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Characterization and Performance Evaluation of Ultrafiltration Membrane for Humic Acid Removal

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Abstract

Background/Objectives: Humic Acid (HA) appears in conventional water treatment processes will compose to carcinogenic disinfection by-products. This has sparked this study to examine the effectiveness of polymeric membranes in HA removal. **Methods/Statistical Analysis**: Different types of membranes with a wide range of Molecular Weight Cut-Off (MWCO) were used in this study and their separation performances were evaluated by varying the Transmembrane Pressure (TMP) and HA concentrations. The permeates and feeds were analyzed by measuring the UV absorbance at wavelength of 254 nm. **Findings:** Among four membrane modules that used in this study, it was found that membrane Modules 1, 2 and 3 demonstrated similar performances in HA removal with a separation rate of at least 50%. Excellent HA separation (>90%) was reported with the use of membrane Module 4. Increasing of HA concentration from 0.1 to 0.2 mg/L did not expressively reduce membrane efficiency. These membranes however having severe fouling which contributed to a low permeate flow rates after a few runs. The permeate flux was initially high but reduced over the operation time. Simple cleaning could be conducted to recover the permeate flux but not 100% recovery as compared to the original fresh membranes. **Application/ Improvements:** Based on the experiments, it can be established that the hollow fiber UF membrane is suitable for HA removal.

Keywords: Humic Acid, Membrane Filtration, Ultrafiltration, Water Treatment

1. Introduction

With the rapid population and improper industrialization practices over the last two decades, it leads to unfavorable water pollution. Nowadays, the severity of water pollution problem has attracted great attention in the public. Many efforts have been made to minimize the water pollution problem such as developing advanced technology for water treatment to increase both drinking water quantity and quality strictly implementing the environmental legislation.

Humic Acid (HA) is a major contaminant that presents in water supplies in water industry. The presence of HA in water source raises a problem for conventional water treatment process for human consumption. The presence of widely-used oxidants, such as chlorine, ozone, chlorine dioxide and chloramines in conventional water treatments are reacting with HA to produce several Disinfection By-Products (DBPs), such as Haloacetic Acids (HAAs), Trihalomethanes (THMs) and other halogenated organics[1].

These DBPs are carcinogens in which direct contact of DBPs with human brings can lead to miscarriages, nervous system sickness and cancers. According to World Health Organization (WHO), the concentration of HA in potable water should be limited to less than 100 ppm[2]. Attribute to this, research study for the development of advance water treatment technologies is highly demanded for the production of clean and reliable drinking water from various industrial and natural source[3].

Membrane filtration is one of the techniques that can be applied to filter HA particles from the water source[4,5]. During membrane filtration process, water is permeate through the membrane with the application of pressure as driving force. HA particles with larger particle size than the membrane pores will prohibit from entering the

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membrane. As the water molecules are relatively smaller than membrane pore size, it causes all the solutes to permeate easily through membrane, resulting in purified water, which is free of contaminants.

Pressure-driven membranes such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) can be employed depending on the molecular weight of solute to be separated, a particular membrane type (with different pore size) can be selected to achieve desirable degree of separation. Superior water quality, smaller footprint and easy maintenance have possibly led membrane technology to replace conventional HA treatment process, such as coagulation, ozonation, precipitation, chlorination, flocculation and gravel filtration[6]. The main objectives of this study are: (1) To investigate the efficiency of polymeric membranes with different structural properties on HA removal and (2) To evaluate the separation performance of membrane by varying the operating pressure and concentration of HA.

2. Materials and Methods

2.1 Materials and Membranes

The HA used in this work for model solution was purchased from ALDRICH Chemistry, Malaysia. Different concentration of HA solutions (0.10 g/L, 0.15 g/L and 0.20 g/L) were prepared by dissolving HA powder into deionized water (MiliQ). The quantity of HA required was measured using Perkin Elmer digital weighing machine.

Four different types of membranes were kindly provided by Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, Skudai. The properties of these membranes are shown in Table 1.

Table 1. Properties of hollow fibre membrane

Module	Composition (wt%)	Air Gap (cm)	Bore Fluid Composition
1	[a]PES/NMP/PEG 400/H_2O (16/38.5/38.5/7)	0	H_2O
2	PES/NMP/PEG 400/H_2O (16/38.5/38.5/7)	0	H_2O/NMP (70/30)
3	PES/NMP/PEG 400/H_2O (16/38.5/38.5/7)	10	H_2O/NMP (70/30)
4	[b]PES/NMP/PVP K15 (20/70/10)	10	H_2O

[a]PES: Polyethersulfone, NMP: N-methyl-2-pyrrolidone, PEG 400:Polyethylene glycol 400, H_2O: Water
[b]PVP K15: Polyvinylpyrrolidone K15

All the membranes were fabricated using hollow fibre spinning technique with the inner and outer diameter of 300 and 600 μm respectively.

2.2 Membrane Morphology Analysis

Field Emission Scan Electron Microscope (FESEM) was used to observe the membrane surface and cross-section morphology.

The water-wetted membrane samples were dehydrated by storing the samples in an oven overnight at temperature around 60 °C. Sputter coater was used to coat the outer surface of the sample with platinum prior to analysis. For cross-section analysis, the dry hollow fibre membrane samples were frozen and then cryogenically fractured after immersing in liquid nitrogen in order to reduce damage on morphology. After acquisition, images were treated by the public domain images processing and analysis program.

2.3 Membrane Performance Evaluation

2.3.1 Membrane Permeation System

MiliQ water is initially used as the background solution. Each membrane module was tested with MiliQ water to investigate the Pure Water Flux (PWF) at various applied Pressure (P). RO booster pump, purchased from Kemflo, Malaysia was used in this work to generate the desired pressure.

Figure 1 shows the lab-scale permeation unit which was used to evaluate the performance of membrane throughout the study. The feed was kept in a storage tank (4-5 liter) and then delivered to the membrane housing by controlling the booster pump. Pressure gauge was used to indicate the applied pressure in the membrane housing.

Figure 1. Experimental set-up of membrane permeate unit.

The maximum operating pressure was set to 50 psig (~3.4 bar). The filtrate (permeate) was then collected using cylinder measurement as shown in Figure 2.

2.3.2 Membrane Water Flux

The lab-scale modules were prepared with length and number of membrane tubes. The fiber in the module was shorter than the length of the membrane tubes due to the coated surface area at the two end of the membrane module.

There are four test modules used to measure PWF. Mili-Q ultrapure water was circulated through the shell side of the membrane modules under various Transmembrane Pressure (TMP) through the fouling layer and the membrane to get the PWF. The rejection of HA feed solution by UF membranes is attributed by the sieving mechanism and Donnan exclusion effective in the filtration process. The PWF of each membrane module can be described by Darcy's law:

$$J_{WF} = \frac{1}{A}\frac{dV}{dt} = \frac{\Delta P}{\eta(R_m + R_C)} \tag{1}$$

Where J is the specific hollow fiber membrane water flux (L/ m^2 h), A is the membrane effective area (m^2), V is the volume of permeating water (L), t is the filtration time required to collect V (h), ΔP represents the TMP, η is the dynamic viscosity of the water, R_m is the membrane resistance to the PWF and R_c stands for the deposit resistance.

2.3.3 Humic Acid Rejection

The effectiveness of a membrane on HA removal was determined under 30 psig using HA aqueous solution at the concentration of 0.1 to 0.2 mg/L. The efficiency of HA removal is calculated using the equation as follows:

$$R(\%) = \left(1 - \frac{Abs_p}{Abs_f}\right) \times 100\% \tag{2}$$

Where and are the absorbance of permeate and feed solution, respectively.

The absorbance of the solutions was measured using UV/visible spectrophotometer (CARY 100 Conc). In UV absorption spectroscopy analysis, the sample solutions were placed in a 4 mL quartz cuvette and UV absorbance values of the sample solutions were measured at a wavelength of 254 nm. The analyzer was required to be calibrated prior to sample analysis. The standard calibration curve of UV254 absorbance was produced by varying the concentration of HA.

Figure 2. Permeate solution collected in cylinder measurement.

3. Results and Discussion

3.1 Pure Water Flux of Membranes

In this study, PWF of membranes with different morphologies was first measured and calculated by using Equation (1). The experiments were conducted using MiliQ water as solution and operated at room temperature (~25°C). Since the flow rate of this filtration process is varied depending on the pressure applied, controlling the parameter thus was not considered in this study. It is generally known that the water flux of membrane is independent of the flow rate if a low pressure booster pump is used. This low booster pump used is only able to generate maximum flow rate less than 1 Litre per Minute (LPM), thus insignificant on membrane water permeation.

Equation (1) expresses that water molecules permeate faster through membrane by applying higher operating pressure from feed side, leading to greater water flux. This indicates membrane is a pressure-driven filtration process7. It was thus experienced an increase of membrane permeate flux with increasing of operating pressure for all types of modules. Figure 3 shows the variation of membrane water fluxes as a function of operating pressure for four different membrane modules. These figures established based on the data collected experimentally. Comparing between these figures, it is found that Module 3 exhibited the highest value of PWF, while Module 4 was the lowest one. Slight deviation from linearity at higher feed pressures could be due to compaction of the membranes.

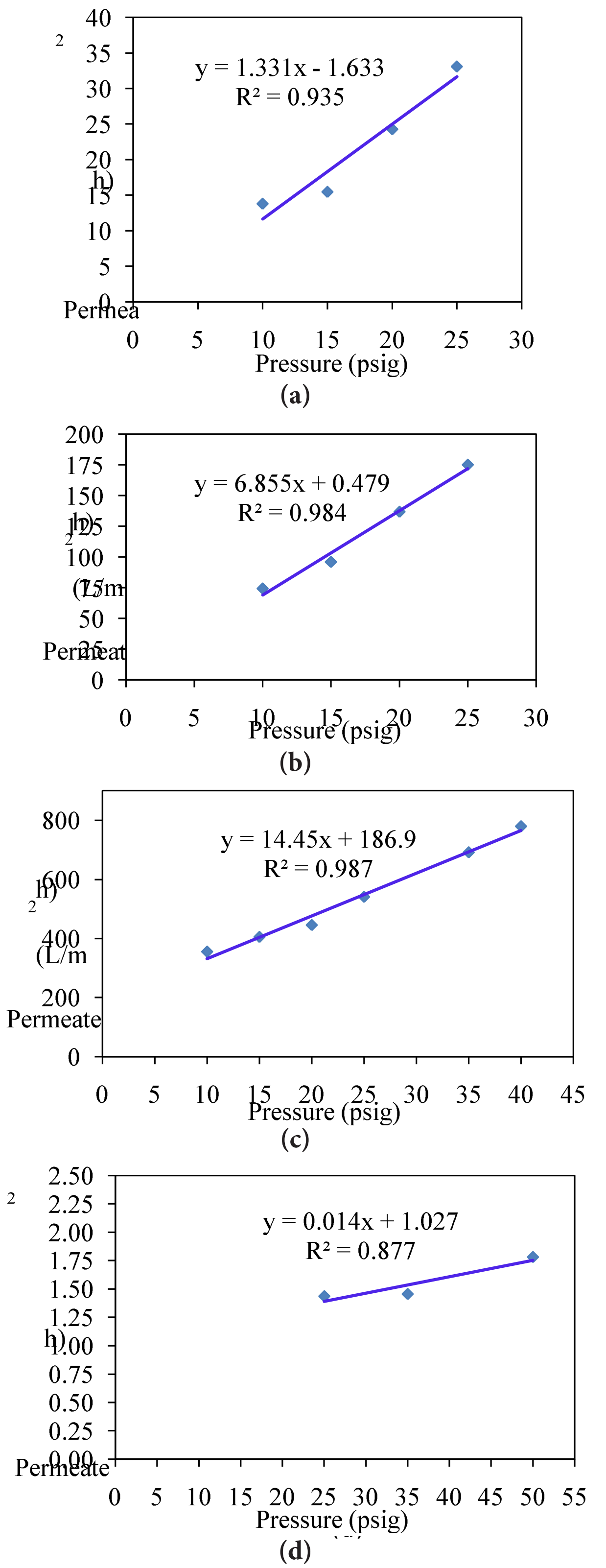

Figure 3. Permeate water flux of membranes with different applied pressure **(a)** Module 1, **(b)** Module 2, **(c)** Module 3, **(d)** Module 4.

Furthermore, Equation (1) also shows that PWF is inversely proportional to membrane resistance, R_m. As shown in Table 2, highest the PWF of membrane, lowest the membrane resistance or vice-versa. With the increasing of membrane resistance, most of the water molecules will be retained at the feed side of the membrane, causing lower water permeation. The increasing of membrane resistance might attribute to the decrease of membrane pore size, which will be further investigated in the following section through the solute rejection measurement of HA.

3.2 Membrane Morphological Studies

In fabricating polymeric hollow fibre membrane, the dope solution characteristics and spinning conditions have been known to play main role in influencing asymmetric membrane structure which in turn affecting membrane permeation and selectivity.

In this study, two different compositions of dope solution as shown in Table 1 were prepared (PES/NMP/PEG 400/H_2O and PES/NMP/PVP K15). The latter solution contained much higher polymer (PES) concentration (20 wt%) compared to the PES/NMP/PEG 400/H_2O system of 16 wt% PES. Therefore, it is agreed that this PES/NMP/PVP K15 solution has higher viscosity and thus the solvent and non-solvent exchange rate across the membrane is relatively lower[8–10]. As a consequence, it creates smaller membrane pores which may contribute to lower membrane permeate flux.

Figure 4 illustrates FESEM micrographs of the cross-sectional morphologies and outer surfaces for all four modules of membrane prepared. As can be clearly seen, membrane Module 4 exhibited dense structure on outer surface even at magnification of 50,000×, indicating that the average membrane pore size of this module was the smallest ones compared to other membranes prepared using PES/NMP/PEG 400/H_2O solution. It resulted in the

Table 2. Relationship between water flux coefficient and membrane resistance of different types of membrane

Module	Water Flux Coefficient, L_p L/m² h psig	Membrane Resistance, R_m 1/m × 10^{12}
1	1.331	32.52
2	6.855	63.15
3	14.450	2.996
4	0.014	3092

lowest permeate water flux of membrane Module 4. The low water flux of this module however will cause a higher degree of HA removal which will be further investigated.

By varying the spinning conditions such as air gap and bore fluid compositions, it was found that membranes with different morphological structures could also be created, even with the use of same composition of dope solution. Comparing between membrane Modules 1 and 2, it was experienced that the additional of NMP into bore liquid could delay the liquid-liquid de-mixing process, causing slow precipitation during phase inversion process. Attributed to this phenomenon, membrane with a sponge structure is formed, as displayed in Figure 4(b).

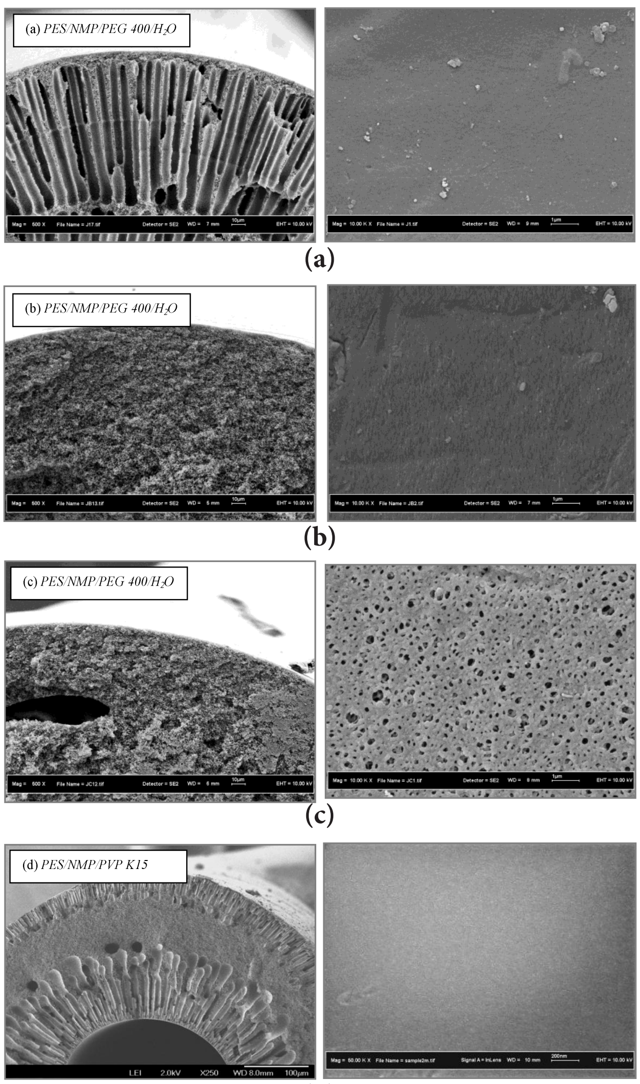

Figure 4. FESEM images of the partial cross-section **(left)** and outer surface **(right)** of hollow fibre membranes **(a)** Module 1, **(b)** Module 2, **(c)** Module 3, **(d)** Module 4.

However, by using pure water as bore composition, it induced a faster phase separation during membrane formation and was able to produce a relatively porous structure, as shown in Figure 4(a).

On the other hand, by increasing the air gap during the spinning process, it can induce a vapour penetration of non-solvent (H_2O from air) at the outer surface of membrane, which may delay the process of liquid-liquid de-mixing as membrane was not immersed instantaneously into the coagulation bath after spinneret. This consequently forms lagger membrane pores as evidenced by FESEM micrograph shown in Figure 4(c). With the bigger pore size on membrane surface, membrane Module 3 was able to provide higher water flux. The result was supported by the pure water permeability of membrane obtained (Figures 3).

3.3 Humic Acid Rejection

In order to evaluate the membrane pore structure, the rejection of HA of each membrane module was measured. Figure 5 shows the HA rejection rate of each membrane module at different HA concentrations while Figure 6 illustrates the image of permeate solution compared with initial feed solution. To obtain membrane solute rejection, it is required to measure the solute content of feed and permeate solutions.

As shown in Figure 5, membrane Module 4 demonstrated the highest rejection of HA for all different concentration of HA solution (form 0.1 to 0.2 g/L), implying that the average pore size for this membrane was

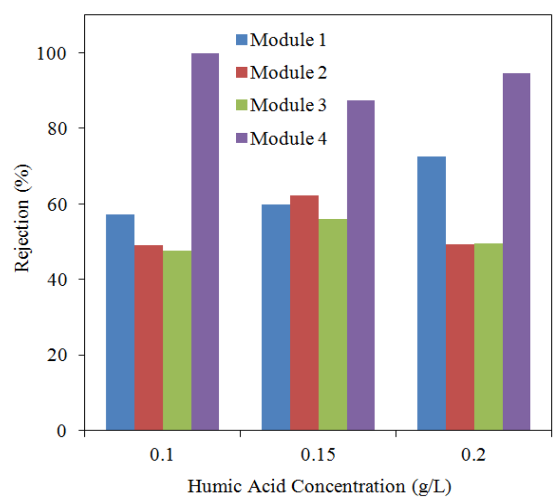

Figure 5. Rejection rate of membranes at different Humic Acid concentrations (operating conditions: pressure = 50 psig, temperature = 25 °C).

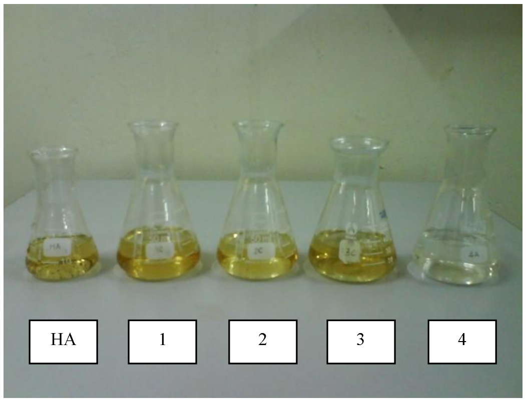

Figure 6. Observation of permeate compared with feed solution using different types of membranes.

* The number represents membrane module

the smallest ones compared to other modules. Obviously, it was found that membrane Module 4 could achieve excellent separation (~100%) at HA concentration of 0.1 g/L. The separation rate though decreased when a higher concentration of HA solution was used, it still showed promising HA removal with near to 90% of solute retention at solute concentration of 0.15 and 0.2 g/L. On the other hand, membrane Module 3 with the lowest rejection rate was due to its bigger pore structure as shown in FESEM micrographs of previous section.

When HA particles filtered with a membrane, HA particles were deposited on the pore wall and thus reducing the membrane pore radius. Teow et al. (2012) experienced that HA deposition on membrane surface reduced the membrane pore effective diameter. This change was contributing in altering the performance of the membrane in HA rejection[11]. Typically, HA deposition was found to be influenced by the bulk concentration[12–14]. As feed concentration increased, the amount of deposited HA particle increased, resulting in higher membrane rejection. However, in this study, the percentage of membrane module rejection was not consistent. This can be elucidated by the fact that the membrane module was physically cleaned each time before carrying out a new set of experiments.

3.4 Membrane Fouling

Filtration or rejection of multivalent solute such as HA with the UF membranes has the tendency to form a deposit layer of foulant on top of the membrane surface. This fouling layer is mainly contributed by sieving mechanism and Donnan exclusion effect15.

Darcy's law presented in Equation (1) is used to explain the permeate flux of the pressure-driven membrane[15]. The membrane fouling resistance is generally increased with the separation time due to deposition of foulant layer on top of the membrane surface.

Figure 7 shows the water flux of membrane Module 4 against the time. The solution containing 0.15 g/L of HA was prepared for this investigation. In comparison, the membrane displayed a much lower water flux than the PWF achieved at the same operating pressure of 55 psig. This is because the existence of HA in the feed solution might attached on membrane outer surface and blocked the open pores of membrane, resulting in a flux decline. Although there was a decrease in water flux, the values of water flux achieved remained almost constant. This phenomena is due to the extremely small average pore size of membrane Module 4 (smaller than the HA particle size), therefore no fouling occurs. Deposited HA particles on membrane surface were easily flashed away by the water flux at feed side. Only certain segment on membrane surface was fouled (pore blockage) by small fraction of HA particles with smaller size.

Figure 8 presents a direct observation on membrane Module 4 before and after filtration process. As can be clearly seen, no fouling layer developed on membrane surface, conversely there has only pore blocking occurred at certain potion throughout the membrane surface. It is known that the HA powder purchased from ALDRICH Chemistry, Malaysia displayed a wide range of particles size distribution. According to normal distribution curve of HA particle size, it is found that only small part of tiny particles, in which the particle size was comparable to average membrane pore size could block the membrane pores, constructing brown colour spot on the membrane

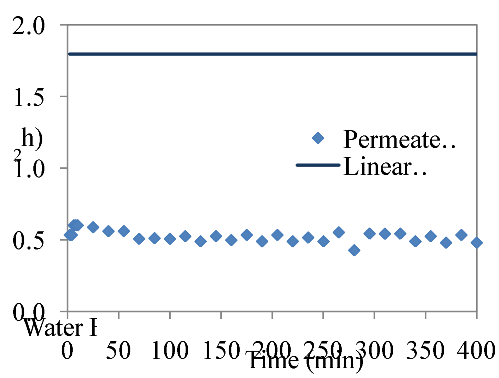

Figure 7. Water flux of membrane Module 4 as a function of time at operating pressure of 55 psig.

Figure 8. Direct observation on membrane (Module 4) surface **(a)** before and **(b)** after filtration process.

surface. Since fouling layer was not enthusiast in this investigation, thus it was predicted the water permeations were not decreased over the operation time, though it displayed much lower values as compared to initial pure water permeability.

4. Conclusions

Based on the experiments performed with using four different types of hollow fiber membranes, the following conclusions were established:

- Due to the highest value of membrane resistance, the membrane Module 4 exhibited the lowest permeate flux compared to the other three types of membranes. The low permeability of membrane Module 4 can be attributed to its relatively dense structure on the top of membrane.
- Morphological analysis using FESEM provided better understanding of membranes' structure. These images captured showed the evidences that membrane with bigger pore size on top layer exhibiting greater water permeation than the dense structure of membrane.
- In terms of HA removal, membrane Module 4 demonstrated the highest separation efficiency than other three types of membranes. It showed promising results of approximately 90% HA removal in comparison to less than 60% rejection rate achieved by other membranes. This is due to the relatively dense structure on the top of membrane Module 4 which is evidenced by FESEM morphological analysis. Membrane Module 4 exhibited dense structure on outer surface even at magnification of 50,000×, indicating that the average membrane pore size of this module was the smallest and could achieve highest degree of HA removal.
- Increasing HA feed concentration solution from 0.1 - 0.20 mg/L resulted in a variation in HA removal efficiency for all types of membranes. The phenomenon might be due to the pore blockage which restricts the molecules to pass through membrane.
- Fouling problem was common in membrane water separation processes. This was evidenced in this study in which the permeation of membrane tended to decrease over the time. The membrane Module 4 is having the most severe membrane fouling which is mainly contributed by the deposition of HA molecules on the membrane surface or into the membrane pores.

5. Acknowledgment

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