

Performance of membrane filtration in the removal of iron and manganese from Malaysia's groundwater

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Abstract. The aim of this research was to investigate the ability of nanofiltration (NF) and ultrafiltration (UF) membranes as a filtration unit for groundwater treatment for drinking water resources. Commercial membranes denoted as TS40, TFC-SR3 and GHSP were used to study the performance based on rejections and fluxes. The investigation has been conducted using natural groundwater obtained from a deep tube well with initial concentration of iron (Fe) and manganese (Mn) at 7.15 mg/L and 0.87 mg/L, respectively. Experimental results showed that NF membranes exhibited higher fluxes than UF membrane with pure water permeability at 4.68, 3.99 and 3.15 L.m⁻².h⁻¹.bar⁻¹, respectively. For metal rejection, these membranes have performed higher removal on Fe with TS40, TFC-SR3 and GHSP membranes having more than 82%, 92% and 86% respectively. Whereas, removal on Mn only achieved up to 60%, 80% and 30%, for TS40, TFC-SR3 and GHSP membranes respectively. In order to achieve drinking water standard, the membranes were efficient in removing Fe ion at 1 and 2 bar in contrast with Mn ion at 4 and 5 bar. Higher rejection of Fe and Mn were achieved when pH of feed solution was increased to more than 7 as TFC-SR3 membrane was negatively charged in basic solution. This effect could be attributed to the electrostatic effect interaction between membrane material and rejected ions. In conclusion, this study proved that NF membrane especially the TFC-SR3 membrane successfully treated local groundwater sources for public drinking water supply in line with the WHO standard.

Keywords: iron and manganese; drinking water; groundwater treatment; membrane filtration

1. Introduction

In 2013, population growth in Malaysia has been estimated to reach approximately about 29.9 million (Department of Statistics 2013). Water use in Malaysia by 2020 is estimated to increase to approximately 16 500 million liter per day (MLD) (Mohammad and Karim 2010). Nowadays,

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about 97% of raw water supply for domestic, agricultural and industrial needs are derived from surface water sources primarily rivers (Malek *et al.* 2013). The common problem of surface water as drinking water resources are easily exposure to pollution, and reduction of water level during dry season. Therefore, utilization of groundwater may help especially during water crisis due to water shortage in areas where surface water is limited.

In the northern part of Kelantan, groundwater has become the main freshwater resources for drinking water production since 1935 (SMHB 2000). High level of Fe and Mn that exceeded allowable values for potable consumption was reported as the major problem of groundwater quality in Kelantan. The World Health Organization (WHO) suggested that Fe and Mn concentrations in drinking water should be less than 0.3 and 0.1 mg/L, respectively (WHO 2008). Fe and Mn usually present in natural groundwater in their most soluble form as divalent ions, Fe(II) and Mn(II). Presence of excess amount of metal such as Fe and Mn may cause slightly reddish colored water, rusty-brown stains on laundry and bad odor or taste of beverages (Marchovecchio *et al.* 2011). In addition, their presence for long period may also cause deposits in distribution pipes, pressure tanks or heaters that may lead to high cost of maintenance either for domestic or industrial usage (Chaturvedi and Dave 2012). Metal contaminants even at low doses and in a long period may lead to kidney or liver damage, anemia, neurodegenerative and Alzheimer's disease (Merrill *et al.* 2012).

Most of water treatment plant in the northern part of Kelantan had applied the conventional method for removal of Fe and Mn in groundwater. This conventional method consists of aeration, flocculation, sedimentation, filtration and disinfection. These methods require a huge plant area, high cost of maintenance and a lot of manpower. Efforts have been taken by researchers to investigate and improve the treatment method to remove these metals such as ion exchange, oxidation-filtration, sulphide precipitation-filtration, absorption by granular activated carbon, adsorptive filtration, biosorption, pH-conditioning and ionic liquid extraction (Van Halem *et al.* 2010, Lin *et al.* 2013, Jusoh *et al.* 2005, Chaudhuri *et al.* 2008, Abdul Kadir *et al.* 2012, Bordoloi *et al.* 2013a, Hussin *et al.* 2013, Berbenni *et al.* 2000, Ma *et al.* 2010, Pacini *et al.* 2005, Sharma *et al.* 2005, Sim *et al.* 2001).

This study investigated an alternative method for groundwater treatment by NF and UF membrane to remove Fe and Mn. Membrane processes in production of drinking water have been used for softening, desalting, removal of dissolved organic and color, removal of particle and microbe (Bruggen and Vandecasteele 2003). Nanofiltration membranes are employed to remove turbidity, microorganisms, hardness and some dissolved salts (Hilal *et al.* 2004). Ultrafiltration membranes have the potential to remove microparticles and macromolecules, which generally include inorganic particles, organic colloids such as microorganisms and dissolved organic matter.

Numerous studies have been reported in investigating the ability of membrane filtration in water treatment. However, only a limited number of studies have examined the removal of Fe and Mn in groundwater by using NF membranes. Previous studies have reported that, Fe and Mn at high concentration can be removed by combination process of oxidation and microfiltration (Ellis *et al.* 2000). The removal efficiencies were improved by prechlorination with enhanced mixing during oxidation which influenced the performances of microfiltration (Lin *et al.* 2013). Prechlorination with large dosage was required for Mn removal by means of oxidation followed by ultrafiltration, while substantial Fe removal was possible even without chlorine addition (Choo *et al.* 2005). Nanofiltration employing hydrogen peroxide oxidation was capable of treating Fe and Mn from water with high organic carbon loading (Potgieter *et al.* 2004b). Removal of Mn-humic acid by NF membranes was preferable at pH higher than 10 in order to meet Mn regulatory limit

for drinking water production (De Munari and Schäfer 2010).

In conjunction with transformation towards “Integrated Water Resources Management” (IWRM) which is still in the state of inertia, efforts must be taken by researchers in Malaysia to overcome problems with water quality issue especially in water supply. Available surface water resources are depleting in many regions and states in Peninsular of Malaysia (Malek *et al.* 2013). Therefore, this study was conducted with the aim to investigate the potential of membrane filtration for groundwater treatment as alternative water resources for drinking water production. In order to study Fe and Mn removal, NF membrane (TS40 and TFC-SR3) together with UF membrane (GHSP) membrane were selected. Experiments were carried out at low applied pressures, various range of feed solution pH and various metal concentrations in feed solution.

2. Materials and methods

2.1 Membranes, chemicals and reagents

Commercially available flat sheet NF and UF membranes were employed in this study. TFC-SR3, TS40 and GHSP membranes from different manufacturers were used to identify their performances. The polyamide TFC-SR3, polypiperazine amide TS40 and thin film composite GHSP membranes were supplied by Sterlitech Corp., USA. The properties of these membranes were summarized in Table 1.

Ultra pure water with conductivity less than 1 μ S/cm was used to prepare fresh samples of synthetic groundwater with ferrous ion by using ferrous chloride tetrahydrate (FeCl₂.4H₂O, HmbG[®] Chemicals) and manganese ion by using manganese chloride tetrahydrate (MnCl₂.4H₂O, Bendosen Laboratory Chemicals). Ferrous iron reagent powder (HACH Permachem[®], USA) was used to determine the content of Fe(II) in permeate for each filtration. Manganese reagent set (HACH Permachem[®], USA) that consists of buffer powder citrate type for Mn and sodium periodate were used to detect the concentration of Mn(II) in permeate. Individual salt solutions such as sodium chloride (NaCl, Merck, Germany), sodium sulphate (Na₂SO₄, Sigma USA), and magnesium chloride (CaCl₂, Sigma USA) were freshly prepared. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) at low concentration were used in order to investigate the effect of pH adjustment. All chemicals, solvents and reagents used were analytical grade with high purity.

Table 1 Specification of commercial NF and UF membranes

Parameter	TFC-SR3	TS40	GHSP
Manufacturer	Koch	TriSep	GE Osmonics
MWCO ^a (Da)	200	200	1000
pH ^a range at 25°C	4-10	2-11	2-11
Contact angle ^b (°)	44 ± 2.5	32 ± 2.5	66 ± 2.5

^a – data provided by manufacturer

^b – data obtained from contact angle measurement at ambient temperature

MWCO – molecular weight cut off

Table 2 Physical and chemical characteristics of groundwater samples

Sample	^a KB 12	^b KB 31	^c KB 39	^d NAHRIM	^e DWQS
pH	7.2	4.2	7.3	5.5	6.5-9.0
Turbidity (NTU)	13	12	148	14	5
TDS (mg/L)	480	784	48	25	1000
Cation (mg/L)					
Ca	12	35	4.9	3.21	500
Mg	14	35	2.5	1.18	150
Na	94	100	15	7.02	200
K	11	34	3.2	1.26	-
Fe	10	90	0.3	7.15	0.3
Mn	0.2	0.8	0.4	0.87	0.1
Zn	< 0.1	< 0.1	< 0.1	0.1	3
Cd	< 0.01	< 0.01	< 0.01	< 0.01	0.003
Pb	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Cu	< 0.1	< 0.1	< 0.1	< 0.1	1.0
As	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Al	< 0.1	< 0.1	< 0.1	0.15	0.2
Anion (mg/L)					
F	< 0.5	< 0.5	< 0.5	< 0.1	0.4-0.6
Cl	235	436	15	6.6	250
SO ₄	< 5	< 5	15	3.5	250
HCO ₃	114	< 1	28	13	-
CO ₃	< 1	< 1	< 1	< 0.5	-
NO ₃	2.5	< 0.5	< 0.5	0.1	10

(Source: ^{a,b,c} Minerals and Geoscience Department of Kelantan, Malaysia (KB: well reference code);

^d Hydrogeology Research Centre, National Hydraulic Research Institute of Malaysia (NAHRIM);

^e Drinking Water Quality Standard (DWQS), Ministry of Health Malaysia)

2.2 Groundwater sampling

Along with synthetic groundwater, natural groundwater was also used throughout the experiments. Groundwater samples were collected from a deep tube well that located at the Natural Hydraulic Research Institute of Malaysia (NAHRIM) in Serdang, Selangor. This sampling location was selected because of the water quality is almost similar to groundwater in the northern part of Kelantan as presented in Table 2. The depth of this tube well is 100 m with its diameter at 0.15 m. A volume of 20 L groundwater sample was collected for experimental runs and water quality analyses. The natural groundwater was abstracted using a stand in hydrocontrol pump that connected to the well. Samples were kept in a cold room right after sampling as a standard preservation procedure. The characteristics of the natural groundwater samples which collected at NAHRIM were analyzed by ALS Technichem Laboratory as also reported in Table 2.

2.3 Membrane characterization

2.3.1 Pure water permeability

The pure water permeability of the selected TFC-SR3, TS40 and GHSP membranes was determined as the slope of a linear relationship between the applied feed pressure and permeate flux. The applied pressure was varied from 1 to 5 bar at room temperature by using nitrogen gas. Membranes were immersed in ultra-pure water and kept for overnight before compacted at 5 bar for about 30 to 45 min prior to use. The permeate flux (J , $L \cdot m^{-2} \cdot h^{-1}$) as a function of permeability (L_p , $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and applied pressure (ΔP , bar) taking the osmotic pressure difference between feed and permeate ($\Delta \pi$, bar) is given in Eq. (1).

$$J = L_p(\Delta P - \Delta \pi) \quad (1)$$

2.3.2 Contact angle measurement

The hydrophilicity of membrane surface was analyzed by contact angle measurements using a static sessile drop method by Goniometer contact angle (Ramé-Hart, Model 290, Netcong, USA) with three series of measurements at three different spots. A volume of 4 μ L droplet of deionized water was dropped on the membrane surface at ambient temperature. Then, the contact angle image was captured from the membrane surface via an optical camera connected to a computer using the DROPIimage software.

2.3.3 Membrane surface morphology

Images of the top surface and cross-sectional morphology of membranes were provided by a field emission scanning electron microscope (FESEM), Zeiss SUPRA 55VP (Oberkochen, Germany). The instrument was equipped with an Energy Dispersive X-ray (EDX) analysis system to identify components filtered by the membranes. Prior to FESEM analysis, the membranes were frozen in liquid nitrogen, broken and sputter coated with gold for better resolution.

2.4 Membrane performance measurements

2.4.1 Membrane test unit and experimental procedures

Filtration experiments were performed with a bench-scale dead-end separation unit. The setup comprises of a nitrogen gas tank, 2000 mL reservoir tank, 300 mL stainless steel stirred cell and a precision balance (Sartorius AG, Germany, Model AX6202) connected to a data acquisition personal computer. The dead-end stirred cell (Sterlitech Corporation, WA, Model HP4750) that houses a 49 mm diameter flat sheet membrane with effective area of 14.6 cm^2 . Experiments were conducted for 1 to 3 hr depending on the operational condition with minimum collection of 50 mL of permeate for analysis of Fe(II) and Mn(II) ions using spectrophotometer (HACH, Model DR3900).

Filtration experiments were performed to investigate the ability of applied membranes based on permeability, flux and rejection using ultra pure water, synthetic, and actual samples of groundwater obtained from the sampling point. A part of investigation using synthetic groundwater samples have already been described in earlier publication (Kasim and Mohammad 2013) to replicate the concentrations of Fe and Mn in natural groundwater that exist in the state of Kelantan, Malaysia. All membranes were soaked in ultra-pure water for overnight before used. This step was purposely to remove preservatives, and the soaking step also considered as a wetting process for the membrane. Then, compaction of membrane was conducted for 30 to 45 minutes by

pressurizing the stirred cell with nitrogen gas at 5 bar without stirring. After compaction, the pure water permeability test was conducted and determined by Eq. (1). For determination of flux and rejection of sample (natural and synthetic groundwater), 250 mL of feed solution was placed into the stirred cell and filtered for permeate collection.

2.4.2 Individual salt rejection

Rejection of monovalent and divalent salts, such as NaCl, Na₂SO₄ and MgCl₂ was evaluated in order to determine their rejection mechanism and estimate the charge of membranes. Rejection measurements of membranes with charged solutions provide information about selective character of the membrane and the charge of membrane will be a function of the measured rejection. The concentration of each salt was fixed at 1000 mg/L and the pressure applied was set at 5 bar. The single salt rejection test was held at room temperature with 500 rpm of stirring rate. Conductivity of salt before and after filtration test was measured to identify its rejection.

2.4.3 Iron and manganese removal performance

Performances for the removal of metallic ions namely Fe(II) and Mn(II) from natural groundwater by using the selected membranes were directly investigated via filtration tests with respect to the effects of applied pressure in the range of 1 to 5 bar. Sample of natural groundwater was kept at room temperature before used. The initial concentration of divalent Fe and Mn ions in the natural groundwater was reported at 7.15 and 0.87 mg/L, respectively. The stirring rate was constantly set at 500 rpm and conducted at ambient temperature for all experiments.

A study on the removal of these metals to investigate the effect of concentration to the performance of membranes was conducted by using synthetic groundwater samples. The fresh prepared samples with initial Fe(II) concentration (10, 100, 250, 500 and 1000 mg/L) and Mn(II) concentration (5, 100, 250, 500, 750 and 1000 mg/L) were used as single component solution. Experiments were conducted at natural pH of the prepared samples without any adjustment (5.7 to 6.8) which were initially measured before each filtration test.

Lastly, the membrane capacity for metals separation from natural groundwater was measured via experiments with regard to investigate the effect of pH at range of 3 to 9. This effect was studied to explore and validate previously reported separation performance of these metals, that had been claimed significantly improved their removal from water. In this study, the pH of samples were adjusted by adding 0.1 M HCl or 0.1 M NaOH.

Removal measurements in this study was expressed as observed rejection. The percentage of observed rejection ($R_o, \%$) of membrane for a particular component were measured as Eq. (2) with ($C_f, \text{mg/L}$) and ($C_p, \text{mg/L}$) are the component concentration in the feed and permeate, respectively.

$$R_o = \left(1 - \frac{C_p}{C_f} \right) \times 100\% \quad (2)$$

2.5 Analytical methods

Physical-chemical parameters such as conductivity, total dissolved solids (TDS), turbidity and color were also measured to investigate efficiencies of the selected membranes. Conductivity and TDS were measured using conductivity meter (Hanna Instrument HI2550), whereas turbidity and color were analyzed by turbidimeter (HA 2100AN) and spectrophotometer (HACH DR3900), respectively. All parameters were analyzed according to the APHA standard methods.

3. Results and discussions

3.1 Membrane characterization

3.1.1 Water permeability

Fig. 1 shows the pure water flux of the selected NF and UF membranes. The pure water flux for these membranes was obtained at low applied pressure. The membrane permeability, L_p of each membrane was defined as the slope of pure water flux versus pressure. From this figure, TS40 membrane was found to have the highest water permeation in comparison to other membranes with its permeability of $4.68 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. The TFC-SR3 membrane with permeability, $3.99 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ has provided higher permeation in comparison to GHSP membrane with only $3.15 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. The MWCO of GHSP membrane as reported by manufacturer is 1000 Da while both NF membranes exhibit 200 Da. Therefore, GHSP membrane could be characterized as looser membrane than the NF membranes in this study. For this reason, it was expected that the looser UF membrane contributed to higher flux than the tighter NF membranes. However, results presented in Fig. 1 showed that the GHSP membrane is less water permeable than TFC-SR3 membrane. Perhaps, results of contact angle could further explain this behaviour.

3.1.2 Contact angle measurement

The surface hydrophobicity of each selected NF and UF membrane was determined by the contact angle technique. From the sessile drop method, the contact angle of both NF membranes were determined less than 60° , implying that TFC-SR3 and TS40 were characterized as hydrophilic membranes. In comparison between these two NF membranes, it was found that TS40 membrane was characterized as more hydrophilic than TFC-SR3 membrane with average contact angle after three measurements at 32° and 44° , respectively. Whereas, the GHSP membrane proved that it is a hydrophobic membrane with contact angle has reached more than 60° as presented in Table 1. The UF membrane resulted with low permeability was found correspond to its characteristic as hydrophobic membrane based on the measured contact angle at 66° . Therefore, it is less water permeable than the NF membranes. Hydrophilic membranes are preferable in industrial application such as water treatment process (Ahmad *et al.* 2004). Therefore, NF membrane such TFC-SR3 and TS40 membrane were preferable for further investigations as they were more hydrophilic.

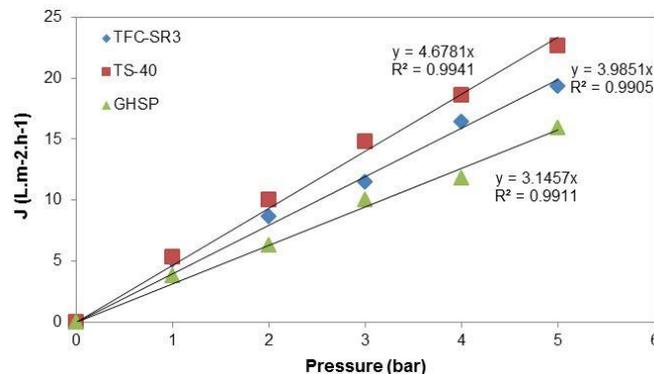


Fig. 1 Pure water flux of TFC-SR3, TS40 and GHSP membrane

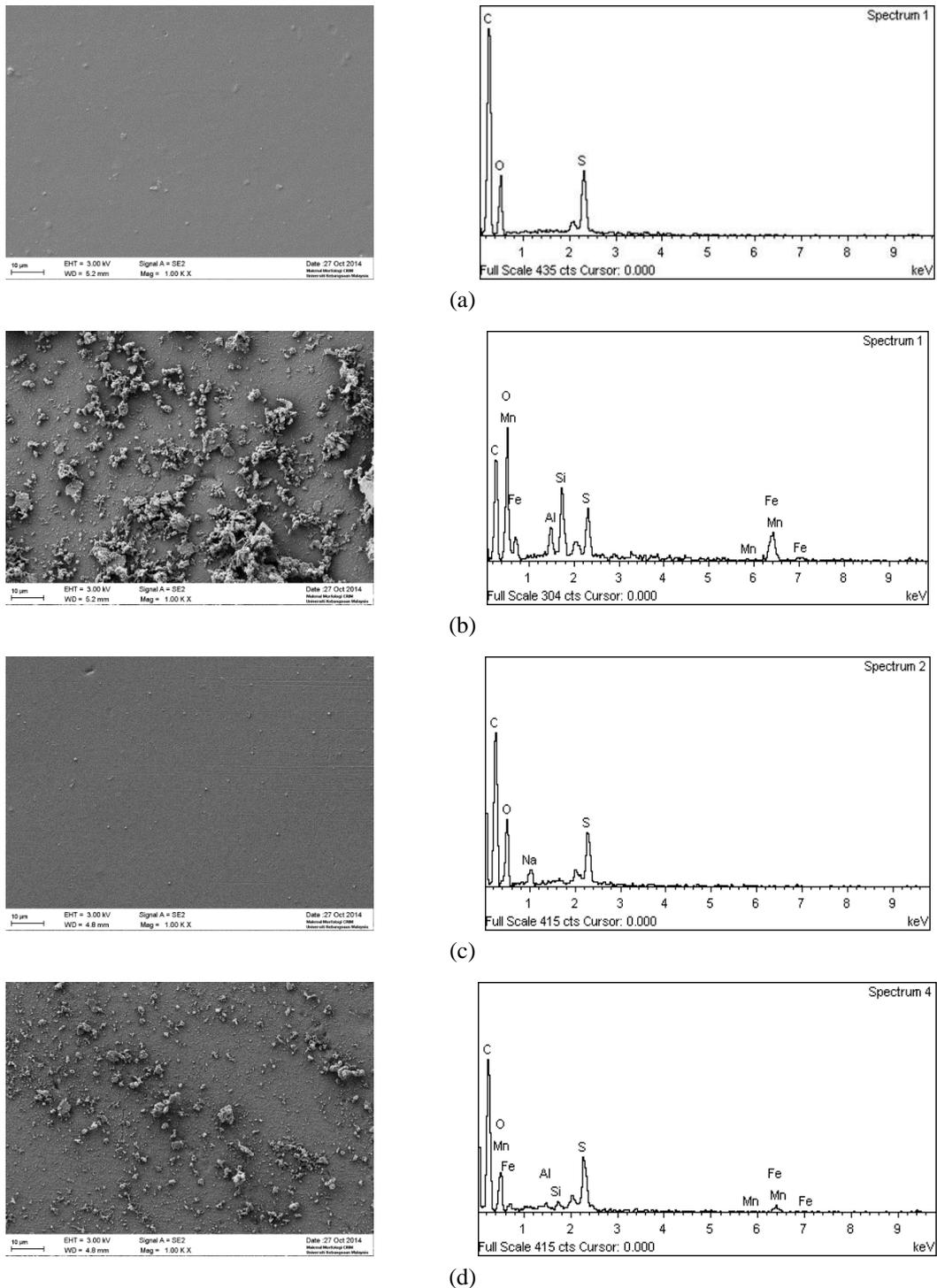


Fig. 2 FESEM coupled with Energy Dispersive X-Ray microanalysis spectra of: (a) cleaned TFC-SR3 membrane; (b) fouled TFC-SR3 membrane; (c) cleaned TS40 membrane; and (d) fouled TS40 membrane

Table 3 EDX analysis of NF membranes

Element	Clean TFC-SR3 (%)	Fouled TFC-SR3 (%)	Clean TS40 (%)	Fouled TS40 (%)
Carbon (C)	65.22	38.38	59.05	64.30
Oxygen (O)	27.58	32.73	31.58	22.19
Sodium (Na)	-	-	1.75	-
Sulphur (S)	7.21	4.81	7.61	7.52
Aluminium (Al)	-	2.27	-	0.33
Silicon (Si)	-	5.43	-	0.66
Manganese (Mn)	-	0.23	-	0.56
Iron (Fe)	-	16.16	-	4.44

3.1.3 Surface characterization using FESEM-EDX

FESEM analysis was performed to observe surface morphological of clean and fouled membranes. Representative results were presented in Fig. 2 along with the respective EDX for each case. The peak heights in the EDX spectra are proportional to the weight percentage of the elements on the membrane surface as depicted in Table 3.

Figs. 2(a) and (c) illustrated the surface morphological for clean NF membrane, TFC-SR3 and TS40. Whereas, Figs. 2(b) and (d) depicted results of FESEM-EDX for fouled membrane after natural groundwater treatment process. The percentage of iron and manganese retained on the TFC-SR3 membrane surface were higher in comparison to TS40 as presented in Table 3. The EDX analyses revealed that the presence of two major elements, iron and manganese, with iron being the predominant element on the surface of membrane.

3.2 Individual salt rejection

Fig. 3 showed rejection efficiencies of single salt system (NaCl, Na₂SO₄, and MgCl₂) at 5 bar. The influent salt concentration was 1000 ppm and performance test was conducted at ambient temperature. Results depicted that both NF membranes (TFC-SR3 and TS40) had performed with similar salt rejection sequence of R (Na₂SO₄) > R (MgCl₂) > R (NaCl). These results indicated that they were classified as amphoteric membrane in which it can be positively charged in acidic condition or negatively charged in basic environment. This type of NF membranes, neither surface charge nor size effects fully determined the separation mechanism (Peeters *et al.* 1998). According to Peeters (1998), a salt rejection such as this sequence falls into the second category of polymeric membranes whose rejection was determined by differences in diffusion coefficients between salts.

This type of NF membrane cannot be explained by Donnan exclusion only because both rejection for Na₂SO₄ and MgCl₂ are high. Rejection sequence for this case is caused by differences in diffusion coefficients between the different salts. The diffusion coefficient increases from Na₂SO₄, MgCl₂, and NaCl as shown in Table 4. The sequence of rejection is proportional to the order of their diffusion coefficients.

Result for single salt rejection measurement using GHSP showed that the sequence was R (Na₂SO₄) > R (NaCl) > R (MgCl₂). The sequence of rejection was in disagreement with diffusivity coefficient order of associate solutes. It was reported that the sequence of single salt rejection such this is typical for a negatively charged membrane. The highest rejection of Na₂SO₄ was attributed to the highest Donnan exclusion of the negative divalent ion (SO₄²⁻). It was found that similar

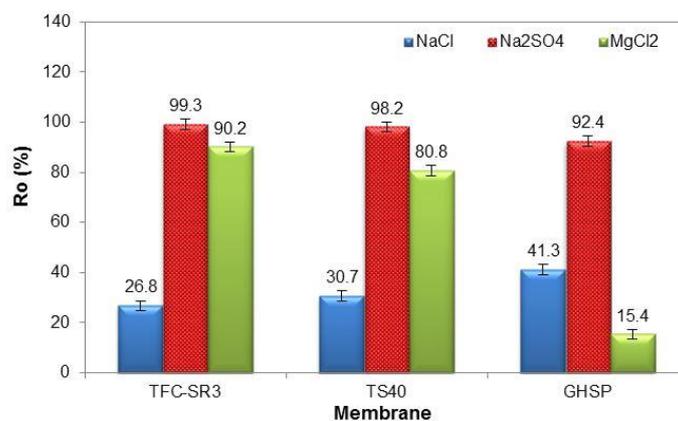


Fig. 3 Rejection of single salt at concentration of 1000 ppm and pressure of 5 bar

Table 4 Summary of solute characteristics

Species/Salt	D (10^{-9} m ² /s)	Molar weight (Da)	Ionic radius (nm)	Reference
Fe ²⁺	0.72	55.8	0.078	Buffle <i>et al.</i> 2007
Mn ²⁺	0.71	54.9	0.084	Buffle <i>et al.</i> 2007
Na ²⁺	1.33	23.0	0.098	Nguyen <i>et al.</i> 2009
Mg ²⁺	0.71	24.3	0.072	Buffle <i>et al.</i> 2007
Cl ⁻	2.03	35.5	0.167	Nguyen <i>et al.</i> 2009
SO ₄ ²⁻	1.06	96.1	0.125	Nguyen <i>et al.</i> 2009
Na ₂ SO ₄	1.23	142.0	-	Peeters <i>et al.</i> 1998
MgCl ₂	1.24	95.2	-	Peeters <i>et al.</i> 1998
NaCl	1.61	58.4	-	Peeters <i>et al.</i> 1998

sequence of the same salt rejection was in accordance with the negative charge characteristics of NF90 as reported by other scholar (Hilal *et al.* 2005). Therefore, this UF membrane is characterized as negatively charged and further analysis on the membrane surface charge by zeta potential measurement is recommended in future. In this study, relatively high rejection for monovalent NaCl salt by the UF membrane because of its membrane materials. The GHSP membrane is a thin film composite (TFC) UF membrane as reported by manufacturer. Most TFC membranes are made with a porous, highly permeable support such as polysulfone, which is coated with a cross-linked aromatic polyamide thin film and the coating provides salt rejection properties of the membrane. Result of NaCl rejection by GHSP membrane was found concurrence with typical membranes which exhibits NaCl rejection of 99%.

3.3 Iron and manganese ions removal performance

Permeate flux is one of the main factor to evaluate the performance of membranes. It reflects the amount of permeate and products collected for a specific time and is a factor that demonstrate the membrane's efficiency. In the case of producing drinking water, rejection of contaminant or

pollutant is the most counted for consideration. In order to select the best performing of membranes for groundwater treatment in Malaysia, membranes permeability and rejection capability of selected ions such Fe(II) and Mn(II) were investigated.

3.3.1 Effect of pressure

The effect of applied pressure to the removal of metal ions such Fe(II) and Mn(II) were studied at low pressure. In order to study this factor on the removal of these metallic ions by the selected membranes, retention experiments by using natural groundwater were carried out. The pH of natural groundwater was measured at 6.5 and the water quality analysis results reported that Fe(II) and Mn(II) ions in fresh samples were detected at concentration of 7.15 mg/L and 0.87 mg/L, respectively. The observed rejection of Fe(II) ions from natural groundwater by the three membranes as a function of applied pressure as depicted in Fig. 4(a). Results showed that ferrous ions rejection by these membranes were decreased as the applied pressure increased. This phenomena indicated that the increase in the applied pressure leads to an increase of water flux, but the Fe(II) transport by the selected membranes were not dominantly hindered by steric effect. The increase of pressure has caused more transport on solute to the surface of membrane which lead to increase on concentration polarisation. Thus, this condition led to a decrease in solute rejection by decreasing the charge effect on the membrane surface.

The rejection capability by TFC-SR3 membrane was found the best in comparison to TS40 and GHSP membrane with rejection rate of ferrous ions was in the range of 92 to 98%. Results also showed that the hydrophobic UF membrane, GHSP had performed better than the hydrophilic NF membrane, TS40. The TS40 membrane has the highest permeability but had achieved lower rejection in the range of 82 to 96% in comparison to GHSP with rejection of 87 to 96%. Similar trends also presented by Qin and co-researcher (Qin *et al.* 2007) whereby dyeing wastewater was treated for reuse using three types of NF membranes designated as NE-70, Desal-5 and TS40. They reported that TS40 membrane had a lower efficiency for dye removal even though its flux was the highest.

The opposite behavior was obtained for rejection of Mn(II) ions from groundwater samples as depicted in Fig. 4(b). It showed that Mn(II) ions rejection by TFC-SR3 and GHSP membrane were gradually increased with increasing of applied pressure but not for TS40 membrane which seems to slightly declined for filtration at applied pressure more than 2 bar. Similar trend as performed by TFC-SR3 and GHSP membranes was reported by Gherasim and Mikulášek (2014) with Pb(II) rejection by using AFC 80 membrane. They explained that metal rejection increases with increase of pressure due to the dilution effect, as the higher solvent flux would result in a dilution of permeate and therefore, provided higher rejection. Results in this study indicated that TFC-SR3 membrane was having the greatest Mn(II) rejection which was preferable for further investigation. The concentration of Mn(II) ions decreased with increased of flux due to the so called "dilution effect". As the applied pressure increases, permeate water flux through the membrane increases while the ion flux remains virtually unchanged, therefore resulting in lower solute concentration in permeate (Seidel *et al.* 2001).

The main aim of this treatment method is to ensure that the treated groundwater is safe as for drinking water resources. Therefore, concentration of Fe(II) and Mn (II) ions in permeate was the main priority to be considered even though high percentage of rejection was achieved by the selected membranes. In order to reach the allowable limits for Fe in drinking water that set by WHO, it is a compulsory to make sure that the concentration of Fe in permeate should be lower than 0.3 mg/L. The Fe(II) ion concentrations in permeate after filtration using NF and UF membranes were increased as the applied pressure increased as depicted in Fig. 4(c). Results

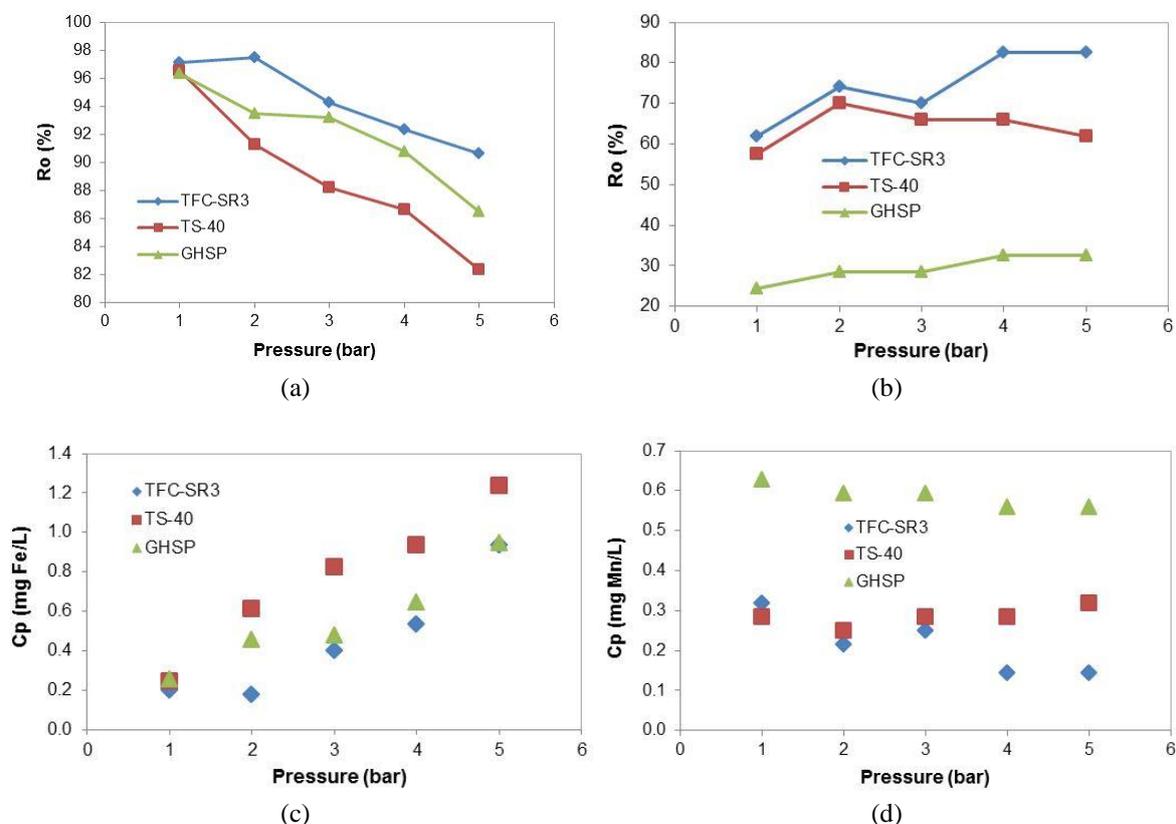


Fig. 4 Rejection of (a) Fe(II) and (b) Mn(II) ions from natural groundwater by the selected NF and UF membranes at pH6.5 together with permeate concentration of (c) Fe(II) and (d) Mn(II) ions detected after treatment

showed that permeate concentration of Fe(II) ions by TFC-SR3 and GHSP were almost identical for every applied pressure except at 2 bar. These results indicated that rejection of Fe(II) ions by TFC-SR3 membrane was preferable at low pressure of 2 bar in order to reach the drinking water standard.

Rejection of Mn(II) ions from natural groundwater using these membranes showed an opposite behaviour in comparison to ferrous rejection. Results in Fig. 4(d) showed that Mn(II) ion concentration in permeate were gradually decreased with increasing of applied pressure for filtration using TFC-SR3 and GHSP membrane. However, the measured Mn(II) ion concentration from permeate by filtration using TS40 were almost unchanged at all applied pressures. In order to reach the drinking water standard for Mn which is 0.1 mg/L, filtration using TFC-SR3 membrane at 4 and 5 bar was preferable since the C_p values were almost achieving the allowable value.

Therefore, results in Figs. 4(a) and (b) showed that rejections of divalent ions such as Fe(II) and Mn(II) were higher for TFC-SR3 membrane which was in good agreement with salt rejection study as given in Fig. 3. These phenomena probably indicated by the concentration of permeate for both metals that depend on the applied pressure. The applied pressure was significantly influenced the Fe rejection but not for Mn rejection especially while using the GHSP membrane. The increase

of pressure leads to a strong increase in permeate flux but decrease of Fe rejection indicating that it could be due to increase of solvent permeability at higher pressure compared to the solute permeability.

3.3.2 Effect of pH

Further studies were conducted to investigate the influence of pH on the performance of membrane. For this case, TFC-SR3 membrane was selected based on its good rejection rates and moderate permeability. Fig. 5(a) presented the rejection of Fe(II) ions from natural groundwater with adjustment of pH in the range of 3 to 9 with addition of HCl or NaOH. Results showed that rejection of Fe(II) ions were more than 90% for feed solution at pH 5, 7 and 9. At these pH range, the concentration of Fe(II) ions detected in permeate were well below than the acceptable limit for drinking water standard set by WHO. At pH 5, 7 and 9, the permeate concentration were 0.27, 0.18 and 0.11 mg Fe/L respectively. These results indicated that rejection rates were improved with increasing pH to 9. Whereas for pH 3, poor rejection rate of Fe(II) ions at nearly 70% with permeate concentration at 2.3 mg Fe/L. The soluble divalent ions were slowly oxidized to become insoluble and stable ions of Fe(III) by increasing the pH of feed solution. Precipitation of Fe(OH)₃ was due to the feed solution having bigger size of particles formed once the pH increased. Therefore, size exclusion was expected to become the domain rejection mechanism that has been significantly influenced by the feed pH adjustment.

Thus, pH has importantly impacted Fe removal as also reported by Bordoloi and co-workers (Bordoloi *et al.* 2013a). They found that the Fe removal is significantly improved with the adjustment of pH conditioners. In addition, Al-Rashdi and friends (Al-Rashdi *et al.* 2013) in their study on removal of heavy metals by NF membranes discovered that the feed pH may change the nature of membrane surface charge and pore size, as well as that of dissolved metal species and therefore can affected the membrane separation efficiency.

Similar phenomenon has been observed for the removal of Mn(II) ions. However, it was found that Fe(II) is more easily and rapidly oxidized than Mn(II). Fig. 5(b) showed that rejection was the best at pH 7 which resulted 96% with detected permeate concentration at 0.04 mg Mn/L. The achieved value was well below than the toxicity level of Mn. This result was agreed well with De Munari and Schäfer (2010) study in which TFC-SR3 membrane has achieved more than 95% of rejection at pH 7. At pH 5 and 9, the rejection rates were 79 and 84% while the C_p value of Mn(II) were 0.22 and 0.28 mg Mn/L, respectively. Poor rejection at only 38% also resulted at pH 3 with C_p value at 0.65 mg Mn/L. Rejection of Mn(II) ions at pH 3, 5 and 9 were above the limit of 0.1 mg Mn/L and thus, unsafe for drinking water resources. Kabsch-Korbutowicz and Winnicki (1996) have mentioned in their studies that Mn occurs in the dominant form at pH 6.6. The retention of Mn compounds by the sulfonated polysulfonated UF membrane was not very high in comparison to the retention of iron. This effect should be attributed solely to the electrostatic effect interaction between membrane material and Mn(II) ions.

Figs. 5(a) and (b) showed that TFC-SR3 membrane has performed higher rejection rate for Fe(II) in comparison to Mn(II) ions. Similar findings were also presented by Jusoh and colleague (2005) as they related this phenomenon with adsorbing characteristic in terms of electronegativity and ionic radius. The electronegativity of Fe(II) is higher than Mn(II) and higher electronegativity corresponded to higher adsorption levels of metal ions onto the negative charge at granular activated carbon surface. De Munari and co-researchers (De Munari *et al.* 2013) reported that TFC-SR3 membrane is amphoteric and it is positively charged at acidic pH while negatively charged at basic pH. Therefore, results from this study proved that it was expected that rejection of

Fe(II) ions increased as increasing of feed solution pH. The good rejection at this condition was also contributed by the solute-membrane charge interactions. At higher pH, TFC-SR3 membrane was negatively charged and therefore, higher electronegativity of Fe(II) ions contributed to higher retention on the membrane surface if compared to Mn(II) ions. The charge of solute influence the extent of retention by NF membranes though the precise mechanism of retention will depend upon the particular membrane in use (Waite 2005).

The solution pH is very important factor in which it may also affected the pore size (or pore volume) of membrane in use. The adjustment of pH on feed solution possibly may cause expansion or shrinkage of membrane pore size. In this study, results presented in Fig. 6 indicated that permeate flux of feed solution increased as the pH increased from 3 to 9. This result showed that the pore size of TFC-SR3 membrane could probably expanded as the solution pH increased. It has been explained in previous section that this membrane is negatively charged at higher solution pH and the isoelectric point (IEP) of the same membrane is in the range of 6 to 8 as reported by De Munari and friends (De Munari *et al.* 2013). The expansion of membrane pore size determines the increase of flux. However, the increase rejections of both metallic ions determines by both sieving and electrostatic interactions of solute-membrane. Childress and Elimelech (2000) reported that ionic species rejection is directly related to membrane pore charge and is attributed to co-ion

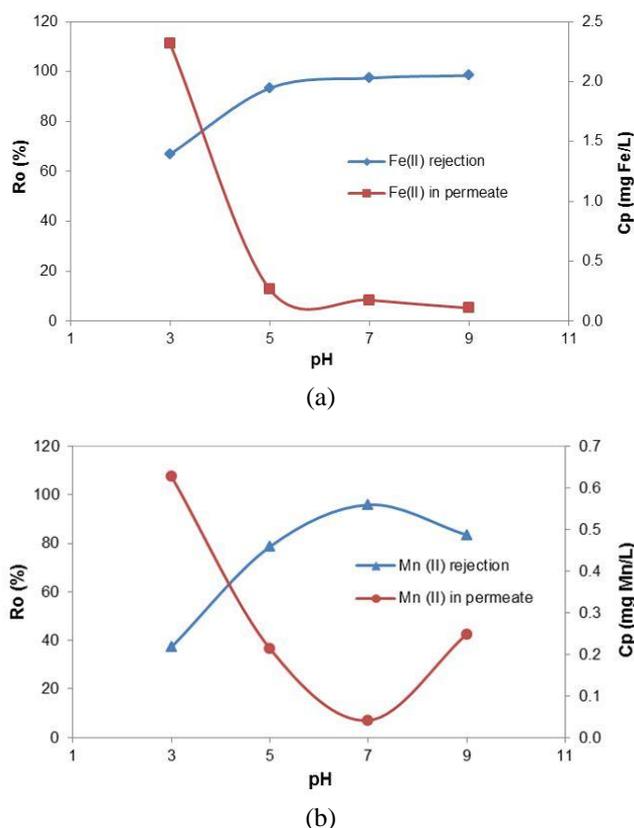


Fig. 5 Rejection at applied pressure of 2 bar and permeate concentration of (a) Fe(II) ions; and (b) Mn(II) ions by using TFC-SR3 with initial concentration of 7.15 mg Fe/L and 0.87 mg Mn/L in feed solution of natural groundwater

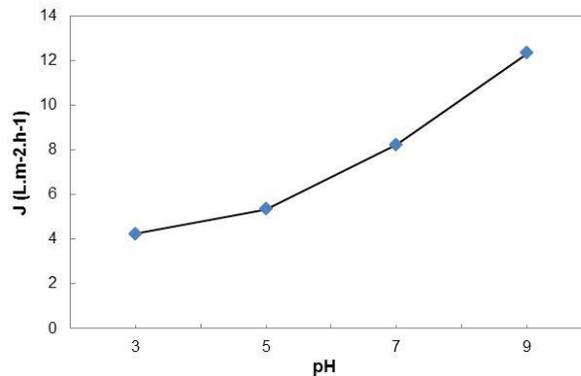


Fig. 6 Permeate flux of natural groundwater as feed solution for treatment using TFC-SR3 membrane as a function of pH at pressure of 2 bar

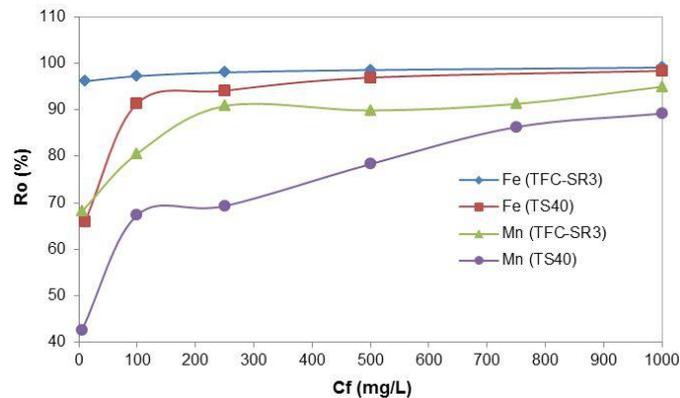


Fig. 7 Rejection of Fe and Mn by using NF membranes at various concentration of feed solution

electrostatic repulsion (exclusion). Therefore, the charge of membrane is significant to the membrane performance (solute rejection and permeate flux) because it may affect the electrostatic repulsion between the ionic species and the membrane surface.

3.3.3 Effect of concentration

The Department of Mineral and Geoscience, Malaysia has reported that natural concentrations of Fe(II) in groundwater sources were typically range from 0.7 to 94 mg/L, with an average concentration of 15.6 mg/L. Whereas, manganese occurs in lower concentration by the range from less than 0.1 to 2.7 mg/L, with an average concentration of 0.43 mg/L. In order to determine the effectiveness of using the selected membranes for treating groundwater with higher concentration range of heavy metals, therefore synthetic water at various concentrations of Fe(II) and Mn(II) were prepared. The effect of initial feed concentration on the rejection of these metallic ions as presented in Fig. 7. Filtration experiments were conducted at applied pressure of 5 bar, room temperature and stirring rate of 500 rpm. This comparative study was conducted by using both NF membranes with initial feed concentration of Fe(II) and Mn(II) were from 10 to 1000 mg/L and 5 to 1000 mg/L, respectively.

Table 5 Comparative assessments of Fe and Mn removal by membrane technology and other available methods

Feed water	Source of water	Process	Pretreatment	Fe and Mn removal (%)	Reference
Membrane technology treatment method					
Fe and Mn	Synthetic and Natural GW	NF UF	None	Fe: 92-99 Mn: 68-94	Present study
Fe and Mn	Synthetic	MF	Mixing-enhanced preoxidation	80-90	Lin <i>et al.</i> 2013
Mn with HA	Synthetic	NF	pH conditioning electrolyte sol. NaHCO ₃	45-90	De Munari and Schäfer 2010
Fe and Mn with NOM	Dam water spiked with MnCl ₂ and FeCl ₂	UF	Chlorination: 3 mg Cl ₂ /L	Fe: 70 Mn: 31	Choo <i>et al.</i> 2005
Fe and Mn	River water loaded with HA	NF	H ₂ O ₂ Oxidation-FeCl ₃ Coagulation	Fe: 95 Mn: 47	Potgieter <i>et al.</i> 2004a
Mn	Synthetic	RO NF	None	99 80	Molinari <i>et al.</i> 2001
Mn	Synthetic	MF	AOP Mn sand self-catalytic oxidization	95	Teng <i>et al.</i> 2001
Fe and Mn	Synthetic and Natural GW	MF	Oxidation - KMnO ₄	96	Ellis <i>et al.</i> 2000
Fe and Mn with HA	Synthetic	UF	None	Fe: 95 Mn: 45	Karbsc-Korbutowicz and Winnicki 1996
Other treatment method (Malaysia's case study)					
Fe	Synthetic	Ionic liquid extraction	None	< 95	Husin <i>et al.</i> 2013
Fe and Mn	Natural GW	Biosorption (Rosa Centifolia)	None	< 95	Adul Kadir <i>et al.</i> 2012
Fe	Synthetic Natural GW	Sulfide precipitation	Anaerobic process with H ₂ S	83	Jusoh <i>et al.</i> 2011
Fe	Natural GW	Coal and carbonaceous shale filtration	None	80-90	Chaudhuri <i>et al.</i> 2008
Fe and Mn	Synthetic	Granular activated carbon	None	Fe: 80 Mn: 45	Jusoh <i>et al.</i> 2005

(GW – groundwater, HA – humic acid, NOM – non organic matter, AOP – advanced oxidize processes)

Results showed that rejection of Fe(II) and Mn(II) ions were increased with increasing initial feed concentrations. Very high observed rejection of Fe(II) values from 96 to 99% were obtained by using the less hydrophilic TFC-SR3 membrane, indicating that the membrane has very good

separation properties. Whereas for the more hydrophilic TS40 membrane, Fe(II) rejection increased from 66 to 98%. These results confirmed that the presence of Fe(II) ions in synthetic groundwater even at high concentration was effectively rejected by both NF membranes. The same behavior of TFC-SR3 membrane was observed by other scholar, (De Munari *et al.* 2013).

It was observed that a similar trend also depicted for Mn(II) removal from synthetic groundwater. Rejection of Mn(II) using TFC-SR3 was from 68 to 94% and 42 to 89% by using TS40. It was clearly determined that the less hydrophilic TFC-SR3 membrane has potentially rejected both metallic ions. However, it should be noted that the metal concentration in permeate was not always below than the acceptable limit for drinking water standard. Therefore, further investigation by other operating conditions was suggested to optimize the performance of both membranes in the production of drinking water. In this study, the findings on Fe and Mn rejection percentage revealed that the selected TFC-SR3 membrane has outstanding performance in comparison to other commercial membranes or other treatment methods, as shown in Table 5.

Steric (sieving) and electrical (Donnan) effects are separation mechanism that both normally involved by NF membranes (Mohammad *et al.* 2004). It is effectively able to reject multivalent ions and allow the monovalent ions pass through. For this study, both metallic ions were proportionally rejected with increasing metal concentration in the aqueous solution. Thus, by considering only the corresponding charge effects, both metallic ions rejection were expected to increase with increasing feed concentration.

4. Conclusions

The performance of membrane filtration using NF (TFC-SR3 and TS40) and UF (GHSP) membranes in treating Malaysia's groundwater were identified and evaluated in this study. The efficiencies of these membranes were assessed based on their permeability and rejection capabilities at low applied pressures, various range of feed solution pH and various metal concentrations in feed solution. The rejection rates for metal component (Fe and Mn) using these membranes were significantly influenced by the operating conditions. Particularly, rejections of both metals by TFC-SR3 membrane were higher than TS40 and GHSP membrane for all investigated operating conditions. In addition, results proved that TFC-SR3 membrane has efficiently rejected Fe(II) and Mn(II) ions to the allowable value for drinking water based on WHO standards.

The contribution of solute-membrane charge interactions was evaluated by investigation on the influence of feed solution pH. It was observed that an increase of pH determined a higher efficiency of Fe and Mn rejections by TFC-SR3 membrane. Higher pH of the feed solution contributed to transformation of the soluble divalent ferrous(II) and manganese(II) ions to insoluble ferric(III) and manganic(IV) ions which easily precipitated and rejected by the membranes. In conclusion, all findings in this study contributed to possibility of developing the membrane technology for Malaysia's groundwater treatment for drinking water resources .

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