# Effect of applied pressure on iron and manganese rejection by polyamide and polypiperazine amide membranes

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## Abstract

The aim of this research is to investigate the removal behavior of iron and manganese that naturally exist as divalent ions in groundwater by using nanofiltration and ultrafiltration membranes. The main focus of this study is to better understand the effect of applied pressures during the rejection of these metallic ions from synthetic groundwater in order to achieve drinking water standard. Polyamide and polypiperazine amide membranes denoted as PA-NF, PPA-NF and PA-UF were selected to investigate the iron and manganese rejection at low applied pressure range (1-5 bar). In single solute solution with feed concentration at 10 ppm and initial pH of 6.8 ± 0.5, the rejection of iron was ≥96% by PA-NF membrane at applied pressure of 2 bar. However, the rejection percentage by PPA-NF and PA-UF were 86.6% and 81.1%, respectively whereby both membranes were unable to remove iron to the allowable drinking water standard. The rejection of manganese with single solute at concentration of 1 ppm with initial pH of 6.8 ± 0.5 by using the PA-NF membrane was ≥98% and almost all of manganese were rejected at 5 bar. Nevertheless, manganese removal by PPA-NF and PA-UF membranes were found less than 70% and 40%, respectively. Findings from this work showed that the applied pressure was significantly influenced the water flux however the removal of iron and manganese were independent. The increased of applied pressure contributed to concentration polarization effect on the membrane surfaces leading to a decrease in solute rejection by decreasing the charge effect mainly for iron removal from synthetic groundwater.

**Keywords:** Polypiperazine amide, nanofiltration membrane, groundwater, iron removal, manganese removal, metallic ions rejection, water treatment.

## Introduction

Membranes have gained an important place in chemical technology and are used in a broad range of applications [1]. Membrane filtration has attracted much attention in water treatment fields since the past two decades. It has shown great potential over the conventional processes of being a compact size which reduces operating area and less manpower. Membrane systems have been used in specialized applications for more than 30 years, largely for water treatment, including desalination of seawater and brackish water [2]. Membrane technologies are receiving special recognition as alternatives to conventional water treatment and as a means of polishing treated wastewater effluent for reuse applications. These technologies are energy intensive because the use of low pressure systems that significantly resulted to reduce of energy use and also diminish operation costs [3-6]. In fact, membrane filtration offers several advantages over conventional water treatment such as fewer need of chemical agents, good quality of produced water, compact process and easy automation [6]. In addition, this filtration technology has superior treatment capability and performance characteristics in removing suspended solids and colloidal materials, which are the main cause of turbidity and important carrier of metal elements and microorganisms [7].

Membrane separation process in water treatment has gained popularity because it effectively removes variety of contaminants from raw water resources. Membranes are commonly used for the removal of dissolved solids, color and hardness of drinking water [2]. Microfiltration (MF) and ultrafiltration (UF) membranes can mainly remove suspended particles from raw water. Whereas, nanofiltration (NF) membranes are effective technology to remove dissolved organic contaminants with molecular weights larger than 200 Da and about 70% of monovalent ions by electrostatic repulsion (charge effect), size exclusion (sieving effect) and a combination of the rejection mechanism [8]. Meanwhile, reverse osmosis (RO) is more prone to be used for desalination or treatment of brackish water as it demonstrates the best overall removal of total dissolved solids (TDS) and organic compounds [9]. The separation characteristic of NF is in between UF and RO membranes. It is commonly used when low molecular weight (MW) solutes have to be separated from a solvent. In comparison to UF, NF membranes have a smaller pore size therefore, smaller organic molecules ($MW > 200$) can be rejected [10]. If compared to RO, a lower rejection is for monovalent ions.

In recent years, various treatment technologies have been employed to enhance water quality by removing inorganic contaminants. Among the inorganic contaminants that yet still being discussed all over the world is the removal of Fe and Mn because the existence of these dissolved metallic ions in groundwater or surface water is a long lasting issue to be highlighted. The groundwater in the aquifer of the northern Kelantan contains high concentrations of Fe and Mn, and is therefore unsuitable for use as drinking water without appropriate treatment. The benchmark of Fe and Mn in drinking water based on World Health Organization (WHO) is 0.3 ppm and 0.1 ppm, respectively.

Numerous studies have been reported in investigating the ability of membrane filtration in water treatment. It has been studied and proved by other scholars that NF and UF membranes were widely applied as tools in water treatment [11-15]. However, only a limited number of studies have examined the removal of Fe and Mn in groundwater by using NF membranes [16-18]. Therefore, commercially available PA-NF, PPA-NF and PA-UF membranes were examined to investigate the removal behavior of Fe and Mn from groundwater with the aim to achieve drinking water standards by WHO.

In this work, performance of each membrane was systematically investigated to identify the membrane with the best performance that could potentially support the treatment system even at high concentration of contaminants. The membrane performances were discussed mainly based on permeate fluxes, metallic ions rejection and water quality. The investigation was started by applying the PA-NF and PPA-NF commercial membranes for batch filtration with the use of synthetic groundwater as feed solution. Then, the ability of the best performance NF membrane was compared with the PA-UF membrane in order to achieve higher flux with higher rejection of both divalent metallic ios.

## Materials and methods

### Membranes, chemicals and reagents

Ferrous chloride tetrahydrate ($FeCl_2.4H_2O$, HmbG® Chemicals) and manganese chloride tetrahydrate ($MnCl_2.4H_2O$, Bendosen Laboratory Chemicals) were used in order to prepare synthetic groundwater contains of divalent metallic ions of Fe and Mn. Ultra pure water with conductivity less than 1 $\mu$S/cm was used to prepare fresh samples of the synthetic groundwater. In determination of $Fe^{2+}$ ions in permeate after each filtration, ferrous iron reagent powder (HACH Permachem®, USA) was used whereas 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 $Mn^2$ ions in permeate by using spectrophotometer (DR3900, HACH, USA). All chemicals, solvents and reagents used were analytical grade with high purity.

Commercially available flat sheet polyamide (PA) and polypiperazine amide (PPA) membranes for both NF and UF were employed throughout this study. The NF and UF membranes designated as TFC-SR3, TS40 and GHSP from different manufacturers were used to identify their performances for treating groundwater contains of Fe and Mn. The PA and PPA membranes were supplied by Sterlitech Corp., USA. Each membrane was named as PA-NF, PPA-NF and PA-UF respectively to the TFC-SR3, TS40 and GHSP membrane for easier recognition of them. These membranes were chosen based on their polymers and molecular weight cut off (MWCO). The properties of these membranes were summarized in Table 1.

Table 1 Specification of NF and UF membranes

| Parameter | PA-NF | PPA-NF | PA-UF |
|---|---|---|---|
| Designation | TFC-SR3 | TS40 | GHSP |
| Manufacturer | Koch | TriSep | GE Osmonics |
| MWCO[a] (Da) | 200 | 200 | 1000 |
| Polymer[a] | PA | PPA | PA |
| pH range at 25°C[a] | 4-10 | 2-11 | 2-11 |
| Standard pressure[a] (bar) | NR | 2-14 | NR |
| Contact angle[b] (°) | 46 | 28 | 68 |

NR – not reported

[a] Information obtained from manufacturer

[b] Value obtained from experimental measurement

**Membranes performance test**

Separation experiments were performed to investigate the ability of NF and UF membranes in term of permeability, flux and rejection using ultra-pure water and samples of synthetic or natural groundwater. Ultra-pure water with conductivity less than 1μS/cm was used for determination of water permeability. Natural groundwater was used to measure removal efficiency of organic and inorganic constituents in the aim to reach drinking water standard. Synthetic groundwater was mainly used to investigate the performance of membranes in terms of metallic ions removal in order to well understand the rejection mechanism involved. Filtration experiments have been conducted by applied pressures in the range of 1 to 5 bar, feed solution concentration of low range at 1 to 10 mg/L and pH of feed solution as recorded by synthetic groundwater (6.8±0.5). Filtration experiments were carried out at room temperature similar to the filtration protocol carried out previously by other scholars [19, 20].

The performance of membranes was conducted using a bench-scale stirred cell separation unit. All membranes were soaked in ultra-pure water for overnight before used in order to remove preservatives, and the soaking step was considered as a wetting process for the membrane. The wetted flat sheet membrane was placed at the bottom of a dead-end stirred cell. Then, compaction of membrane was conducted for 30 to 45 min by pressurizing the stirred cell with nitrogen gas at 5 bar without stirring. The compaction step is conducted purposely to ensure a complete removal of residual chemicals inside the membrane's porous structures. After compaction, the pure water permeability test was conducted and the water flux was measured. The pure water flux was calculated by the following Eq. 1 [20]:

$$J_w = \frac{Q}{A\Delta t} \tag{1}$$

where, $J_w$ is pure water flux ($L\cdot m^{-2}\cdot h^{-1}$), $Q$ is amount of water collected (L) for $\Delta t$ (h) which is time duration using a membrane coupon with area $A$ ($m^2$).

The pure water permeability ($L_p$, $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$) was determined by measuring the slope of a linear plot of pure water flux against applied pressures. Initial measurement for water quality analysis such as pH, conductivity, color, turbidity, total dissolved solid (TDS) and salinity (% NaCl) of the feed solution were conducted at the beginning of each filtration experiment. After the initial water quality analysis, a sample of feed solution was then placed into the stirred cell to further determine the solute rejection and permeate flux according to Eq. 2 and Eq. 3, respectively. The rejection of sample of feed solution and the removal efficiency of NF and UF membranes during the filtration was measured by Eq. 2:

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

where $R_o$ is the observed rejection and $C_p$ and $C_f$ are the concentration of permeate and feed, respectively [20].

Filtration test were conducted for 2 to 3 hours or by the collection of minimum permeate volume at least 70 mL for permeate quality analysis. For this test, 250 mL of feed solution was placed into the stirred cell and constantly stirred with a plastic magnetic stirrer guided by a magnetic stirring plate. The applied pressures were supplied in the range from 1 to 5 bar with fixed stirring rate at 500 rpm for all experiments to minimize concentration polarization. Data of permeate mass collected every 60 s was recorded by a LabView software installed in the personal computer.

The flux of sample of feed solution was measured by the following Eq. 3:

$$J = L_p\,(\Delta P - \Delta\pi) \tag{3}$$

where $J$ is the sample flux ($L\cdot m^{-2}\cdot h^{-1}$), as a function of permeability, $L_p$ ($L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$) and applied transmembrane pressure, $\Delta P$ (bar) taking the osmotic pressure difference between feed and permeate, $\Delta\pi$ (bar) into account [20, 21].

The osmotic pressure may affect membrane walls during the calculation of flux, thus $\Delta\pi$ was calculated based on the Van't Hoff law as given in the following Eq. 4:

$$\Delta\pi = R_g T\left(C_{i,w} - C_{i,p}\right) \tag{4}$$

where $R_g$ is the universal gas constant (L/bar), T is the absolute temperature (Kelvin), and $C_{i,w}$ and $C_{i,p}$ are the concentrations of feed (mol/L) and permeate (mol/L), respectively [21]. It should be noted that all concentrations of salt solutions were below 1000 mg/L in this study, therefore the osmotic pressure was not overestimated, as it can be when Eq. 3 is applied to highly concentrated salt solutions.

## Results and discussion

### Water permeability

In this study, flux of PA-UF membrane was found lower than the PA-NF and PPA-NF membranes mainly due to the hydrophilicity of membranes. The PA-UF membrane is less hydrophilic than PA-NF and PPA-NF meaning that both NF commercial membranes are more water permeable in comparison to the UF membrane. This is proven by the value of contact angle between pure water drop and the surface of clean membrane using the sesile drop method that was reported in Table 1. Results show that PPA-NF is the most hydrophilic membrane with contact angle 28° and followed by the PA-NF membrane with contact angle 46°. The contact angle of PA-UF membrane is 68° which is considered as less hydrophilic in comparison than the other two NF membranes and since the magnitude is slightly higher than 60° therefore it was categorised as hydrophobic membrane. Hydrophilicity of a membrane is normally expressed in terms of contact angle ($\theta$) which is a measurement of membrane's wettability of water. Hydrophilic membranes usually are more preferable in industrial application such as water treatment processes [22].

In water treatment processes using membrane technology, UF membranes are more preferable due to their ability to provide higher water flux in comparison to the NF membranes. However, it was proven by other scholars [23-26] that NF membranes have the advantages on reducing heavy metals, nitrates, sulfates, color, tannins, turbidity, TDS content of slightly brackish water, softening hard water and at the same time able to lower the operating and energy cost since NF system can be operated at low pressures. Therefore, the performance study was primarily conducted using synthetic groundwater that was prepared by dissolving Fe and Mn salts in ultra pure water. The capability of PA-NF, PPA-NF and PA-UF membranes on removal of Fe and Mn was mainly further discussed based on the influence of applied pressure.

### Influence of applied pressure

Permeate flux is one of the main factors 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 [19]. In most of water process industries, UF membranes with high flux are always preferable. In the case of producing drinking water, rejection of contaminant or pollutant is the most priority for health consideration. Therefore, in order to select the best performing membrane for groundwater treatment in Malaysia, membranes with high water permeability and high rejection capability of the selected ions, $Fe^{2+}$ and $Mn^{2+}$ ions were investigated. The PPA-NF membranes exhibited higher water permeability in comparison to the PA-UF membrane. The average volumetric water fluxes at 5 bar by these membranes are summarized in the following Table 2.

Table 2 Water flux for commercial NF and UF membranes at applied pressure of 5 bar

| **Membrane** | **PA-NF** | **PPA-NF** | **PA-UF** |
|---|---|---|---|
| Average volumetric water flux ($L\cdot m^{-2}\cdot h^{-1}$) | 15.85 ± 0.5 | 23.39 ± 0.5 | 10.75 ± 0.5 |

Three different coupons of each PA-NF, PPA-NF and PA-UF were used for measurement of their water fluxes. The average volumetric water flux at applied pressure of 5 bar for PA-NF membrane was found at 15.85 ± 0.5 $L\cdot m^{-2}\cdot h^{-1}$. The result obtained was much lesser than for the PPA-NF membrane with flux at 23.39 ± 0.5 $L\cdot m^{-2}\cdot h^{-1}$. Even though both membranes have similar MWCO at 200 Da, but they performed differently due to the membrane's surface hydrophilicity. It was proven by the contact angle measurement that PPA-NF is more hydrophilic than the PA-NF membrane. From this behavior, PPA-NF membrane was considered as more water permeable than PA-NF membrane. For the case of PA-UF membrane, the average volumetric water flux was 10.75 ± 0.5 $L\cdot m^{-2}\cdot h^{-1}$ which is the lowest flux in comparison to the other NF membranes. This result has confirmed that PA-UF membrane is less water permeable than PA-NF membrane and with this behavior, it was considered as hydrophobic UF membrane since the MWCO is 1000 Da.

Results of water fluxes for the three membranes are summarized in Table 2 and these results showed that the separation layer of PA-UF membrane was less permeable to water in comparison to PA-NF. Data obtained from the manufacturers had reported that the MWCO for PA-NF and PA-UF were 200 and 1000 Da, respectively. Therefore, results of water flux were congruent with their hydrophilicity and not mainly based on the MWCO of the NF and UF membranes as reported by manufacturers. Fig.1 shows positive linear relationship between pressures and permeate fluxes for each membrane for filtration using synthetic groundwater. The increase of applied pressure leads to a strong increase in permeate flux as also reported by other researchers [27].

Application of appropriate applied pressure plays a critical role in membrane processes that ca influence the changes in membrane permeate flux throughout the operation changes [28]. However, relationship between rejection and the applied pressure in Figure  shows an unreliable behavior.

Rejections of metallic ions are expected to decrease as applied pressures are increased from 1 to 5 bar. At higher pressure, water flux could be increased due to an increase of the preferential sorption of water and thus, the solvent permeability increases rather than solute permeability. The performance study of the selected membranes was started by applying synthetic groundwater with single solute of metallic ion at 10 mg Fe/L and 1 mg Mn/L. These are values in which the total Fe and Mn commonly exist in groundwater as reported by the Department of Minerals and Geoscience, Malaysia.

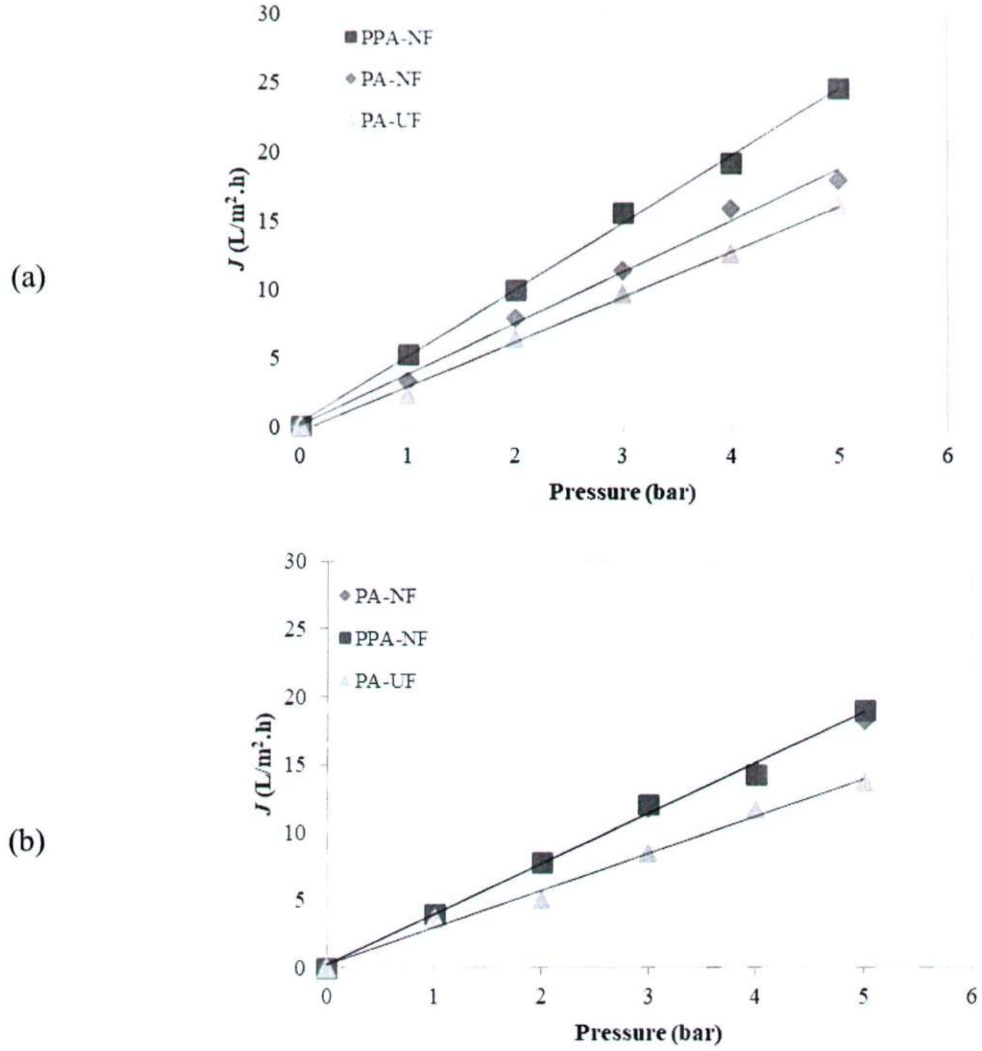


Figure 1 Flux of NF and UF membranes using synthetic groundwater with (a) 10 mg Fe/L and (b) 1 mg Mn/L

Fig. 2 presents the rejection of ferrous iron ($Fe^{2+}$) for ferrous chloride ($FeCl_2$) solution with concentration of 10 mg/L at initial pH of the feed solution measured at pH 6.8 ± 0.5. Fig. 2(a) shows that Fe removal by using PA-NF membrane at this operating condition have reached more than 96%. Results show that at low concentration of $Fe^{2+}$ ion, the PA-NF membrane is capable to totally remove the divalent ions in order to achieve drinking water standard at the selected range of applied pressure. In the aim to reach the allowable limits for Fe that is set by WHO drinking water standard [29], therefore rejection for this condition should be more than 97%. Thus, the applied pressure at 2 bar was preferable since the measured permeate concentrations were well below than the allowable value for drinking water which is 0.3 mg Fe/L.

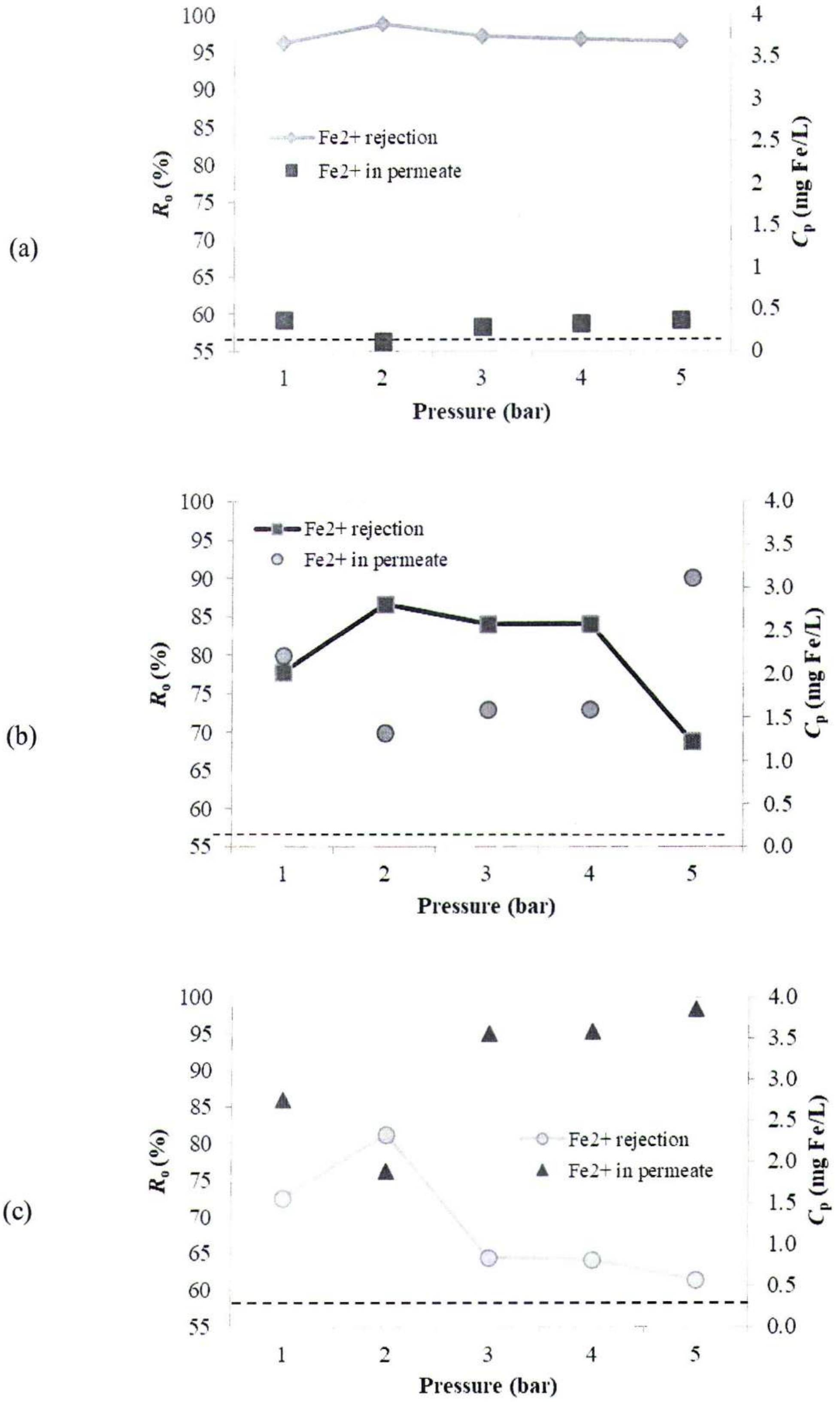


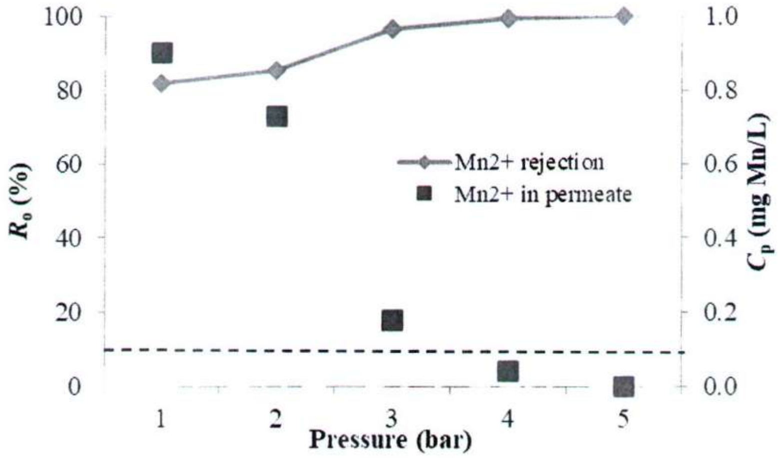
Figure 2 Percentage of rejection and concentration of $Fe^{2+}$ ion in permeate by filtration using (a) PA-NF, (b) PPA-NF and (c) PA-UF membranes for feed concentration at 10 mg Fe/L

Fig. 2(b) and 2(c) show the percentage of rejection for $Fe^{2+}$ and also permeate concentration for filtration by using PPA-NF and PA-UF membranes, respectively. Results showed that both membranes were unable to remove the divalent ions even at low concentration of Fe content in groundwater. At applied pressure of 2 bar, the highest rejection percentage by PPA-NF and PA-UF were 86.6% and 81.1%, respectively. The detected level of Fe$^{2+}$ in permeate was found at the concentration of 1.34 and 1.88 mg/L, respectively. These values were much higher than the benchmark. Therefore, only PA-NF has managed to remove Fe$^{2+}$ ions to the allowable limit for drinking water with concentration of Fe$^{2+}$ in groundwater at 10 mg/L treated at 2 bar. This result indicated that the increase of pressure will transport more solute ions to the membrane surface and, therefore, the concentration polarization will also increase, then leading to a decrease in solute rejection by decreasing the charge effect. At low pressure of 2 bar, high rejection is mainly dominated by the charge effect on membrane surfaces.

Figure presents the rejection of Mn$^{2+}$ ion from MnCl$_2$ solution with a concentration of 5 mg/L at initial pH of the feed solution that was measured at pH 6.5 ± 0.5. Among the selected membranes, the PA-NF membrane had the best performance to reject low concentration of Mn$^{2+}$ in order to achieve drinking water standard. Fig 3(a) showed that the removal of Mn increased with increasing applied pressure and was found preferable at 4 and 5 bar since the solute concentration in permeate were less than 0.1 mg Mn/L. However, the PPA-NF and PA-UF were found to have the best performance at 2 bar. Mn removal by both membranes was found less than 70% and 40%, respectively. Results in Figure (b) and 3(c) clearly displayed that PPA-NF and PA-UF membranes were unable to treat Mn$^{2+}$ effectively from the prepared synthetic groundwater at applied pressure range of 1 to 5 bar.

In order to investigate the potential of NF membranes in groundwater treatment, therefore a comparative study was carried out to explain the performance of PA-NF and PPA-NF membranes. The properties of PA-NF and PPA-NF membranes with respect to the contact angle and pure water flux are as shown in Table 3. Results showed that pure water permeability was found to be governed mainly by membrane MWCO and its surface hydrophilicity. As reported by manufacturers, both membranes have similar MWCO at 200 Da.

(a)



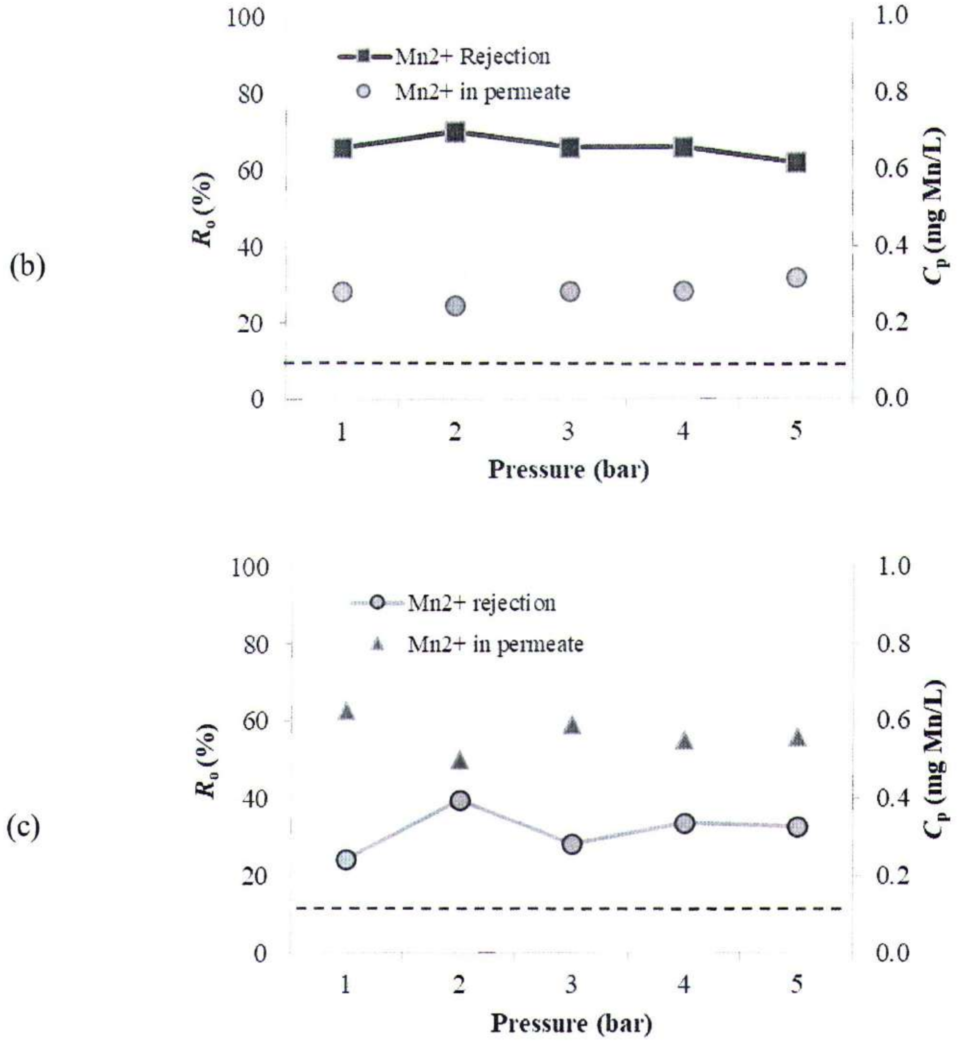


Figure 3 Percentage of rejection and concentration of $Mn^{2+}$ ion by filtration using (a) PA-NF, (b) PPA-NF and (c) PA-UF membranes for feed concentration at 1 mg Mn/L

Table 3 Properties of NF membranes

| **Membrane** | **MWCO (Da)** | **Pure water flux[a] ($L \cdot m^{-2} \cdot h^{-1}$)** | **Mean contact angle (°)** |
|---|---|---|---|
| PA-NF | 200 | 10.75 (± 0.5) | 46 (± 2.5) |
| PPA-NF | 200 | 23.40 (± 0.5) | 28 (± 2.5) |

[a] value obtained from experimental measurement at P = 5 bar

However, PPA-NF membrane exhibited higher water flux mainly because of its surface morphology that offers minimum transport resistance for water molecules to permeate. In fact, this behaviour was proved by its contact angle at 28° ± 2.5 showing that this membrane is hydrophilic. This phenomenon can be explained by the fact that PPA-NF 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 was experienced. In contrast with PA-NF 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 46° ± 2.5, this proved that it is less hydrophilic than PPA-NF membrane. Thus, contact angle and pure water flux results that were reported in Section 4.4, have supported the fact that PA-NF was less water permeable than PPA-NF membranes. A recent work conducted by Zulaikha et al. (2014) [30] also reported the same behaviour as NF-270 membrane which is made by piperazine and benzenetricarbonyl trichloride (PIP-TMC) monomer resulted in higher pure water flux than NF-90 membrane.

Filtration of synthetic groundwater consists of single salt of ferrous chloride ($FeCl_2$) and manganese chloride ($MnCl_2$) were further tested at similar pressure range and at room temperature. However, the feed concentration of synthetic groundwater were maintained at 10 mg Fe/L but reduced to 1 mg Mn/L, respectively. The reduction on Mn concentration is purposely to aim for higher removal of this metallic ions from the prepared synthetic groundwater. Figure 1 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 for filtration using both PA-NF and PPA-NF membranes. As pressure increased, convective transport and concentration polarization become more important [31]. Fig. 4(a) for Fe removal, reveals that changes in the permeate fluxes remained linear with increasing pressure, which indicated that insignificant of concentration polarization. A similar observation has been made for Mn as depicted in Fig. 4(b). The permeate fluxes for Fe and Mn using PPA-NF were higher than PA-NF at this operating condition. All of the permeate flux results were as expected and thus, indicated that PPA-NF is more water permeable than the PA-NF membrane.

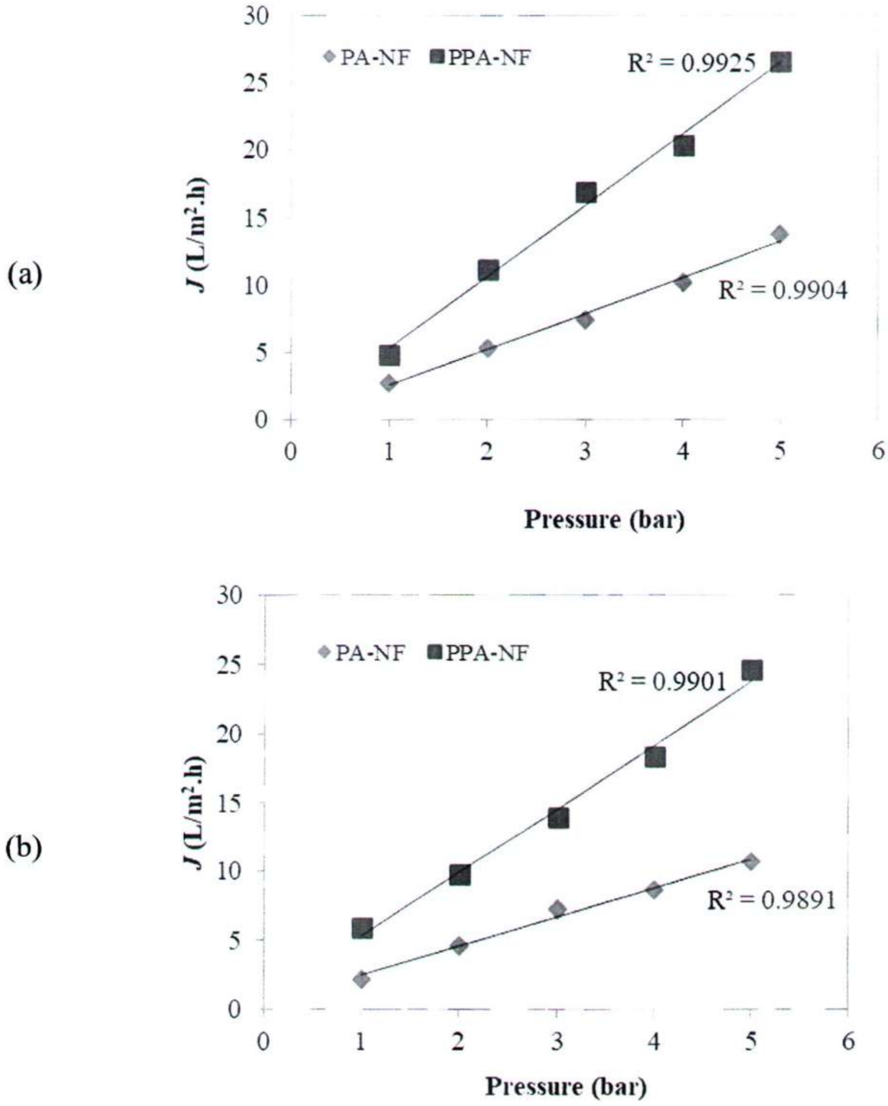


Figure 1 Effect of applied pressure on permeate flux of PA-NF and PPA-NF membrane with (a) $Fe^{2+}$ and (b) $Mn^{2+}$ at feed concentration 10 mg Fe/L and 1 mg Mn/L, pH 6.8 ± 0.5 and at room temperature

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 contaminants from groundwater. Results depicted in Figure 2 shows that rejection of $Fe^{2+}$ and $Mn^{2+}$ ions from synthetic groundwater decreased with increasing applied pressures. Rejection of both metallic ions were pereferable by using PA-NF in comparison to PPA-NF. This might be because of the tight membrane structure of PA-NF which resulted in good rejection of both metallic ions in the synthetic water.

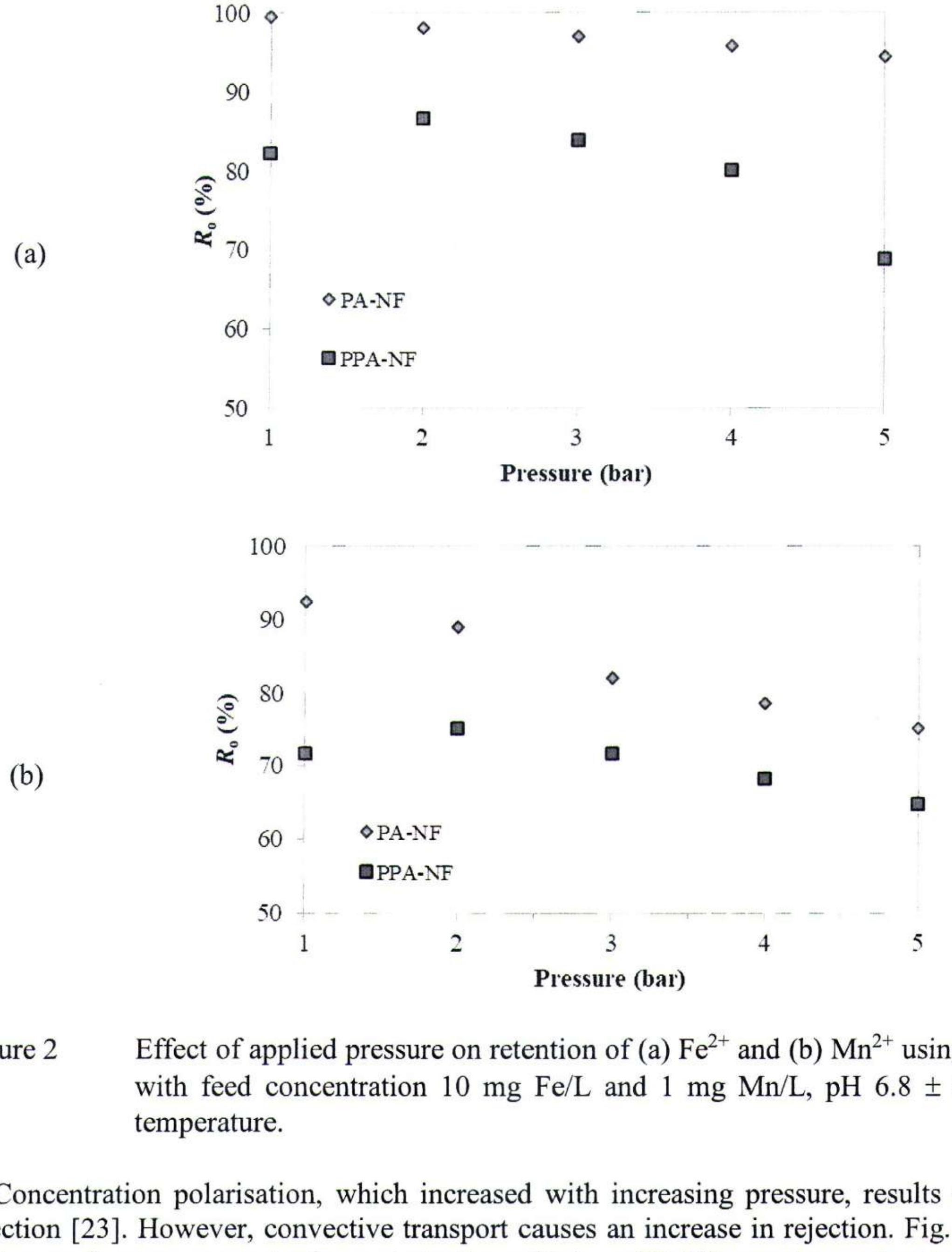


Figure 2 Effect of applied pressure on retention of (a) $Fe^{2+}$ and (b) $Mn^{2+}$ using NF membranes with feed concentration 10 mg Fe/L and 1 mg Mn/L, pH 6.8 ± 0.5 and at room temperature.

Concentration polarisation, which increased with increasing pressure, results with decrease in rejection [23]. However, convective transport causes an increase in rejection. Fig. 5(a) reveals that Fe has undergone concentration polarisation effect on PA-NF membrane due to rejection to this metallic ions were decreased from 99% to 94% as the applied pressure increased. As for PPA-NF membrane, rejection of Fe at 1 bar was 83% and then increased to 86% at 2 bar. However, it has dropped to 69% by the operation at 5 bar. These behaviors confirmed that Fe has experienced convective transport effect on PPA-NF membrane then followed by concentration polarisation. Similar trends and mechanism of rejection had occured for Mn as presented in Fig. 5(b).

In comparison to $Fe^{2+}$ ions by using PA-NF, $Mn^{2+}$ ions rejection were slightly lower and decreased from 92% to 75%. While the rejection for PPA-NF has dropped from 86% to 65%. The reason for higher $Fe^{2+}$ ions removal and lower $Mn^{2+}$ ions removal possibly credited to the ionic radius of cations $Fe^{2+}$ and $Mn^{2+}$ which are 75 and 81 pm, respectively. Ions with lower ionic radius tend to hold their hydration shells and therefore would have higher removal by membrane [32]. Therefore, $Fe^{2+}$ ions with lower ionic radius tend to hold their hydration shells and thus minimize the tendency to permeate through the membrane pores and highly removed by the membrane. In addition, with more hydrophilic NF membrane such PPA-NF, size exclusion was expected to be the main mechanism to explain both metallic ions rejection. The illustrations of hydration shell for $Fe^{2+}$ and $Mn^{2+}$ ions are as presented in Figure 3. However, a study by Haddad et. al (2018) [33] claimed that in the absence of groundwater hardness, charge exclusion was mainly responsible for rejection of dissolved Mn and Fe.

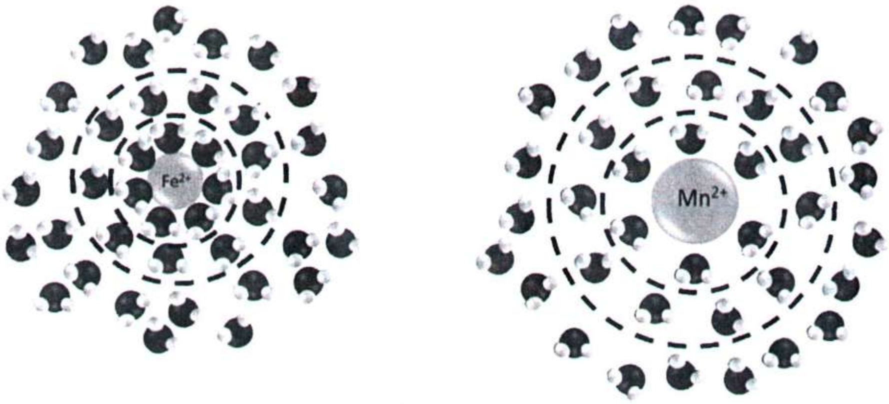


Figure 3 $Fe^{2+}$ and $Mn^{2+}$ ions with their hydration shells

For this operating condition, $Fe^{2+}$ ions rejection should be higher than 97% in order to reach the allowable limits for drinking water that is set by WHO. Thus, applied pressure at 2 bar is preferable for $Fe^{2+}$ ions rejection at natural pH of the prepared synthetic water which is pH $6.5 \pm 0.5$. This was due to the measured permeate concentration that was well below than the allowable value. As for $Mn^{2+}$ ions, preferable rejection should be 90% for the acceptable limit of drinking water standard.

## Conclusion

The performance of membrane filtration using NF (PA-NF and PPA-NF) and UF (PA-UF) 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, and various metallic ions concentrations in the feed solution. Results of membrane performance tests using the commercial membranes indicated that membrane permeability decreasing with this sequence, PPA-NF > PA-NF > PA-UF mainly because of their surface hydrophilicity. The removal of metallic ions ($Fe^{2+}$ and $Mn^{2+}$) using these membranes are significantly influenced by the operating conditions especially by the applied pressure. Particularly, rejections of both divalent metallic ions by PA-NF membrane were higher than PPA-NF and PA-UF membrane for all investigated operating conditions. In addition, results proved that PA-NF membrane has efficiently rejected $Fe^{2+}$ and $Mn^{2+}$ ions to the allowable value for safe drinking water based on WHO standard. At low concentration of contaminants, applied pressure at 2 bar is the optimum operating condition for Fe removal by using PA-NF membrane. However, pressure at 4 bar is more preferable for Mn removal in order to achieved allowable drinking water standard. At higher concentration of Fe and Mn, pH of feed solution at higher than pH 7 contributed to better rejections of these constituent ions in groundwater.

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