Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1110048

57 (2016) 20388–20400
September

Taylor & Francis
Taylor & Francis Group

Removal of heavy metal ions from its low concentrated lake water via LiBr/PES hollow fiber membrane module system

Muhammad Irfan, Ani Idris*, Nur Farahah Mohd Khairuddin

Faculty of Chemical Engineering, Department of Bioprocess Engineering, c/o Institute of Bioproduct Development, Universiti Teknologi Malaysia UTM, 81310 Johor Bahru, Johor, Malaysia, Tel. +60 75535603; Fax: +60 75588166; email: ani@cheme.utm.my (A. Idris)

Received 8 February 2015; Accepted 7 October 2015

ABSTRACT

The treatment of river or lake water for heavy metal removal is of special concern due to their persistence and recalcitrance in the environment. In the current study, an ultrafiltration (UF) system consisting of polyethersulfone (PES) UF hollow fiber (HF) membranes spun from Liberia doped solutions was used for the removal of most critical, heavy metals (Mg^{2+}, K^+, Ca^{2+}, Mo^{2+}, Cr^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, As^{3+}, Na^{1+}, Fe^{2+}, Cd^{2+}, and Co^{2+}) and Cl^{1-} ions from lake water at high-flux rate filtration through the commercial grade filtration setup. The 300 UF HF having potted length of 1.07 m with 0.95 m^2 of total permeation surface area was positioned on the final stage in a commercial grade module consisting of multimedia filter, iron filter, active carbon filter, and water softener filter. In addition, the performance of formulated HF membranes was characterized in terms of raw lake water flux, turbidity, total dissolved solids, water hardness, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) experiments. The results revealed that the UF filtration system cleaned the water at a high flux rate (417 L/h) with a reduction of 58% water hardness, 77.4% turbidity, 73.7% BOD, and 67.76% COD. Moreover, PES/LiBr HF showed electrostatic repulsion on most of the dissolved heavy metals and 74% of total tested heavy metals demonstrated 44–99% rejection rate of passing through the membranes.

Keywords: Hollow fiber; Polyethersulfone; Heavy metals; BOD; Turbidity

1. Introduction

The demand for drinking water is growing every day due to the increased human population and their lifestyle [1]. Water pollution has been drawing international anxiety, particularly non-biodegradable and toxic heavy metal ions present in aquatic and drinking systems which cause severe environmental and health problems [2]. The heavy metal ions discharged in clean water resources by human activities have limited its use for drinking purpose. Toxic heavy metal ions are extremely soluble in aquatic environments, simply entering and gathering in living organisms. High ingestion of heavy metals beyond a permitted limit can cause severe health disorders, including skin, bladder, kidney, and lung cancer [3].

Several scientific techniques have been developed for the exclusion of heavy metal ions from water, including coagulation/co-precipitation, precipitation, ion exchange, reverse osmosis (RO), adsorption, and nanofiltration techniques, each of which has inherent

---

*Corresponding author.

limitations and advantages [4–7]. These techniques are not appropriate for the treatment of low concentrated heavy metal-containing water. Activated carbon sorption and ion exchange processes are exceptionally costly, especially when dealing with large amounts of water containing low heavy metal concentration [8].

In water treatment systems, membrane technologies are increasingly used because of their guaranteed treated water quality and small space utilization [9,10]. The use of membranes to treat water containing heavy metal ions permits the implementation of water recycling systems in industrial facilities. Nanofiltration (NF) and RO membrane filtration techniques are significantly cost effective and more practical but are less efficient due to membrane fouling and management costs [11]. For low concentration heavy metal water, ultrafiltration (UF) membranes are considered as a suitable method for producing municipal drinking water due to their higher water permeability and low operating pressure than RO/NF membranes. Polyethersulfone (PES) is a polymer whose hollow fiber (HF) membranes are preferably used in the treatment of industrial wastewater through UF techniques, due to its relatively low flammability, water sorption and dielectric loss, and high glass transition temperature of 230°C that makes the polymer chemically resistant [12,13]. The blending of different additives with polymeric material in UF membrane is a normal trend. These additives are used to produce a spongy hydrophilic membrane structure with little macrovoid formation, enhanced pore interconnectivity, and improved pore formation [14].

In general, the blending of inorganic lyotropic salts (like iodide, nitrate, thiocyanate, chloride, bromide, and perchlorate as the anion and calcium and magnesium, lithium, and zinc as the cation) was reported to be extremely efficient in casting solutions for membrane preparations [15]. These salts can influence the interactions between the macromolecule chains, the solvent and form complexes in polar aprotic solvent via ion–dipole interaction with carbonyl groups present in acetone, DMAc, DMF, DMSO, and NMP [16]. Some of the less frequently used low-molecular weight inorganic salt additives are magnesium chloride, calcium chloride, lithium chloride, zinc chloride, calcium perchlorate $Ca(ClO_4)_2$, and magnesium perchlorate $Mg(ClO_4)_2$). However, when they are used with cellulose acetate, they are found to improve their flux rate with hydrophilicity [17].

In our previous studies, different weight % of LiBr with PES were found to influence the viscosity behavior of the dope solution prepared via both the microwave and conventional heating techniques [18]. The flat sheet membranes were then used for the treatment of a palm oil effluent which was high in pollutant concentration [19] and effect of LiBr on the morphology, contact angle, and pure water flux rate of PES [20] were studied. Most of the previous studies were performed on flat sheet membranes in lab-scale studies and none of them uses the formulation for HF membranes and used them for the removal of heavy metal ions from river or lake water at a large scale. Thus, in this study, the dope solution containing PES/LiBr/DMF was spun to form HF membranes which were then potted to membrane module (107 cm in length) and fitted in specific lab-designed commercial grade water filter system (Fig. 1) that contained multimedia filter, iron filter, activated carbon filter, and water softener filter with controlled pressure system. The lake water was utilized as the incoming feed and heavy metal rejection with BOD and COD analyses, hardness, total dissolved solids (TDS), turbidity, and color diminution ratio was quantitatively measured.

2. Experimental section

2.1. Materials

PES (Ultrason E6020P; molecular weight = 58 000 g/mol) were provided by BASF Co. (Germany). Analytical grade dimethylforamide (DMF) (HCON(CH 3)2; molar mass = 73.10 g/mol) was purchased from Merck (Germany) and analytical grade anhydrous LiBr (molecular weight = 86.85 g/mol) was obtained from Sigma. Distilled water was used in the coagulation bath.

2.2. Preparation of dope solution

The polymer dope solution was prepared in a one liter three-necked round-bottomed flask with refluxing condenser and stirrer using microwave technique as described elsewhere [20]. The formulation of dope solutions consist of 20 wt % PES, 3% LiBr in DMF solvent.

2.3. Spinning of HF membranes

HFs from the PES/LiBr dope solutions were spun via the dry–wet phase inversion. From 1-L pressure vessel, the dope solution was pumped to the spinneret by means of a gear pump. The gear pump (SPH0292) has a capacity of 0.3 cm^3/rev and has a 30-watt double-gear motor which provided a steady rotation even at low speed. The distilled water was assigned as the internal coagulant, pumped via a high-pressure precision metering pump (ISCO Model 500 D; series D) to

Fig. 1. The front and back view of the UF system with HF membrane module.

the tube side of the spinneret. The internal coagulation fluid, partially solidified the nascent HF as it emerged out of the spinneret. The spinneret was fixed at a height of 3 cm above the coagulation bath so that the outer surface of the HFs was exposed to air for fractional evaporation of solvent prior to being immersed in the coagulation bath, where coagulation occurred on the external surface of the membrane due to solvent–nonsolvent exchange. Consequently, asymmetric HF membranes were formed in the coagulation bath, where it is passed through a series of rollers and the fully formed fiber was then continuously collected onto a windup drum. The final fibers remained in the water bath so as to complete the coagulation process before being taken out. The HF spinning conditions are listed in Table 1.

2.4. Post-treatment protocol and leaching test

In this protocol, the HFs were washed three times with deionized water and then immersed in deionized water and covered with aluminum foil. The glass container was placed on a hot plate and gradually heated for 45 min at 90˚C. The post-treatment was performed so as to modify the performance of the membrane; increase the rejection rate and decrease the flux rate.

After post-treatment to check the leaching/stability behavior of salt, the HFs was dipped into deionized water and the change in conductivity was observed using conductivity meter. Three meters of long fiber of membranes was cut into small pieces (1 cm sized) dipped in deionized water (2 L), stirred with magnetic stirrer, and measured the conductivity after every 12 h for 48 h. The change in conductivity represents the leaching of salt and calibration curve method was used to quantify the leaching phenomena. It was observed that after post-treatment, the formulation of fiber was fixed and no change in conductivity of HFs (leaching of salt) occurred.”

2.5. Potting

After post-treatment, the HFs membranes were dried for 24 h at room temperature and then potted in bundles of about 300 fibers each with a 107 cm length. A high fiber packing density is needed in HF membranes to minimize any axial diffusional effects and channeling. The geometrical characteristics of the module are given in Table 2.

Table 2
Geometrical characteristics of the HF module

Geometrical characteristics	
Total number of fiber	300
Average fiber outer diameter (cm)	0.0619
Average fiber inner diameter (cm)	0.031813
Potted length (cm)	107.0
Diameter of module (cm)	11.0
Total permeation surface area of HFs $(cm)^2$	9,450.51

2.6. Water Sample

The performance of the commercial grade filter system with potted HFs was estimated using 600 L of lake water that was collected randomly from different sections of the Tasik Ilmu lake in Universiti Teknologi Malaysia.

2.7. Mechanical specifications of commercial grade water filter machine

The commercial grade water filter system was designed by Ecowerks Pte Ltd. The system consists of a control panel, iron, active carbon, and water softener filters. The control panel was used to control the on/off switches and set the water pressure of the whole system and for observing the pure water and retentate fluxes with their relevant pressures gauges. The system is equipped with a water pump to deliver the raw lake water from the storage tank to the whole membrane system as shown in Fig. 1. The raw lake water from storage vessel passed through a series of filters (multimedia filter → iron filter →, active carbon filter → water softener filters) and finally into the HFs membrane module which separated the incoming water into retentate and permeates. The permeate was further passed through UV sterilizer and then stored in a clean water storage container, whereas the retentate was pumped back into the storage vessel.

Table 1
Spinning conditions of HF membranes

Spinning parameters	
Internal bore fluid rate	2 ml/min
Fiber take-up speed	6.5–7.78 m/min
Fiber take-up roller diameter	20 cm
Air gap between spinneret and coagulant bath	3.0 cm
Dope extrusion rate	3.95–4.0 ml/min
Dope solution temperature	25˚C
Relative humidity	60–70%
Spinning temperature	22˚C

2.8. Membrane morphology

Field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) were used to analyze the morphology of cross-section and surface roughness of HFs, respectively. For FESEM (Model SUPRA 35VP, Gemini column), the membrane sample was snapped in liquid nitrogen and then sputter coated with platinum and mounted onto brass plates using double-sided cellophane tapes in a lateral position. AFM (SII Nanotechnology SPM- SPI3800 N) was used to analyze the roughness of the membranes (5 μm × 5 μm) with 3D micrographs, and all roughness parameters of membranes were determined by an AFM software program from the AFM images. In roughness data, "Ra" and "RMS" represent the mean roughness and root mean square roughness of the membrane surface, respectively, whereas "P − V" is the main difference in the heights between the five highest peaks and the five lowest peaks valley. "Rz" represents the average roughness of 10 points.

2.9. Flux rate

The HFs module was tested for lake water permeation flux at a pressure of 1 and 2 bars. The volume of permeate was collected and measured after every 30 min for 4 h so as to determine the flux rate of clean water. The lake water flux of the HFs was obtained using Eq. (1):

$$\text{Flux} = J_{\text{w1}} = \frac{Q}{A \times h} = \frac{Q}{N\pi d_{\text{o}} l h} \tag{1}$$

where "Q" is the volume flow rate of permeate (L), "A" is the effective membrane area (m^2), "h" is the time (hrs), "N" is the number of fibers, "d_{o}" is the outer diameter of fiber (m), and "" is the effective length of fiber (m).

UF experiment was continued to determine the antifouling property of membranes, by replacing lake water with feed solution (J_{w1}) containing 1,000 ppm of clay [21]. The experiment was performed under the same condition for the next 2 h and clay water flux was noted as "J_{c}." After that, the HFs membrane was cleaned by allowing tap water to flow for 30 min under the same condition. Then, lake water flux (J_{w2}) was remeasured to obtain the flux recovery ratio percentage (R_{FR}) as expressed in Eq. (2):

$$R_{\text{FR}}(\%) = \frac{J_{\text{w2}}}{J_{\text{w1}}} \times 100 \tag{2}$$

Generally, the fouling of UF membrane is caused by reversible and irreversible foulants. To better analyze the mechanism, the total resistance rate (R_{t}), the reversible resistance (R_{r}), and the irreversible resistance (R_{ir}) rate were calculated using Eqs. (3)–(5), respectively [21]:

$$R_{\text{t}}(\%) = 1 - \frac{J_{\text{c}}}{J_{\text{w1}}} \times 100 \tag{3}$$

$$R_{\text{r}}(\%) = \frac{J_{\text{w2}} - J_{\text{c}}}{J_{\text{w1}}} \times 100 \tag{4}$$

$$R_{\text{ir}}(\%) = \frac{J_{\text{w1}} - J_{\text{w2}}}{J_{\text{w1}}} \times 100 \tag{5}$$

2.10. Porosity and pore size and molecular weight cut-off of HFs

Membrane porosity ($\in$) was measured by dry–wet weight method. After the membrane was equilibrated in water, the volume occupied by water and the volume of the membrane in the wet state was determined. The membrane porosity is obtained by Eq. (6):

$$\in = \frac{W_{\text{Wet}} - W_{\text{Dry}}}{V \cdot \delta_{\text{w}}} \tag{6}$$

where "W_{wet}" and "W_{dry}" are the weights (g) of wet and dry membranes, respectively, and "V" is the volume (cm^3) of membrane and "δ_{w}" is the density of pure water (g/cm^3) [22].

The solute rejection of HFs membranes was evaluated using different polyethylene solutions (1,000 ppm) having molecular weight 400, 600, 1, 3, 6, and 10 K Daltons, whereas the rejection rate was calculated by Eq. (7):

$$R = \left(1 - \frac{C_{\text{p}}}{C_{\text{f}}}\right) \times 100\% \tag{7}$$

where C_{p} and C_{f} are the concentrations of the permeate and feed, respectively. Modified Dragendorff methods were used to detect PEG concentrations in solution [23].

The pore sizes of the membranes were determined using solute transport data as derived by Singh et al. [24]. Solute diameter (d_{s}) is given by:

$$d_{\text{s}} = 2a \tag{8}$$

The data of solute separation vs. solute diameter were plotted on a log normal graph paper to determine the mean pore size of the membranes. The mean pore size corresponding to $R = 50\%$ on the linear regression line was calculated.

2.11. Color

The color of filtered and raw lake water was measured by "visual" and the American Dye Manufacturers Institute (ADMI) Hach Standard Methods "10048." The ADMI examination of clean and waste water was performed on a Hach DR/4000 U, UV–vis spectrophotometer. The ADMI scale uses a spectral or a tristimulus method to calculate a single color value that is independent of hue. It is used for tinted effluents with colors that are different from the widely used Pt–Co/Hazen/APHA/Hazen units which was used with water with values of more than 25 TCU (true color unit). The value of ADMI color number is comparable to platinium/cobalt (TCU) color number.

2.12. Turbidity

Water turbidity is a measurement of water clarity and is measured using a turbidity meter. The instrument works by collecting the amount of light that is scattered by material in the water. The higher the intensity of scattered light, the higher is the turbidity. The material that caused water to be turbid and losses its transparency is called suspended solid which consist of inorganic and organic materials. In this study, the Thermo Corporation Orion Aquafast™ II Turbidimeter Model was used to measure the turbidity of lake samples. This instrument works on the nephelometric and ratiometric principles of turbidity measurement.

2.13. TDS and pH

TDS of lake and filtered water was calculated using Hach DR/4000 U, UV–vis spectrophotometer at a wavelength of 522 nm, and the Hanna 211 microprocessor-based pH, and the temperature bench meter was used to measure the pH of different water samples at different time intervals.

2.14. Hardness

Hardness of water is caused by the high content of magnesium and calcium carbonates, sulfates, and chlorides that normally are dissolved in water as the water pass through soils and rock. It does not give adverse effects to humans, but it can cause damage to pipes and boiler due to scaling. The hardness of water was determined using atomic absorption spectrometer (AAS). This instrument measured the absorption of light at specific wavelengths of calcium and magnesium. A standard curve of absorbance vs. concentration was used to measure the calcium and magnesium concentration of the lake water sample. Four different concentration standards 1, 4, 7, and 10 ppm were prepared each from stock solution of 601.2 ppm calcium and 10,000 ppm magnesium in a 250-ml volumetric flask. The absorbance was measured for each concentration and plotted against the concentration. The sample of lake water was inserted into AAS and was measured for its absorption. The metal concentration was determined using the prepared standard curve.

2.15. Biochemical oxygen demand

BOD measures the amount of dissolved oxygen consumed by aerobic organism in water to break down organic materials at specific temperature and time. BOD_5 is the measurement of oxygen consumed by the organism after 5 d of incubation at 20°C. To measure BOD_5, dilution water and sets of samples were prepared. Dilution water consists of nutrients for the organism. It was prepared by mixing 1 ml each of phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride into a 1-L flask of distilled water. Then sets of samples were prepared as follows:

(1) Pure sample (300 ml sample + 0 dilution water).
(2) Diluted sample (200 ml sample + 100 dilution water).
(3) Control (300 dilution water).

BOD_5 (mg/L) was calculated using Eq. (9):

$$BOD_5 = \frac{DO_{initial} - DO_{final}}{\text{Dilution factor}} \quad (9)$$

where DO is the dissolved oxygen and dilution factor is the volumetric ratio between the total sample size of the water used and the BOD bottle used. DO value was determined using YSI model 58 Dissolved Oxygen Meter.

2.16. Chemical oxygen demand

COD measures the amount of oxygen required to oxidize organic matter in water using strong oxidizing agents under acid conditions. The COD test was carried out using Hach DRP 200 COD digester and

"Hach" reagents. Briefly, 1 ml of sample was mixed with 2.5 ml of potassium dichromate reagent and 3.5 ml of sulfuric acid reagent in a COD digestion tube. Then, it was placed inside the COD digester at 150°C for 2 h. After that the content of the COD digestion tube was poured in a 100-ml beaker and distilled water was added up to 50 ml. 1–2 drops of "Ferroin" indicator were added in the solution and titrated with ferrous ammonium sulfate (FAS). The COD of the sample was then calculated as follows:

$$\text{COD as mg}\,\frac{\mathrm{O_2}}{\mathrm{L}} = \frac{(A - B) \times M \times 8000}{\mathrm{V}} \tag{10}$$

where "A" is the volume of FAS used for blank (ml), "B" is the volume of FAS used for sample, "M" is the molarity of FAS, and "V" is the volume of sample (ml).

2.17. Chlorides (Cl^{1-})

The quantitative estimation of chloride ions was performed by Hanna HI 701 instrument having range 0.00–2.50 ppm with accuracy ±0.03. This instrument worked on "USEPA method 330.5" with light-emitted diode and light detector made from the silicon photo cell which showed absorbance at 525 nm. For detecting chloride ion in the water sample, DPD reagent (causes a pink tint in the sample) was added in 10 mL of testing sample in the instrument-specified bottles.

2.18. Heavy metals

The determination of 15 heavy metals; Mg^{2+}, K^{+}, Ca^{2+}, Mo^{2+}, Cr^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, As^{3+}, Na^{1+}, Fe^{2+}, Cd^{2+}, and Co^{2+} ions in the lake water were carried out using inductive coupled plasma-mass spectrometer (ICP-MS) (Perkin Elmer). This instrument can detect multi-element and various heavy metals in water. It is completed with Meinhart nebulizer and silica cyclonic spray chamber and continuous nebulization for analysis. Before being tested with ICP-MS, the samples were prepared at first. Samples were placed in polyethylene containers that have been previously washed with 10% of nitric acid and rinsed. Then, 60% nitric acid was added in the sample for stabilization, heated, and filtered using 0.2-μm nylon filter paper.

3. Results and discussion

In our previous lab-scale studies, it was concluded that the 3 wt.% of LiBr in membrane matrix with PES provided the best performance in terms of hydrophlicity, flux rate, and molecular weight cut-off (2.83 kDa) as compared to pristine PES and others LiBr-contained membranes [18–20]. In this study, the same formulation (3% LiBr) of PES/LiBr membrane was used to fabricate the HFs for treatment of lake water for heavy metal rejection. The lake water was initially in class 1/II where it is potable and suitable for irrigation purposes [25]. The filtration of lake water through PES/LiBr HFs module system had improved the water quality.

3.1. Membrane morphology

Figs. 2 and 3 represents the FESEM results and the 3D image of HFs, respectively. Several studies have reported that the membrane morphology is sturdily affected by the addition of nonsolvent salt additives that enhanced the formation of macrovoids (finger like pores) while too much nonsolvent suppressed their formation [26,27]. In this study, not only the

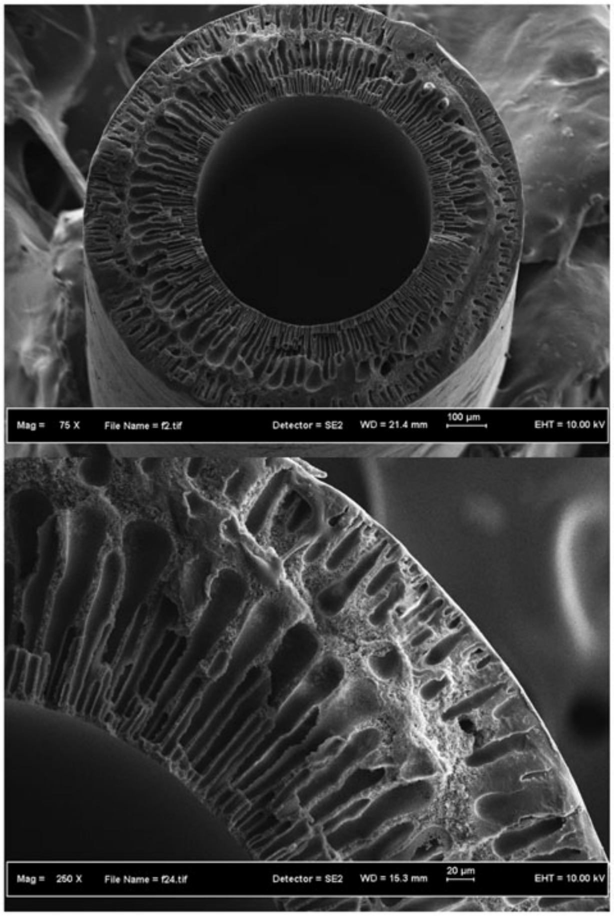
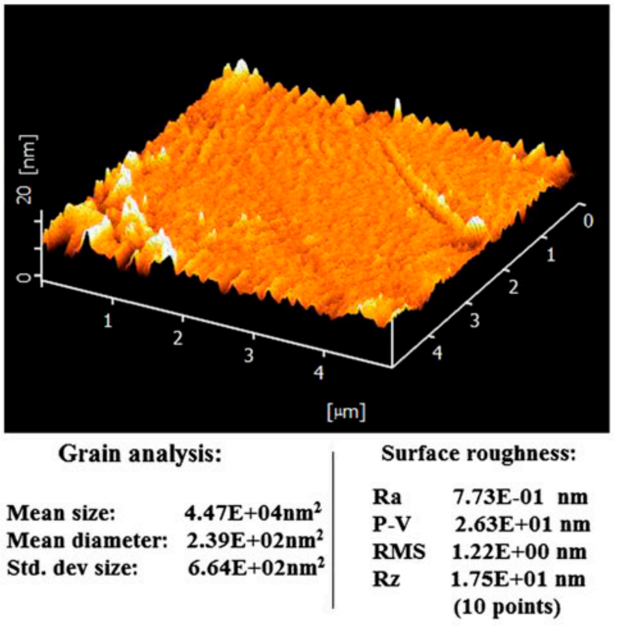


Fig. 2. Cross-section images of PES/LiBr membrane at 75× and 250× magnification power.



Grain analysis:

Mean size:	4.47E+04nm^2
Mean diameter:	2.39E+02nm^2
Std. dev size:	6.64E+02nm^2

Surface roughness:

Ra	7.73E-01 nm
P-V	2.63E+01 nm
RMS	1.22E+00 nm
Rz	1.75E+01 nm (10 points)

Fig. 3. AFM results of HF membrane.

hydrophilicity, but also the membrane morphology is influenced by the addition of LiBr. As we mentioned earlier [20], the addition of LiBr into the PES reduced the sponge-like structure in the middle and the finger-like structure elongates and extends through the sponge-like structure. Such morphological change, enhanced the flux rates of the HF membranes.

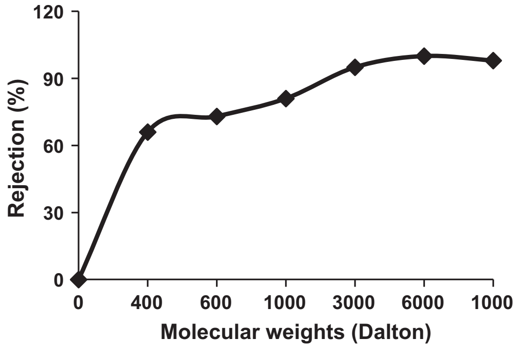


Fig. 4. The MWCO profile of HF membrane.

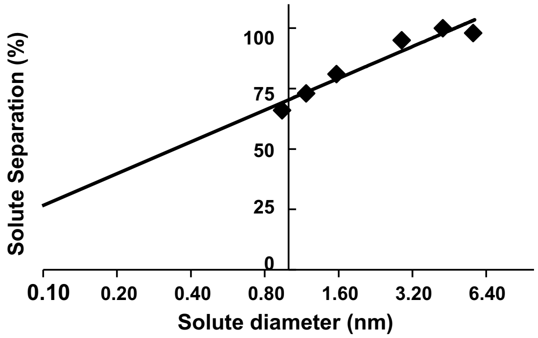


Fig. 5. The pore size calculation of HFs.

3.2. Molecular weight cutt-off and Pore size

Figs. 4 and 5 represent the MWCO results and pore size estimation of HFs. As compared to our previous reported studies [20], the presence of LiBr has not only enhanced the rejection rates, but also improved the permeation rates. The MWCO at 90% rejection rate for membranes with 3 wt.% LiBr was estimated to be 2.8 kDa and the pore size and porosity was found to be 0.35 nm and 26.63, respectively, which were approximately similar to the previous reported work. However, without LiBr in PES the rejection rate of the membrane was extremely low with high MWCO [20].

3.3. Flux rate and antifouling properties of membrane

In previous lab-scale studies, the small membrane module having area of 18.59 cm^2 with 30 HFs and the PWP rates achieved by the HFs membranes containing (3 wt.%) LiBr were approximately 43% higher than those without LiBr. In this study, we used a quite bigger module of HF as compared with previous one, having water permeation area of 9,450.51 cm^2 with 300 packed fibers (Table 2). The flux rate results are mentioned in Fig. 6, were approximately in agreement with our small-scale lab studies (222.16 L m^{-2} h^{-1} bar^{-1} with 3 wt.% LiBr), although in this study, lake water with contaminants was used instead of using pure water. The LiBr has high swelling properties and through its blending, the PES became “hydrophilised” and its contact angle decreased from 84° to 58° [20]. The higher flux rate of lake water with LiBr HF membranes could be due to the formation of the LiBr and DMF complexes that had created a hydration effect and caused swelling of the polymer gel. Fig. 6 shows that increment in pressure from 1 to 2 bars, doubled the flux rate from 209 to 417.8 L/h m^2, and at this high flux rate nearly more than 60% (average) of heavy metal rejection were achieved (discussed in detail in Section 3.10).

The antifouling performance of the hybrid membranes was evaluated in terms of flux recovery ratio and membrane resistance parameters. The results for fouling test are designated in Fig. 7 The flux rate of the lake water decreased sharply when the lake water

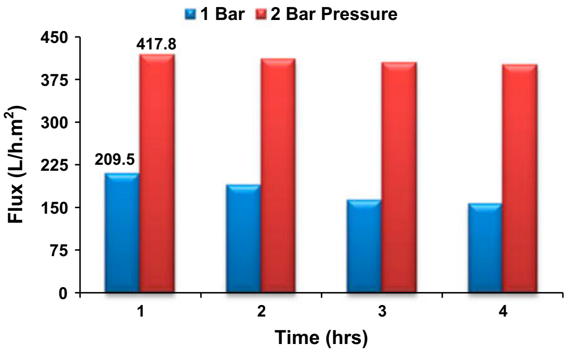


Fig. 6. Flux rate of HF membranes at 1 and 2 bar pressure.

was replaced by clay solution. This result was due to the fouling induced by the deposition and adsorption of the clay onto the membrane surface. Fig. 8 illustrates the fouling parameters for HF membrane in terms of R_t, total resistance rate, R_r, the reversible resistance, R_{ir}, irreversible resistance rate, and R_{FR}, flux recovery ratio. Based on terms, more than 80% flux recovery ratio (R_{FR}) was achieved after washing the HFs with tap water. Moreover, HFs showed 41% to total resistance against fouling in which 25% resistance was reversible foulants. The data represent the outstanding behavior of HFs membrane toward flux recovery ratio, and resistance parameters of the removal of heavy metals.

3.4. pH

The pH value of water before and after filtration was slightly changed (6.6–7.02). This showed that the pH of water was not influenced by the membrane treatment. This also indicated that the PES/LiBr membrane is resilient, i.e. no material was leached out during the filtration process which can influence the water pH. Nevertheless, the pH value of both feed and permeate is under the Class I and in the neutral [25].

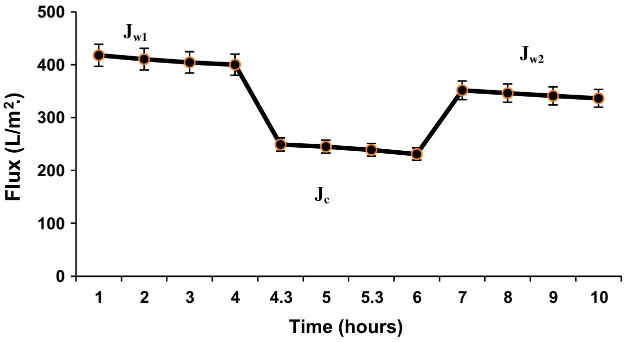


Fig. 7. Initial lake water flux (J_{w1}), clay solution flux (J_c), and after-washing with tap water, lake water flux (J_{w2}) for prepared membrane.

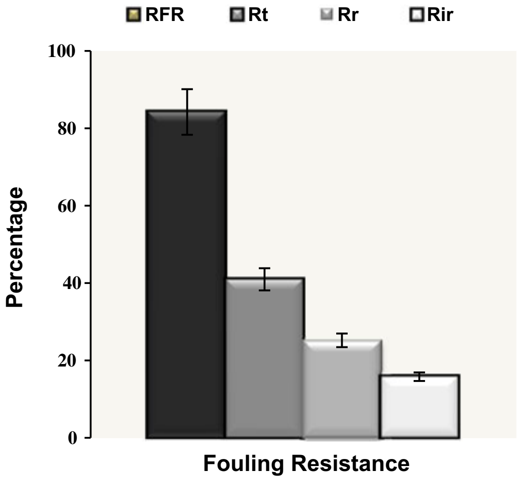


Fig. 8. Fouling parameters for HF membrane; where R_t = total resistance rate, R_r = the reversible resistance, R_{ir} = irreversible resistance rate, and R_{FR} = flux recovery ratio.

3.5. Turbidity

UF is known as a promising treatment that could constantly remove turbidity. The result had shown that the filtration through HFs reduced the turbidity up to 77.41%. Generally, turbidity involves the attendance of suspended solid in the water. Suspended solid in river water may consist of silt, clay, sand, or any other particles. These particles are bigger than the dissolved ions. Therefore, these materials could be easily retained by the UF membrane. Previous study also reported that the UF membrane was able to remove turbidity due to the cake layer formation by particulate materials on the membrane surface. In this commercial grade UF membrane system, multimedia filter worked together with HF membranes to minimize the turbidity which brought its value under drinking water acceptance range [28].

3.6. Total dissolved solid

The PES/LiBr membrane demonstrated a good rejection of TDS with approximately 50% of rejection. As the dissolved solids were already in small amount in the raw lake water so this rejection seems lesser. Generally, TDS is the total amount of ions dissolved in water, including salts and minerals. It can be seen from the Table 3, the feed water contains high sodium (Na^+) content is believed to attribute to the high TDS content. Moreover, the result obtained for Na^+ rejection in Table 3 validates the reason for low TDS rejection by the membrane. Interaction between these ions to the membrane surface has possibly influenced the TDS rejection. Increase of high counter ion mineral would actually reduce Donnan exclusion effect as reported by Seidel and Elimelech [29]. They reported that TDS rejection by the NF membrane decreased with the increase in calcium (Ca^{2+}) due to the behavior of negatively charged membrane with higher valence counter ions that reduced the Donnan exclusion. The rejection of TDS in water by membrane might be higher if the feed water contains higher amounts of Na^+, which were the dominant ions in the feed water.

3.7. Colors

Fig. 9 shows the visuals of the raw and filtered lake water, which clearly indicates that after filtration, the suspended particles (like mud and algae) and the light brown color of water are removed. These changes were also observed when operating the membrane system in the flow meters of pure and the retentate waters (Fig. 1).

A reduction of 59% in color was observed which indicated satisfactory results of water clearance at high flux rate. The degree of color removal by membrane is determined by the pore size of the membrane and is also influenced by the electrostatic repulsion between the colored molecules and membrane materials [30]. As the size of some dissolved particles were smaller in the feed water than the reported molecular weight cut-off (2.83 kDa) of PES/LiBr membranes [20], thus suggesting that the color removal was due to the electrostatic repulsion which was also confirmed in heavy metal rejection results (discussed in Section 3.8). Previous study has reported that the membrane's pressure and pore size played an important role in color removal. Low color removal was found to be associated with high transmembrane pressure and larger pore size [31]. However, in this experiment, only low transmembrane pressure was applied; 1–2 bars thus suggesting that the color removal demonstrated by PES/LiBr membrane was influenced by the membrane pore size and its electrostatic repulsion. The presence of LiBr additive could have contributed to the electrostatic repulsion property of the PES membranes. Nevertheless, the PES/LiBr membrane has shown its ability to remove the color contaminant and meet the class I water standard set by the Malaysian government [25].

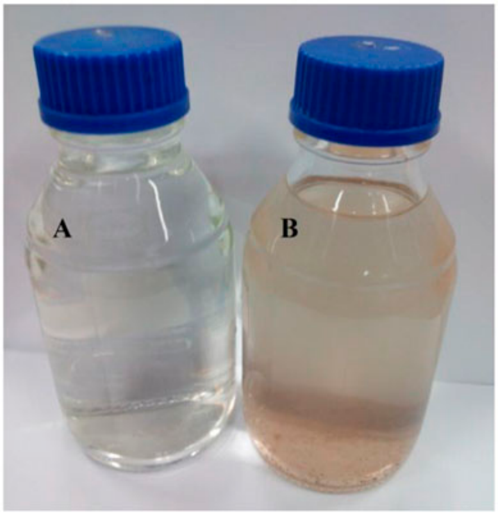


Fig. 9. Visual result of (A) Permeate and (B) Feed waters, feed water from the lake.

3.8. Hardness

NF membrane usually provides high hardness removal than the UF membrane due to its pore size. Moreover, the NF membrane would be able to retain

Table 3
The quality of the lake water after passing through PES/LiBrHF membrane module

Test	Before filtration	After filtration (%)	Reduction (%)
Color (visual)	Highly yellowish	Transparent	–
Color (ADMI)	29	12	58.62
Hardness (mg/l)	123	52	57.72
Turbidity	15.5	3.5	77.41
BOD	2.70	0.71	73.70
COD	121	39	67.76
TDS (mg/L)	154	79	48

both divalent and monovalent ions and can result in low hardness concentration in permeate but with low flux rate. In our case, as the hardness in raw lake water was already at low level (i.e. 123 mg/L), therefore, it is expected that the percentage of hardness removal would be lower than NF membrane, but is still at the level of nearly 58% (Table 3). In the reduction of hardness, not only HF membranes were involved, but the softener filter also plays an important role. Even though the hardness percentage removal is low, the PES/LiBr membrane has produced permeate water under the very soft category (0–60 mg/L, soft water scale of $CaCO_3$) [25].

3.9. BOD and COD

The result of BOD/COD achieved in this experiment corresponded to the retention of organic materials by the PES/LiBr membrane. In this study, the lake water was subjected directly to the membrane system without any pre-treatment. Apparently, the level of organic pollutant in raw water resembled by the initial BOD/COD reading was in low concentration, and thus, reduction of almost 70% of BOD/COD is acceptable. This indicates that there were some dissolved organic matters which is low in molecular weight. Organic matters or better known as natural organic matter (NOM) or effluent organic matter (EfOM) consist of soluble microbial products (SMP). SMPs are comprised mainly of organic acid, organic colloids, polysaccharide, and proteins. The characteristics of SMP such as the quality and quantity depend on the biological system operational condition. As the retention time of biological entities increased in biological reactor, the COD of effluent decreased [32]. Since, this study belong to high flux rate filtration, only 30% of organic matters were passed through the membrane but the filter water still contains BOD/COD values in the acceptable range of drinking water.

3.10. Heavy metals

Generally, UF membrane will not be able to remove dissolved material itself since the pore size of the UF membrane is always larger than the dissolved ions. The micellar-enhanced ultrafiltration (MEUF) and polymer-enhanced ultrafiltration (PEUF) were common method used to obtain high metals ion removal. MEUF system is, where surfactant is used as the ions binder. Surfactant added in the wastewater would become very concentrated at one stage which is called critical micelle concentration (CMC). At this stage, the surfactant would aggregate into micelles and bind with the metal ions to form a large micelle that would be retained by the UF membrane. On the other hand, PEUF involved the use of water-soluble polymer which bind with metal ions and form macromolecules. Since the macromolecules have larger particle size than that of UF membrane, they would be retained. The retentate would be treated to obtain the metallic ions and polymer [33]. In this experiment, none of these two systems were applied and instead the water was directly subjected to the HF membranes after passing the multimedia filter, iron filter, activated carbon, and softener filter. Nonetheless, the result obtained for heavy metals removal showed that the

Table 4
Heavy metal weight percentage of feed and filtered lake water

Sr#	Metals name	Before filtration (ppb)	After filtration (ppb)	Percentage reduction (%)
2	Cr	5.380	2.289	57.454
3	Mn	0.244	0.081	66.803
4	Ni	9.284	6.091	34.393
5	Co	0.041	0.03	26.829
6	Cu	5.939	1.08	81.815
7	Zn	1.563	1.316	15.803
8	As	2.179	1.233	43.414
9	Cd	1,105.516	793.509	28.223
10	Pb	17.217	2.689	84.382
11	Ca	169.86	31.802	81.278
12	Fe	27.438	15.357	44.030
13	Na	37,093.728	35,152.025	5.235
14	K	3.145	1.413	55.072
15	Mo	3.518	1.491	57.618
16	Cl^{1-}/Chlorine	0.3	0.15	50.000

PES/LiBr membrane has successfully removed half of the heavy metal content with high rejection and some are rejected even more than 80% **(**Table 4**)**. It has been observed that only Zn^{2+}, Cd^{2+}, Na^{1+}, and Co^{2+} of the tested heavy metal showed low rejection (<30%); and 33% of metals (Cl^{1-}, Cr, Mo, Fe, and K) demonstrated 40–60% rejection rate, whereas others 41% of dissolved heavy metal (Mg, Mn, Cu, Pb, and Ca^{2+}) ions showed 61–99% rejection rate.

Thus, it was strongly believed that the ionic interaction and electrostatic repulsion of the membrane surfaces and the dissolved heavy metal ions in lake water are responsible for a higher rejection rate obtained with high flux clean water rate (418 L/h). Higher valence of counter ions has decreased the Donnan exclusion of the negative PES/LiBr membrane which leads to positive charged ions passing through the membrane.

4. Conclusion

Lake water is one of the important drinking water sources in the whole world and most of countries are using lake water for drinking purposes. Heavy metals are the most considerable contaminants in the lake water, which are soluble in the water and their higher concentration changed the water chemistry and makes it extremely unhealthy for human health. The present study focused on the removal of heavy metal from lake water with high flux rate through a UF membrane on a large scale. In short, the PES/LiBr HF membrane modules installed in the filter system setup are superior in terms of flux rate, turbidity reduction, BOD and COD removal, and heavy metals removal although all had been already present in very lesser quantities. The presence of LiBr in the membrane matrix developed some kind of electrostatic forces on the membrane surfaces, thus enabling the removal of heavy metals effectively. The electrostatic forces on the membrane surface applied repulsive effect on most of the dissolved solids, especially toxic heavy metals; hence, they were rejected when passing through the HF at a very high flux rate. Out of 15 heavy metals, 10 elements (Mg^{2+}, K^{+}, Ca^{2+}, Mo^{2+}, Cr^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Cl^{1-} ion) showed more than 50% rejection ratio at a high flux filtration rate which was quite difficult in NF and other filtration techniques. Heavy metals such as Ca^{2+}, Mg^{2+}, Cu^{2+}, and Pb^{2+} were rejected by the HF membranes with more than 80% reduction rate. Moreover, after passing through the membrane module, all the heavy metals concentrations are in the permissible range of National Quality Standard for Malaysia and WHO guidelines [21].

References

[1] R.M. Hassan, R. Scholes, N. Ash, Ecosystems and Human Well-Being: Current State and Trends: Findings of the Condition and Trends Working Group, Island Press, Washington, DC, 2005.

[2] A. Denizli, S. Senel, G. Alsancak, N. Tüzmen, R. Say, Mercury removal from synthetic solutions using poly(2-hydroxyethylmethacrylate) gel beads modified with poly (ethyleneimine), React. Funct. Polym. 55 (2003) 121–130.

[3] A. Sigel, H. Sigel, R.K. Sigel, Metal Ions in toxicology: Effects, Interactions, Interdependencies, Royal Society of Chemistry, Cambridge, England, 2011.

[4] S. Bouranene, P. Fievet, A. Szymczyk, M. El-Hadi Samar, A. Vidonne, Influence of operating conditions on the rejection of cobalt and lead ions in aqueous solutions by a nanofiltration polyamide membrane, J. Membr. Sci. 325 (2008) 150–157.

[5] X. Chen, K.F. Lam, S.F. Mak, K.L. Yeung, Precious metal recovery by selective adsorption using biosorbents, J. Hazard. Mater. 186 (2011) 902–910.

[6] J. Lv, K.Y. Wang, T.-S. Chung, Investigation of amphoteric polybenzimidazole (PBI) nanofiltration hollow fiber membrane for both cation and anions removal, J. Membr. Sci. 310 (2008) 557–566.

[7] K.-H. Yeon, J.-H. Song, S.-H. Moon, A study on stack configuration of continuous electrodeionization for removal of heavy metal ions from the primary coolant of a nuclear power plant, Water Res. 38 (2004) 1911–1921.

[8] C. Cojocaru, G. Zakrzewska-Trznadel, A. Jaworska, Removal of cobalt ions from aqueous solutions by polymer assisted ultrafiltration using experimental design approach. part 1: Optimization of complexation conditions, J. Hazard. Mater. 169 (2009) 599–609.

[9] N.N. Li, A.G. Fane, W.W. Ho, T. Matsuura, Advanced Membrane Technology and Applications, John Wiley & Sons, New Jersey, USA, 2011.

[10] J.R. Pressdee, Integration of membrane filtration into water treatment systems, American Water Works Association, Denver, CO, 2006.

[11] B. Al-Rashdi, C. Somerfield, N. Hilal, Heavy metals removal using adsorption and nanofiltration techniques, Sep. Purif. Rev. 40 (2011) 209–259.

[12] A.W.W. Association, Microfiltration and Ultrafiltration Membranes for Drinking Water (PDF), J. Am. Water Works Assoc. 100 (2008) 84–97.

[13] M.J. Troughton, Sulfone-based resins. in: M.J. Troughton (Ed.), Handbook of Plastics Joining, second ed., William Andrew Publishing, Boston, 2009, pp. 451–463.

[14] B. Jung, J.K. Yoon, B. Kim, H.-W. Rhee, Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes, J. Membr. Sci. 243 (2004) 45–57.

[15] D.R. Lloyd, Materials science of synthetic membranes, ACS Symposium Series, vol. 269, American Chemical Society, Washington, DC, 1985, pp. 1–21.

[16] R.E. Kesting, Synthetic polymeric membranes: A structural perspective, Wiley, New York, NY, 1985.

[17] R.E. Kesting, A.K. Fritzsche, M.K Murphy, A.C. Handermann, C.A. Cruse, R.F. Mahon, Process for forming asymmetric gas separation membranes having graded density skins, US Patent 4, 871, 494, US Patent and Trademark Office, Washington, DC, 1989.

[18] A. Idris, I. Ahmed, Viscosity behavior of microwave-heated and conventionally heated poly(ether sulfone)/dimethylformamide/lithium bromide polymer solutions, J. Appl. Polym. Sci. 108 (2008) 302–307.
[19] A. Idris, I. Ahmed, M.A. Limin, Influence of lithium chloride, lithium bromide and lithium fluoride additives on performance of polyethersulfone membranes and its application in the treatment of palm oil mill effluent, Desalination 250 (2010) 805–809.
[20] A. Idris, I. Ahmed, M. Misran, Novel high performance hollow fiber ultrafiltration membranes spun from LiBr doped solutions, Desalination 249 (2009) 541–548.
[21] G. Arthanareeswaran, T. Sriyamuna Devi, M. Raajenthiren, Effect of silica particles on cellulose acetate blend ultrafiltration membranes: Part I, Sep. Purif. Technol. 64 (2008) 38–47.
[22] Z. Chen, M. Deng, Y. Chen, G. He, M. Wu, J. Wang, Preparation and performance of cellulose acetate/polyethyleneimine blend microfiltration membranes and their applications, J. Membr. Sci. 235 (2004) 73–86.
[23] Z. Jia, C. Tian, Quantitative determination of polyethylene glycol with modified Dragendorff reagent method, Desalination 247 (2009) 423–429.
[24] S. Singh, K. Khulbe, T. Matsuura, P. Ramamurthy, Membrane characterization by solute transport and atomic force microscopy, J. Membr. Sci. 142 (1998) 111–127.
[25] State of water: Malaysia, 2015. Available from: http://www.wepa-b.net/policies/state/malaysia/river.htm.
[26] F.G. Paulsen, S.S. Shojaie, W.B. Krantz, Effect of evaporation step on macrovoid formation in wet-cast polymeric membranes, J. Membr. Sci. 91 (1994) 265–282.
[27] C. Smolders, A. Reuvers, R. Boom, I. Wienk, Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids, J. Membr. Sci. 73 (1992) 259–275.
[28] W.H. Organization, Guidelines for Drinking-Water Quality: First addendum to, vol. 1, Recommendations, World Health Organization, Geneva, Switzerland, 2006.
[29] A. Seidel, M. Elimelech, Coupling between chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes: Implications for fouling control, J. Membr. Sci. 203 (2002) 245–255.
[30] S. Yu, M. Liu, M. Ma, M. Qi, Z. Lü, C. Gao, Impacts of membrane properties on reactive dye removal from dye/salt mixtures by asymmetric cellulose acetate and composite polyamide nanofiltration membranes, J. Membr. Sci. 350 (2010) 83–91.
[31] S. Muthukumaran, D.A. Nguyen, K. Baskaran, Performance evaluation of different ultrafiltration membranes for the reclamation and reuse of secondary effluent, Desalination 279 (2011) 383–389.
[32] M. Esparza-Soto, S. Núñez-Hernández, C. Fall, Spectrometric characterization of effluent organic matter of a sequencing batch reactor operated at three sludge retention times, Water Res. 45 (2011) 6555–6563.
[33] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418.