เอกสารหมายเลขที่ 4.2(1)

บันทึกข้อความ

ส่วนราชการ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ โทร. 3343

ที่ ศธ 0529.8.3/ [illegible] **วันที่** 4 มิถุนายน 2553

เรื่อง ขออนุมัติค่าตอบแทนการตีพิมพ์ในวารสารวิชาการระดับชาติ เรื่อง "ประสิทธิภาพและสมรรถนะของนาโนฟิลเตรชันของสารละลายสังกะสี: ผลกระทบของความแรงประจุและพีเอช"

เรียน รองคณบดีฝ่ายวิจัยและบริการวิชาการ ผ่านหัวหน้าภาควิชาวิศวกรรมเคมี

อ้างถึงประกาศฉบับที่ 40/2550 ประกาศ ณ วันที่ 22 ตุลาคม 2550 คณะวิศวกรรมศาสตร์ เรื่อง "หลักเกณฑ์การจ่ายค่าตอบแทนการตีพิมพ์ผลงานวารสารวิชาการ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยอุบลราชธานี" ตามความทราบแล้วนั้น

เนื่องจากบทความทางวิชาการของผู้ช่วยศาสตราจารย์ ดร.สุพัฒน์พงษ์ มัตราช เรื่อง "ประสิทธิภาพและสมรรถนะของนาโนฟิลเตรชันของสารละลายสังกะสี: ผลกระทบของความแรงประจุและพีเอช" ได้รับการตีพิมพ์ในวารสารวิชาการระดับชาติ วารสารวิศวกรรมสิ่งแวดล้อมไทย (สวสท.) ปีที่ 24 ฉบับที่1: หน้า 9-17 (2553) มกราคม – เมษายน 2553 ดังนั้น ภาควิชาวิศวกรรมเคมี จึงใคร่ขออนุมัติค่าค่าตอบแทนการตีพิมพ์ผลงานในวารสารวิชาการในเรื่องดังกล่าว

จึงเรียนมาเพื่อโปรดพิจารณา

(ผู้ช่วยศาสตราจารย์ ดร.สุพัฒน์พงษ์ มัตราช)
อาจารย์ประจำภาควิชาวิศวกรรมเคมี

1. เรียน หัวหน้าภาควิชาวิศวกรรมเคมี เพื่อโปรดพิจารณา

2. [illegible]

3. เรียน รองคณบดี [illegible]

4. เห็นควร ERIS [illegible] 8/6/53

แบบฟอร์มการมีส่วนร่วมในผลงานทางวิชาการ

☐ ตำรา ☐ งานวิจัย ☐ ผลงานทางวิชาการในลักษณะอื่น

เรื่อง "ประสิทธิภาพและสมรรถนะของนาโนฟิลเตรชันของสารละลายสังกะสี: ผลกระทบของความแรงประจุและพีเอช"

Nanofiltration performance and capacity of zinc solution: Impacts of ionic strength and solution pH, Thai Environmental Engineering Journal, Vol.24, No. 1, pp. 9-17, January – April, 2010. ISSN 1686-2961.

ผู้ร่วมงาน จำนวน 3 คน แต่ละคนมีส่วนร่วมดังนี้ :

ชื่อผู้ร่วมงาน	ปริมาณงานคิดเป็นร้อยละ
1. นายวุฒิกร สายแก้ว	35
2. ผศ.สุพัฒน์พงษ์ มัตราช*	60
3. ศ.รัตนา จิระรัตนานนท์	5

ลงชื่อ .....

(นายวุฒิกร สายแก้ว)

ลงชื่อ .....

(ผศ.สุพัฒน์พงษ์ มัตราช)

ลงชื่อ .....

(ศ.รัตนา จิระรัตนานนท์)

ENVIRONMENTAL ENGINEERING
ASSOCIATION OF THAILAND

THAI ENVIRONMENTAL ENGINEERIN JOURN

Vol.24 No.1 January - April 2010 ISSN 1686 - 2961

วารสารวิศวกรรมสิ่งแวดล้อมไทย

เจ้าของ

สมาคมวิศวกรรมสิ่งแวดล้อมแห่งประเทศไทย (สวสท.)

www.ecat.or.th

สำนักงาน

122/4 ซอยเรวดี ถนนพระราม 6 แขวงสามเสนใน เขตพญาไท กรุงเทพฯ 10400

ENVIRONMENTAL ENGINEERING
ASSOCIATION OF THAILAND

Thai Environmental Engineering Journal

Vol. 24 No. 1 January - April 2010

ISSN 1686 - 2961

Thai Environmental Engineering Journal Vol. 24 No. 1 : 9-17 (2010)
www.eeat.or.th

Nanofiltration Performance and Capacity of Zinc Solution: Impacts of Ionic Strength and Solution pH

ประสิทธิภาพและสมรรถนะของนาโนฟิลเตรชันของสารละลายสังกะสี: ผลกระทบของความแรงประจุและพีเอช

วุฒิกร สายแก้ว* สุพัฒน์พงษ์ มัตราช**,***,* และ รัตนา จิระรัตนานนท์****

Wuthikorn Saikaew* Supatpong Mattaraj,***,* and Ratana Jiraratananon****

*Department of Environmental Engineering, Ubon Ratchathani University, Ubonratchathani 34190

**Department of Chemical Engineering, Ubon Ratchathani University, Ubonratchathani 34190

***National Center of Excellence for Environmental and Hazardous Waste Management, Ubon Ratchathani University, Ubonratchathani 34190

****Department of Chemical Engineering, King Mongkut's University of Technology Thonburi, Bangkok 10140

*E-mail: mattas@ubu.ac.th, supatpong.m@hotmail.com

Abstract

Nanofiltration performance and capacity (i.e. rejection aod flux decline) of zinc solutioo were 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 on nanofiltration fouling of zinc solution. The experimental results revealed that solution flux decline was dependent on ionic strength, solution pH, and zinc solutions. Solution flux conducted with different zinc solutions (i.e. $ZnSO_4$ and $Zn(NO_3)_2$ decreased with solution pH. At high pH, flux solutions exhibited greater flux decline than those having low solution pH, while zinc rejection presented higher rejection. Increased ionic strength had a greater increase in flux decline, while zinc ion rejection decreased with decreasing solution pH and increasing ionic strength. Such results were related to low solution pH, it suggested an increased fixed charge of proton (H^+), decreasing electrical double layer thickness within membrane, thus allowing increased zinc concentration passing through the membrane surface. In addition, flux solution and rejection decreased further in higher ionic strength, which reduced negatively charged membrane, and thus decreased rejections.

Keywords : Flux decline; fouling; nanofiltration; rejection; zinc

บทคัดย่อ

ประสิทธิภาพและสมรรถนะของนาโนฟิลเตรชัน(เช่น การกำจัดและการลดลงของฟลักซ์) ของสารละลายสังกะสีได้ทดสอบโดยใช้ชุดการทดลองแบบตายตัวที่อุณหภูมิห้อง เยื่อกรองโพลีเอมายด์แบบ NF-90 ถูกใช้ทดสอบเพื่อหาผลกระทบของคุณลักษณะทางเคมีจากการอุดตันของนาโนฟิลเตรชันโดยสารละลายสังกะสี ผลการทดลองพบว่าการลดลงของฟลักซ์ขึ้นอยู่กับความแรงประจุ พีเอชและสารละลายสังกะสี ฟลักซ์สารละลายที่ทดสอบกับสังกะสีที่ต่างชนิดกัน (ได้แก่ $ZnSO_4$ และ $Zn(NO_3)_2$) ให้ค่าลดลงจากผลของพีเอช ฟลักซ์สารละลายที่ค่าพีเอชสูงให้ค่าการลดลงของฟลักซ์มากกว่าสารละลายที่มีค่าพีเอชต่ำ ขณะที่ค่าการกำจัดของสารละลายสังกะสีให้ค่าสูง การเพิ่มความแรงประจุทำให้เพิ่มการลดลงของฟลักซ์ ขณะที่ค่าการกำจัดสังกะสีให้ค่าลดลงเมื่อลดพีเอชและเพิ่มความแรงประจุ ผลเนื่องจากค่าพีเอชที่ต่ำทำให้เพิ่มโปรตอนบนผิวของเยื่อกรองส่งผลต่อการลดชั้นความหนาภายในผิวของเยื่อกรองส่งผลให้ความเข้มข้นของสังกะสีผ่านผิวของเยื่อกรองมากขึ้น นอกจากนี้ฟลักซ์สารละลายและการกำจัดให้ค่าลดลงเมื่อเพิ่มความแรงประจุซึ่งมีผลต่อการลดประจุลบที่ผิวของเยื่อกรองส่งผลให้ค่าการกำจัดลดลง

คำสำคัญ : การลดลงของฟลักซ์; การอุดตัน; นาโนฟิลเตรชัน; การกำจัด; สังกะสี

Introduction

Membrane technologies have been widely used in the field of water treatment due to stringent water quality regulations [1]. They are efficient technologies to remove feed source water in terms of natural organic matter (NOM) [1-5], inorganic scalants [6-8], salt solution [9-11] and heavy metals [12-16]. 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 1000 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 contain high color due to dissolved organic matter (DOM), partially decomposed from plant materials, high hardness from the composition of calcium (Ca^{2+}) and magnesium (Mg^{2+}), and high iron (Fe^{2+}) and manganese (Mn^{2+}) concentration. NF can provide high water quality and large amount of water production in the short period of operation. This can give water quality within drinking water standards. However, membrane fouling caused by organic and inorganic substances can be a major factor for limiting more widespread use of membrane technologies, reducing long-term filtration, and increasing costs for membrane operation through higher labor, cleaning and 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 precipitation (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.* [8]. Molinari *et al.* [13] investigated the interactions between membranes (RO and NF) and inorganic pollutants (i.e. SiO_2, NO_3^-, Mn^{++} and humic acid). They showed that membrane fouling was caused by the interactions between the membranes and other ions. Other factors, which can cause membrane fouling

are solution pH, ionic strength, concentration, solution composition, and operating conditions.

Zinc and its alloys are inorganic substance which mostly used in mechanical engineering and building. It is estimated that 10 million tons of zinc was used in the year 2001. However, industrialization and urbanization are often accompanied by large pollution emissions. Zinc creates serious problems for drinking waters. Against this increased pollution, very strict standards were imposed for heavy metal content water because of their high toxicity. Drinking water standards of zinc is about 5 mg/L [17].

Fouling on membrane surface by nanofiltration may influence by operating condition such as solution pH and ionic strength. Hence, the objective of this study was to investigate the effects of solution chemistry during nanofiltration of zinc solution. The effects of solution chemistry (i.e. solution pH and ionic strength) were determined on nanofiltration fouling. The discussion of this study was adapted to improve membrane filtration for long-term operation.

Materials and Methods

Nanofiltration membrane characteristics

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. According to the manufacturer, the maximum operating pressure is 600 psi (or 4,137.6 kPa), maximum feed flow rate is 16 gpm (3.6 m^3/hr), maximum operating temperature 113°F (45°C) and the operating pH is ranged from 1 to 12. Free chlorine tolerance is less than 0.1 ppm. In operation, membrane flat sheets were stored in 1% sodium meta-bisulfite ($Na_2S_2O_5$) and kept in refrigerator at 4 ^{0}C to prevent microbial activity. The water flux characteristic was determined for 30-min operation with DI water for membrane compaction. The membrane permeability was determined as a slope between cleaned water flux and operating pressures.

Analytical method

Zinc concentration was measured by using atomic absorption (AA) spectrometry (AAnalyst 200 Version 2, Perkin Elmer Corp.). Measurements of solution pH, conductivity and temperature were made using pH meter (Inolab pH level 1 Wissenschaftlich-Technische Werkstatten (WTW) Gmbh & Co (Weilheim, Germany)) and conductivity meter (Inolab cond level 2 Wissenschaftlich-Technische Werkstatten (WTW) Gmbh & Co. (Weilheim,Germany)), respectively. Ionic strength of samples were calculated using a correlation between conductivity and ionic strength of NaCl standards, I.S.[M]=$0.5\sum C_i Z_i^2$.

Flux decline experiments

The experiments were carried out with three liters of solution containing zinc solution ($ZnSO_4$ and $Zn(NO_3)_2$) in fixed concentration of 0.31 mM (about 20 mg/L), while varying solution pH from 4 to 8 and ionic strengths (0.01, 0.05 M as NaCl). Flux decline experiments were tested by using an 400 ml dead-end membrane filtration apparatus (Amicon 8400, USA) with magnetic stirrer (LABINCO, LD-12) and the magnetic spin bar fitted into the cell provided the agitation. The velocity speed was about 300 rpm. A membrane sheet can be fitted to the cell. The membrane active area is 41.38 cm^2. 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 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.

Analysis of Results

The parameters taken into account were:

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

$$J_v = L_p(\Delta P - \sigma\Delta\pi) = \frac{Q_p}{A} \quad (1)$$

Where L_p is the membrane permeability; ΔP is the transmembrane pressure; σ is the osmotic reflection coefficient; π is the osmotic pressure; Q and A represent flow rate of permeate and the membrane area, respectively.

- The observed rejection was calculated by the following relation:

$$\%R = (1-\frac{C_p}{C_i})\times 100 \quad (2)$$

Where C_p and C_i are the solution concentrations in the permeate and in the initial feed solution, respectively.

Results and Discussion

Water flux characteristics

Before the experiments, the membrane permeability was measured after membrane compaction by the effects of pressure on water flux or permeate flux produced from deionized water (DI water). As shown in fig. 1, the effects of pressure at 0, 10, 20, 30, 40 and 50 psi on permeate flux increased linearly with increasing operating pressure with high correlation of 0.9986. The slope represents the membrane permeability (L_p) about 0.4925 $LMH.psi^{-1}$. The membrane permeability measured was considered as reference to evaluate cleaning procedure, concentration polarization and fouling.

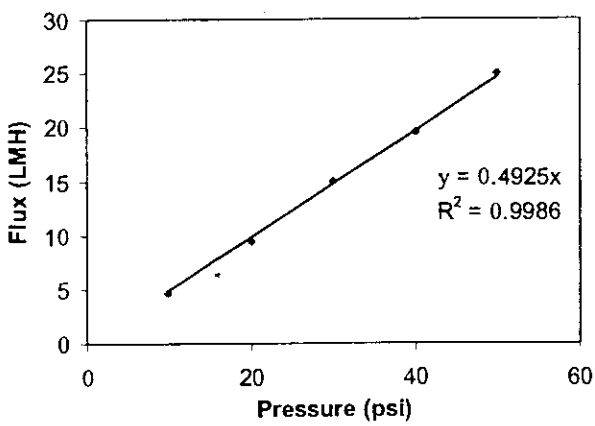


Fig. 1 Effect of pressure on cleaned water flux

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 Fig. 2, the cleaned water flux after system cleaning of $ZnSO_4$ and $Zn(NO_3)_2$ at pH 6 had similar flux as water flux after membrane compaction, where hydrodynamic cleaning showed lower flux. However, flux observed after hydrodynamic cleaning was not significantly low when compared with cleaned flux after membrane compaction. This suggested that inorganic zinc could not significantly affect membrane fouling during filtration experiments. Increased flux caused by chemical cleaning was possibly due to protons from acid which dissolved efficiently inorganic zinc from the membrane surface. A common trend of increase in flux was found for the membrane sheets when cleaned by deionized water and chemical agent. The comparisons of cleaned water fluxes were similarly found with different zinc solutions. This indicated that ionic zinc ($ZnSO_4$ and $Zn(NO_3)_2$) showed less non-recoverable fouling after system cleaning, indicating high water flux recovery.

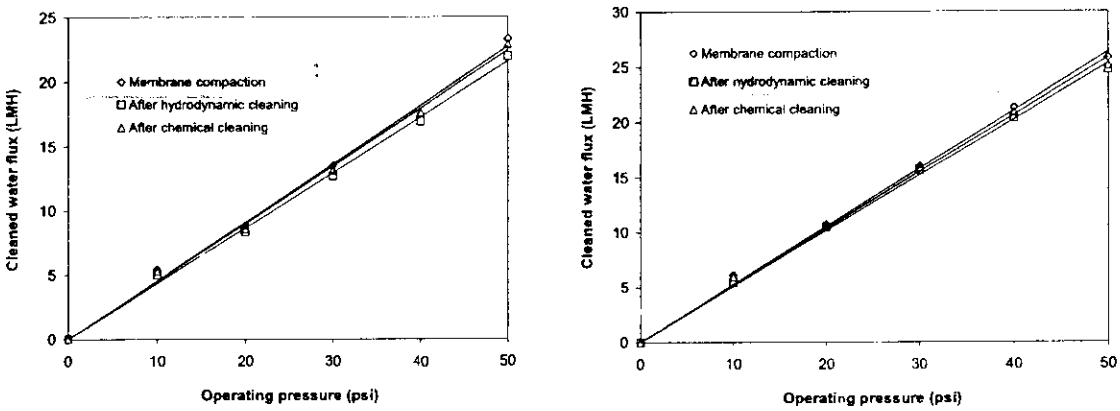
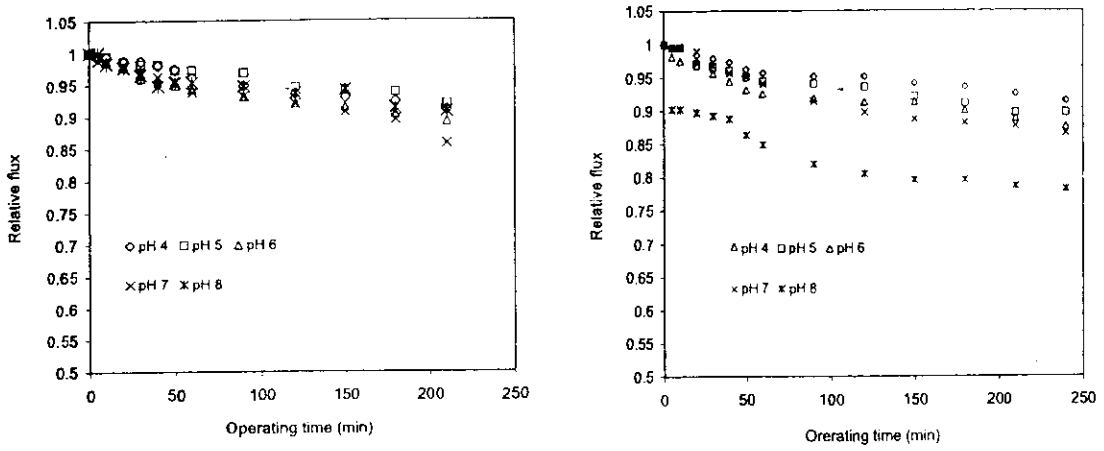


Fig. 2 Cleaned water flux after system cleaning at pH 6 (a) $ZnSO_4$ and (b) $Zn(NO_3)_2$

Effects of solution pH on flux

The effects of the solution pH on flux decline of $ZnSO_4$ and $Zn(NO_3)_2$ were carried out at pH 4,5,6,7 and 8 with keeping constant ionic strength 0.01 M as NaCl at 60-psi operating pressure. Zinc concentration was about 0.31 mM. Fig. 3 showed relative flux with function of operating period. It can be seen that the rate and extent of flux decline increased with increasing solution pH for both solutions of $ZnSO_4$ and $Zn(NO_3)_2$. At the higher pH, flux solutions of $Zn(NO_3)_2$ (J_v/J_{vo} = 0.78 at pH 8) showed higher flux decline than those of low solution pH (J_v/J_{vo} = 0.91 at pH 4). At low pH, it suggested an increased fixed charge of H^+, decreasing electrical double layer thickness within membrane or both, thus decreased the concentration at the membrane surface. At high pH, the membrane surface and pores become both more negatively charged due to the presence of anion (inorganic). As a result, the pore size of the membrane is reduced because of the repulsion between neighbor negatively charged groups and adopts an extended conformation [18, 19]. In addition, the osmotic pressure near the membrane surface increase at high due to the high salt rejections, which decreased the driving pressure. Together, these mechanisms lead to a



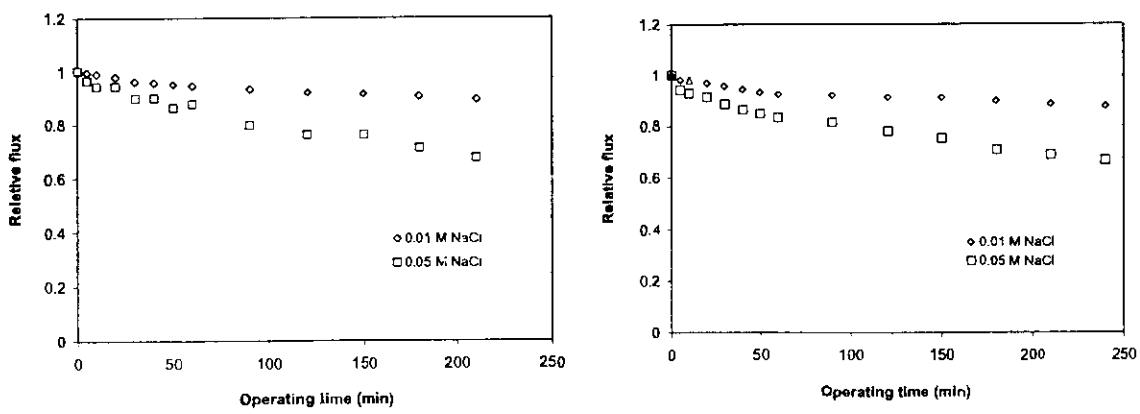
(a) (b)

Fig. 3 Effect of solution pH on flux ; (a) $ZnSO_4$ and (b) $Zn(NO_3)_2$

decrease in permeate flux and an increase in salt rejection with pH. From the figure, it was found that solutions having $Zn(NO_3)_2$ showed greater flux decline that those having $ZnSO_4$, possibly due to higher salt rejections for $Zn(NO_3)_2$ solution, thus increased osmotic pressure at the membrane surface.

Effects of ionic strength on flux

Fig. 4 presents the effect of ionic strength on flux that was 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 due to avoid zinc precipitation at high pH and high hydrogen ion concentration at low pH, which could affect membrane performance. It was observed that the extent and rate of solution flux decline increased with increasing ionic strength. This was possibly due to increased reduced electrostatic repulsion at the membrane surface, thus suggesting high flux decline. Previous study indicated that increases in ion concentration could reduce the permeability of charged membranes [20-22], thus reduced permeate flux. The results showed similar trend for both $ZnSO_4$ and $Zn(NO_3)_2$ solution with increasing sodium salt at the membrane surface.



(a) (b)

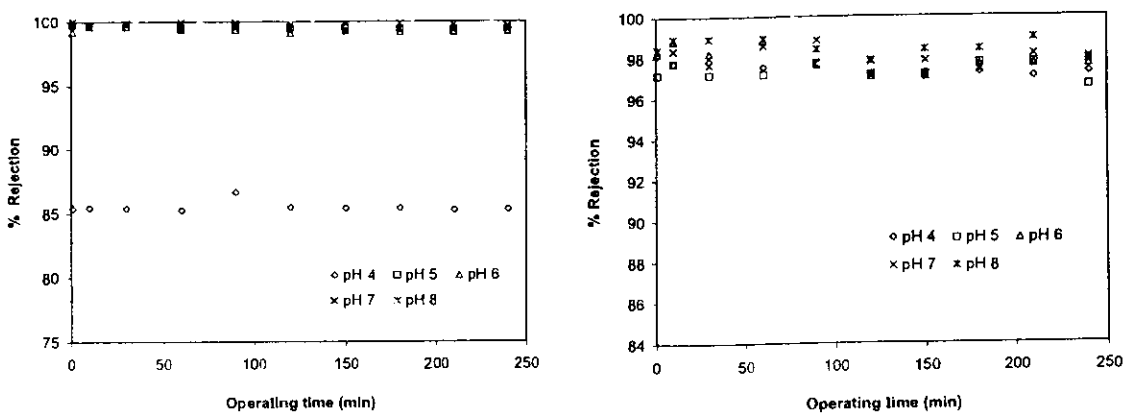
Fig. 4 Effect of ionic strength on flux; (a) $ZnSO_4$ and (h) $Zn(NO_3)_2$

Effects of solution pH on rejection

The effect of the solution pH on rejection of $ZnSO_4$ and $Zn(NO_3)_2$ was carried out with different solution pH from 4, 5, 6, 7 and 8. Ionic strength of 0.01 M NaCl, 60-psi operating pressure and solution concentration of 0.31 mM were maintained constant during filtration. The obtained results were presented in Fig. 5. Zinc ion rejection was found to be decreased with decreasing solution pH level. At higher solution pH, membrane surface take more negative charges, thus attracting greater zinc ion. Consequently, solution pH of 6-8 for $ZnSO_4$ had greater ion rejection, about 97-98%, while low solution pH exhibited lower rejection about 85-86%. For $Zn(NO_3)_2$ solution, the ion rejection percentages were approximately 96-99%. At low pH, the zinc ion rejection of $ZnSO_4$ solution showed lower than that of $Zn(NO_3)_2$ solution, possibly due to H^+ ion reducing negative charge at the membrane, causing larger membrane pores. This allowed negatively charged anion ion passing through the membrane, thus increasing zinc ion concentration in the permeate in order to maintain electroneutrality condition. This result showed higher zinc ion concentration for $ZnSO_4$ solution than that for $Zn(NO_3)_2$ solution, thus lowering zinc ion rejection.

Effect of ionic strength on zinc ion rejection

The effect of salt solution on zinc ion rejection was carried out with ionic strengths of 0.01 and 0.05 M as NaCl as shown in Fig. 6. Solution pH of 6 for $ZnSO_4$ and $Zn(NO_3)_2$ solution was kept constant during filtration. It was found that the trend of ionic strength at 0.05 M indicated lower zinc ion rejection than those of 0.01 M. Increased salt concentration can provide positively charged Na^+ 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. This can allow zinc ion passage through the membrane surface, suggesting a decrease in ion rejection. The zinc ion rejection for $ZnSO_4$ solution showed higher than that of $Zn(NO_3)_2$ solution was possibly caused by higher charge repulsion of negatively charged SO_4^{2-}, when compared with negatively charged NO_3^-, thus increased zinc concentration for $ZnSO_4$ solution in order to satisfy an electroneutrality condition, an equivalent number of zinc ion retained on the membrane surface, thus resulting high zinc rejection.



(a) (b)

Fig. 5 Effect of solution pH on zinc ion rejection; (a) $ZnSO_4$ and (b) $Zn(NO_3)_2$

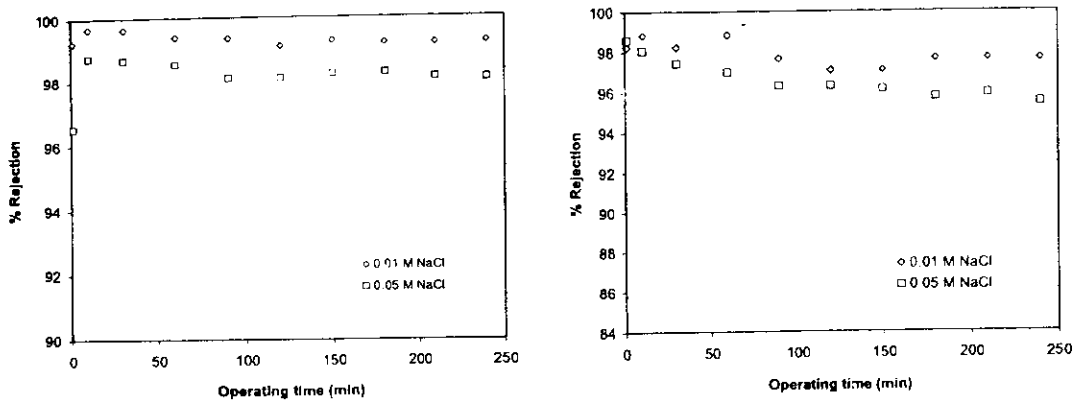


Fig. 6 Effect of salt solution on zinc ion rejection; (a) $ZnSO_4$ and (b) $Zn(NO_3)_2$

Conclusions

Zinc ions rejection and flux decline from aqueous solution by nanofiltration was strongly influenced by solution pH and ionic strength. Flux decline for experiment conducted both in $ZnSO_4$ and $Zn(NO_3)_2$ solution decreased for solution pH. At higher solution pH, flux solutions showed higher flux decline than those of low solution pH, while zinc rejection exhibited higher rejection. Increased ionic strength had a greater increase in flux decline. Zinc ion rejection was found to be decreased with decreasing solution pH and increasing ionic strength. The experimental results of the study can be determined to improve system performance by adjusting system feed solution (i.e. avoiding low solution pH and high ionic strength) in order to control high removal efficiency and low fouling potential for long-term operation.

Acknowledgements

This work was financially supported by Professor Dr. Rattana Jiraratananon as the head of Senior Membrane Technology Project and Office of Commission on Higher Education, Ministry of Education, Thailand. The authors are also grateful to the faculties for their assistance during experiments at the chemical engineering laboratory, Ubon Ratchathani University.

References

[1] Hong, S. and Elimelech, M. 1997. Chemical and Physical Aspects of Natural Organic Matter (NOM) Fouling of Nanofiltration Membranes, J. Membrane Sci. 132: 159-181.

[2] Alborzfar, M., Jonsson, G., and Gron, C. 1998. Removal of Natural Organic Matter from Two Types of Humic Ground Waters by Nanofiltration, Water Res. 32(10): 2983-2994.

[3] Cho, J., Amy, G. and Pellegrino, J. 1999. Membrane Filtration of Natural Organic Matter: Initial Comparison of Rejection and Flux Decline Characteristics with Ultrafiltration and Nanofiltration Membranes, Water Res. 33(11): 2517-2526.

[4] Schafer, A.I., Fane, A.G. and Waite, T.D. 2000. Fouling Effects on Rejection in the Membrane Filtration of Natural Waters, Desalination. 131: 215-224.

[5] Kilduff, J.E., Mattaraj, S. and Belfort, G. 2004. Flux Decline during Nanofiltration of Naturally-Occurring Dissolved Organic Matter: Effects of Osmotic Pressure, Membrane Permeability, and Cake Formation. J. Membrane Sci. 239(1): 39-53.

[6] Lisdonk, C.A.C., van Paassen, J.A.M. and Schippers, J.C. 2000. Monitoring Scaling in Nanofiltration and Reverse Osmosis Membrane Systems". Desalination. 132: 101-108.

[7] Lin, C.J., Shirazi, S., Rao, P. and Agarwal, S. 2006. Effects of Operational Parameters on Cake Formation of $CaSO_4$ in Nanofiltration. Water Res. 40: 806-816.

[8] Jarusutthirak, C., Mattaraj, S. and Jiraratananon, R. 2007. Influence of Inorganic Scalants and Natural Organic Matter on Nanofiltration Membrane Fouling. J. Membrane Sci. 287: 138-145.

[9] Childress, A.E. and Elimelech, M. 2007. Effect of Solution Chemistry on the Surface Charge Of Polymeric Reverse Osmosis and Nanofiltration Membrane. J. Membrane Sci. 119: 253-268

[10] Anne, C.O., Trebouet, D., Jaouen, P. and Quemeneur, F. 2001. Nanofiltration of Seawater: Fractionation of Mono-and Multi-valent Cations. Desalination. 140: 67-77.

[11] Labbez, C., Fievet, P., Szymczyk, A., Vidonne, A., Foissy, A. and Pagetti, J. 2003. Retention of Mineral Salts by a Polyamide Nanofiltration Membrane. Sep. Purif. Technol. 30: 47-55.

[12] Mehiguene, K., Garba, Y., Taha, S., Gondrexon, N. and Dorange, G. 1999. Influence of Operating Conditions on the Retention of Copper and Cadmium in Aqueous Solutions by Nanofiltration: Experimental Results and Modelling. Sep. Purif. Technol. 15: 181-187.

[13] Molinari, R., Argurio, P. and Romeo, L. 2001. Studies on Interactions between Membranes (RO and NF) and Pollutants (SiO_2, NO_3^-, Mn^{++} and humic acid) in Water. Desalination. 138: 271-281.

[14] Ku, Y., Chen, S.W. and Wang, W.Y. 2005. Effect of Solution Composition on the Removal of Copper Ions by Nanofiltration. Sep. Purif. Technol. 43: 135-142.

[15] Ipek, U. 2005. Removal of Ni(II) and Zn(II) from an Aqueous Solution by Reverse Osmosis. Desalination.174: 161-169.

[16] Turek, M., Dydo, P., Trojanowska, J. and Campen, A. 2007. Adsorption/Co- Precipitation-Reverse Osmosis System for Boron Removal. Desalination. 205: 192-199.

[17] Ministry of Public Health Notification. 1981. The quality of bottled drinking water in Thailand, no. 61.

[18] Teixeira, M.R., Rosa, M.J. and Nystrom, M. 2005. The role of membrane charge on nanofiltration performance, J. Membrane Sci. 265: 160-166.

[19] Schaep, J. and Vandecasteele, C. 2001. Evaluating the charge of nanofiltration membranes, J. Membrane Sci. 188: 129-136.

[20] Yaroshchuk, A. and Staude, E. 1992. Charged membranes for low pressure reverse osmosis properties and applications. Desalination. 86: 115-134.

[21] Eriksson, P. 1988. Water and salt transport through two types polyamide composite membrane. J. Membrane Sci. 36: 297-313.

[22] Van Reenan, A.J. and Sanderson, R.D. 1992. Dynamically formed hydrous zirconium (IV) oxide-polyelectrolyte membranes. VII. Poly (acrylic acid-co-vinyl acetate) and poly (acrylic acid-co-vinyl alcohol) membranes: the effect of feed salt concentration on membrane properties. Desalination. 85: 247-262.

เอกสารหมายเลขที่ 4.2 (2)

บันทึกข้อความ

ส่วนราชการ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ โทร. 3343

ที่ ศธ 0529.8.3/ [illegible] **วันที่** 4 มิถุนายน 2553

เรื่อง ขออนุมัติค่าตอบแทนการตีพิมพ์ในวารสารวิชาการระดับนานาชาติ เรื่อง "Nanofiltration performance of lead solutions: effects of solution pH and ionic strength"

เรียน รองคณบดีฝ่ายวิจัยและบริการวิชาการ ผ่านหัวหน้าภาควิชาวิศวกรรมเคมี

อ้างถึงประกาศฉบับที่ 40/2550 ประกาศ ณ วันที่ 22 ตุลาคม 2550 คณะวิศวกรรมศาสตร์ เรื่อง "หลักเกณฑ์การจ่ายค่าตอบแทนการตีพิมพ์ผลงานวารสารวิชาการ คณะวิศวกรรมศาสตร์ มหาวิทยาลัย-อุบลราชธานี" ตามความทราบแล้วนั้น

เนื่องจากบทความทางวิชาการของผู้ช่วยศาสตราจารย์ ดร.สุพัฒน์พงษ์ มัตราช เรื่อง "Nanofiltration performance of lead solutions: effects of solution pH and ionic strength" ได้รับการตีพิมพ์ในวารสารวิชาการระดับนานาชาติ วารสาร Water Science and Technology: Water Supply, ฉบับที่ 2: หน้า 193 - 200 (2010) ดังนั้น ภาควิชาวิศวกรรมเคมี จึงใคร่ขออนุมัติค่าค่าตอบแทนการตีพิมพ์ผลงานในวารสารวิชาการในเรื่องดังกล่าว

จึงเรียนมาเพื่อโปรดพิจารณา

(ผู้ช่วยศาสตราจารย์ ดร.สุพัฒน์พงษ์ มัตราช)
อาจารย์ประจำภาควิชาวิศวกรรมเคมี

1. เรียนหัวหน้าภาควิชาวิศวกรรมเคมี เพื่อโปรดพิจารณา

2. [illegible]

3. เรียนรองคณบดีฝ่ายวิจัยและบริการวิชาการ ตามที่ผศ.ดร.สุพัฒน์พงษ์ มัตราช ได้ขอค่าตอบแทนในการตีพิมพ์ผลงานวิชาการ ในวารสารวิชาการระดับนานาชาติ ซึ่งเป็นไปตามเกณฑ์การจ่ายค่าตอบแทนฯ ข้างต้น จึงเรียนมาเพื่อโปรดพิจารณา

4. [illegible] ERB [illegible] 8/6/53

FRACTION FORM FOR ACADEMIC WORK

☐ Book ☐ Research ☐ Other academic papers

Title "Nanofiltration performance of lead solutions: effects of solution pH and ionic strength" Water Science and Technology: Water Supply, (2010) Vol. 2, 193-200.

Collaborative work consists of 3 persons whose fractions are:

Collaborative Person	Fraction of Academic Work
1. Mr. Wuthikorn Saikaew	40
2. Asst. Prof. Supatpong Mattaraj*	55
3. Prof. Rattana Jiraratananon	5

Signature.....

(Mr. Wuthikorn Saikaew)

Signature.....

(Asst. Prof. Supatpong Mattaraj)

Signature.....

(Prof. Rattana Jiraratananon)

Water Science and Technology: Water Supply

Editor in Chief: Professor Helmut Kroiss, Vienna University of Technology, Austria

Important Announcement

Water Science and Technology and *Water Science and Technology: Water Supply* have adopted a new editorial policy to invite direct submission of papers on all aspects of the science and technology of water and wastewater.

The submitted papers will be peer reviewed under the control of the Editorial Board led by Professor Gustaf Olsson, Editor-in-Chief, using the Editorial Manager online submission and peer review system.

Water Science and Technology: Water Supply is published as an adjunct to *Water Science and Technology*, in 6 issues per year, covering new developments in water supply.

Papers are selected by a rigorous peer review procedure and the journal publishes the best papers on all aspects of water supply.

IWA Publishing Open
IWA Publishing Open is a new service which gives authors the option of having their accepted paper made freely available online immediately on publication. Click here to find out more about IWA Publishing Open.

ISSN Print: 160
Published by IW

Acknowledgement to Reviewers
The high scientific standards maintained by the journal in its papers owe much to the continuing dedication of the journal's reviewers, who give freely of their time and expertise. IWA is pleased to pay tribute to this contribution by recognizing those who have participated in the review process. A full list of those who reviewed papers for the journal last year can be found here.

Indexed/Abstracted in:
EMBASE/Excerpta Medica, Geo Abstracts, GEOBASE, Elsevier Biobase, Engineering Information Inc.

Note to contributors: All manuscripts should be submitted electronically through our Online Submission and Peer Review System.

Journal details

Water Science & Technology (Water Sci Tech)
Publisher: *International Association on Water Pollution Research; International Association on Water Quality; International Water Association, IWA Publishing*

Follow

Impact factor:	1.24
Cited half life:	8.3
Immediacy index:	0.11

Water Research publishes refereed, original research papers on all aspects of the science and technology of water quality and its management worldwide. A broad outline of the journal's scope includes: Treatment processes for water and wastewaters, municipal, agricultural and industrial, including residuals management. Water quality standards and the analysis, monitoring and assessment of water quality by chemical, physical and biological methods. Studies on inland, tidal or coastal waters, including surface and ground waters, and point and non-point sources of pollution. The limnology of lakes, impoundments and rivers. Solid and hazardous waste management, including source characterization and the effects and control of leachates and gaseous emissions. Environmental restoration, including soil and groundwater remediation. Analysis of the interfaces between sediments and water, and water/atmosphere interactions. The application of mathematical and modelling techniques. Public health and risk assessment. Education and training.

ISSN: 0273-1223, OCLC: 7004034
Website: Water Science and Technology website
Other titles: Water science and technology, Water science & technology
Material type: Periodical, Internet resource
Document type: Journal / Magazine / Newspaper, Internet Resource

Publisher details

IWA Publishing

Pre-print:	Archiving status unclear
Post-print:	Author cannot archive a post-print version
Conditions:	▪ On Intranet (not publicly accessible) only
Classification:	white

Publications in this journal

Upgrading of sewage treatment plant by sustainable and cost-effective separate treatment of industrial wastewater
Authors: *W R Abma, W Driessen, R Haarhuis, M C M van Loosdrecht*
Water science and technology : a jo.... 01/2010; 61(7):1715-22.
"The Olburgen sewage treatment plant has been upgraded to improve the effluent quality by implementing a separate and dedicated treatment for industrial (potato) wastewater and reject water. The separate industrial treatm..."

Harvested rainwater quality: the importance of appropriate design
Authors: *S Ward, F A Memon, D Butler*
Water science and technology : a jo.... 01/2010; 61(7):1707-14.
"This paper summarises the physicochemical and microbiological quality of water from a rainwater harvesting (RWH) system in a UK-based office building. 7 microbiological and 34 physicochemical parameters were analysed dur..."

Analysis of constructed wetland performance for irrigation reuse
Authors: *Helena Marecos do Monte, António Albuquerque*
Water science and technology : a jo.... 01/2010; 61(7):1699-705.
"Most of the wastewater treatment systems in small rural communities of the Cova da Beira region (Portugal) consist of constructed wetlands (CW) with horizontal subsurface flow (HSSF). It is believed that those systems al..."

Treatment of hospital wastewater effluent by nanofiltration and reverse osmosis
Authors: *S Beier, S Köster, K Veltmann, H Schröder, J Pinnekamp*
Water science and technology : a jo.... 01/2010; 61(7):1691-1698.
"Considerable concern exists regarding the appearance and effects of trace and ultra trace pollutants in the aquatic environment. In this context, it is necessary to identify relevant hot spot wastewater - such as hospita..."

Treatment of farm dairy effluent with hybrid upflow multilayer bioreactor and activated sludge module
Authors: *D F Shams, N Singhal, P Elefsiniotis, A Johnson*
Water science and technology : a jo.... 01/2010; 61(7):1683-90.
"Biological removal of nitrogen and carbon from farm dairy effluent (FDE) was studied with two laboratory-scale systems following nitrification and denitrification processes. Each system consisted of an upflow multilayer..."

A comparison study on Acid Red 119 dye removal using two different types of waterworks sludge
Authors: *S Sadri Moghaddam, M R Alavi Moghaddam, M Arami*
Water science and technology : a jo.... 01/2010; 61(7):1673-81.
"This study aims to compare the performance of two waterworks sludge samples, ferric chloride sludge (FCS) and polyaluminium chloride sludge (PACS), as coagulants to remove Acid Red 119 (AR119) dye from aqueous solution...."

Removal of endocrine disrupting compounds from wastewater treatment plant effluents by means of advanced oxidation

Keywords

Sewage
Water
Water Pollution
Water quality management
Water Supply

Related Journals

Check out related Journals.

Water Research
International Association on Water...
ISSN: 0043-1354, Impact factor: 3.43

Bioresource technology
ISSN: 1873-2976

Journal of Environmental Management
Elsevier Science B.V., Amsterdam
ISSN: 0301-4797, Impact factor: 1.45

Huan jing ke xue= Huanjing kexue / [bian...
Chinese Journal of Environmental Science
ISSN: 0250-3301

Journal of Environmental Science and Hea...
Informa UK (Marcel Dekker)
ISSN: 1093-4529, Impact factor: 0.97

Environmental Technology
Informa UK Ltd.,
ISSN: 0959-3330, Impact factor: 0.74

Journal of Hazardous Materials
Elsevier Science B.V., Amsterdam
ISSN: 0304-3894, Impact factor: 2.34

Bioresource Technology
Biomass Energy Research Association;...
ISSN: 0960-8524, Impact factor: 3.1

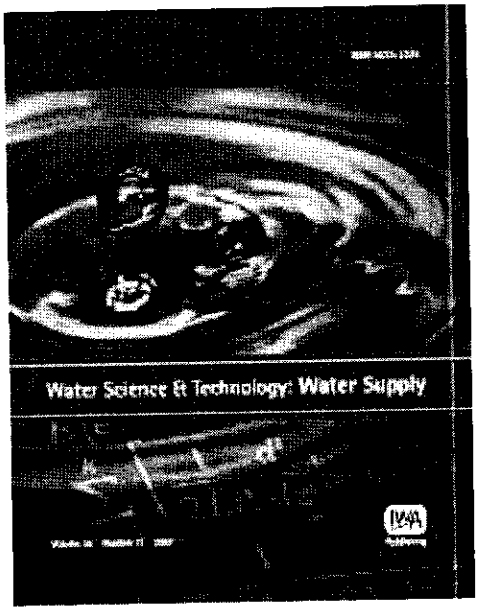
Next Journal

Sociological Spectrum
Mid-South Sociological Association,...
ISSN: 0273-2173

Water Science and Technology: Water Supply

ISSN Print:
Published b

Editorial Board



Nanofiltration performance of lead solutions: effects of solution pH and ionic strength

Wuthikorn Saikaew, Supatpong Mattaraj and Ratana Jiraratananon

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. $PbCl_2$ and $Pb(NO_3)_2$) 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 $PbCl_2$ solution exhibited higher rejections than that of $Pb(NO_3)_2$ solution.

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

Wuthikorn Saikaew
Environmental Engineering Program, Department of Chemical Engineering,
Ubon Ratchathani University,
Ubonratchathani 34190,
Thailand

Supatpong Mattaraj (corresponding author)
Department of Chemical Engineering, Faculty of Engineering,
Ubon Ratchathani University,
Ubonratchathani 34190,
Thailand
E-mail: *mattas@ubu.ac.th*, *supatpong.m@hotmail.com*

Supatpong Mattaraj
National Center of Excellence for Environmental and Hazardous Waste Management,
Ubon Ratchathani University,
Ubonratchathani 34190,
Thailand

Ratana Jiraratananon
Department of Chemical Engineering,
King Mongkut's University of Technology Thonburi,
Bangkok 10140,
Thailand

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 (Mehiguene *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 (Ca^{2+}) and magnesium (Mg^{2+}), and high iron (Fe^{2+}) and manganese (Mn^{2+}) 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

doi: 10.2166/ws.2010.062

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 effects of solution chemistry (i.e. solution pH and ionic strength) were determined to evaluate nanofiltration performance of lead solutions. The results of this study could be used to provide system performance of membrane filtration throughout the long operating period.

MATERIALS AND METHODS

Nanofiltration membrane characteristics

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 ($Na_2S_2O_5$) 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 (AAnalyst 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, $I.S.[M] = 0.5\Sigma C_i Z_i^2$ (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

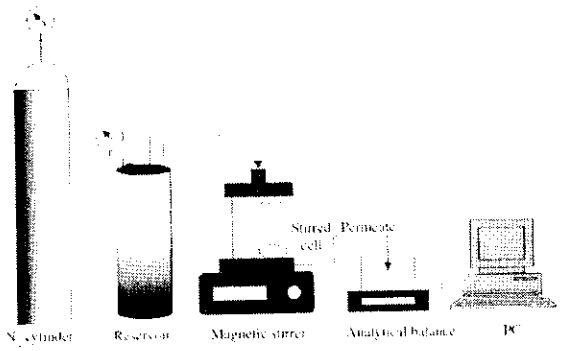


Figure 1 | Schematic diagram of the experimental setup.

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 cm^2. 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:

$$J_v = L_p(\Delta P - \sigma\Delta\pi) = \frac{Q_p}{A} \quad (1)$$

where L_p is the membrane permeability (LMH kPa^{-1}); ΔP is the transmembrane pressure (kPa); σ is the osmotic reflection coefficient (−); π is the osmotic pressure (kPa); Q_p and A represent flow rate of permeate ($L\,h^{-1}$) and the membrane area (m^2), respectively.

The observed rejection was calculated by the following relation:

$$\%R = \left(1 - \frac{C_p}{C_i}\right) \times 100 \quad (2)$$

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 $PbCl_2$ and $Pb(NO_3)_2$ 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

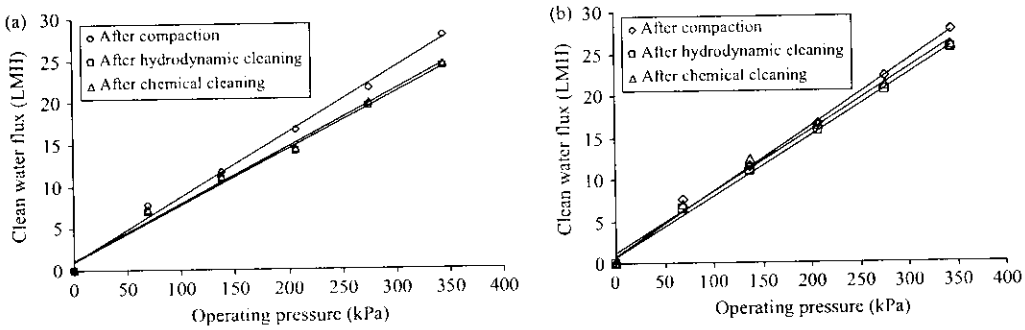


Figure 2 | Clean water flux after system cleaning; (a) $PbCl_2$ and (b) $Pb(NO_3)_2$.

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 ($PbCl_2$ and $Pb(NO_3)_2$ 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 $PbCl_2$ and $Pb(NO_3)_2$ 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 $PbCl_2$ and $Pb(NO_3)_2$ solutions. For higher pH, relative fluxes of $Pb(NO_3)_2$ solution ($J_v/J_{v0} = 0.88$ at pH 6) showed higher flux decline than those of low solution pH ($J_v/J_{v0} = 0.90$ 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-

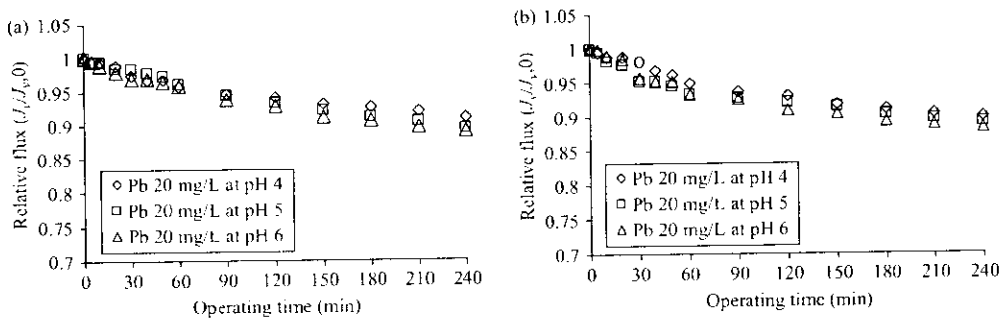


Figure 3 | Effect of solution pH on relative flux, (a) $PbCl_2$ and (b) $Pb(NO_3)_2$.

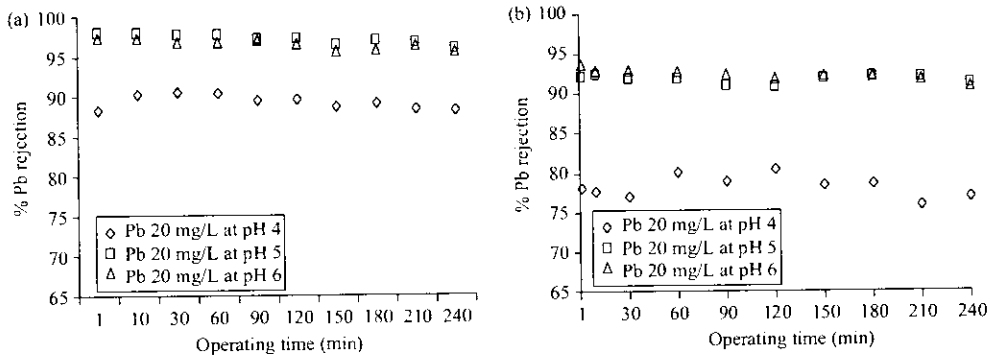


Figure 4 | Effect of solution pH on lead ion rejection; (a) $PbCl_2$ and (b) $Pb(NO_3)_2$.

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 $PbCl_2$, 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 $Pb(NO_3)_2$ 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 $Pb(NO_3)_2$ solution were lower than that of $PbCl_2$ 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 $Pb(NO_3)_2$ solution than that for $PbCl_2$ 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.

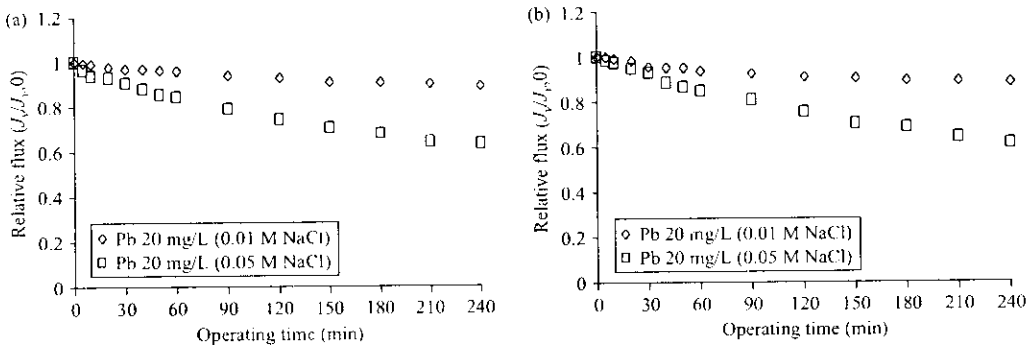


Figure 5 | Effect of ionic strength on relative flux, (a) $PbCl_2$ and (b) $Pb(NO_3)_2$.

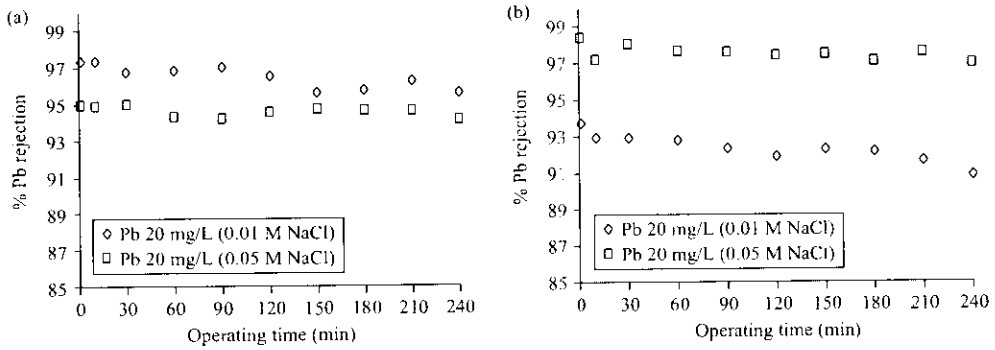


Figure 6 | Effect of ionic strength on lead ion rejection; (a) $PbCl_2$ and (b) $Pb(NO_3)_2$.

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 $PbCl_2$ and $Pb(NO_3)_2$ solutions with increasing ionic strengths, thus suggesting an increase in flux decline.

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.

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 Pb^{2+} ($PbCl_2$ and $Pb(NO_3)_2$ 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

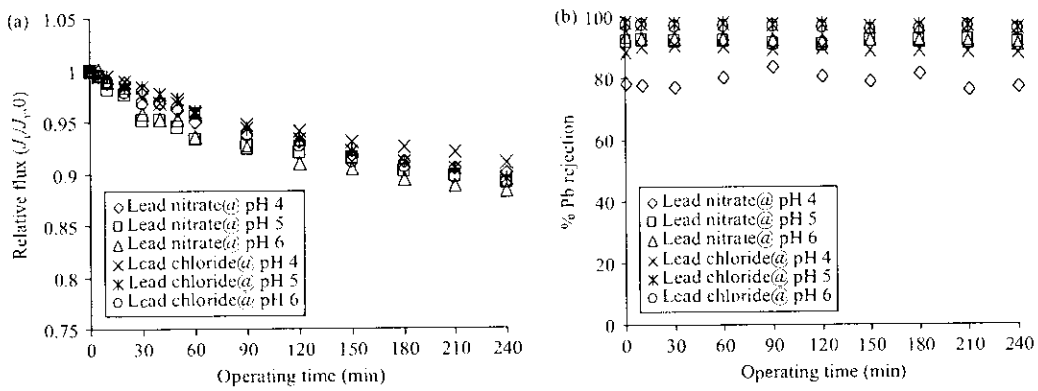


Figure 7 | Comparisons of co-ion on nanofiltration performance of lead solution; (a) relative flux and (b) rejection.

during filtration. Figure 7 shows the comparisons of co-ion on nanofiltration performance of lead solution. It was observed that $Pb(NO_3)_2$ solution showed higher flux decline than $PbCl_2$ solution, while $PbCl_2$ solution presented higher rejections than $Pb(NO_3)_2$ solution. Since the NF membrane is more negatively charged, the monovalent anion of Cl^- ion is more excluded than NO_3^- ion resulting in greater rejection. The lead ion rejections for $PbCl_2$ solution showed higher than those of $Pb(NO_3)_2$ solution. It was possibly caused by higher charge repulsion of negatively charged Cl^- ion, when compared with negatively charged NO_3^- ion, thus increased lead concentration for $PbCl_2$ 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 NO_3^-) 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) (Frares *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 $PbCl_2$ and $Pb(NO_3)_2$ 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.

ACKNOWLEDGEMENTS

This work was granted by the Office of the Higher Education Commission, which was supported by Strategic Scholarship Fellowships Frontier Research (CHE-Ph.D. THA-NEU). The authors also gratefully acknowledge support from the Thailand Research Fund (TRF) for TRF senior research scholar grant (No. RTA5080014) and the Commission on Higher Education, Thailand. The authors would like to thank the Department of Chemical Engineering, Faculty of Engineering, Ubon Rachathani University, and the National Center of Excellence for Environmental and Hazardous Waste Management, Ubon Ratchathani University, Ubonratchathani, Thailand, for all experimental equipments applied in this research.

REFERENCES

Amiri, M. C. & Samiei, M. 2007 Enhancing permeate flux in a RO plant by controlling membrane fouling. *Desalination* **207**, 361–369.

Anne, C. O., Trebouet, D., Jaouen, P. & Quemeneur, F. 2001 Nanofiltration of seawater: fractionation of mono-and multivalent cations. *Desalination* **140**, 67–77.

Bellona, C. & Drewes, J. E. 2005 The role of membrane surface charge and solute physico-chemical properties in the rejection of organic acids by NF membranes. *J. Membr. Sci.* **249**, 227–234.

Childress, A. E. & Elimelech, M. 2007 Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membrane. *J. Membr. Sci* **119**, 253–268.

Cho, J., Amy, G. & Pellegrino, J. 1999 Membrane filtration of natural organic matter: initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes. *Water Res.* **33**(11), 2517–2526.

Choi, S., Yun, Z., Hong, S. & Ahn, K. 2001 The effect of co-existing ions and surface characteristics of nanomembranes on the removal of nitrate and fluoride. *Desalination* **133**, 53–64.

Cotruvo, J. A. & Vogt, C. D. 1990 Rationale for water quality standards and goals. *Water Quality and Treatment*, 4th edition. McGraw-Hill, Inc, New York, USA.

Donnan, F. G. 1995 Theory of membrane equilibria and membrane potentials in the presence of non dialysing electrolytes. A contribution to physical-chemical physiology. *J. Membr. Sci.* **100**, 45–55.

Eriksson, P. 1988 Water and salt transport through two types of polyamide composite membrane. *J. Membr. Sci.* **36**, 297–313.

Frares, N. B., Taha, S. & Dorange, G. 2005 Influence of the operating conditions on the elimination of zinc ions by nanofiltration. *Desalinatian* **185**, 245–253.

Hong, S. & Elimelech, M. 1997 Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *J. Membr. Sci.* **132**, 159–181.

Ipek, U. 2005 Removal of Ni(II) and Zn(II) from an aqueous solution by reverse osmosis. *Desalination* **174**, 161–169.

Jarusutthirak, C., Mattaraj, S. & Jiraratananon, R. 2007 Influence of inorganic scalants and natural organic matter on nanofiltration membrane fouling. *J. Membr. Sci.* **287**, 138–145.

Kilduff, J. E., Mattaraj, S. & Belfort, G. 2004 Flux decline during nanofiltration of naturally-occurring dissolved organic matter: effects of osmotic pressure, membrane permeability, and cake formation. *J. Membr. Sci.* **239**(1), 39–53.

Ku, Y., Chen, S.-W. & Wang, W.-Y. 2005 Effect of solution composition on the removal of copper ions by nanofiltration. *Sep. Purif. Technol.* **43**, 135–142.

Labbez, C., Fievet, P., Szymczyk, A., Vidonne, A., Foissy, A. & Pagetti, J. 2003 Retention of mineral salts by a polyamide nanofiltration membrane. *Sep. Purif. Technol.* **30**, 47–55.

Lin, C. J., Shirazi, S., Rao, P. & Agarwal, S. 2006 Effects of operational parameters on cake formation of $CaSO_4$ in nanofiltration. *Water Res.* **40**, 806–816.

Lisdonk, C. A. C., van Paassen, J. A. M. & Schippers, J. C. 2000 Monitoring scaling in nanofiltration and reverse osmosis membrane systems. *Desalination* **132**, 101–108.

Mattaraj, S., Jarusutthirak, C. & Jiraratananon, R. 2008 A combined osmotic pressure and cake filtration model for crossflow nanofiltration of natural organic matter. *J. Membr. Sci.* **322**, 475–483.

Mehiguene, K., Garba, Y., Taha, S., Gondrexon, N. & Dorange, G. 1999 Influence of operating conditions on the retention of copper and cadmium in aqueous solutions by nanofiltration: experimental results and modelling. *Sep. Purif. Technol.* **15**, 181–187.

Molinari, R., Argurio, P. & Romeo, L. 2001 Studies on interactions between membranes (RO and NF) and pollutants (SiO_2, NO_3^-, Mn^{++}, and humic acid) in water. *Desalination* **138**, 271–281.

Schaep, J. & Vandeeasteele, C. 2001 Evaluating the charge of nanofiltration membranes. *J. Membr. Sci.* **188**, 129–136.

Tahaikt, M., El Habbani, R., Ait Haddou, A., Achary, I., Amor, Z., Taky, M., Alami, A., Boughriba, A., Hafsi, M. & Elmidaoui, A. 2007 Fluoride removal from groundwater by nanofiltration. *Desalination* **212**, 46–53.

Taylor, J. S. & Jacobs, Ed. P. 1996 Reverse osmosis and nanofiltration. In: Mallevialle, J., Odendaal, P. E. & Weisner, M. R. (eds) *Water Treatment Membrane Processes*. McGraw-Hill, New York, USA.

Teixeira, M. R., Rosa, M. J. & Nystrom, M. 2005 The role of membrane charge on nanofiltration performance. *J. Membr. Sci.* **265**, 160–166.

Turek, M., Dydo, P., Trojanowska, J. & Campen, A. 2007 Adsorption/co-precipitation reverse osmosis system for boron removal. *Desalination* **205**, 192–199.

Van Reenan, A. J. & Sanderson, R. D. 1992 Dynamically formed hydrous zirconium (IV) oxide-polyelectrolyte membranes. VII. Poly (acrylic acid-co-vinyl acetate) and poly (acrylic acid-co-vinyl alcohol) membranes: the effect of feed salt concentration on membrane properties. *Desalination* **85**, 247–262.

Yaroshchuk, E. & Staude, A. 1992 Charged membranes for low pressure reverse osmosis properties and applications. *Desalination* **86**, 115–134.