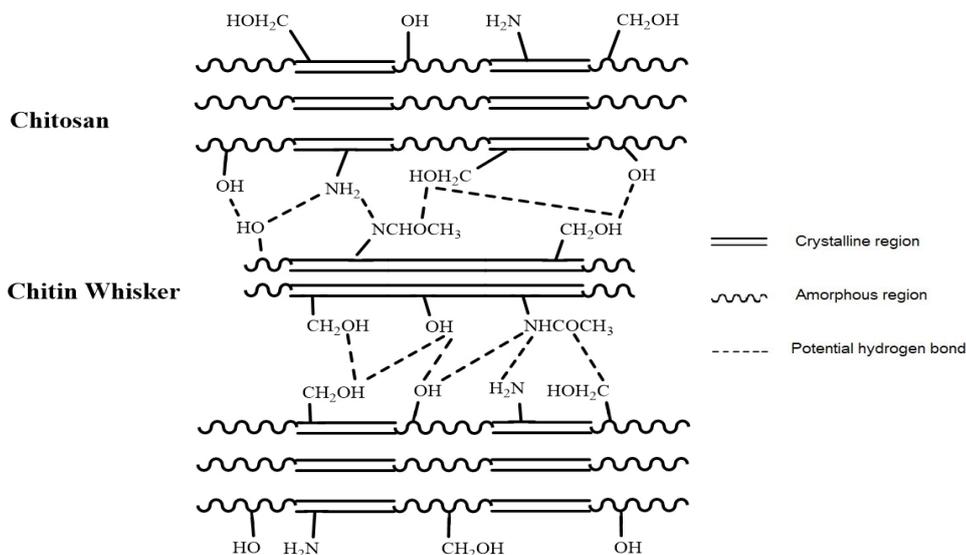


Fig. 4. Potential electrostatic and hydrogen bonds between both of the polymers.

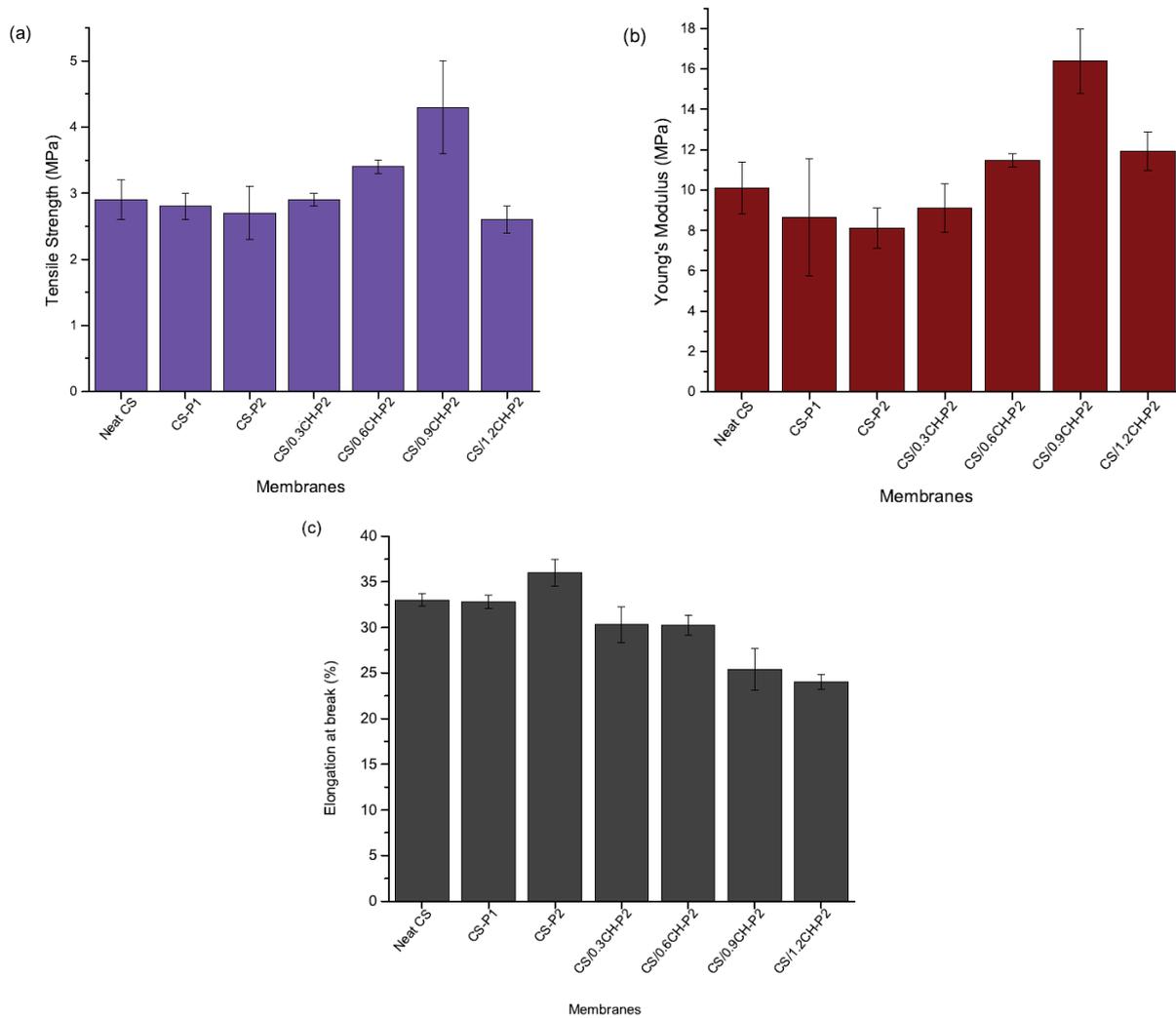


Fig. 6. Mechanical properties of composite membranes (a) tensile strength, (b) Young's modulus and (c) elongation at break.

composite membrane with optimum addition of chitin whiskers are adaptable to be used as ultrafiltration membrane.

3.6. Pure water flux

Based on the characterization studies performed, membranes with optimum PEG concentration (CS-P2) and chitin reinforced chitosan membranes were selected for further analysis. Fig. 6 shows the pure water flux obtained for the membranes at various operating pressure. It is found that neat CS has extremely low water flux which is below than $0.5 \text{ L/m}^2 \text{ h}$ at 4 bar from preliminary studies (not shown in Fig. 7). On the other hand, CS-P2 depicted higher water flux at $25.1 \text{ L/m}^2 \text{ h}$ when the pressure was set to 4 bar. This indicates the addition of pore forming agent helps to enhance the water permeation through the membrane by inducing larger pore structure in the matrix.

However, the water flux decreases gradually with the increase of chitin whiskers content. This can be due to hydrophobic properties exhibited by the chitin reinforced membranes as observed in water uptake and contact angle results.

Furthermore, the improved biocompatibility between the chitosan and chitin causes the interfacial adhesion between them becomes stronger. As a result, the pore size reduces and the compactness of the membrane increases which leads to low water flux [43]. However, it can be deduced that the interconnected porous channels in the matrix able to provide supplementary passage for the water flow for membranes reinforced with 0.3%, 0.6% and 0.9% chitin content. The minimum water flux obtained for 1.2% chitin reinforced chitosan membrane can be correspond to pore blockage and high surface roughness [44].

3.7. Performance evaluation of membranes

The removal efficiency of cadmium for membrane with 0.3% chitin whiskers increases as portrayed in Fig. 8 due to the introduction of amide and hydroxyl functional group which bind with cadmium ions. Nevertheless, decreasing trend can be observed with further increasing of chitin content beyond 0.3%. This is may be attributed to the strong bond formation between chitosan and chitin whiskers which

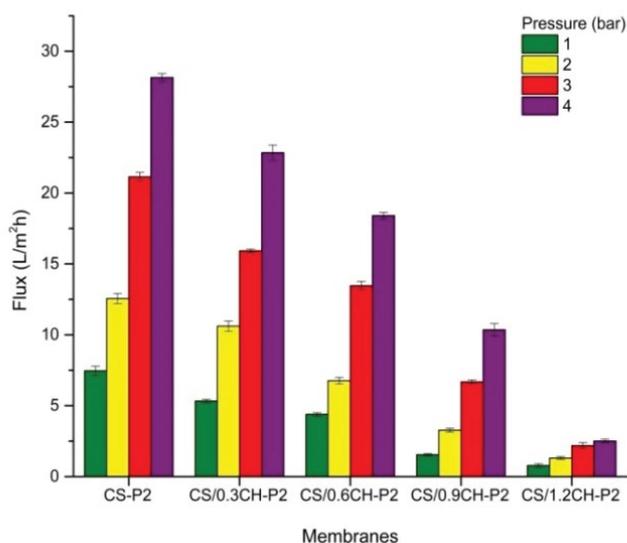


Fig. 7. Pure water flux for composite membranes at various operating pressure.

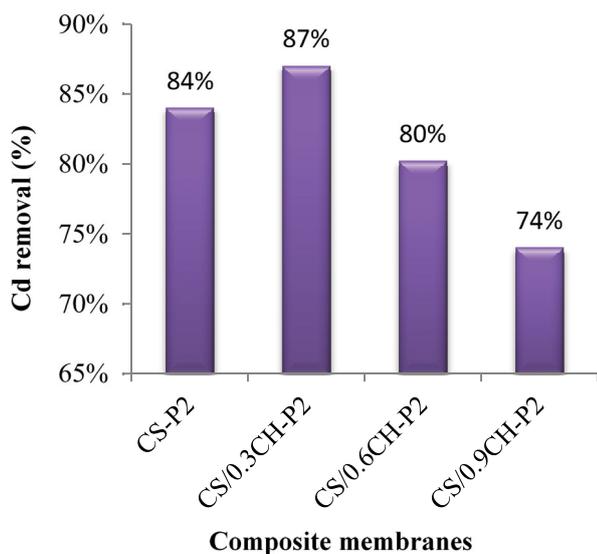


Fig. 8. Cd²⁺ removal efficiency for composite membranes.

lessens the affinity towards cadmium ions. This result is in good agreement with water uptake findings. In fact, reduction of chitosan mass ratio may also be one of the factors that decrease the adsorption capacity. In this context, the lower availability of functional groups (amino and hydroxyl) in chitosan has lesser tendency to capture the divalent cations via complexation [45]. Similar findings were reported by Rahmi et al. [45] where the addition of cellulose in chitosan reduces the adsorption capacity of Cd²⁺ ions.

4. Conclusion

A promising bio-composite membrane with porous structure through the extraction of PEG is considered as

ultimate success of this study as it is an efficient way to produce composite membrane with tailored permeability properties. Despite of obtaining satisfactorily low water flux, these membranes are still sufficient to be utilized as membrane adsorbent and this is attributed to; (1) chitosan is rich with functional groups (amine and hydrogen), the target pollutants can be eliminated using these composite membranes, (2) reinforcement of chitin whiskers which enhanced the mechanical stability of chitosan membrane and adequate to be used for membrane application (3) chitosan and chitin whiskers are proven to be biocompatible and does not cause agglomeration or large aggregation. In future, evaluation on reinforcement of natural based nanofiller in these composite membranes can be performed to improve the hydrophilicity and water permeability of membranes. To summarize, porogen (PEG) and chitin whiskers utilization in chitosan matrix turns out to form a new family of composite membranes with unique properties. These membranes have great potential to extensively exploit in wastewater treatment field as membrane adsorbent. Thus, finding the optimum concentration of PEG and chitin is crucial to obtain benefits in terms of both physicochemical and mechanical properties

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