Nanofiltration Performance of Zinc Solution: Effects of Solution Chemistry

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ABSTRACT

The effects of solution chemistry (i.e. solution pH and ionic strength) on nanofiltration systems were investigated using a dead-end test cell at room temperature. An aromatic polyamide NF-90 membrane was chosen to determine the effects of zinc solution on nanofiltration fouling. The experimental results revealed that solution flux decline was dependent on ionic strength and solution pH. Flux decline conducted in $ZnSO_4$ solution decreased for solution pH. At pH 6-8, 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. Solution pH of 6-8 had greater ion rejection about 97% - 98%, whereas solution pH of 4 exhibited lower rejection approximately 85-86%.

Keywords: Flux Decline, Fouling, Nanofiltration, Rejection, Zinc

บทคัดย่อ

ผลกระทบทางเคมีของสารละลาย เช่น ค่า pH และความแรงประจุของสารละลาย ต่อระบบนาโนฟิลเตรชัน ซึ่งได้ทำการศึกษาด้วยชุดทดสอบเมมเบรนแบบไหลตามแนวดิ่ง (dead-end test cell) ณ อุณหภูมิห้อง เมมบรนชนิดอะโรเมติกโพลีเอไมด์ NF-90 ได้เลือกนำมาใช้เพื่อศึกษาผลกระทบของสารละลายสังกะสีต่อการอุดตันในระบบนาโนฟิลเตรชัน ผลการทดลองพบว่า

การลดลงของฟลักซ์ในสารละลายขึ้นอยู่กับความแรงประจุ และค่า pH ของสารละลาย การลดลงของฟลักซ์สารละลาย $ZnSO_4$ จะลดลงในสารละลายที่มีค่า pH ลดลง โดยพบว่าที่ pH 6-8 การลดลงของฟลักซ์ในสารละลายจะสูงกว่าสารละลายที่มีค่า pH ที่ต่ำกว่า ขณะที่การกำจัดสังกะสีจะมีค่าการกำจัดที่สูงกว่า ความแรงประจุที่เพิ่มมากขึ้นส่งผลให้การลดลงของฟลักซ์เพิ่มมากขึ้น การกำจัดไอออนของสังกะสีลดลงเมื่อค่า pH ของสารละลายลดลงและเมื่อเพิ่มความแรงประจุ ค่า pH ของสารละลายที่ 6-8 มีค่าการกำจัดไอออนโดยเฉลี่ย 97-98% ในขณะที่ที่ pH 4 มีค่าการกำจัดที่น้อยกว่า โดยเฉลี่ย 85-86%

คำสำคัญ : การลดลงของฟลักซ์ การอุดตัน นาโนฟิลเตรชัน การกำจัด สังกะสี

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Introduction

Membrane technologies have been widely used in the field of water treatment due to stringent water quality regulations (Hong and Elimelech, 1997). They are efficient technologies to remove feed source water in terms of natural organic matter (NOM) (Hong and Elimelech, 1997; Alborzfar, Jonsson, and Gron, 1998; Cho, Amy and Pellegrino, 1999; Schafer, Fane, and Waite, 2000; Kilduff, Mattaraj, and Belfort, 2004; Lisdonk, van Paassen, and Schippers, 2000; Lin, Shirazi, Rao, and Agarwal, 2006; Jarusutthirak, Mattaraj and Jiraratananon, 2007) salt solution (Childress and Elimelech, 2007; Anne, Trebouet, Jaouen and Quemeneur, 2001; Labbez, et. al., 2003) and heavy metals (Mehiguene, Garba, Taha, Gondrexon, and Dorange, 1999; Molinari, Argurio, and Romeo, 2001; Ku,Chen, Wang, 2005; Ipek, 2005; Turek, Dydo, Trojanowska, and Campen, 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 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. (Jarusutthirak, Mattaraj, and Jiraratananon, 2007). Molinari et al. (2001) 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 mostly used in mechanical engineering and building. 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 (Ministry of Public Health Notification, 1981).

Fouling on membrane surface by nanofiltration may influence by operating condition such as solution pH and ionic strength. 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 will be adapted to improve membrane filtration for long-term operation.

Materials and Methods

Nanofiltration 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 m3/hr), maximum operating temperature 113°F (45°C) and the operating pH is ranged from 1 to 12. 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.

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

Lux decline experiments

The experiments were carried out with three liters of solution containing zinc solution $(ZnSO_2)_4$ in fixed concentration of 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. A membrane sheet can be fitted to the cell. The membrane active area is 41.38 cm2. The operating pressure was employed via high-pressure regulator of nitrogen cylinder. The permeate flux will be kept in a beaker on the electrical balances (Mettler Toledo Monobloc PB-3002-S, USA).

Analysis of Results

The parameters taken into account were:

- The volumetric flux Jv (L/m2/h or LMH) was determined by measuring the volume of permeate collected in a given time interval divided with membrane area by the relation:

$$Jv = Q/A$$

Where, Q and A represents flow rate of permeate and the membrane area, respectively.

- The observed rejection was calculated by the following relation:

$$\% R = (1- C_p /C_f) \times 100$$

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

Results and Discussion

Effects of pressure on cleaned water flux

As shown in fig. 1, the effects of pressure at 0, 10, 20, 30, 40 and 50 psi on permeate flux or water flux produced from deionized water (DI water) increased linearly with increasing operating pressure with high correlation of 0.9986. The slope represents the membrane permeability about 0.4925 $LMH.psi^{-1}$.

After filtration experiments, the membrane sheet was cleaned with DI water and citric acid to investigate water flux. As shown in Fig. 2, the cleaned water flux with chemical cleaning had similar flux as water flux after compaction, where hydrodynamic cleaning showed lower flux. It was possibly due to protons from acid which dissolved inorganic zinc from the membrane surface.

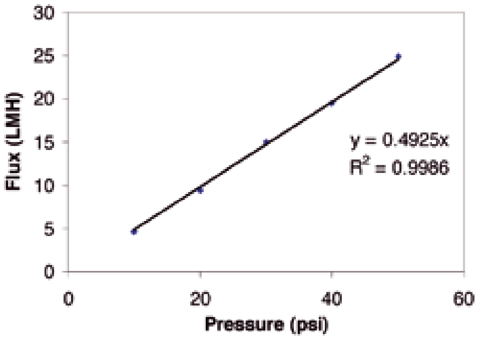

Fig. 1 Effect of pressure on cleaned water flux

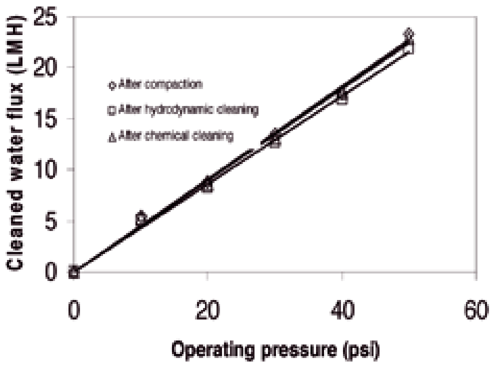

Fig. 2 Cleaned water flux of ZnSO4

Effects of solution pH on flux

The effects of the solution pH on flux decline of $ZnSO_4$ was carried out at pH 4,6,7 and 8 with keeping constant ionic strength 0.01 M as NaCl at 60-psi operating pressure. Zinc concentration was about 20 mg/L. 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. At pH 6-8, flux solutions showed higher flux decline than those of low solution pH. 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.

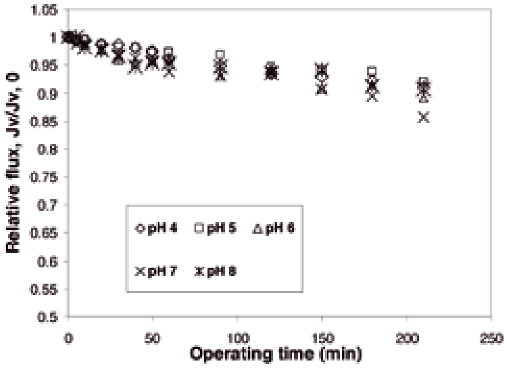

Fig. 3 Effects of solution pH on flux

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. It was observed that the extent and rate of solution flux decline increased with increasing ionic strength. In the study, increases in ion concentration can reduce the permeability of charged membranes (Yaroshchuk and Staude, 1992; Eriksson, 1988; Van Reenan and Sanderson, 1992), thus reduced permeate flux.

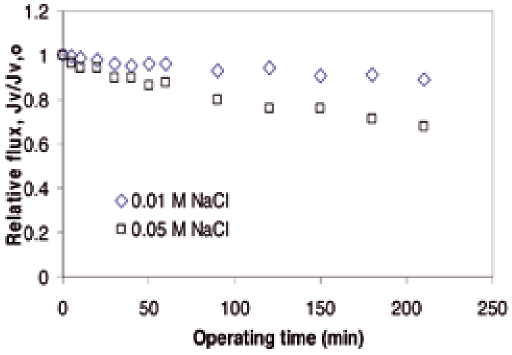

Fig. 4 Effects of ionic strength on flux

Effects of solution pH on zinc ion rejection

The effect of the solution pH on rejection of $ZnSO_4$ 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 20 mg/L were maintained constant during filtration. The obtained results are 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 had greater ion rejection, about 97%-98%, while low solution pH exhibited lower rejection about 85%-86%.

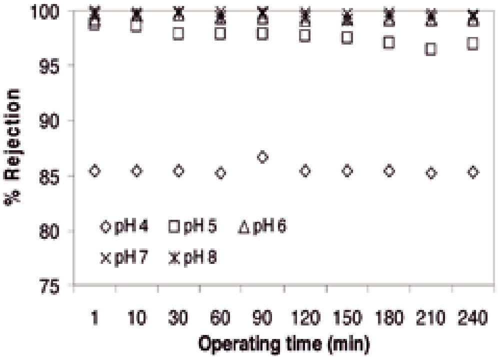

Fig. 5 Effect of solution pH on zinc ion rejection

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 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. This was possibly due to increasing salt concentration, reducing membrane permeability, thus allowing zinc ion passage through the membrane surface.

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 in $ZnSO_4$ solution decreased for solution pH. At pH 6-8, 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.

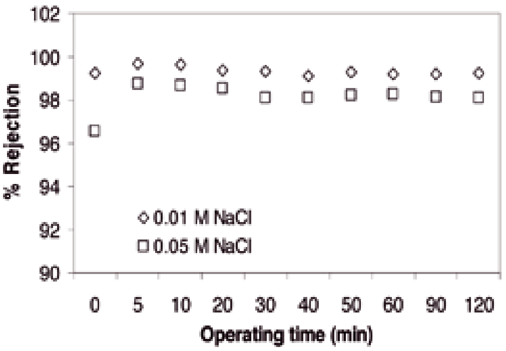

Fig. 6 Effect of ionic strength on zinc ion rejection

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