

Effect of *Chitosan* concentration on antifouling performance of thin film composite

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Abstract

Wastewater treatment is an approach to make sure the water supply is clean and free from unwanted particles. Membrane technology is one of the methods applied to the treatment process. This study describes the production of thin film composite (TFC) membrane, which was formulated from polysulfone as a porous support membrane, and hybrid membrane as a barrier layer. The hybrid membrane was formulated from a blend of chitosan, polyethylene glycol (PEG) and tetraethylorthosilicate (TEOS). The objective of this study is to investigate the effects of varying chitosan concentrations (1, 2 and 3 wt.%) on the properties of the thin-film composite membrane in terms of thermal, pure water flux and antifouling properties. It was found that the membrane with 2 wt.% chitosan yields the highest water flux and good antifouling property. The findings of this study are very significant as it provides a wide knowledge of separation performance of thin film composite (TFC) membrane.

Article Info

Article history:

Received date: 24 March 2019

Accepted date: 26 April 2019

Keywords:

Antifouling
Chitosan
Water flux
Thin film composite
Hybrid membrane

1.0 Introduction

Nowadays, water supply is highly dependent on the nature sources such as rainwater and seawater. Therefore, the wastewater treatment is very crucial to ensure a continuous water sustainability (Zheng et al., 2015). The world population growth increases at the same rate with the requirement for the water supply. Estimation of freshwater resources in the world indicates that 50 percent of the population will live near water area in 2025, thus action must be taken in water management and treatment processes for the next generation (Palma et al., 2016).

In treating wastewater, membrane technologies play an important part in water sources and energy sustainability (Le et al., 2016). This technology had been used widely in industrial application especially in water filtration. Benefits of this technologies include high selectivity, compact modular equipment, low energy cost and reduced chemical use (Ghiggi et al., 2017). In the water filtration process using membranes, common types of membrane processing used are reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) (Kajekar, 2015).

However, membrane fouling is a common challenge faced in the membrane processes technology. Membrane fouling is a serious problem that has negative impact to the membrane technology application. The reduction in the membrane fouling can increase water productivity,

reduce requirement of maintenance in cleaning process, lengthen membrane life and increase cost saving in term of the operational costs (Le et al., 2016).

Common types of membrane materials used in the preparation of membrane are organic polymer and inorganic materials (Shao & Huang, 2007). The combination of these two materials produces a hybrid membrane, which is a new material with multifunctional chemical or physical properties.

In this research, a thin-film composite (TFC) membrane consists of polysulfone as a porous support membrane, and hybrid membrane as a barrier layer was fabricated. The hybrid membrane was formulated from a blend of polyethylene glycol (PEG) with chitosan (Cs). The PEG/Cs blend interactions are a combination of intramolecular hydrogen bonds and intermolecular hydrogen bonds that make the polymer blend compatible. Chitosan is N-deacetylated derivative of chitin is a hydrophilic material with film-forming properties and biodegradable.

2.0 Methodology

2.1 Material

In the preparation of thin film composite membrane, polysulfone 99.5% (PSf) beads (MW~22000), 1-methyl-2-pyrrolidone 99.5% (NMP), chitosan (Cs) powder (MW 1000~3000), polyethylene glycol (PEG) flakes (MW 1500), acetic acid 100%, tetraethylorthosilicate

98% (TEOS), and hydrochloric acid 37% (HCl) were purchased from Merck, Malaysia.

2.2 Methods

2.2.1 Preparation of porous support membrane

An amount of 13 wt.% PSf dope solution was prepared by dissolving 13 g of PSf into the solvent 1-methyl-2-pyrrolidone. The solution was stirred continuously at 300 rpm for approximately 4 to 6 hours at 60 °C until PSf beads were completely dissolved and formed a homogenous mixture (Zhang et al., 2011). The dope solution was then left at room temperature for 12 hours to remove air bubbles. Porous support membrane was fabricated by using phase inversion method. The thickness of a casting blade was adjusted to 90 µm and PSf solution was casted onto a glass plate by using the casting blade. The membrane was then immersed in a water bath at room temperature for 24 hours to remove any excess residual solvent.

2.2.2 Preparation of thin film composite

The membrane was prepared by coating PSf support membrane with the hybrid membrane solution and uniformly spreading by using a glass rod. The thin film composite membrane was left for 24 hours at room temperature and subsequently cured in an oven for 1 hour at 45 °C (Shaari et al., 2017). Table 1 shows the formulation of hybrid membranes prepared in this study.

Table 1: The formulation of hybrid membranes

Membrane code	PEG (wt%)	Cs (wt.%)	TEOS (wt.%)	HCL (mL)
M1	1.5	1	3	1
M2	1.5	2	3	1
M3	1.5	3	3	1

2.2.3 Membrane characterisation

The IR spectra were recorded on a Perkin Elmer Fourier transform infrared (FTIR) Spectrum One spectrometer with a wavelength range from 400–4000 cm⁻¹ (Ghiggi et al., 2017). Thermal analysis was performed on a Mettler Toledo thermogravimetric analyser (TGA). The 10 mg hybrid membrane sample was heated from 30 to 1000 °C at a rate of 10 °C/min under nitrogen gas (Samiey et al., 2014).

2.2.4 Performance testing

Pure water permeation (PWP) test was carried out by using dead-end filtration mode. Deionised water was used as the feed solution (Hamzah et al., 2014). The thin film composite membrane was cut into a piece with an

area of 19.63 cm² and was placed inside the membrane holder. The pressure of nitrogen gas was set at 4 bar. Flux measurement was done at 15 min intervals for 1 hour. The permeated sample was collected and pure water flux (PWF) was calculated using Eq. (1) (Arthanareeswaran et al., 2010). The procedure was repeated for another two pieces of membrane, and the average value was recorded.

$$I_w = \frac{V}{\Delta t \times A} \quad (1)$$

where,

I_w = pure water flux (L/m²·h)

V = volume of permeates collected (L)

t = sampling time (h)

A = membrane area (m²)

Antifouling performance test was carried out by using the humic acid (HA) solution as a foulant model. HA solution was prepared by dissolving 10 g of HA powder in 500 ppm NaOH solution in a 1 L volumetric flask and was stirred for 24 hours as a stock solution. The stock solution was stored away from the sunlight (Zhu et al., 2013).

Pure water flux was recorded for 30 minutes. The stabilised flux was denoted as J_o . HA solution was then filtered through the membrane for 2 hours. The stabilised flux was denoted as J_p . The membrane was immersed in 50 mL deionised water and was stirred in a shaker at 200 rpm for 30 minutes. Pure water flux was recorded again for 30 minutes and this flux was denoted as J_1 . The permeate flux change was recorded versus filtration time for a total of 3 hours. The relative flux decay (RFD) and relative flux recovery (RFR) for each membrane were calculated by using Eq. (2) and Eq. (3), respectively (Zhu et al., 2013).

$$RFD = \frac{J_o - J_p}{J_o} \times 100 \quad (2)$$

$$RFR = \frac{J_1}{J_o} \times 100 \quad (3)$$

3.0 Results and Discussion

3.1 FTIR Analysis

FTIR spectra of PEG, Cs powder, Cs/PEG blend and Cs/PEG/TEOS hybrid membrane are shown in Fig. 1. A broad peak at 3286.42 cm⁻¹ can be either O–H or N–H (primary amine) bonds or both while a peak at 2876.53 cm⁻¹ indicates an alkyl group (2990–2855 cm⁻¹) stretching vibration for chitosan powder. The peak at

1148.41 cm^{-1} is attributed to the symmetrical stretching C–O–C bond, meanwhile the peak at 1030.94 cm^{-1} is due to C–O stretching vibration and commonly referred to as the fingerprint peak for chitosan structure. FTIR spectrum of PEG exhibits the characteristic of C–O stretch at 1058.93 cm^{-1} . A broad peak at 3341.28 cm^{-1} corresponds to the hydroxyl group. FTIR spectrum of Chitosan/PEG/TEOS shows the broad band gradually shifts to the left at 3413.70 cm^{-1} and the intensity increases because an addition of the O–H bond from the PEG and TEOS. The peak in the range of 1000–1100 cm^{-1} is assigned to Si–O–C stretch as a result of cross-linking reaction between polymer blend PEG/Cs with TEOS (Shao & Huang, 2007).

Fig. 2 shows the FTIR spectra for hybrid membranes with different Cs concentration. The O–H stretching vibration is in the range of 3540–3200 cm^{-1} and N–H deformation (primary amine) in the range of 1650–1590 cm^{-1} increases with the increase in chitosan concentration. The intensity of peak in the range of 1030–1085 cm^{-1} , which corresponds to C–O–C or Si–O–C stretching vibration also increases with the concentration of chitosan. This phenomenon represents the rapid cross-linking reaction during hybrid formulation.

3.2 Thermal Analysis

The thermal stability of the hybrid membranes is presented in Fig. 3. The decomposition process occurs in a few stages, around 15% weight loss is accounted on the

first stage of decomposition process where it occurs at ambient and up to 140 °C. This is due to the dehydration or evaporation of the residual water present in the polymer sample. For the second stage, decomposition starts at 150 °C to 310 °C, where about 17% of weight loss is due to the decomposition of polymeric network. For the third stage, the thermograms for hybrid membrane M1 and M2 show weight losses around 340 °C to 630°C, meanwhile for M3 was around 330°C to 570°C. As the amount of chitosan concentration increases, the intramolecular interactions between the terminal hydroxyl groups (–OH) of chitosan dominate, the polymer blend becomes compatible that leads to the increase in the thermal stability of the hybrid membrane M3 as compared to the hybrid membranes M2 and M1. The weight loss observed at 375 °C is attributed to the degradation of the alkyl chain with production of volatiles and eventually having a thermally stable Si–O–Si bond residue at 700 °C (Sánchez-fernández et al., 2016).

3.3 Pure Water Permeation (PWP) Test

The graph of flux decline versus operating time intervals is shown in Fig. 4. It can be observed that all the thin-film composite membranes show a decreasing trend for a period of 1 hour.

This flux reduction was due to some factors such as membrane fouling, concentration polarisation and changes in the properties of the feed solution. Concentration polarisation and membrane fouling are the most general and major problem corresponds to the flux declining phenomenon during membrane filtration process (Arthanareeswaran et al., 2010).

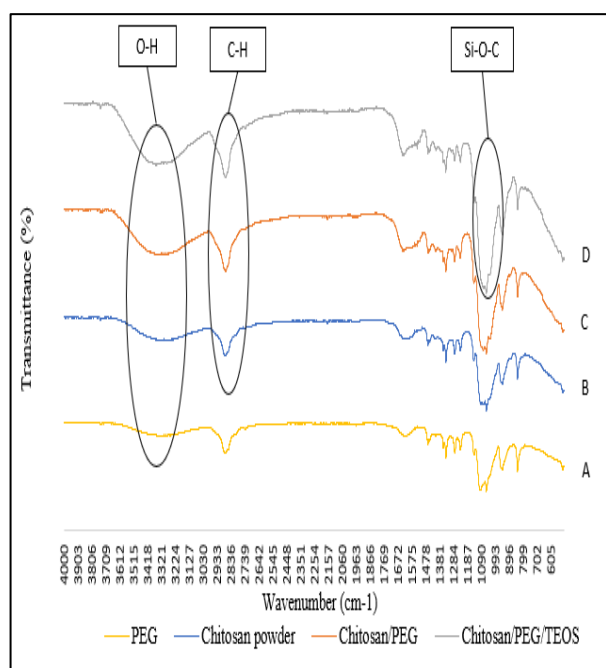


Fig. 1: The FTIR spectra of PEG (A), Chitosan powder (B), Chitosan/PEG (C) and Chitosan/PEG/TEOS (D).

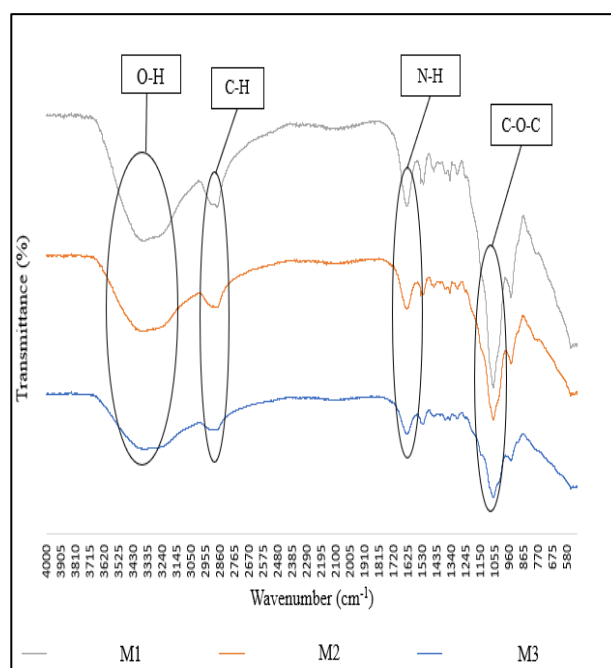


Fig. 2: The FTIR spectra of hybrid membranes

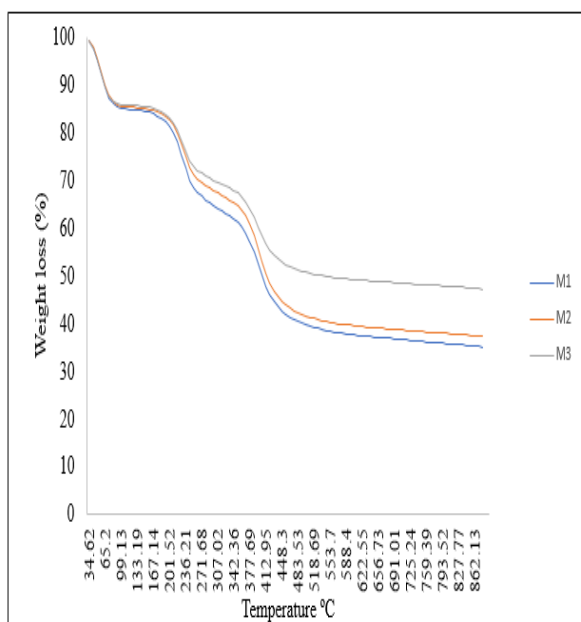


Fig. 3: TGA thermograms of hybrid membranes: M1, M2, M3.

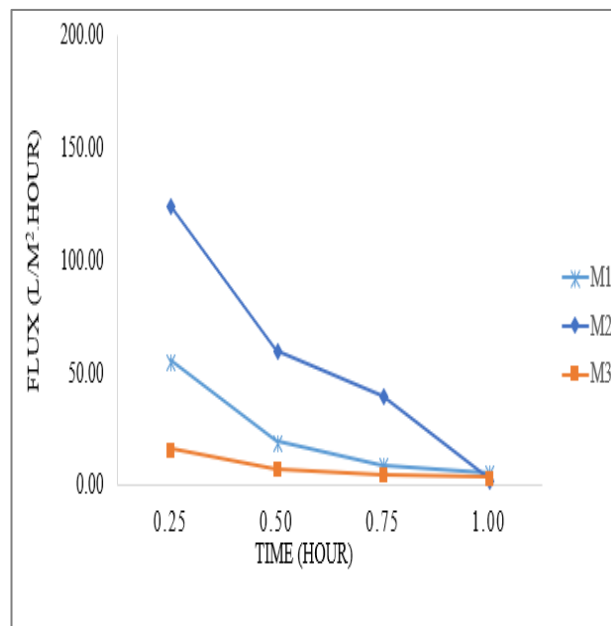


Fig.4: Graph of pure water flux of thin film composite membranes: M1, M2 and M3.

Concentration polarisation is able to decrease the driving force of water flux through the membrane. It is the point at which incipient gel precipitation can occur if the concentration of the solute at the membrane surface increases. This could lead to a formation of a polarisation layer on top of the membrane surface which contributes to the serious resistance to flow.

The thickness of this polarisation layer increases until the pressure-activated convective transport of solute with solvent towards the membrane surface equals to the concentration gradient-activated diffusive transport away from the surface (Hamzah et al., 2014).

By comparing water flux between these three thin-film composite membranes, the best performance is exhibited by thin film composite membrane with M2 as a barrier layer. This result is consistent with Fig. 2, where M2 shows a moderate cross-linking degree with sufficient amount of hydroxyl group. Furthermore, M2 formulation has the optimum amount of blend ratio between PEG and chitosan

3.4 Antifouling Performance Test

The antifouling performances of the thin film composite (TFC) membranes were evaluated through the filtration of HA solution as a foulant model. As shown in Table 2, all membranes portray high relative flux decay (RFD). However, based on the table, a comparable flux declining rates for filtration of HA solution for all membranes was observed and it could be seen that the flux declining rate for M1 during filtration of pure water is the highest as compared to M2 and M3.

Table 2: Relative flux decay (RFD) and relative flux recovery (RFR) of the membranes

Membrane	J_0 (L/m ² ·h)	J_p (L/m ² ·h)	J_1 (L/m ² ·h)	RFD (%)	RFR (%)
M1	40.34	4.52	20.75	88.78	51.43
M2	27.66	5.36	21.32	80.62	77.08
M3	25.36	3.40	12.56	86.59	49.54

This observation is also in agreement with lower relative flux recovery (RFR) of M2 as shown in Table 2. After backwashing process for 30 minutes, the pure water flux for TFC with barrier layer from M2 recovers to 77.08% of its original water flux, which is the highest as compared to M1 and M2. Higher RFR of M2 would justify that the concentration polarisation occurs in this membrane is low because of the enhancement in hydrophilicity of the membrane’s surface (Shaari et al., 2017).

TFC with M2 as the barrier layer shows the best performance in effectiveness of the membrane to resist organic fouling caused by natural organic matter (NOM) which is humic acid (HA) and 2 wt.% chitosan used has contributed in enhancing the hydrophilicity. The antifouling test would reflect the reversible fouling which can be removed by backwashing to recover water permeance and cross-flushing known as hydraulic cleaning (Shahkaramipour et al., 2017).

4.0 Conclusion

Hybrid membrane M3 as a barrier layer has a higher thermal stability compared to M1 and M2 but it suffers from low water flux and relative flux recovery. M2 on

the other hand, has the highest water flux and has the ability to resist organic fouling caused by NOM. Therefore, thin film composite with M2 has the potential to be used in the treatment of wastewater containing organic matters.

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Acknowledgement

The authors would like to thank Universiti Teknologi MARA (UiTM) for sponsoring the research through grant Bestari Perdana with file number 600-IRMI/DANA 5/3/BESTARI (P) (009/2018).