Effect of Operating Variables in Ionic Solutes Removal from Groundwater by Nanofiltration Membranes

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Abstract. The presence of heavy metals in groundwater is a persistent problem in many parts of the world. Membrane technology could be considered as an alternative technology for heavy metals removal from water. Iron and manganese naturally occur in groundwater. These metallic ions at excessive amount, contribute to rusty taste with reddish color that is unsuitable for drinking or daily usage. In this study, rejection of heavy metals (iron (Fe) and manganese (Mn)) by two commercially available nanofiltration membranes, TS-40 and TFC-SR3 were investigated. Low applied pressure and adjustment on feed pH have influenced the metallic ions rejection mechanism. Experimental results showed that rejection of both metals by using TFC-SR3 was much higher than TS-40 membrane. An increase of applied pressure has decreased Fe rejection for TFC-SR3 (99-94%) and TS-40 (86-69%) due to solvent permeability. A similar decreasing trend was also observed for Mn rejection by TFC-SR3 (92-75%) and TS-40 (75-65%). In the aim to achieve drinking water standard, feed pH was adjusted in the range of 3 to 9. Rejection of both metals was improved. At pH 9, permeate concentration (C_p) has reached the drinking water standard for TFC-SR3 (0.07 mg Fe/L and 0.04 mg Mn/L) and TS-40 (0.14 mg Fe/L and 0.18 mg Mn/L). The pH adjustment has significantly influenced membrane performance due to solute-membrane interaction. As for conclusion, all findings proved that nanofiltration is a promising method for groundwater treatment in drinking water production.

INTRODUCTION

Heavy metals in water are always being the main concern especially if regarding on drinking water resources. This is because they are extremely dangerous to human health, wildlife and for the environment based on their toxicity, non-biodegradability and tendency to accumulate in living organisms. Along with surface water, groundwater resources play a vital role in the production of clean and adequate drinking water supply all around the world. Iron (Fe) and manganese (Mn) are common metallic elements that occurs together naturally especially in deeper wells (Ahmad, 2016). Presence of excess amount Fe and Mn result in metallic taste of water, slightly reddish colored water and rusty-brown stains of different products like paper, cloths, and plastics (Cai et al. 2021). The World Health Organization (WHO) suggested that Fe and Mn concentrations in drinking water should be less than 0.3 mg/L 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). In soluble form they are colorless in groundwater but when exposed to air, they get oxidized then turn to insoluble form of Fe(III) and Mn(IV), respectively and leave the water with brown-red color. Several techniques have been applied to remove these metals from groundwater including ion-exchange and water softening, absorption by activated carbon, aeration and filtration, biosorption and ionic liquid extraction (Chaturvedi and Dave 2012, Jusoh et al. 2015, Kadir et al. 2012, Hussin et al. 2013). Recently, membrane technology including nanofiltration (NF) has been increased rapidly in water treatment for producing drinking water resources. NF technology able to overcome operational problems that used to associate with conventional technique. In addition, other advantages of NF are high rejection of divalent ions at lower operating pressure and higher flux with lower energy consumption.

Numerous studies have been reported in investigating the ability of membrane filtration in water treatment (Ezugbe et al. 2020, Lin et al. 2013). However, only a limited number of studies have examined the removal of Fe and Mn in groundwater by using NF membranes (De Munari and Schäfer 2010). Therefore, this study was conducted with the aim to investigate the influence of operating variables on the rejection of Fe and Mn in groundwater by using NF membranes. In this work, Fe and Mn removal were investigated using TS-40 and TFC-SR3. The effect of the following factors on separation was studied: applied pressure (1-5 bar) and feed pH (3-9). Separation efficiency of membranes were also studied based on rejection of color, turbidity, total dissolved solids and conductivity which further explained according to surface morphology images measured by field emission scanning electron microscopy (FESEM).

MATERIALS AND METHODS

Feedwater and Chemicals

Synthetic groundwater samples in this studies were prepared based on the quality of water sources from monitoring wells that abstracted in the north part of Kelantan, Malaysia. The key water quality characteristics are as given in Table 1. Ultra pure water with conductivity less than 1µS/cm was used to prepare samples of synthetic groundwater with Fe by using ferrous chloride tetrahydrate, $FeCl_2.4H_2O$ (HmbG® Chemicals) and Mn by using manganous chloride tetrahydrate, $MnCl_2.4H_2O$ (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. All chemicals, solvents and reagents used were of analytical grade with high purity.

TABLE 1 Physical and chemical characteristics of groundwater samples and treated water

Sample	^{a}**KB 12**	^{b}**KB 31**	^{c}**KB 39**	^{d}**Legal**
pH	7.2	4.2	7.3	6.5-9.0
Turbidity (NTU)	13	12	148	5
TDS (mg/L)	480	784	48	1000
Cation (mg/L)				
Fe	10	90	24	0.3
Mn	0.2	0.8	0.4	0.1

(*Source*: ^{a,b,c} Minerals and Geoscience Department of Kelantan, Malaysia; ^{d} Drinking Water Quality Standard, Ministry of Health Malaysia)

Membrane Characterization

Two types of commercially available flat sheet NF membranes were employed in this study. Both membranes, TFC-SR3 and TS-40 were supplied by Sterlitech Corp., USA. The polyamide and polypiperazine amide membranes, respectively had a molecular weight cut-off (MWCO) of 200 Da. The membranes characteristics are summarized in Table 2. 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 measurement at three different spots. Images of the top surface morphology of membranes were provided by Zeiss SUPRA 55VP FESEM (Oberkochen, Germany). The instrument was equipped with an energy dispersive X-ray (EDX) analysis system to identify components filtered by the membranes. The membrane pure water permeability, L_p was determined by measuring at operating pressure range of 1 to 5 bar using ultra-pure water at room temperature. Membranes were immersed in ultra-pure water and kept for overnight before compacted at 5 bar for 30 min prior to use.

TABLE 2 Specification of NF membranes

Parameter	TFC-SR3	TS-40
Manufacturer^{a}	Koch	TriSep
pH range at 25°C^{a}	4-10	2-11
Standard pressure^{a} (bar)	NR	2-14
Contact angle^{b} (°)	46	32
Rejection NaCl^{b} (%)	28-35	34-42

NR – not reported

[a] Information obtained from manufacturer
[b] Value obtained from experimental measurement

Membrane Performance Measurements

Filtration experiments were performed to investigate the ability of NF membranes based on permeability, flux and rejection using ultra pure water and samples of synthetic groundwater. The performance of membranes were tested using a bench-scale stirred cell separation unit. The setup comprises of a nitrogen gas tank, 2000 mL reservoir tank, 300 mL stainless steel stirred cell and a precision balance (Sartorious AG, Germany, Model AX6202) connected to a data acquisition personal computer. The stirred cell (Sterlitech Corporation, WA, Model HP4750) that houses a 49 mm diameter flat membrane sheet with an effective area of 14.6 cm^2.

All membranes were soaked in ultra-pure water for overnight before used in order to remove preservatives, and the soaking step also considered as a wetting process for the membrane. Then, compaction of membrane was conducted for 30 min 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 measuring the slope of a linear plot of pure water flux against applied pressures. For determination of flux and rejection of sample, 200 mL of feed solution was placed into the stirred cell and filtered for permeate collection with minimum ammount of 50 mL for further analyses.The applied pressure for filtration tests were ranged from 1 to 5 bar. The pH of feed solution was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH) in the range of 3 to 9. The stirring rate was fixed at 500 rpm for all experiments. The initial feed concentration of both metals was fixed and tested as referred to the natural groundwater that exists in the east part of Peninsular Malaysia.

Sample Analysis

The collected permeate after separation process was checked for water quality analysis in identifying the best operating variables to meet the drinking water standards. Physical-chemical parameters such as pH, conductivity, total dissolved solids (TDS), turbidity and color were also measured to investigate efficiencies of membranes. Conductivity, pH and TDS were measured using Hanna Instrument HI2550, whereas turbidity were analyzed by using Turbidimeter (HA 2100AN). Color, Fe and Mn in permeate were detected by using Spectrophotometer (HACH, Model DR3900). All parameters were analyzed according to the APHA standard methods.

RESULTS AND DISCUSSIONS

Properties of Membranes

The properties of NF membranes with respect to contact angle and pure water flux are as shown in Table 3. Results show that pure water permeability was found to be governed mainly by the membrane hydrophilicity. As reported by the manufacturer, both membranes have the same pore sizes. However, TS-40 membrane exhibited higher water flux mainly because of its loose membrane structure that offers minimum transport resistance for water molecules to permeate. This behaviour was proved by its contact angle at 46°. This phenomenon can be explained by the fact that TS-40 which is made of piperazine (PIP) monomer is superhydrophilic (i.e. low contact angle value). Thus, showing very high affinity for water during filtration process and as a result, higher water flux is experienced. In contrast with TFC-SR3 membrane, its water flux was reported to be relatively lower when tested at the same condition. In conjunction with results from contact angle measurement at 32°, this proved that it is less hydrophilic than TS-40 membrane. Figure 1 shows the purewater flux as a function of applied pressure which provided permeability for both NF membranes. Thus, contact angle and pure water flux results supported the fact that TFC-SR3 membrane provides lower permeability than the TS-40 membrane.

TABLE 3 Properties of NF membranes

Membrane	MWCO (Da)	Pure water flux[a] (L/m^2.h)	Mean contact angle (°)
TFC-SR3	200	13.90 (±2.5)	32 (±3.6)
TS-40	200	23.40 (±2.5)	46 (±3.7)

MWCO – molecular weight cut-off
[a] measured at applied pressure of 5 bar and room temperature

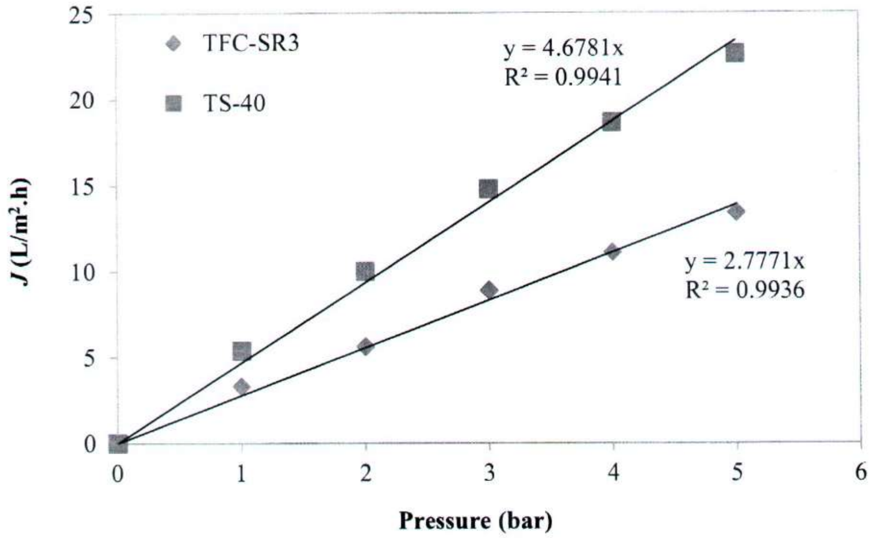


FIGURE 1 Pure water flux as a function of pressure

Influence of Applied Pressures

Permeate Flux

In order to investigate this effect to the NF membranes performance, filtration of synthetic groundwater consists of single salt of ferrous chloride ($FeCl_2$) and manganous chloride ($MnCl_2$) were tested at low applied pressure and at room temperature. The feed concentration of synthetic groundwater were fixed at 10 mg Fe/L and 1 mg Mn/L, respectively. Figure 2 shows the fluxes of NF membranes as a function of pressure tested by using samples of synthetic groundwater. Results show that with both metals, the permeate flux increased with increasing pressure using both TFC-SR3 and TS-40. The increase of applied pressure leads to strong increase in permeate flux (Kasim and Mohammad 2013). As pressure increases, convective transport and concentration polarization become more important (Mehiguene et al., 1999, Jose et al., 2018). Figure 2(a) for Fe removal reveal that changes in the permate fluxes remain linear while increasing pressure, which indicate that insignificant of concentration polarization. A similar observation was made for Mn as depicted in Figure 2(b). The permeate fluxes for Fe and Mn using TS-40 were higher than TFC-SR3 at this operating condition. All these permeate flux results were as expected and thus, indicated that TS-40 is a higher wettability membrane than TFC-SR3.

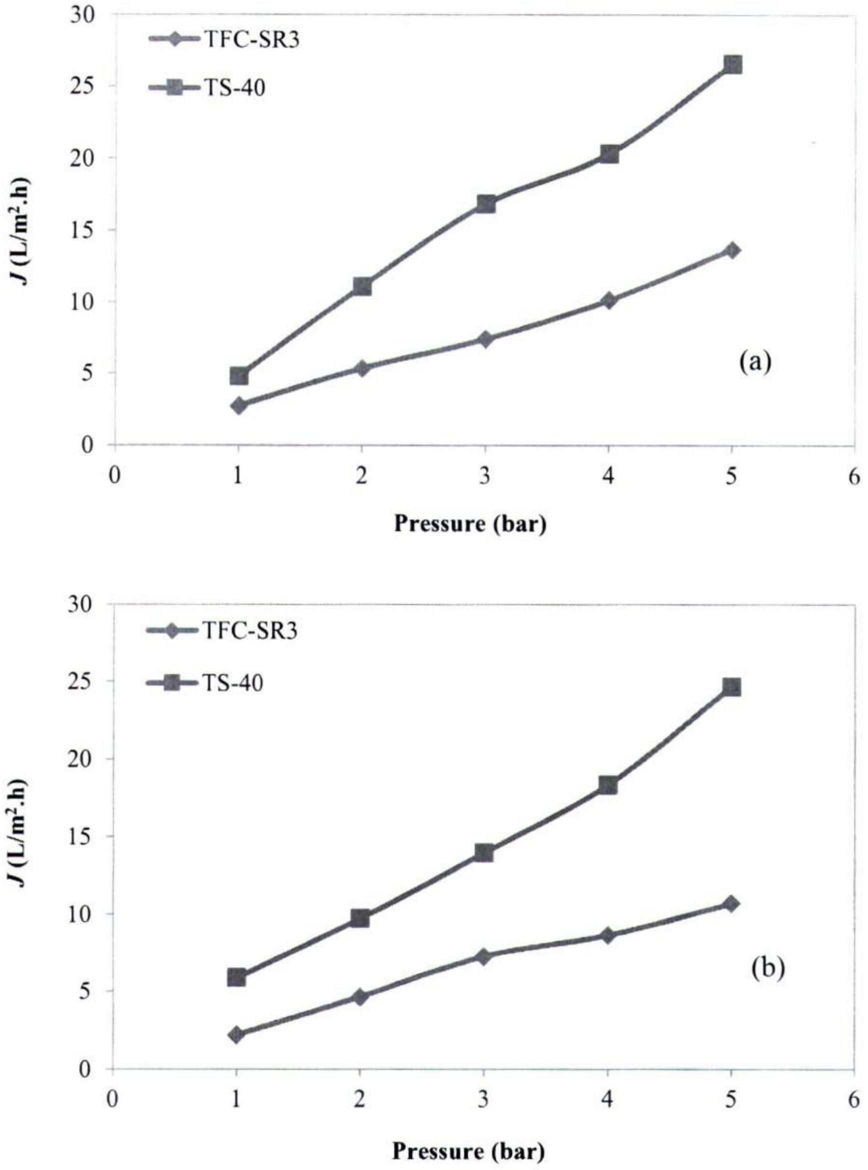


FIGURE 2 Effect of applied pressure on permeate flux of TFC-SR3 and TS-40 membrane with (a) Fe(II) and (b) Mn(II) at feed concentration 10 mg Fe/L and 1 mg Mn/L, pH 6.5±0.4 and at room temperature.

Rejection

The effect of applied pressure to the removal of selected metal ions such Fe^{2+} and Mn^{2+} are important to identify the optimum conditions for an effective removal of these parameters from groundwater. Results depicted in Figure 3 shows that rejection of Fe^{2+} and Mn^{2+} ions from synthetic groundwater were decreased with increasing of applied pressures. Rejection of both metals ions were pereferable by using TFC-SR3 in comparison to TS-40. This is may be because of tight membrane structure of TFC-SR3 which resulted with good rejection on both targeted metallic ions in the synthetic water.

Concentration polarisation, which increased with increasing pressure, results with decrease in rejection (Al-Rashdi et al. 2013). However, convective transport causes an increase in rejection. Figure 3(a) reveals that Fe has concentration polarisation effect on TFC-SR3 membrane due to rejection to this metal were decreased from 99% to 94% as the applied pressure increased. As for TS-40 membrane, rejection of Fe at 1 bar was 83% and then increased to 86% at 2 bar however dropped to 69% by operation at 5 bar. These behaviors confirmed that Fe has convective transport effect on TS-40 membrane then followed by concentration polarisation. Similar trends and mechanism of rejection had occured for Mn as presented in Figure 3(b). In comparison to Fe by using TFC-SR3, Mn rejection were slightly lower and decreased from 92% to 75%. Whereas, for TS-40 had dropped from 86% to 65%. The reason for higher Fe removal and lower Mn removal might be credited to the ionic radius of cations Fe^{2+} and Mn^{2+} are 75 and 81, respectively. Ions with lower ionic radius tend to hold their hydration shell and therefore would more removed by membranes (Tansel, 2012). In addition, with looser NF membrane such TS-40, size exclusion probably is the main mechanism to explain metallic ions rejection.

For this condition, Fe rejection should be more than 97% in order to reach the allowable limits set by WHO for drinking water. Thus, applied pressure at 2 bar is preferable for Fe rejection at natural pH of prepared synthetic water which is 6.5±0.5. This is due to the measured permeate concentration was well below than the allowable value. As for Mn, preferable rejection rate should be 90% for acceptable limit of drinking water standard. Therefore, applied pressure at 2 bar is also recommended for Mn rejection at natural pH of groundwater.

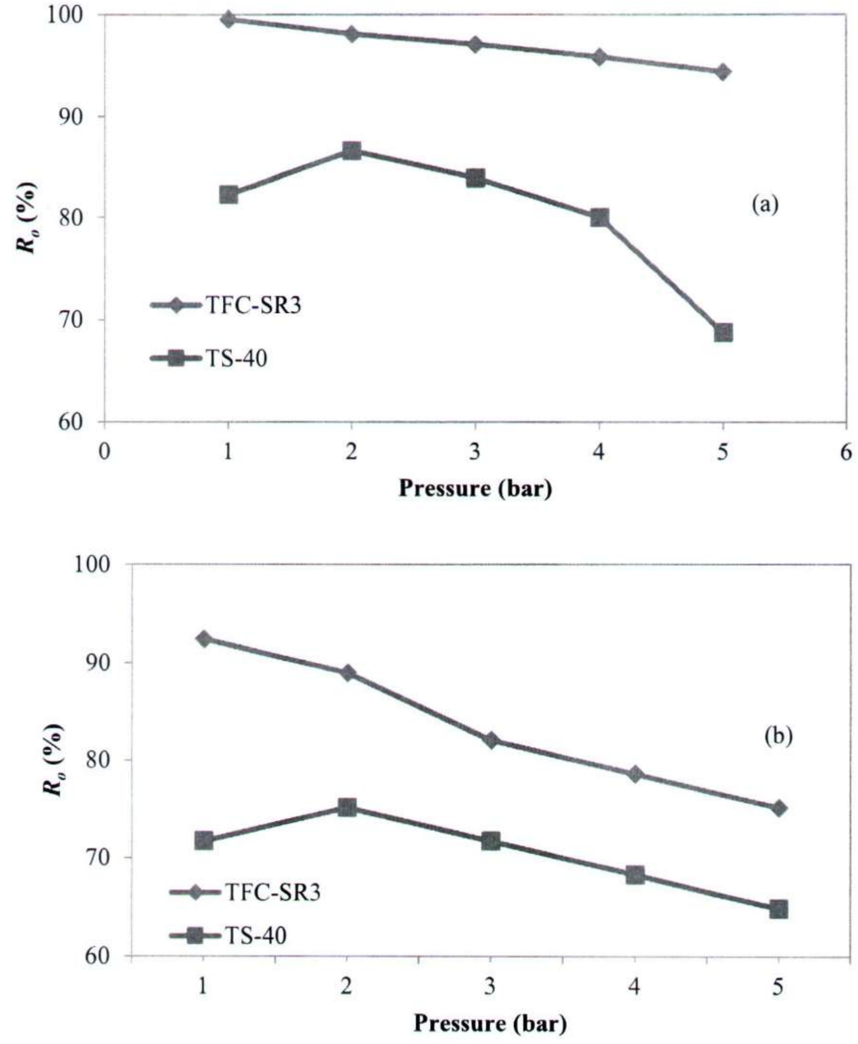


FIGURE 3 Effect of applied pressure on rejection of (a) Fe(II) and (b) Mn(II) using NF membranes with feed concentration 10 mg Fe/L and 1 mg Mn/L, pH 6.5±0.5 and at room temperature.

Influence of feed pH on TFC-SR3 membrane performance

Permeate Concentration

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 due to its property as tight NF membrane. Figure 4 presents the permeate concentration measured after filtration with feed solution with adjustment of pH in the range of 3 to 9 by adding HCl or NaOH. Results show that at these pH range, the concentration of metal ions detected in permeate decreased with increasing pH. For Fe removal at pH 7 and 9, permeate concentration measured were well below the acceptable limit for drinking water standard set by WHO which were 0.20 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 with permeate concentration at 2.3 mg Fe/L was detected. Thus, results proved that pH has importantly impacted Fe removal as also reported by other scholar (Nagandran et al. 2020, Bordoloi et al. 2013). The feed pH may change the nature of the membrane surface charge and pore size, as well as that of dissolved metal species and therefore can affect the membrane separation efficiency (Al-Rashdi et al. 2013). Between pH 3 and 7, almost all Fe is present as soluble Fe^{2+}. Higher than pH 8, Fe is predominantly present as insoluble Fe^{3+} and easily precipitate as $Fe(OH)_3$ on the surface of membrane. Therefore, Fe removal at this point were mainly by size exclusion.

For Mn removal, highest rejection occured at pH 9 with detected permeate concentration at 0.18 mg Mn/L. The achieved value at this point was nearly the allowable limit for Mn in drinking water standard and perhaps can be improved at higher pH. The occurence and behavior of Mn is not similar to Fe. Fe^{2+} is easily and rapidly oxidized than Mn^{2+}. At higher than pH 9, Mn is slowly exist as stable Mn^{4+} and insoluble as MnO_2 then precipitate on the surface of membrane. At this point, Mn removal could be attributed solely by size exclusion. Between pH 3 and 7, Mn exist as soluble Mn^{2+} and thus, easily permeate and pass through membrane pores. As a result, poor rejection occured especially at pH 3 with high value of permeate concentration at 0.83 mg Mn/L was detected. In acidic feed solution, membrane pores could be expand. At this point, TFC-SR3 was reported to be positively charged. Low rejection at pH 3 explained that solute-membrane interaction is the main mechanism and dominated by the nature of membrane pores.

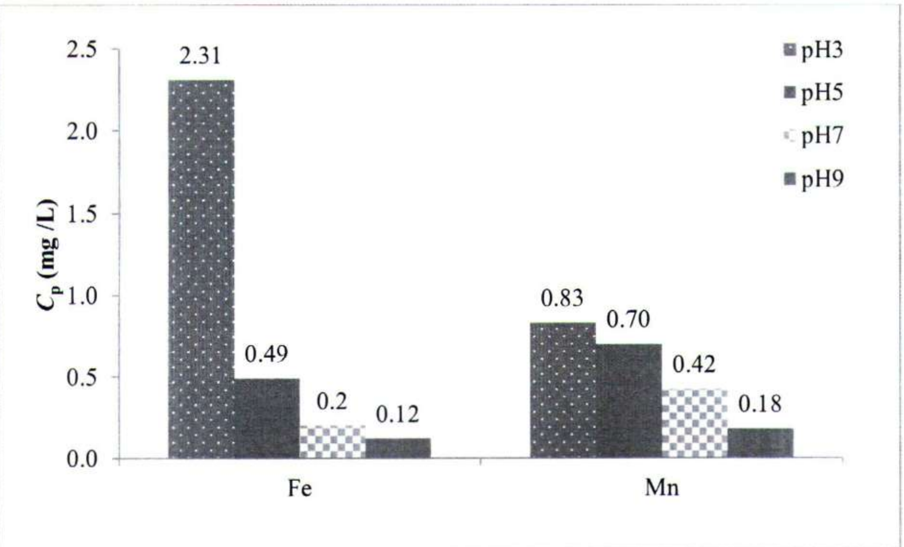


FIGURE 4 Permeate concentrations from filtration by using TFC-SR3 at various feed pH with 10 mg Fe/L and 1 mg Mn/L, pressure 5 bar and room temperature.

Rejection

Figure 5 presents the effect of feed pH on Fe and Mn rejection by using TFC-SR3 membrane. In general, as the pH increased from 3 to 9, the rejection of these metals inreased. This can be mainly caused by the solute-membrane charges interactions. It is obviously shows that rejections of Fe at various feed pH were higher than Mn. Lower rejection of Mn could be attributed solely to the electrostactic effect interaction between membrane material and Mn(II) ions (Kabsch-Korbutowicz and Winnicki 1996). The isoelectric point (IEP) of TFC-SR3 is in the range of 6 to 8 (De Munari et al. 2013). It is positively charge in solution less than pH 6 and negatively charge in solution more than pH 8. Between pH 3 and 5, the membrane is positively charged and lower Fe rejection could be due to dissolved Fe^{2+} were easily permeate the membrane pores. Thus, charge repulsion and size exclusion are less important at this feed pH range. At pH 7, high Fe rejection mainly because of electrostatic interaction between the membrane and the ions was zero. Therefore, the ions did not easily permeate membrane and contribute to higher rejection of Fe at IEP of membrane.

The feed pH may change the nature of the membrane surface charge and pore size, as well as that of dissolved metal species and therefore can affect the membrane separation efficiency. TFC-SR3 membrane has higher rejection rate for Fe(II) in comparison to Mn(II) ions as explain in the earlier sub-section. A simillar findings for Fe removal has previously been reported (Jusoh et al. 2005, De Munari et al. 2013). Regarding to Mn(II) ions, De Munari and Schäfer (2010) reported that TFC-SR3 membrane has achieved more than 95% of rejection at pH 7. In this study, Mn rejecntion at pH 7 had inreased very well to 58% from 30% rejection at pH 5. At pH 9, higher Mn rejection was achieved and mainly because of changes of solute charges to a stable form which easily removed by membrane as further explained in the earlier section. The good rejection at this condition was mainly contributed by solute-membrane charge interactions. The charge of solute influence the extent of rejection by NF membranes though the precise mechanism of rejection will depend upon the particular membrane in use (Waite, 2005).

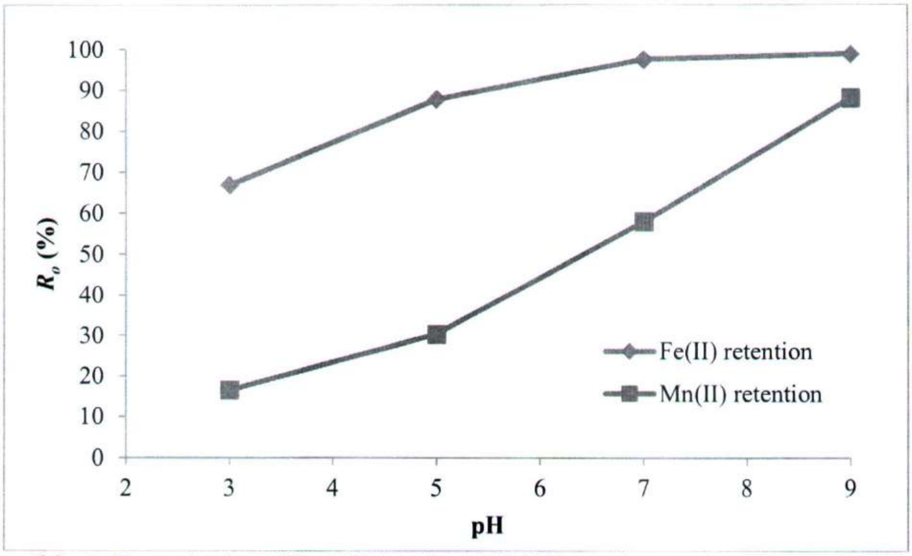


Figure 5 Effect of feed pH on rejection of Fe and Mn using TFC-SR3 membrane using 10 mg Fe/L and 1 mg Mn/L at 2 bar and room temperature.

Separation Efficiency on Membrane

Figure 6 presents the separation efficiency of both NF membranes for synthetic groundwater treatment with feed solution was adjusted to pH 9. The filtration test was conducted at applied pressure of 5 bar in order to gain higher flux within a shorter duration. As mentioned in the earlier section, rejection rates for both metals by TFC-SR3 membrane were improved at higher feed pH. It has a significant impact to the membrane performances. Thus, in order to prove this fact Figure 6(a) presents the separation efficiency using 100 mg Fe/L and Figure 6(b) using 10 mg Mn/L, respectively as the feed solutions. These results show that looser membrane, TS-40 has improved its efficiency and almost similar to the tight TFC-SR3 membrane. From these figures, both membranes demonstrated excellent metallic ions, color and turbidity removal (at least 94%) regardless of the membrane pore structure and sample characteristics. High rejection rate of turbidity and color can be attributed to large particle size of metals precipitated on the membrane surface as can be proven by FESEM images depicted in Figure 7. Principally, it can be concluded that turbidity and color separation were mainly governed by sieving mechanism due to steric hindrance. The performance of membranes in reducing conductivity and TDS was greatly dependent on the membrane pore size and surface charge property. With adjustment of pH, results show that both membranes demonstrated reasonable rejection rate (50-89%).

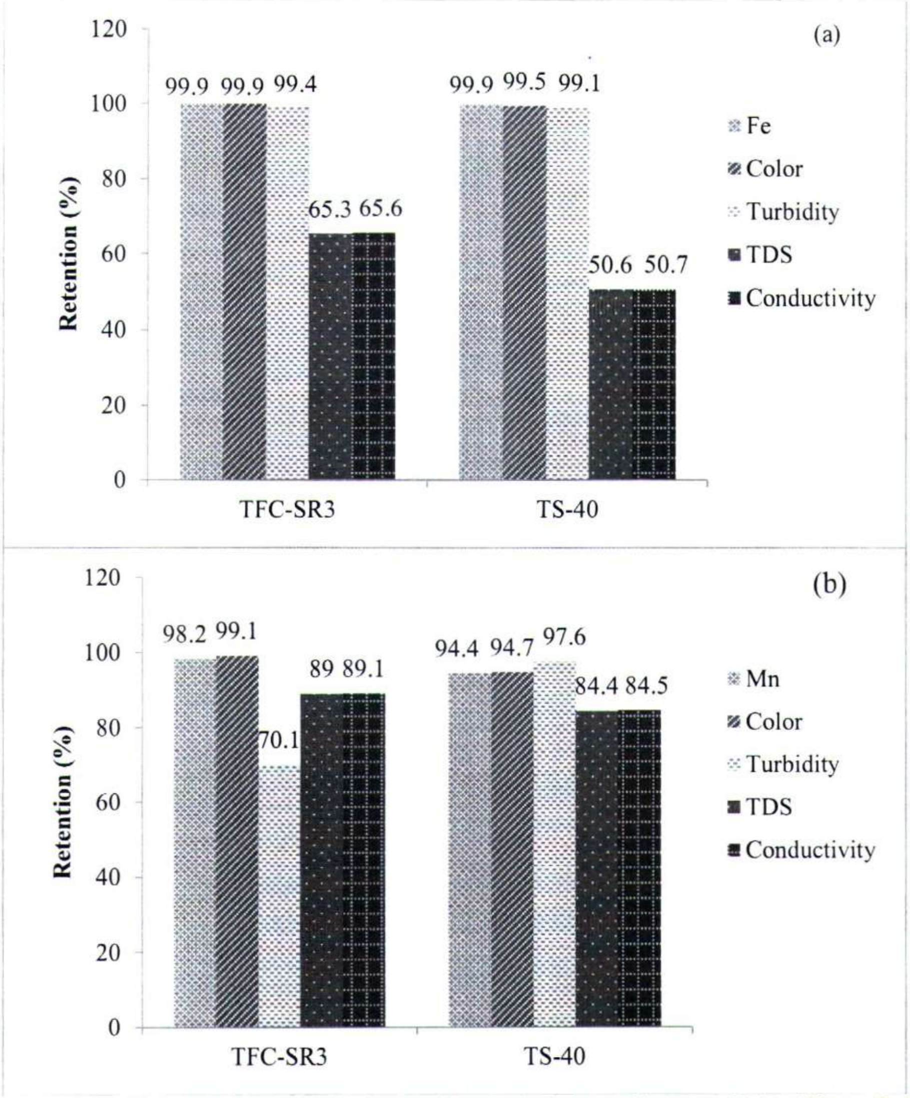
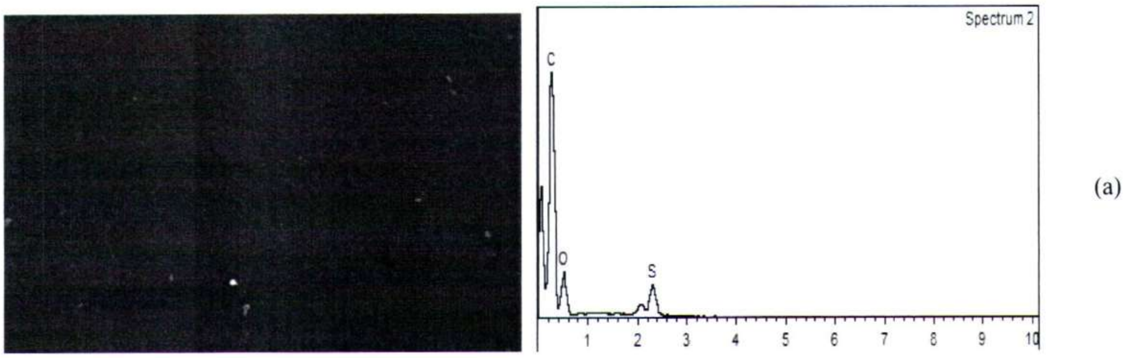


FIGURE 6 Separation efficiency of membranes in treating synthetic groundwater with (a) 100 mg Fe/L and (b) 10 mg Mn/L at applied pressure 5 bar and pH9.



CONCLUSION

The rejection mechanism using a loose (TS-40) and tight (TFC-SR3) NF membranes in treating Fe and Mn in groundwater were identified and evaluated in this study. The efficiencies of these membranes were assessed based on permeability, water flux and rejection rates at low applied pressure and feed solution pH. The rejection rates for metal component (Fe and Mn) using these membranes were significantly influenced by low pressure (2 bar) and basic feed solution (pH 9). Particularly, rejections of both metals by TFC-SR3 were higher than TS-40 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. Excellent separation performance of TFC-SR3 membrane was mainly due to its tighter membrane structure.

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. Higher pH of the feed solution contributed to transformation of soluble divalent Fe^{2+} and Mn^{2+} ions to insoluble Fe^{3+} and Mn^{4+} ions which are more stable and easily precipitated on membrane surfaces. Therefore, precipitation of metallic ions on the surface of membrane conducted to higher rejection of metal compounds from groundwater. In conclusion, all findings in this study contributed to possibility of developing the membrane technology for Malaysia's groundwater treatment as for drinking water resources.

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