



## Technical Note

## Rejection of divalent ions in commercial tubular membranes: Effect of feed concentration and anion type



Danial Qadir\*, Hilmi B. Mukhtar, Lau K. Keong

Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Sri Iskandar 32610, Malaysia

## ARTICLE INFO

## Article history:

Received 15 August 2016

Received in revised form

25 October 2016

Accepted 14 December 2016

Available online 24 December 2016

## Keywords:

Tubular membranes

Calcium salts

Tin salts

Sulphate retention

Chloride retention

## ABSTRACT

Four commercial tubular membranes (AFC80, AFC30, PU608, and ES404) have been investigated in this study for their performance of binary metal ions rejection under different feed conditions. A range of salts (tin chloride, tin sulphate, calcium chloride, calcium sulphate) with divalent cations were chosen to assess the effects of different anions (chloride and sulphate) on performance of the membranes. All membranes were tested by varying the feed concentration (2500, 5000, 10,000 mg L<sup>-1</sup>) at fixed cross flow velocity of 1.5 LPM and feed pressure 1400 kPa. Observed retention ( $R_{obs}\%$ ) and permeate flux ( $J_v$ ) were key parameters to evaluate the performance of studied tubular membranes. It was found that increase in concentration adversely affected the both evaluation parameters, i.e., permeate flux and rejection. Nevertheless, nanofiltration type tubular membranes (AFC80 and AFC30) showed higher rejection than their counterparts, i.e., ultrafiltration type tubular membranes (ES404, PU608) for all investigated salts. Maximum observed rejection for all salts was noted for AFC80 for all salts followed by AFC30, ES404 and PU608 tubular membranes. Furthermore, it is reveal that anion types ( $SO_4^{2-}$ ,  $Cl^-$ ) of these salts played a vital role in retention of these tubular membranes when the salts with same cations were used as feed solution.

© 2016 Chinese Institute of Environmental Engineering, Taiwan. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Heavy metal ions removal from water bodies is of a great significance since their toxicity and hazardous nature could cause harm for living beings. Disposal of industrial wastes usually to land and water stream is a main source of environmental pollution. These metals could exist either as ions, compounds or in the form of complexes. Many studies have been conducted to investigate the effects of various heavy metals on human bodies which resulted in identifying their hazards of their exposure to environment and human population. These heavy metals could cause not only severe diseases in humans but it could also pose a serious threat to our ecosystem [1–4].

Tin in its very nature is not as hazardous as other heavy metals but it could cause severe health problems such as eye and skin irritations, depression, severe sweatiness, urinating problems, liver and kidney damage, tumour formation, shortage of red blood cells

and weak immune systems. Tin is found excessively in tin mining areas and in waste of industries such as paints, plastics and food. It is naturally present in very low amount in environment and usually its presence is in the form of tin oxide which is of insoluble nature. Nevertheless, tin based organic compounds, e.g., tributyltin and trifenylytin, are of highly hazardous nature because they are very difficult to biodegrade resulting in the accumulation in water bodies or soil. Its dangerous nature is of serious concern for ecosystems as well since it not only disturbs the growth of aquatic life (algae, fungi, fish, phytoplankton, etc.) but it also damages their reproduction and feeding pattern [1,5–7].

Over the years, many treatment technologies have been developed and successfully employed to remove the different pollutants from the water. Among technologies are solvent extraction, liquid–liquid extraction, chemical precipitation, ion flotation, ion exchange and adsorption. But most of these methods are slow, time consuming, low quality product and generate waste sludge [2,8]. Membrane separation technology has gained its reputation because of its distinctive features such as high quality product, cost effectiveness, low waste and low energy requirements [9,10]. Ultrafiltration and more specifically nanofiltration have been proven to be of great value for removal of heavy metals from waste or

\* Corresponding author.

E-mail address: [daniel2715@gmail.com](mailto:daniel2715@gmail.com) (D. Qadir).

Peer review under responsibility of Chinese Institute of Environmental Engineering.

polluted streams. These membranes are classified based on their pore sizes basis with ultrafiltration membranes generally having larger pore sizes of 2–100 nm while nanofiltration lies between ultrafiltration and reverse osmosis with their relatively smaller pore size of 0.5–2 nm. These membranes have gained their due importance because of their characteristics such as low operational cost, absence of toxic sludge, compactness, low energy consumption and better rejections of heavy metal ions [11,12].

In this study, four commercially available tubular membranes (AFC80, AFC30, ES404, PU608) were evaluated for their ability to remove the tin ions from aqueous solution of various tin salts. This study also evaluates the effect of different feed concentration on membrane performance. A review of recent literature has revealed that tin ion removal has not been studied extensively and no study has been found in context of tin ion removal for aforementioned commercially available membranes. Thus, the present work would add not only a valuable investigation into body of water treatment literature but also be used as a benchmark studies for further investigation in removal of tin salts from aqueous solutions.

## 2. Experiments

A self-assembled tubular membrane set up was installed to investigate the performance of aforementioned commercially available tubular membranes. Tubular membranes were designed in parallel configuration for testing purposes. Aqueous solutions of different salts were introduced as feed solutions under varying feed conditions. Effect of various salt types, salts concentrations and feed pressure were evaluated in terms of permeate flux and salt rejection.

### 2.1. Materials and methods

Deionized water from ion-exchange unit was used for aqueous solution preparation. Salts such as calcium chloride, calcium sulphate, tin chloride and tin sulphate of pure analytical grade were purchased from Merck (Germany). Tubular membranes (single tube) were bought from PCI (UK). All these membranes were 1.2 m long and of 12.5 mm diameter. Among four investigated tubular membranes, two membranes AFC80 and AFC30 were polyamide nanofiltration type while other two membranes (ES404, PU608) were polysulfone based ultrafiltration membranes. The specifications of commercial tubular membranes are shown in Table 1.

In this study, a self-assembled tubular unit from SOLTEQ (TR08) was used. Feed was introduced to the tubular setup in a cross flow pattern at fixed value by the pump. Concentration of salts in feed and permeate was determined by HANA EDGE meter while permeate was collected in a beaker placed on weighing balance attached to computer following the gravimetric method.

### 2.2. Retention studies

Retention measurements were made at room temperature, fixed cross flow velocity (1.5 LPM) and constant feed pressure (1400 kPa).

**Table 1**  
Specifications of commercial tubular membranes.

Membrane type	Apparent retention	Hydrophilicity <sup>a</sup>	pH range	Surface charge
AFC80	80% NaCl	2	1.5–10.5	Strong negative
AFC30	75% CaCl <sub>2</sub>	2	1.5–9.5	Strong negative
ES404	4000	4	1.5–12	Slightly negative
PU608	8000	4	1.5–12	Slightly negative

<sup>a</sup> On a Scale where “5” being the highest value of hydrophilicity and “1” the lowest.

All aqueous salt solutions were prepared from deionized water at neutral pH and no pH adjustment was made to the solutions. Concentration of salts investigated here was as follows; 2500, 5000 and 10,000 mg L<sup>-1</sup>. Calibration curves were prepared for each salt before the testing and concentration of permeate and feed were calculated through these curves. For each salt testing, new membranes were used and compaction of membranes was also performed at 1600 kPa till steady state flux was achieved. At each operational condition, a fixed 0.5 L permeate was collected for further analysis. Observed rejection and permeate flux of salts was calculated by the formulae [13];

$$R_{obs}(\%) = 1 - \frac{C_p}{C_f} \quad (1)$$

$$J_v = \frac{Q}{A} \Delta t \quad (2)$$

where  $C_p$  and  $C_f$  is the concentration of permeate and feed, respectively,  $Q$  is flow rate (L h<sup>-1</sup>),  $A$  is area (0.05 m<sup>2</sup>) and  $J_v$  is membrane flux (L h<sup>-1</sup> m<sup>-2</sup>).

## 3. Results and discussion

An investigation of feed parameters is a vital part of membrane filtration to choose the optimum operating conditions for certain filtration purpose. Feed concentration is one of the important parameters to be evaluated for any filtration process since it directly affects the filtration efficiency of membranes. In order to study the effect of feed concentration on performance of chosen tubular membranes, aqueous solutions of following feed concentrations; 2500, 5000, 10,000 mg L<sup>-1</sup> were prepared for all salts such as CaCl<sub>2</sub>, CaSO<sub>4</sub>, SnCl<sub>2</sub>, and SnSO<sub>4</sub>. A detailed result of membrane performance is presented in Table 2 for tested tubular membranes.

It is interesting to note that nanofiltration membranes (AFC30 and AFC80) being negatively charged and of same type exhibited different rejection behaviours for same salts at similar feed conditions. Also the rejection of these membranes for each salt followed the similar trend here, i.e., rejection decreased slightly when concentrations of salts were increased. Among the two nanofiltration membranes, AFC-80 showed better rejection for each salt because of its tighter nature as claimed by manufacturer. Nevertheless, it is important to mention that metal salts containing the sulphate anions had better rejection than their counterpart (Cl<sup>-</sup> ion). Likely reason as discussed in literature is that chloride ions get less hydrated in comparison to the sulphate ions and they diffuses through membranes easily resulting in poor performance of the membrane [14,15]. Another reason that has been widely acclaimed is valence of anions. It is believed that anions with higher valence are easily rejected than the lower valence anions because of the less repulsion forces of the membranes pushing them away from membrane surface. This behaviour of anion rejection is widely observed in case of charged membranes and has been reported by many researchers as “Donnon Exclusion” [16,17]. These phenomena play an active role where tin sulphate had better rejection than tin chloride. Same can be said for calcium cations, where calcium sulphates show better rejection than calcium chloride for both nanofiltration membranes. The rejection order in all studied membranes is as follows; SnSO<sub>4</sub> ≥ CaSO<sub>4</sub> > SnCl<sub>2</sub> > CaCl<sub>2</sub>. It is of great importance to notice that in case of two different cations (Ca<sup>2+</sup>, Sn<sup>2+</sup>) with same type of anion (SO<sub>4</sub><sup>2-</sup>), rejection is dominated not only by their respective ionic sizes but also strong repulsion forces due to membrane surface charge. Here, it is safe to deduce that rejection of these salts is a complex mechanism where anion types, anion concentration, membrane charge played their effective

**Table 2**  
Permeate flux ( $J_v$ ) and observed rejection ( $R_{obs}$  %) data for commercial tubular membranes at cross flow velocity of 1.5 LPM and 1400 kPa feed pressure.

Concentration (mg L <sup>-1</sup> )	CaCl <sub>2</sub>		CaSO <sub>4</sub>		SnCl <sub>2</sub>		SnSO <sub>4</sub>	
	$J_v$ (L <sup>-1</sup> h <sup>-1</sup> m <sup>2</sup> )	$R_{obs}$ (%)	$J_v$ (L <sup>-1</sup> h <sup>-1</sup> m <sup>2</sup> )	$R_{obs}$ (%)	$J_v$ (L <sup>-1</sup> h <sup>-1</sup> m <sup>2</sup> )	$R_{obs}$ (%)	$J_v$ (L <sup>-1</sup> h <sup>-1</sup> m <sup>2</sup> )	$R_{obs}$ (%)
(a) AFC30								
2500	75	38	76	47	75	39	74	57
5000	74	36	67	45	71	38	70	54
10,000	54	33	62	43	68	36	58	52
(b) AFC80								
2500	36	80	17	89	32	87	30	89
5000	28	78	14	86	28	85	27	87
10,000	21	76	12	84	24	83	19	86
(c) ES404								
2500	139	27	149	37	138	29	137	36
5000	131	25	144	34	131	27	130	34
10,000	129	23	139	32	129	26	128	33
(d) PU608								
2500	177	15	207	18	176	16	178	19
5000	172	14	203	16	171	14	171	16
10,000	166	12	198	15	165	13	163	14

role among other factors. In particular, pH of a feed solution could have played an important role in rejection of these salts, since membrane charge is greatly influenced by the pH of the feed solution. In literature, isoelectric points (IEP) of these nanofiltration membranes (AFC80 & AFC30) are reported to be 3.6 and 5.3, respectively in KCl solution [2,8]. It is important to note that membranes behave differently under the conditions where pH of solution is different than their respective IEP. Table 3 presents the pH of feed solutions at different concentrations. It can be seen that for all concentrations of calcium salts, pH of feed solutions (6.03–8.45) remained above the IEP's of both nanofiltration membrane tested here whereas for tin salt solutions pH of feed solutions was found to be well below the IEP of membranes used here in highly acidic range (2.22–2.80). It is interesting to note that for tin salt solutions, membranes would have reversed the charge and had acted as positive charged membranes because of the protonation of amine groups on surface of these membranes. Consequently, heavy metal ions (Sn<sup>2+</sup>) got repelled strongly resulting in higher rejections [2,8,18]. Such results have already been reported by Gherasim et al. where lead rejection was found to be greatly affected when membrane acted as positively charged membrane because of charge reversal due to low pH of feed solution [2]. Hence the difference in rejection of these salts for each membrane can be linked to interplay of these factors as shown in this investigation.

In case of ultrafiltration tubular membranes studied here, it is observed that ES404 showed better rejection than PU608 ultrafiltration membrane since PU608 had larger molecular weight cut off. Nevertheless, it is interesting to note that for PU608 membrane, salts containing sulphate anions had slightly better rejection than chloride ones. But this difference in rejection of same salts with different anions becomes bigger for ES404. Since these ultrafiltration membranes are polysulfone based and have slightly negative surface charge so their rejection is influenced by membrane surface charge. The role of membrane surface charge is found to be exactly same as found in case of nanofiltration membranes (Table 2). It is

**Table 3**  
pH of feed solutions of calcium and tin salts at different concentrations.

Salts	2500 mg L <sup>-1</sup>	5000 mg L <sup>-1</sup>	10,000 mg L <sup>-1</sup>
CaCl <sub>2</sub>	6.54	7.63	8.45
CaSO <sub>4</sub>	6.03	6.15	6.23
SnCl <sub>2</sub>	2.80	2.56	2.35
SnSO <sub>4</sub>	2.64	2.45	2.22

evident that ultrafiltration membrane does not perform well for removal of divalent metal salts owing to its larger pore sizes yet it could be assumed that they might be useful for low concentration feed solutions.

Table 2 data also indicate that ultrafiltration membranes have considerably higher  $J_v$  than the nanofiltration membranes. The reason for such behaviour is that ultrafiltration membranes have larger pore sizes with less tight membrane structure in comparison to nanofiltration membranes with pore sizes in few nm ranges. It is also evident from the results that PU608 membrane has the highest  $J_v$  and lowest rejection among all four tubular membranes because of its loose structure. The significant decrease in permeate flux for ultrafiltration membranes here is thought to be the direct result of concentration polarization effect on membrane surface as reported by researchers previously [19,20]. This effect stimulates an increase in solute concentration on membrane surface which consequently generates a greater osmotic pressure [19,21]. This increase in osmotic pressure on membrane surface will decrease the solvent flux during the filtration. Here, it is important to notice that calcium sulphate had better permeate flux than the tin sulphate aqueous solution. The likely reason for such observation could be that membrane surface faced more osmotic pressure in case of tin sulphate aqueous solution because of better rejection of tin ions due to combined effect of sieving mechanism and polarization effect. Hence, solvent flux decreased during the filtration process resulting in less flux than the calcium sulphate solution which had the same anion but smaller ionic size, which helped it to bypass the filtration conveniently.

#### 4. Conclusions

In this study, commercially available nanofiltration and ultrafiltration tubular membranes were evaluated for their performance of rejecting the tin based salt solutions. Key findings are as follows;

- Order of rejection for all tubular membranes at all feed concentrations was as follows, SnSO<sub>4</sub> > CaSO<sub>4</sub> > SnCl<sub>2</sub> > CaCl<sub>2</sub>
- Among tubular nanofiltration membranes, AFC80 showed better rejection than AFC30 for all salts.
- Maximum rejection for tin salts was noticed here for AFC80 tubular membrane as 89% and 87% for tin sulphate and tin chloride salts respectively.
- Increase in feed concentration slightly reduced the tin salts rejection for all membranes.

- Nanofiltration based tubular membranes had Donnon Exclusion as dominant rejection mechanism.
- In a scenario, where common cations ( $\text{Ca}^{+2}$ ,  $\text{Sn}^{2+}$ ) were used among salts, Donnon phenomenon caused the better rejection for salts with sulphate ions (anion) than the salts with chloride ions.

### Acknowledgements

Author is grateful to MyRA funding authority for their financial support (0153AB-J16) and Universiti Teknologi PETRONAS (0153AB-J16) for their lab facilities.

### References

- [1] Mahurpawar M. Effects of heavy metals on human health. *Int J Res-Granthaalayah* 2015;3:1–7.
- [2] Gherasim CV, Cuhorka J, Mikulasek P. Analysis of lead(II) retention from single salt and binary aqueous solutions by a polyamide nanofiltration membrane: experimental results and modelling. *J Membr Sci* 2013;436:132–44.
- [3] Al-Rashdi B, Somerfield C, Hilal N. Heavy metals removal using adsorption and nanofiltration techniques. *Sep Purif Rev* 2011;40:209–59.
- [4] Ashraf MA, Maah MJ, Yusoff I, Ghararibreza M. Speciation of heavy metals in the surface waters of a former tin mining catchment. *Chem Spec Bioavailab* 2012;24:1–12.
- [5] Winship KA. Toxicity of tin and its compounds. *Adverse Drug React T* 1988;7:19–38.
- [6] Lenntech. Chemical Properties of Tin – Health Effects of Tin – Environmental Effects of Tin. Delft, Netherlands: Lenntech; 2016.
- [7] Edward Group DC, NP, DACBN, DCBCN, DABFM. Toxic Metal: The Health Dangers of Tin. Houston, TX: Global Healing Center; 2013.
- [8] Bouranene S, Fievet P, Szymczyk A, Samar MEH, Vidonne A. Influence of operating conditions on the rejection of cobalt and lead ions in aqueous solutions by a nanofiltration polyamide membrane. *J Membr Sci* 2008;325:150–7.
- [9] Qadir D, Mukhtar H, Keong LK. Mixed matrix membranes for water purification applications. *Sep Purif Rev* 2017;46:62–80.
- [10] Thakur VK, Voicu SI. Recent advances in cellulose and chitosan based membranes for water purification: a concise review. *Carbohydr Polym* 2016;146:148–65.
- [11] Van der Bruggen B, Vandecasteele C, Van Gestel T, Doyen W, Leysen R. A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environ Prog* 2003;22:46–56.
- [12] Zhou D, Zhu LJ, Fu YY, Zhu MH, Xue LX. Development of lower cost seawater desalination processes using nanofiltration technologies – a review. *Desalination* 2015;376:109–16.
- [13] Li NN, Fane AG, Ho WSW, Matsuura T, editors. *Advanced Membrane Technology and Applications*. Hoboken, NJ: John Wiley & Sons; 2011.
- [14] Mehdipour S, Vatanpour V, Kariminia HR. Influence of ion interaction on lead removal by a polyamide nanofiltration membrane. *Desalination* 2015;362:84–92.
- [15] Chávez-Guajardo AE, Medina-Llamas JC, Maqueira L, Andrade CAS, Alves KGB, de Melo CP. Efficient removal of Cr (VI) and Cu (II) ions from aqueous media by use of polypyrrole/maghemite and polyaniline/maghemite magnetic nanocomposites. *Chem Eng J* 2015;281:826–36.
- [16] Knowles AD, Nguyen CK, Edwards MA, Stoddart A, McIlwain B, Gagnon GA. Role of iron and aluminum coagulant metal residuals and lead release from drinking water pipe materials. *J Environ Sci Heal A* 2015;50:414–23.
- [17] Moradihamedani P, Kalantari K, Abdullah AH, Morad NA. High efficient removal of lead(II) and nickel(II) from aqueous solution by novel polysulfone/ $\text{Fe}_3\text{O}_4$ -talc nanocomposite mixed matrix membrane. *Desalin Water Treat* 2016;57:28900–9.
- [18] Gherasim CV, Mikulasek P. Influence of operating variables on the removal of heavy metal ions from aqueous solutions by nanofiltration. *Desalination* 2014;343:67–74.
- [19] Blatt WF, Dravid A, Michaels AS, Nelsen L. Solute polarization and cake formation in membrane ultrafiltration: causes, consequences, and control techniques. In: Flinn JE, editor. *Membrane Science and Technology: Industrial, Biological, and Waste Treatment Processes*. Boston, MA: Springer; 1970. p. 47–97.
- [20] Abdullah N, Gohari RJ, Yusof N, Ismail AF, Juhana J, Lau WJ, et al. Polysulfone/hydrous ferric oxide ultrafiltration mixed matrix membrane: preparation, characterization and its adsorptive removal of lead (II) from aqueous solution. *Chem Eng J* 2016;289:28–37.
- [21] Kalaiselvi G, Maheswari P, Mohan D, Balasubramanian S. Synthesis and characterization of poly 3-methyl 2-vinyl pyridinium nitrate incorporated polyvinylidene fluoride ultrafiltration membrane for metal ion removal. *Sep Purif Technol* 2015;143:105–14.