



A study on acid reclamation and copper recovery using low pressure nanofiltration membrane

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ABSTRACT

In this study, nanofiltration membrane is used to separate proton (H^+) and copper ions from a ternary ions mixture (H^+ , Cu^{2+} , SO_4^{2-}). The performance of membrane in separating Cu^{2+} and H^+ was tested under the effect of pressure, concentration and different acid strength (pH). It was found that the H^+ rejection is independent of the applied pressure. Permeability of solution decreased linearly with the increase of $CuSO_4$ concentration. In terms of H^+ rejection, there is a continuous drop in rejection from 0.1 mM $CuSO_4$ to 10 mM $CuSO_4$ solution. H^+ was poorly retained and concentrated in the permeate stream in corresponding to the electro-neutrality requirements, on the other hand, the rejection of copper ion was almost constant with pH. In overall, optimum acid reclamation and copper recovery can be achieved at higher volume flux. A Three Parameters-Combined Film-Extended Nernst-Planck Equation (CF-ENP) model is successfully applied to predict the performance of nanofiltration membrane in separating the ternary ions.

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1. Introduction

Copper is widely used in the production of wire brass, boiler pipe, cooking utensils, and fertilizers, etc. Copper plating is very common either as preparation to further electro-deposition process of nickel or as end treatment for many items in the daily use [1]. Therefore, copper is frequently found in water and wastewater at significant quantities. Although copper is known to be a biologically essential and beneficial element, ingestion of excessive copper can cause nausea, vomiting, diarrhea, epigastric pain, and dizziness. Victims of Wilson's disease will steadily accumulate copper in the liver, central nervous system, and kidneys [2]. To protect the public health and aquatic life, it is necessary to remove copper from industrial effluent before discharging it to public wastewater treatment plant or receiving waters.

The concentration of the copper in the waste stream was found varied with type of industry and influent. For example, a rinse stream reported by GE Water Technologies has 27.70 ppm of copper [3] with pH 1.5–3.5, while the influent of printed circuit board fabrication wastewaters reported by L&T Technologies consists of 1200 ppm copper ion with pH 2.0 [4]. The copper rinsed water also reported having 1020 mg/l copper with pH 1.76 [5].

Membrane method has been introduced in quite recently to recover or remove copper from the effluent or plating rinse water.

The pre-treated emulsion was subsequently purified by nanofiltration (NF-90-2540) and a 98% rejection of copper ions was achieved [6]. Application of NF to leachate treatment was studied to separate metals from less toxic salts by low retention NF membranes [7]. A comparative study has been investigated for the treatment of wastewater containing copper and cadmium [8]. The results showed that high removal efficiency of the heavy metals (more than 90% of the copper ion) could be achieved by NF process. Recently, Copper rejections of a nanofiltration (NF) and a reverse osmosis (RO) membrane are investigated with copper sulfate and copper–nitrate solutions as test wastewaters. The copper content of the solutions represents the typical copper ion concentration of process waters from a textile coating plant. The applied conditions (e.g. pressure or pH) are in the applicable range of parameters. Permeate flux, conductivity, pH, and copper concentration of the permeate are measured to determine the membrane characteristic and rejection [9].

In this work, a laboratory produced hydrophilic nanofiltration membrane which carry pendant carboxylic group was investigated for its ability to separate proton from the copper ion under the effect of pressure, concentration and different acid strength (pH).

2. Materials and methods

2.1. Membrane

The nanofiltration membrane is a polysulfone supported thin film composite polyamide produced by interfacial polymeriza-

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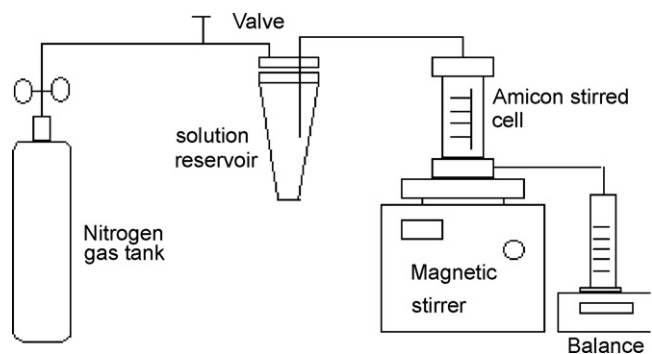


Fig. 1. Schematic diagram of dead end filtration rig.

tion of aqueous diamine containing 1.95% (w/w) piperazine, 0.05% (w/w) 3,5-diaminobenzoic acid (moieties which have high affinity to the proton) and 0.5% H_2SO_4 , with 0.1% (w/v) trimesoyl chloride in hexane solution. The mean pore size of the membrane is around 0.52 nm [10].

2.2. Membrane permeation test

The membrane permeation test was carried out using the Amicon 8200 stirred cell (Fig. 1). The effective area of the membrane mounted under the cell is 28.27 cm² (excluding the area cover by the O-ring). Throughout the experiment, the stirring speed of the stirrer was fixed at 350 rpm using the controllable magnetic stirrer (Heidoph MR3000D, Germany). For each operating pressure, deionized water (18.2 M Ω) was first tested to determine the pure water permeability (PWP) constant. The membrane permeation test was carried out at eight different pressures: 100 kPa, 150 kPa, 200 kPa, 250 kPa and 300 kPa, 350 kPa, 400 kPa and 450 kPa. Two copper sulfate solutions with concentration of 1 mM were prepared as feed solution, one with original pH (pH 4.83) and the other was adjusted to pH 2.5. For effect of concentration study, the membrane permeation test was carried out at the pressure of 450 kPa. The concentrations of the copper sulfate solution used are 0.1 mM, 1 mM, 5 mM, 10 mM and 100 mM. Each series was repeated for solution with original pH 4.83 and pH 2.5. The membrane performance under different pH conditions was carried out at pH 2.00, 2.50, 3.00, 3.50, 4.00, 4.50 and 5.00 using pure sulfuric acid. For each pH value, three different concentrations of copper sulfate solution were tested namely 0.1 mM, 0.5 mM and 5.0 mM. All the results presented are averaged data obtained through three membrane samples with a variation of $\pm 10\%$. The observed rejection of the salt are defined in Eq. (1)

$$\text{Observed rejection} = R_{obs} = 1 - \frac{C_p}{C_f} \quad (1)$$

where C_p and C_f are permeate and feed concentration (mol/l) respectively.

2.3. Measurement of ions content

The copper ion was checked using a copper high range ISM meter (Hanna HI 93702, Italy). The copper meter measures the copper content in the 0.00–5.00 mg/l (ppm) range with accuracy ± 0.02 mg/l. Sulfate ion was checked using Sulfate ISM meter (Hanna HI 93751, Italy). The sulfate meter measures the sulfate content in the 0–150 mg/l (ppm) range with accuracy ± 1 mg/l. In order to get the H^+ concentration for the feed and permeate, the electro-neutrality condition was applied in which the H^+ concentration was

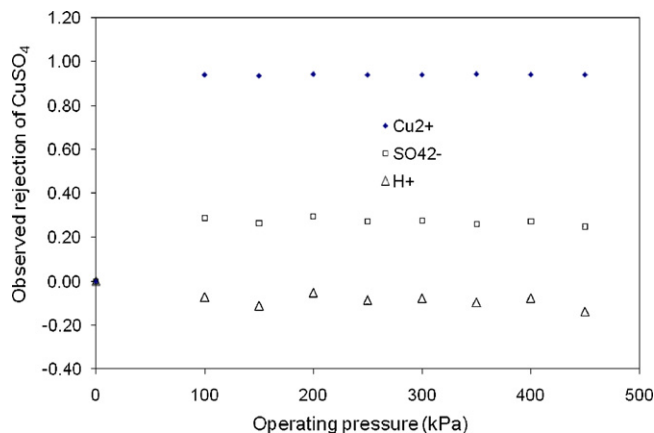


Fig. 2. Effect of pressure on ions rejection in ternary solution (pH 2.5).

calculated by using Eq. (2):

$$m_{H^+} (\text{ppm}) = 2 \left[\frac{m_{SO_4^{2-}} \text{ mg/l}}{96.06 \text{ mg/mmol}} - \frac{m_{Cu^{2+}} \text{ mg/l}}{63.54 \text{ mg/mmol}} \right] \quad (2)$$

2.4. Modeling of Cu^{2+} , H^+ and SO_4^{2-} rejection in ternary solution

Three Parameters-Combined Film-Extended Nernst-Planck model is adopted to predict the ions permeation and rejection. The three components are Cu^{2+} (1), SO_4^{2-} (2) and H^+ (3). The concentration of copper sulfate solution was prepared at 18.88 mM $CuSO_4$ or 1200 ppm copper ion. Pure sulfuric acid was added to reduce the solution pH to 2.00, 2.50, 3.00 from the initial pH of 4.83.

The following equation for the flux of component i , can be derived [11]:

$$J_i = -F_{1,i} \Delta C_1 - F_{2,i} \Delta C_2 + F_{3,i} J_v C_{1,0} + F_{4,i} J_v C_{2,0} \quad (i = 1, 2) \quad (3)$$

The expression for the rejection of component i in a ternary system is given by following equation:

$$R_i = \frac{R_{s,i}(J_v)J_v - B_{i,j}(J_v)(C_{f,j}/C_{f,i})R_j}{J_v + B_{s,i}(J_v)} \quad (i = 1, 2, j = 1, 2, i \neq j) \quad (4)$$

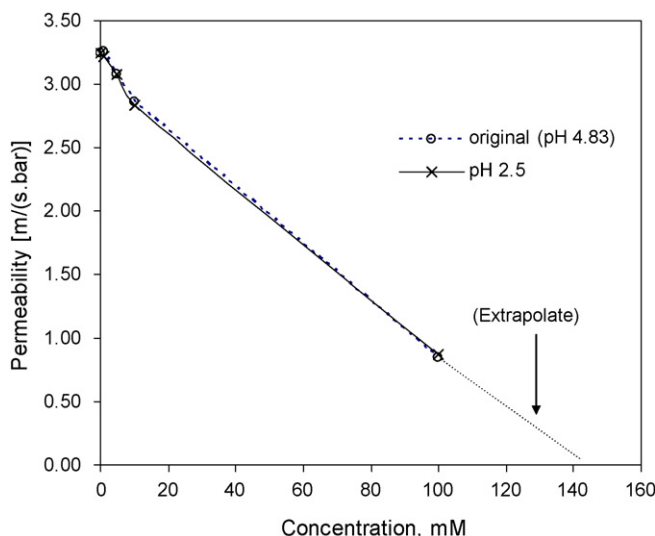


Fig. 3. Effect of $CuSO_4$ concentration on volume flux.

The rejection of component 3 (H^+) is given by:

$$R_3 = 1 - \left[\frac{(1 - R_2) - (C_{f,1}/C_{f,2})(1 - R_1)}{1 - (C_{f,1}/C_{f,2})} \right] \quad (5)$$

The following expressions for $R_{si}(J_v)$, $B_{si}(J_v)$, and $B_{2i}(J_v)$ are obtained.

$$R_{si}(J_v) = \frac{1 - F_{3,i}}{1 + F_{3,i}(\exp(J_v/k_i) - 1)} \quad (i = 1, 2) \quad (6)$$

$$B_{si}(J_v) = \frac{F_{1,i} \exp(J_v/k_i)}{1 + F_{3,i}(\exp(J_v/k_i) - 1)} \quad (i = 1, 2) \quad (7)$$

$$B_{ij}(J_v) = \frac{F_{2,i} \exp(J_v/k_j)}{1 + F_{3,i}(\exp(J_v/k_j) - 1)} \quad (i = 1, 2, j = 1, 2, i \neq j) \quad (8)$$

By solving Eqs. (4)–(8), the observed rejection of each ion could be expressed as below:

$$R_i = \frac{J_v(R_{si}(J_v) \cdot (J_v + B_{s,j}) - R_{s,j}(J_v) \cdot B_{ij}(C_{f,j}/C_{f,i}))}{(J_v + B_{s,i}(J_v))(J_v + B_{s,j}(J_v)) - B_{ij}B_{ji}} \quad (i = 1, 2, j = 1, 2, i \neq j) \quad (9)$$

3. Result and discussion

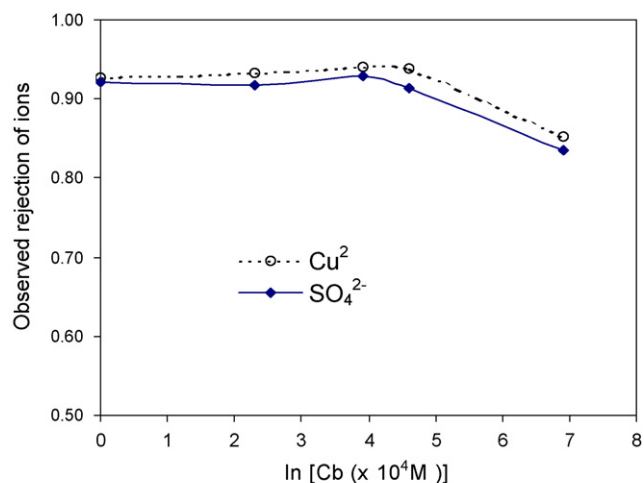
3.1. Effect of operating pressure on $CuSO_4$ rejection

Fig. 2 shows the effect of operating pressure on membrane rejection at pH 2.5. The rejection approached the respective maximum value or reflection coefficient at the pressure as low as 100 kPa. This operating pressure was low enough for NF, indicating the economic advantage of applying this NF to remove $CuSO_4$. A variation of pressure or volume flux (since volume flux is a function of pressure) is unlikely to cause any changes to the ternary ions rejection. Copper and sulfate ions were positively rejected whereas proton (H^+) shows negative rejection. Negative rejection means that membrane would rather concentrate H^+ in the permeate stream than reject it. This phenomenon was due to higher permeability of proton compared to copper and sulfate ions. The proton was extensively transported through the membrane to maintain the electro-neutrality conditions with the sulfate ion in permeate.

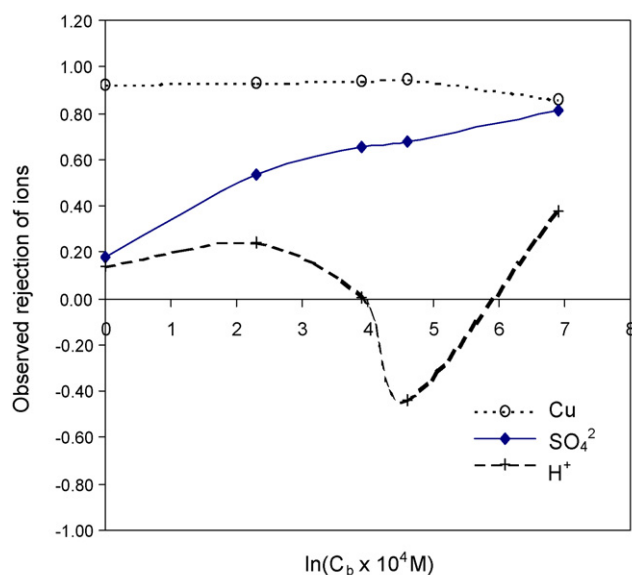
3.2. Effect of $CuSO_4$ feed concentration on rejection

Fig. 3 shows the effect of copper sulfate concentration (0.1 mM, 0.5 mM, 1 mM, 5 mM, 10 mM and 100 mM) on membrane permeability. Two groups of solution with the above concentration were prepared. The pH of first group is 4.83 (original) and the second group is pH 2.5. It was noticed from Fig. 3 that, the permeability of solution decreased linearly with the increase of $CuSO_4$ concentration. This linear relationship is agreed well with the trend observed in solution diffusion model [12–14] in which the volume flux increased linearly with the driving force across the membrane. Increasing the feed concentration will reduce the volume flux across the membrane due to the osmotic pressure that opposed the permeate flow [15]. Similar profile was observed for the salt solution, which was acidified to pH 2.5. If the permeability of the membrane in Fig. 3 is extrapolated to zero permeability, one finds that at $CuSO_4$ concentration of 140 mM, no permeability was obtained. This means that for the concentration of $CuSO_4$ that are less than 140 mM, the solute is dissociated at the membrane surface and the volume flux is just a simple function of the pressure different (between applied pressure and osmotic pressure) and the membrane permeability constant.

Fig. 4(a) shows the effect of $CuSO_4$ concentration on binary ions (Cu^{2+}/SO_4^{2-}) rejection while Fig. 4(b) exhibits the effect of



(a) binary ion system



(b) ternary ion system

Fig. 4. Effect of $CuSO_4$ concentration on ions rejection in (a) binary ions system (Cu^{2+}/SO_4^{2-}) and (b) ternary ions system ($Cu^{2+}/SO_4^{2-}/H^+$).

$CuSO_4$ concentration on ternary ions ($Cu^{2+}/SO_4^{2-}/H^+$) rejection. The $CuSO_4$ concentrations were varied for 0.1 mM (0), 0.5 mM (1.6), 1 mM (2.3), 5 mM (3.9), 10 mM (4.6) and 100 mM (6.9) (which is well below 140 mM). The concentrations of the feed solution were reported on log scale in Fig. 4 with their respective calculated value shown in bracket.

For binary ions system, Fig. 4(a) shows that as the concentration of $CuSO_4$ increased the rejection of Cu^{2+} ions and SO_4^{2-} ions was decreased. The magnitudes of rejection for both ions were about the same, which corresponding with the electro-neutrality requirements [16–18]. As shown in Fig. 3, when the feed salt concentration increased, the volume flux will be decreased due to the increased of osmotic pressure that opposed the permeate flow. This effect of concentration polarization is more pronounced with high feed concentration. Besides that, the solute activity at the influent side becomes higher which resulted in higher diffusion of the salt through the membrane. These reasons explains why at higher concentration (100 mM or $\ln(C_b \times 10^4 M) = 6.9$), the rejection was slightly dropped. Similar rejection profile for copper sulfate at different concentration was also reported [19].

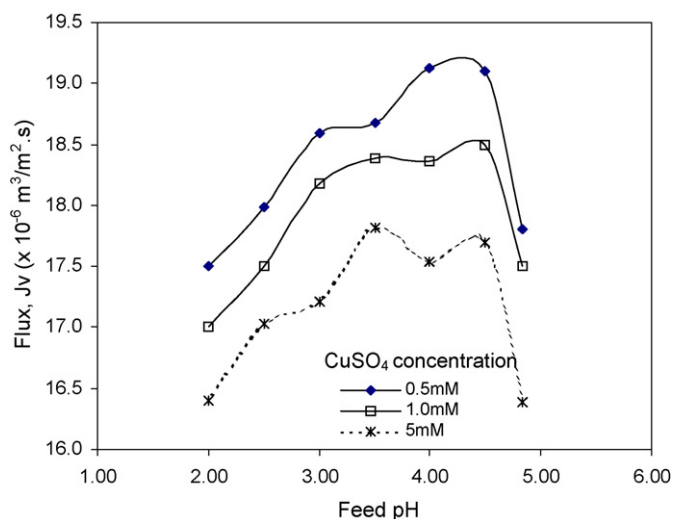


Fig. 5. Effect of feed solution pH on volume flux.

In contrary to the rejection characteristic of binary ions system, Fig. 4(b) shows the effect of CuSO_4 concentration on membrane rejection for ternary ions system (at pH 2.5). It was found that in the presence of sulfuric acid, the sulfate rejection was enhanced with the increase of CuSO_4 concentration. It was observed that under the condition of same pH, the increase of CuSO_4 concentration did contribute to the higher ratio of SO_4^{2-} to H^+ . The ions content for each CuSO_4 concentration were determined experimentally and the ratio of SO_4^{2-} to H^+ was calculated. The ratio (as indicated in the bracket) increased in the order of 0.1 mM (50.1) < 1 mM (60.8) < 5 mM (106.8) < 10 mM (169.3) < 100 mM (297.0). Basically, anions are less hydrated than cations, so they can more closely approach the membrane surface. The surface will then acquire a more negative zeta potential due to the presence of preferential adsorbed anions beyond the plane of shear [20]. As a result, the membrane with more negative charge could perform better in repelling the sulfate ions. Besides the surface charge, better rejection of sulfate ion at higher sulfate ratio was also probably due to the greater intermolecular repulsion [21].

In terms of H^+ rejection, there was a continuous drop in rejection from 0.1 mM CuSO_4 to 10 mM CuSO_4 solution. H^+ was poorly retained and concentrated in the permeate stream in corresponding to the electro-neutrality requirements. At higher CuSO_4

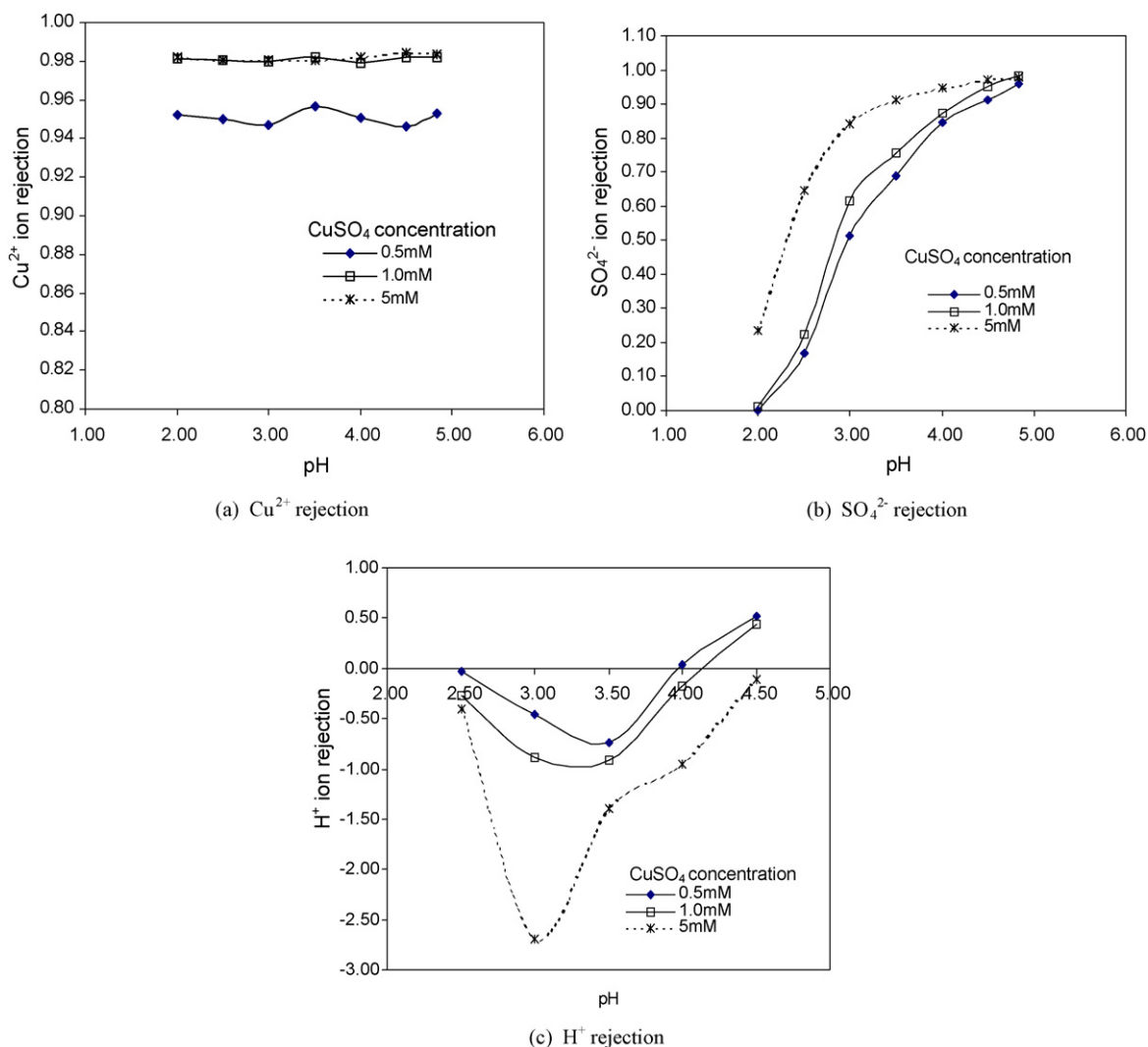


Fig. 6. Effect of pH on (a) Cu^{2+} ion rejection, (b) SO_4^{2-} ion rejection and (c) H^+ ion rejection.

concentration (100 mM) or $\ln(C_b \times 10^4 \text{ M}) = 6.9$, rejection of H^+ was improved due to the improved rejection of SO_4^{2-} . Again, the H^+ was rejected to maintain the electro-neutrality condition in the feed solution.

3.3. Influence of pH on volume flux and ternary ions rejection

Fig. 5 shows the effect of solution pH on volume flux at different concentration of CuSO_4 and constant pressure of 450 kPa. As can be seen from Fig. 5, within pH 2.0 to pH 4.83, the volume flux varied in a narrow range from 16×10^{-6} to $19.5 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$. However, the maximum volume flux was found varied depends on the concentration of CuSO_4 . For concentration of 0.5 mM and 1.0 mM, the maximum volume flux is at pH 4.5 whereas for concentration of 5 mM, the maximum volume flux was found at lower pH of 3.5. Childress and Elimelech reported that for membrane NF-55, the isoelectric point of the membrane is at pH 5 in which a peak in volume flux was observed [20]. Tsuru et al. also found that maximum volume flux was observed near the isoelectric point [22]. Based on that, it would be proposed that the isoelectric point of this membrane is within 3.5–4.5 and depends on the feed concentration. At this isoelectric point, the membrane surface acquired zero charge [23] and its volume flux profile is most likely caused by the change of electroviscous effect due to the pH [24].

Fig. 6 shows the effect of feed solution pH on membrane rejection at different concentrations of copper sulfate. The discussion is based on the rejection of each and individual ions (Cu^{2+} , SO_4^{2-} and H^+). It was expected that the minimum rejection occur at the isoelectric point of the membranes, where the membrane charge is near zero [23,24]. However, neither of the ions shows lowest rejection at this isoelectric point (pH with maximum flux). It can be seen from Fig. 6 that the rejection profile for each ion was differing within the pH range and the concentration of copper sulfate. As shown in Fig. 6(a), the rejection of copper ion was almost constant with pH. Copper ion is characterized by higher hydration energy (2105 KJ/mol) than the monovalent ion, so it would form a particular stable complex, which will reduce electrostatic interactions with the membrane [25]. Therefore, a constant rejection of Cu^{2+} was obtained under varied pH.

On the other hand, Fig. 6(b) shows that by reducing the solution pH, the rejection ability of membranes towards SO_4^{2-} was impaired. At low pH, the surface become positively charged which could repel the cations (Cu^{2+}) more effectively. Under the same pH condition, the rejection of SO_4^{2-} at higher CuSO_4 concentration is comparatively better than the SO_4^{2-} rejection at low copper sulfate concentration. This finding is similar to the results obtained in Fig. 4. At higher copper sulfate concentration, the ratio of SO_4^{2-} to H^+ will be increased. Better rejection of sulfate ions at higher ratio was due to the greater intermolecular repulsion that results in higher rejection.

The rejection profile for H^+ is shown in Fig. 6(c). The rejection ability of the membrane for H^+ is very poor compared to Cu^{2+} and SO_4^{2-} because the membrane allows free permeation of monovalence (proton). Nevertheless, it was found that the rejection was better at higher pH value. At higher pH value, the concentration of H^+ in the feed solution is lower which means that only a small concentration gradient of H^+ is accounted. As a result, the membrane rejection is better at high pH. Besides that, the membrane surface is most likely negatively charged at higher pH [24]. It was expected that the rejection of H^+ should be poorer for negatively charged membrane, however the adverse condition was observed. This phenomenon can be analyzed using Donnan effect in which the diffusion force was superseded by the electro-neutrality condition to be maintained at the feed side. At higher pH value, less penetration of SO_4^{2-} through the membrane was observed; as a result, more H^+ was retained in the feed side to maintain the electro-

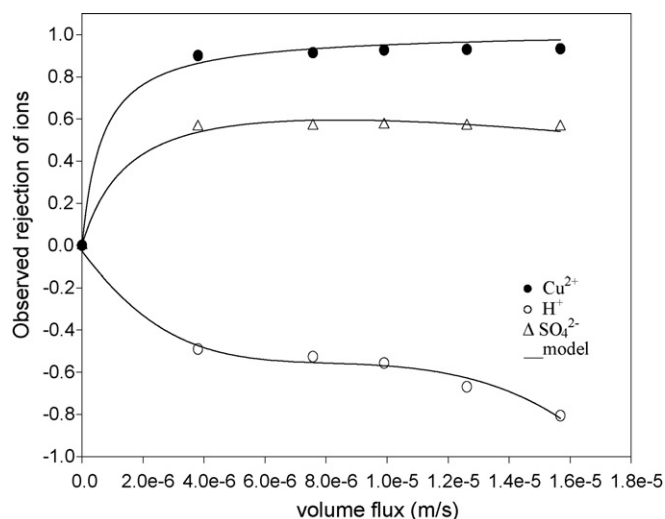


Fig. 7. Ion rejection of ternary solution at different volume flux with concentration of $\text{CuSO}_4 = 18.88 \text{ mol m}^{-3}$ (1200 ppm) and pH = 2.00.

neutrality condition. Consequently, the rejection of proton is better at higher pH compared to lower pH.

Fig. 6(c) shows that the rejection of H^+ reached its minimum value at pH 3.5 for 0.5 mM CuSO_4 and 1.0 mM CuSO_4 while for 5.0 mM CuSO_4 the minimum rejection occurred at pH 3. In other words, the minimum rejection of H^+ depends on the concentration of the copper sulfate also. The minimum rejection shift to lower pH value as the concentration increased. At higher concentration of CuSO_4 , the higher molality of SO_4^{2-} ion create a higher negative charge value on the membrane surface because SO_4^{2-} ion could approach more closely to the membrane surface compare to Cu^{2+} ion [20]. As more H^+ are needed to change the surface charge from negative sign to positive sign, the excessive permeation of H^+ results in poorer rejection. This explains why the minimum rejection could be shifted according to the salt concentration. Similar result were found that as the ionic strength of NaCl in multi-valence electrolyte solution were increased, the pH where the minimum rejection was shift to lower value [26]. As observed in Fig. 6, at lower pH values, the rejection of H^+ was increased again, because the positive ions are repelled more and more by the increase of the positive membrane charge [27,28].

3.4. Rejection and modeling of CuSO_4 in ternary solution system

In order to predict the rejection for ternary ion mixtures, the Three Parameters-CF-ENP model was adopted. From the rejection-volume flux curves, the transfer parameters $F_{1,1}$, $F_{2,1}$, $F_{3,1}$ for copper ion and $F_{1,2}$, $F_{2,2}$ and $F_{3,2}$ for sulfate ion were calculated. $F_{1,1}$ and $F_{2,1}$ are transfer parameters which indicates the diffusive transport of copper ion with relative to the sulfate ion whereas the $F_{3,1}$ is the transfer parameter of copper ion which indicate the convective transport. On the other hand, $F_{1,2}$ and $F_{2,2}$ are transfer parameters which indicates the diffusive transport of sulfate ion with relative to the copper ion whereas the $F_{3,2}$ is the transfer parameter of sulfate ion which indicate the convective transport. The above transfer parameters were determined by solving the nonlinear equation of Eqs. (4)–(9) using Marquadt method (SigmaPlot 2000). Fig. 7 shows the experimental rejection data and the predicted rejection based on the three-parameters CF-ENP model under the pH of 2.0.

As can be seen from Fig. 7, the rejection of copper ion was higher than the sulfate ion while the H^+ ion shows negative rejection. The model was to predict the rejection of copper and sulfate ions under different pH of 4.53, 3.00, 2.50 and 2.00. It was found that the model

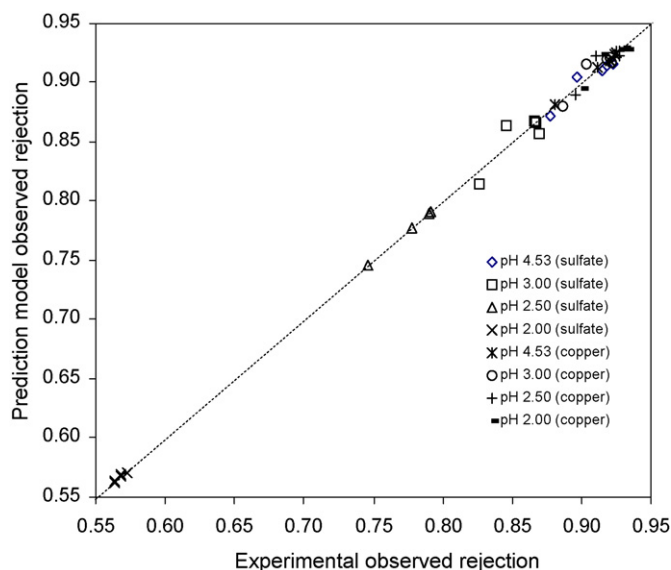


Fig. 8. Comparison of experimental and model predicted observed rejection for copper and sulfate under different pH.

estimations are in good agreement with measured rejections for all the pH value. The difference between experimental rejection and calculated rejection for both copper and sulfate ion under different pH is shown in Fig. 8. It can be concluded that, the Combined Film-Extended Nernst-Planck equation can be successfully applied in the case of this ternary solutions to predict the rejection of ions.

The calculated transfer parameters are reported in Table 1. It can be observed that for Cu^{2+} ion, the calculated $F_{1,1}$ and $F_{2,1}$ value are small, in the order of 10^{-7} m s^{-1} . This means that the transport of Cu^{2+} ion through the membrane was very low, and consequently the corresponding rejections are high as shown in Fig. 9. At lower pH value, the negative value of $F_{3,1}$ was observed, which means that the addition of H_2SO_4 decreases the transfer of copper ions through convective flow. The presence of H^+ can form easily carboxylic group $[\text{RCOO}^- \text{H}^+]$ to reduce the negative charge effect of membrane, hence, repel more copper ion. It was found that the magnitude of $F_{3,1}$ is in the order of $\times 10^{-4}$, hence the $(1-F_{3,1})$ value are very close to 1. This means that the contribution of drag by sol-

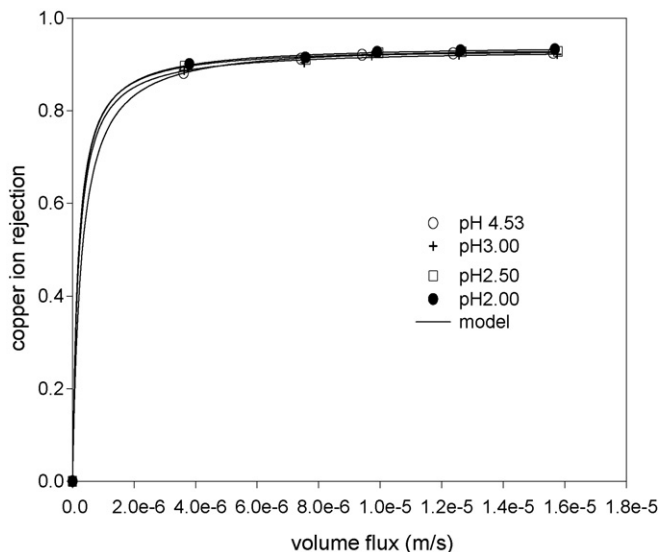


Fig. 9. Rejection of copper ion at various pH and concentration of copper ions 1200 mg/l.

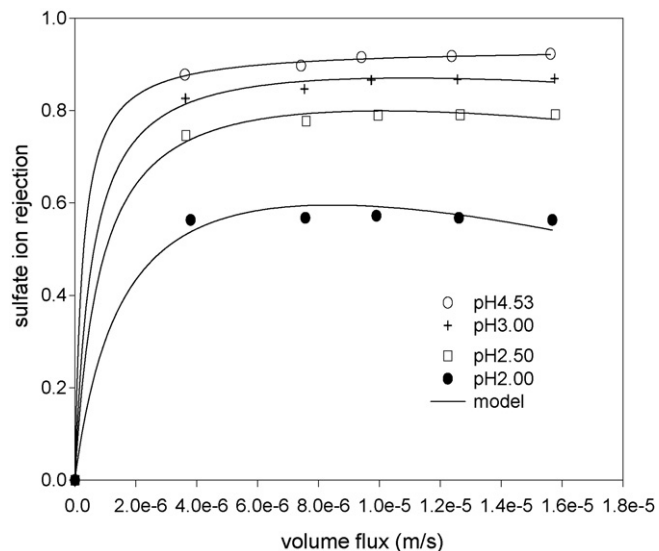


Fig. 10. Rejection of sulfate ion at various pH value and concentration of copper ions = 1200 mg/l.

vent (convective flow) to copper transport is very small and only will be noticed at high fluxes [11].

In the case of sulfate ion, Table 1 shows that the transfer parameters for $F_{1,2}$ is much higher under acidic condition. For example, the $F_{1,2}$ value of sulfate ion increased from $0.3456 \times 10^{-6} \text{ m/s}$ to $9.8940 \times 10^{-6} \text{ m/s}$ when the pH of solution was reduced from pH 3.0 to pH 2.0. The value of $F_{1,2}$ in ternary solution is higher compared to the F_1 value ($0.3090 \times 10^{-6} \text{ m/s}$) in the binary solution which indicates that the diffusion of sulfate ion through the membrane in ternary solution is higher. Subsequently, the rejection of sulfate ion becomes poorer at lower pH. At pH 2 and higher volume flux, sulfate permeation will be increased due to the excessive proton permeation driven by higher concentration gradient as well as pressure gradient. As a result, permeation of sulfate ion is increased to maintain the electro-neutrality condition at the permeate side. Higher permeation of sulfate will result in the drop of rejection. This phenomenon is well illustrated in Fig. 10 which shows decreasing tendency of sulfate rejection at pH 2 and at higher volume flux.

The increased sulfate diffusion or in other words, the reduced sulfate rejection is due to (i) the increased of driving force (concentration) as the ratio of sulfate to copper ion increased at lower pH, (ii) at lower pH value, the increase of H^+ in the solution induces a progressive neutralization of negative sites at the membrane surface [29]. Most of the charged membrane contain carboxylic groups $[\text{RCOO}^-]$, the presence of H^+ reduce the negative charge effect of membrane as discussed earlier, hence, increase the electrical potential across the membrane or induces the electro-migration of the SO_4^{2-} ion.

However, value of $F_{2,2}$ shows an adverse trend in which at lower pH, the smaller the $F_{2,2}$ value was obtained. The negative value of $F_{2,2}$ means that at lower pH the transfer rate of sulfate is lowering. It was deduced that the decreasing transfer rate of sulfate ion is due to the Donnan effect. As discussed earlier, the presence of H^+ at low pH improved the copper ion rejection. The higher concentration of copper in the feed solution consequently reduced the sulfate ions transfer rate in order to maintain the electro-neutrality condition in the feed solution.

It was also observed that the drag force which is indicated by $F_{3,2}$ increased at lower pH which indicated that the convective flow of sulfate through the membrane increased under acidic condition. At lower pH, the concentration of proton is increased, since proton is characterized by high mobility ($34.90 \times 10^{-9} \text{ m}^2/\text{sV}$), small size

Table 1
Calculated ions transport parameters: (a) copper ion and (b) sulfate ion.

(a)	Copper ion rejection in binary solution			Copper ion rejection in ternary solution					R^2 (–)	SS (–)
	pH	R_{∞} (–)	F_1 ($\times 10^{-6}$ m/s)	K ($\times 10^{-5}$ m/s)	K_1 ($\times 10^{-5}$ m/s)	K_2 ($\times 10^{-5}$ m/s)	$F_{1,1}$ ($\times 10^{-6}$ m/s)	$F_{2,1}$ ($\times 10^{-6}$ m/s)		
4.83	0.96	0.29	5.79	–	–	–	–	–	0.9999	0.6950
3.00	–	–	–	1.14	1.17	0.24	0.13	2.83	0.9997	0.6913
2.50	–	–	–	1.12	1.14	0.20	0.14	5.35	0.9997	0.7019
2.00	–	–	–	1.30	0.93	0.24	0.10	5.86	0.9997	0.7073
(b)	Sulfate ion rejection in binary solution			Sulfate ion rejection in ternary solution					R^2 (–)	SS (–)
	pH	R_{∞} (–)	F_1 ($\times 10^{-6}$ m/s)	K ($\times 10^{-5}$ m/s)	K_1 ($\times 10^{-5}$ m/s)	K_2 ($\times 10^{-5}$ m/s)	$F_{1,2}$ ($\times 10^{-6}$ m/s)	$F_{2,2}$ ($\times 10^{-6}$ m/s)		
4.83	0.96	0.31	5.03	–	–	–	–	–	0.9997	0.6853
3.00	–	–	–	1.24	1.13	0.35	0.21	0.01	0.9990	0.6101
2.50	–	–	–	1.29	1.74	6.32	–5.13	0.17	0.9999	0.5075
2.00	–	–	–	2.13	3.77	9.90	–7.89	0.51	0.9999	0.2677

and high diffusion coefficient (9.34×10^{-9} m²/s) [29], therefore, it passes through the membrane more easily than copper. In this case, it enhanced the convective flow of sulfate through the membrane to maintain the Donnan equilibrium in the permeate solution.

4. Conclusion

It was found that the membrane rejection was almost independent of the effect of pressure, which means that the membrane could be operate under lower operating pressure. The membrane shows more than 92% observed rejection for concentration up to 10 mM. The membrane rejection towards copper ion is not affected by the pH value within pH 2.0 to pH 5.0 which means that the membrane is suitable to use even under acidic condition. Although the permeation flux was reduced at low pH, the overall flux is over 1.6×10^{-5} m/s when operated at 450 kPa and 5 mM CuSO₄. The membrane is able to separate the proton and copper ion at higher volume flux. The membrane observed rejection was predicted using the model based on Combined-Film-Extended Nernst-Planck Equation. The model is combined with the film theory to take into account the concentration polarization effect. The mass transfer coefficient calculated is in the same order of volume flux, which means that the concentration polarization effect cannot be neglected. The rejection data for copper and sulfate ions are predicted based on binary ion system and ternary ion system (with the presence of H⁺). The model agrees well with the experimental results in both binary and ternary ions system. The R^2 value of the curve fitting is over 0.95.

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