Nanofiltration performance of lead solutions: effects of solution pH and ionic strength
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ABSTRACT
Nanofiltration performance (i.e. rejection and flux decline) of lead solutions was investigated using a dead-end test cell at room temperature. An aromatic polyamide NF-90 membrane was chosen to determine the impacts of solution chemistry. The experimental results revealed that solution flux decline was dependent on solution pH, ionic strength, and type of lead solutions. Solution flux conducted with different types of lead solutions (i.e. PbCl₂ and Pb(NO₃)₂) decreased with increased solution pH. Solutions having high pH exhibited greater flux decline than those having low solution pH, while lead ion rejections were relatively high. Increased ionic strengths resulted in a greater flux decline, while lead ion rejections decreased with decreasing solution pH and increasing ionic strengths. Such results were related to low solution pH, suggesting an increase in fixed charge of proton (H⁺), decreasing electrical double layer thickness within membrane, thus allowing increased lead concentration passing through the membrane surface. Solution flux and rejection decreased further at higher ionic strengths, which caused a reduced negatively charged membrane, and thus decreased rejections. It was also found that lead ion for PbCl₂ solution exhibited higher rejections than that of Pb(NO₃)₂ solution.

Key words | flux decline, lead solution, nanofiltration, solution chemistry

INTRODUCTION
Membrane technologies have been widely used in the field of water treatment due to stringent water quality regulations (Hong & Elimelech 1997). They are efficient technologies to remove feed source water in terms of natural organic matter (NOM) (Cho et al. 1999; Kilduff et al. 2004; Mattaraj et al. 2008), inorganic scalants (Lisdonk et al. 2000; Lin et al. 2006; Jarusutthirak et al. 2007), salt solution (Anne et al. 2001; Labbez et al. 2003; Childress & Elimelech 2007) and heavy metals (Meighuene et al. 1999; Molinari et al. 2001; Ipek 2005; Ku et al. 2005; Turek et al. 2007). Nanofiltration (NF), one of membrane technologies, is a relatively new membrane process, which is considered to be intermediate between ultrafiltration (UF) and reverse osmosis (RO) in terms of operating conditions. NF membrane processes operate at pressures between 50 and 150 psi much lower than RO (200 to 1,000 psi), but higher than UF (10 to 70 psi). At the present time, NF is increasingly applied in the field of water treatment. For example, ground waters containing high color due to dissolved organic matter (DOM), partially decomposed from plant materials, high hardness from the composition of calcium (Ca²⁺) and magnesium (Mg²⁺), and high iron (Fe²⁺) and manganese (Mn²⁺) concentration. NF can provide high water quality and large amount of water production in the short period of operation. It can give water quality within drinking water standards. However, membrane fouling caused by organic and inorganic substances can be a major factor limiting more widespread use of membrane technologies, reducing long-term filtration performance (i.e. water production), and increasing costs for membrane operation through
higher labor, frequent chemical cleaning, and membrane replacement.

Inorganic fouling (i.e. negative and positive ions) can be a significant factor that enhances permeate flux decline during filtration. This may cause an increased concentration polarization that exceeds solubility limit, resulting precipitative fouling of scale-forming species (i.e. Ca\(^{2+}\), Mg\(^{2+}\), CO\(_3^{2-}\), SO\(_4^{2-}\), and PO\(_4^{3-}\)). This has been recently investigated by Jarusutthirak et al. (2007). Molinari et al. (2001) investigated the interactions between membranes (RO and NF) and inorganic pollutants (i.e. SiO\(_2\), NO\(_3\), Mn\(^{2+}\), and humic acid). They showed that increased flux decline was caused by the interactions between the membranes and other ions. Other factors, which can increase flux decline, are solution pH, ionic strength, concentration, operating conditions, and solution compositions. In addition, inorganic fouling caused by the presence of metal ion in the aquatic environment has also been a subject of importance because of its toxicity for human health and environment, while the applications of nanofiltration for removing metal ions are recently limited in terms of solution chemistry affecting NF performance during filtration period. However, previous study mentioned the efficient use of membrane separation processes for the control of lead and copper corrosion (Taylor & Jacobs 1996), and the feasible recovery of valuable metals (Ku et al. 2005). The metallic ions can also produce stable complexes with organic compounds, which can be more resistant to metal oxidation in natural water. Lead (Pb\(^{2+}\)), known to occur widely as a result of lead plumbing materials and the action of corrosive water, is one of interested inorganic materials used in this study due to relatively low maximum contaminant levels in primary standards (affecting directly to human health) for water quality regulations (Cotruvo & Vogt 1990), while there is a lack of nanofiltration performance of lead solution using various solution pHs and ionic strengths. Therefore, the objective of this paper was to investigate the effects of solution chemistry on nanofiltration performance of different types of lead solutions. The molecular weight cut-off (MWCO) of the NF-90 membrane was about 90 Da, indicating a tight NF membrane (Tahaikt et al. 2007).

An aromatic polyamide thin-film composite NF-90 membrane, produced by Dow-FilmTec., was chosen to determine the effect of solution chemistry on nanofiltration performance of different types of lead solutions. The molecular weight cut-off (MWCO) of the NF-90 membrane was about 90 Da, indicating a tight NF membrane (Tahaikt et al. 2007). According to the manufacturer’s information, the maximum operating pressure is 4,137.6 kPa, maximum feed flow rate is 3.6 m\(^3\) hr\(^{-1}\), maximum operating temperature is 45°C and the operating pH ranges from 1 to 12. Free chlorine tolerance is less than 0.1 ppm. NF-90 is generally a tight NF membrane with a very high surface roughness (Bellona & Drewes 2005).

In operation, membrane flat sheets were stored in 1% sodium meta-bisulfite (Na\(_2\)S\(_2\)O\(_3\)) and kept in refrigerator at 4°C to prevent microbial activity. The water flux characteristics were determined for 30-min operation with clean water for membrane compaction. The membrane permeability was determined from the clean water flux data at different operating pressures.

**Analytical method**

Lead concentration was measured by using atomic absorption (AA) spectrometry (AAAnalyst 200 Version 2, Perkin Elmer Corp.). Measurements of solution pH, conductivity and temperature were made using pH meter (Inolab pH level 1, Weilheim, Germany), and conductivity meter connected with temperature (Inolab cond. level 2, Weilheim, Germany), respectively. Ionic strengths of samples were calculated using a correlation between conductivity and ionic strength of NaCl standards, I.S.[M] = 0.5ΣC\(_i\)Z\(_i\)\(^2\) (C\(_i\) is the ion concentration and Z\(_i\) is the number of ions).

**Flux decline experiments**

The experiments were carried out with three liters of solution containing lead solutions (PbCl\(_2\) and Pb(NO\(_3\))\(_2\)) at fixed concentration about 20 mg L\(^{-1}\), while solution pH from 4 to 6 and ionic strengths (0.01, 0.05 M as NaCl) were varied in this study. As shown in Figure 1, the experiments were tested by using a 400-ml dead end membrane filtration...
apparatus (Amicon 8400, USA) with magnetic stirrer (LABINCO, LD-12), while the magnetic spin bar fitted into the cell provided the agitation. While the dead end filtration system may not be practical compared with the crossflow one, it has been widely used in the laboratory study in order to simulate the situation of severe flux decline and fouling. The stirring speed was about 300 rpm.

A membrane sheet was fitted to the cell with the membrane active area of 41.38 cm². The operating pressure was employed via high-pressure regulator of nitrogen cylinder. The permeate volume was determined during filtration by using the electrical balances (Mettler Toledo Monobloc PB-3002-S, USA). After filtration was terminated, two steps of cleaning, i.e. hydrodynamic cleaning followed by chemical cleaning, were performed. For hydrodynamic cleaning, the membrane sheet was cleaned with deionized (DI) water, then followed with chemical cleaning, acidic solution (using citric acid) with pH of 4 for 30-min each. After each cleaning, water fluxes at different operating pressures were measured to determine water flux recovery. For the next run of the experiment, new membrane sheet was used in order to avoid non-recoverable resistance from the previous filtration experiment. New membrane sheet was initially used to characterize clean water flux for membrane compaction, and subsequently used to determine water flux after hydrodynamic and chemical cleaning.

**Analysis of results**

The parameters taken into account were:

The volumetric flux \( J_v \) (L.m⁻².h⁻¹ or LMH) was determined by measuring the volume of permeate collected in a given time interval divided with membrane area by the relation:

\[
J_v = L_p(\Delta P - \alpha \Delta \pi) = \frac{Q_p}{A}
\]

where \( L_p \) is the membrane permeability (LMH kPa⁻¹); \( \Delta P \) is the transmembrane pressure (kPa); \( \alpha \) is the osmotic reflection coefficient (-); \( \pi \) is the osmotic pressure (kPa); \( Q_p \) and \( A \) represent flow rate of permeate (Lh⁻¹) and the membrane area (m²), respectively.

The observed rejection was calculated by the following relation:

\[
\% R = \left(1 - \frac{C_p}{C_i}\right) \times 100
\]

where \( C_p \) and \( C_i \) are the solution concentrations in the permeate (mg L⁻¹), and in the initial feed solution (mg L⁻¹), respectively.

**RESULTS AND DISCUSSION**

**Water flux characteristics**

Before the experiments, the membrane permeability was measured after membrane compaction by measuring water flux as a function of operating pressure using DI water. The effect of osmotic pressure in Equation (1) was neglected for DI water. Clean water flux increased linearly with increased operating pressure with the correlation coefficient of 0.999. The slope represents the membrane permeability \( (L_p) \) of 0.0714 LMH kPa⁻¹. The measured membrane permeability was considered as reference to evaluate cleaning procedure and water flux recovery after system cleaning.

After filtration experiments, the membrane sheets were cleaned with DI water and followed with citric acid in order to investigate water flux recovery. As shown in Figure 2, the clean water flux after system cleaning of PbCl₂ and Pb(NO₃)₂ solutions at pH 6 was similar to clean water flux after membrane compaction, while water flux observed after hydrodynamic cleaning was lower when compared with clean water flux after membrane compaction. This suggested the inorganic lead resulted in an increase in flow resistance during filtration experiments. Increased flux caused by chemical cleaning was possibly due to...
protons from acid, which could efficiently dissolve inorganic lead from the membrane surface, thus enhancing flux recovery. This suggested that an increase in water flux recovery was found for the membrane sheets cleaned by deionized (clean) water and chemical cleaning agent. The comparisons of clean water fluxes were similarly found with two types of lead solutions. This indicated that ionic lead (PbCl₂ and Pb(NO₃)₂ solutions) showed less non-recoverable resistance after system cleaning, indicating high water flux recovery.

Effects of solution pH on flux and rejection

The effect of solution pH on flux decline of PbCl₂ and Pb(NO₃)₂ solutions were carried out at pH 4, 5 and 6 with constant ionic strength 0.01 M as NaCl at 413.6 kPa operating pressure. Feed concentration was kept at 20 mg L⁻¹. Figure 3 shows the effect of solution pH on relative flux. It was evident that the extent of flux decline increased with increasing solution pH for both PbCl₂ and Pb(NO₃)₂ solutions. For higher pH, relative fluxes of Pb(NO₃)₂ solution \( (J_v/J_{v0} = 0.88 \text{ at pH } 6) \) showed higher flux decline than those of low solution pH \( (J_v/J_{v0} = 0.90 \text{ at pH } 4) \). At low pH, it suggested an increased fixed charge of H⁺, which decreased electrical double layer thickness within membrane or both, thus decreased concentration at the membrane surface. At high pH of 6, the membrane surface and pores became more negatively charged, while the anions from lead dissociation was presented in the feed solution. As a result, the pore size of the membrane was reduced because of the electrostatic repulsion between neighboring negatively charged groups, thus adopting an extended conformation (Schaep & Vandecasteele 2001; Teixeira et al. 2005). In addition, the osmotic pressure near the membrane surface increased due to high salt rejection, resulting in a decrease of the net driving pressure, thus affecting flux reduction. These mechanisms resulted in a decrease of permeate flux and an increase in salt rejection with increased solution pH.

Figure 4 shows the effect of solution pH on lead ion rejection. It was observed that lead ion rejection was relatively constant throughout filtration period. This indi-
cated that high diffusive transport became more important than convective transport for the tight NF membrane at constant operating pressure (413.7 kPa). With increasing pressure, convective transport becomes more important and retention, therefore, increases (Mehiguene et al. 1999). However, concentration polarization can also increase with increasing pressure, which results in a decrease in retention. The counteracting contributions of increased convective transport and increased concentration polarization result in a constant retention value in the pressure range of 5–15 atm (Mehiguene et al. 1999). Lead ion rejection was found to decrease with decreasing solution pH. At higher solution pH, membrane surface became more negatively charged, thus attracting more lead ions. Consequently, for PbCl₂, at solution pH of 5–6, higher ion rejections were achieved (about 96–98%), while solution with low pH exhibited lower rejections about 88–91%. For Pb(NO₃)₂ solution, the ion rejection percentages of high solution pH (5–6) and low solution pH of 4 were 91–94% and 76–81%, respectively. At low pH, the lead ion rejections of Pb(NO₃)₂ solution were lower than that of PbCl₂ solution, possibly due to H⁺ ion reducing negative charge at the membrane, reducing double layer thickness at the membrane, thus increased membrane pores. This allowed negatively charged anion ion passing through the membrane, thus increasing lead ion concentration in the permeate in order to maintain electroneutrality condition. This result showed higher lead ion concentration for Pb(NO₃)₂ solution than that for PbCl₂ solution. Kilduff et al. (2004) concluded that the effective membrane permeability increased when a pH was increased, but the flux decreased as a result of increased osmotic pressure effects resulting from increased solute rejection. Such behavior was in contrast to looser membranes having low salt rejection, for which flux increased with pH as a result of the increased membrane permeability.


Effects of ionic strength on flux and rejection

Figure 5 presents the effect of ionic strength on relative flux. The filtration experiments were carried out at pH 6 with different ionic strengths of 0.01 and 0.05 M as NaCl. The solution pH of 6 was selected in order to avoid lead precipitation at high pH and high hydrogen ion concentration at low pH, which could affect membrane performance. It was observed that the extent of solution flux decline increased with increasing ionic strengths. This was possibly due to reduced electrostatic repulsion at the membrane surface, indicating high flux decline. Many studies indicated that increases in ion concentration could reduce the permeability of charged membranes (Eriksson 1988; Van Reenan & Sanderson 1992; Yaroshchuk & Staude 1992; Mattaraj et al. 2008), thus reducing permeate flux. The results showed similar trend for both PbCl₂ and Pb(NO₃)₂ solutions with increasing ionic strengths, thus suggesting an increase in flux decline.

Effect of co-ion on solution flux decline

The effect of the co-ion of lead solution on flux decline was carried out with two types of Pb²⁺ (PbCl₂ and Pb(NO₃)₂ solutions) at the concentration of 20 mg L⁻¹. The experiments were performed at pH 4, 5 and 6 with constant ionic strength of 0.01 M NaCl and 413.7 kPa operating pressure.

Figure 6 exhibits the effect of ionic strength on lead ion rejection. It was found that at ionic strength 0.05 M lead ion rejections were lower than those of at 0.01 M. Increased salt concentration can provide positively charged Na⁺ ion at the membrane surface, thus decreased electrostatic charge repulsion. The phenomena can enhance a reduction in double layer thickness on the membrane surface, thus affecting a reduction in membrane permeability caused by increased salt concentration on the membrane surface. This can allow lead ion passage through the membrane, suggesting a decrease in ion rejection.

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during filtration. Figure 7 shows the comparisons of co-ion on nanofiltration performance of lead solution. It was observed that Pb(NO3)2 solution showed higher flux decline than PbCl2 solution, while PbCl2 solution presented higher rejections than Pb(NO3)2 solution. Since the NF membrane is more negatively charged, the monovalent anion of Cl⁻ ion is more excluded than NO3⁻ ion resulting in greater rejection. The lead ion rejections for PbCl2 solution showed higher than those of Pb(NO3)2 solution. It was possibly caused by higher charge repulsion of negatively charged Cl⁻ ion, when compared with negatively charged NO3⁻ ion, thus increased lead concentration for PbCl2 solution in order to satisfy an electroneutrality condition. The lead ions were retained on the membrane surface which resulted in high lead rejection.

In addition, Mehiguene et al. (1999) concluded that the retention of metallic cations was enhanced when the charge valency of associated co-ion increased. These observations were explained by Donnan exclusion phenomena (Donnan 1995), and were described by thermodynamic equilibrium. Consequently, as the membrane is negatively charged, co-ions are excluded and cations were also rejected in order to ensure electroneutrality at both side of the membrane. This was an important feature in nanofiltration (Mehiguene et al. 1999). Moreover, the difference effects in hydration energy of co-ions (Cl⁻ and NO3⁻) could be also explained for this experiment. Chloride ion has larger hydration energy than nitrate ion, thus resulting in greater rejection (Mehiguene et al. 1999). Similar results were observed by Choi et al. (2001). The rejection ratio between chloride and nitrate ion was determined about 1.08 for RO membrane (Amiri & Samiei 2007), while the rejection ratio was about 1.14 for NF-90 membrane (Tahaikt et al. 2007) and 1.45 for the loose NF Nanomax 50 (MWCO about 300) (Fraces et al. 2005).

CONCLUSIONS

Lead ion rejection and flux decline from aqueous solution by nanofiltration membrane were strongly influenced by solution pH and ionic strengths. Flux decline of filtration experiments conducted for both PbCl2 and Pb(NO3)2 solutions increased with increased solution pH. Solutions having high solution pH showed greater flux decline than those having low solution pH, while lead rejections exhibited higher rejection. Increased ionic strengths resulted in a greater increase in flux decline. Lead ion rejection was found to be decreased with decreasing solution pH and increasing ionic strengths. The experimental results of the study can be applied to improve system performance by adjusting system feed solution (i.e. avoiding low solution pH and high ionic strength) in order to control high rejection efficiency and high water production throughout the long operating period.

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