EFFECTS OF SOLUTION PH AND IONIC STRENGTH FOR REMOVAL OF COMBINED NATURAL ORGANIC MATTER AND COPPER (II) ION BY MEMBRANE NANOFILTRATION

ผลกระทบของพีเอชและความแรงประจุสำหรับการกำจัดจากการรวมกัน ของสารอินทรีย์ธรรมชาติและทองแดงโดยเยื่อกรองนาโน

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Abstract

Effects of solution pH and ionic strength for removal of combined natural organic matter (NOM) and copper (II) through a nanofiltration (NF) membrane were investigated. Experimental results revealed that the influence of NOM and copper (II) ion on NF performance was dependent on solution chemistry (i.e. solution pH and ionic strength). For copper (II) ion, increased solution pHs exhibited greater flux decline, while there was no significant difference in flux for solutions containing NOM. Solutions containing copper (II) ion alone showed less flux decline than those containing NOM and combined NOM with copper (II) ions. The ion rejections (based on copper and conductivity rejections) followed Donnon exclusion phenomena.

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For combined NOM and copper (II) ion, the rejections of copper ion tended to increase, thus enhancing NOM-copper accumulation at the membrane surface. Increased ionic strength increased both solution flux decline and non-recoverable fouling resistance after system cleaning. A FT-IR spectroscope was successfully used to investigate the binding between NOM and the membrane surface, thus enhancing non-recoverable resistance.

Keywords: Nanofiltration, Membrane fouling, Natural organic matter, Copper (II) ion

บทคัดย่อ

ผลกระทบของพีเอชและความแรงประจุสำหรับการกำจัดจากการรวมกันของสารอินทรีย์ธรรมชาติและทองแดงโดยเยื่อกรองนาโนได้ถูกทดสอบ ผลการทดลองพบว่าอิทธิพลของสารอินทรีย์ธรรมชาติและทองแดงโดยผ่านเยื่อกรองนาโนขึ้นอยู่กับองค์ประกอบเคมีของสารละลาย (เช่น พีเอชและความแรงประจุ) ผลการศึกษาของทองแดงพบว่าการเพิ่มขึ้นของพีเอชส่งผลต่อการเพิ่มการลดลงของฟลักซ์ที่สูงขึ้น ขณะที่ผลของสารอินทรีย์ธรรมชาติให้ผลไม่แตกต่างกันต่อการลดลงของฟลักซ์สารละลายทองแดงอย่างเดียวให้ค่าการลดลงของฟลักซ์น้อยกว่าสารอินทรีย์ธรรมชาติอย่างเดียวและผลร่วมระหว่างสารอินทรีย์ธรรมชาติและทองแดง ค่าการกำจัดไอออนโดยวัดจากค่าการกำจัดของทองแดงและค่าการนำไฟฟ้าเป็นตามปรากฏการณ์การกีดขวางแบบ Donnan สำหรับผลร่วมระหว่างสารอินทรีย์ธรรมชาติและทองแดงพบว่าค่าการกำจัดของทองแดงมีแนวโน้มเพิ่มขึ้นเป็นผลมาจากการจับตัวกันของสารอินทรีย์ธรรมชาติและทองแดงสะสมบนผิวหน้าของเยื่อกรอง การเพิ่มความแรงประจุส่งผลต่อการเพิ่มขึ้นของการลดลงของฟลักซ์สารละลายและค่าความต้านทานที่ไม่สามารถล้างออกได้จากการวิเคราะห์ด้วยเครื่อง FT-IR แสดงให้เห็นการจับตัวกันของสารอินทรีย์ธรรมชาติและผิวหน้าของเยื่อกรองเป็นผลเนื่องมาจากค่าความต้านทานที่ไม่สามารถล้างออกได้

คำสำคัญ: การกรองโดยเยื่อกรองนาโน, การอุดตันแมมเบรน, สารอินทรีย์ธรรมชาติ, ทองแดง

Introduction

Copper is a natural constituent of soil and transported into streams and waterways by runoff either due to natural weathering or anthropogenic soil disturbances. Excessive amounts of copper (II) can cause serious potential health effect such as nausea, headache dizziness, respiratory difficulty, hemolytic anemia, massive gastrointestinal bleeding, liver and kidney failure, and death[1]. Organic matter can be a significant factor that enhances permeate flux decline during filtration. Natural organic matter (NOM) found in surface water and ground water is composed of a heterogeneous mixture of complex organic materials. For example, surface water contains NOM, hardness from the composition of calcium and magnesium, heavy metal ions, iron, manganese, and copper. NOM is a major cause on membrane fouling during the operation period. The cleaning of the membrane to restore the treatment efficiency is needed. In aqueous systems, inorganic matter also can be a significant factor including heavy metal ions which occur in complex with ligands. Takács and Alberts[2] studied the characterization of NOM from eight

Norwegian surface waters, including proton and copper binding. Lee et al.[3] reported that combined fouling was affected by both cake-enhanced osmotic pressure and NOM-calcium complexation. Zularisam et al.[4] found that feed properties, membrane characteristics, operational conditions and solution chemistry also had strong influence on the nature and extent of NOM fouling. The fouling mechanisms appear to be relatively less significant for combined fouling than their separate influences on individual colloidal and NOM fouling. Lee et al.[3] and Zularisam et al.[4] reported that the component of NOM which primarily caused the fouling problem was still not understood very well, especially those relating to the specific fraction that was mainly responsible of flux decline. Lee and Lee[5] indicated that the fouling by NOM adsorption was an important factor on hydrophobic and positively charged membranes, whereas, it was negligible for hydrophilic and negatively charged membranes. However, membrane fouling caused by NOM and inorganic scalants[6-8], resulted in controlling various physical and chemical parameters. Membrane fouling is, therefore, considered as a major factor in the operation and design of membrane system.

Membrane technology has been a significant process in drinking water and wastewater treatment, which facilitates the removal and recovery of pollutants[9]. NF membrane is one of the membrane processes and has been used for the removal of NOM and inorganic matter. Membrane fouling is dependent on solution composition (i.e. NOM concentration, ionic strength, calcium concentration, and solution pH [10]), membrane characteristics (i.e. pore size, charge), and operational conditions (i.e. flux, pressure, and crossflow velocity)[10-12]. Rubia et al.[13] reported that the NOM removal by NF membrane (i.e. NF90, NF270) for all water sources was effective. Murthy and Chaudhari[14] indicated that the rejection of nickel ions increased rise on feed pressure and decreased rise on feed concentration at constant feed flowrate. Qdais and Moussa[15] found that the application of NF for the treatment of wastewater containing copper and cadmium ions, was capable of removing more than 90%. There were primary forms of bound copper in natural waters, where copper complexes were formed by mixing with organic and inorganic ligands, and copper was absorbed into particulate matter[16-18]. Therefore, the objective of this study is to investigate the effect of solution pH and ionic strength for removal of combined NOM and copper (II) ion during NF experiments. Source of NOM was taken from Nong E-jame, which is served raw water resource for University Community. Nong E-jame is located in

Ubon Ratchathani University, north eastern Thailand.

Methods and Materials

Nanofiltration membrane

A commercial polyamine thin-film composite NF membrane, produced by Nitto Denko, USA (ESNA1 serial A154052), was used to determine the effect of NOM and copper (II) ion on nanofiltration fouling. The molecular weight cut-off (MWCO) of the ESNA1 membrane was approximately 80 Daltons[19]. The ESNA1 membrane was designed to remove about 90% of salt from water. According to the manufacturer's information, the maximum applied pressure was 4.16 MPa, while the maximum feed flow was 3.6 m^3h^{-1}. The maximum operating temperature was 45 ^{o}C, and the solution pH of the feed water ranged from 3.0 to 10.0. In this study, the membrane had the effective surface area of 0.0155 m^2 in a flat sheet under a bench-scale cross-flow NF test cell. The membrane sheet was initially cleaned for 30 min with a solution pH of 4 (using citric acid) and further for 30 min with a solution pH of 10 (using NaOH). Membrane permeability was determined with de-ionized water (DI) within a 95% confidence interval. A new membrane sheet was used for each new experiment. The membrane sheets were stored in 1% W/W sodium meta-bisulfate ($Na_2S_2O_5$) and kept in a refrigerator at 4 ^{o}C to prevent bacterial activity.

Filtration experiments

Figure 1 shows the schematic diagram of crossflow NF unit. The filtration experiments were carried out with eight-liter feed solutions containing NOM and copper (II) ion. Solution pH and ionic strengths were ranged from 4 to 6 and from 0.005 to 0.5 M as NaCl, respectively. The initial flux was maintained at 45 LMH with constant pressure during the 500-min filtration period. The recovery was kept constant at 85%. Samples were conducted at 0, 30, 60, 120, 210, 300, 380 and 500 min, while the flow rate was measured along with the filtration period. The removal efficiencies of NOM and copper ion were subsequently determined to compare experimental results. 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, and then followed with chemical cleaning by using acidic solution (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 in order to evaluate flux recovery and resistant fouling
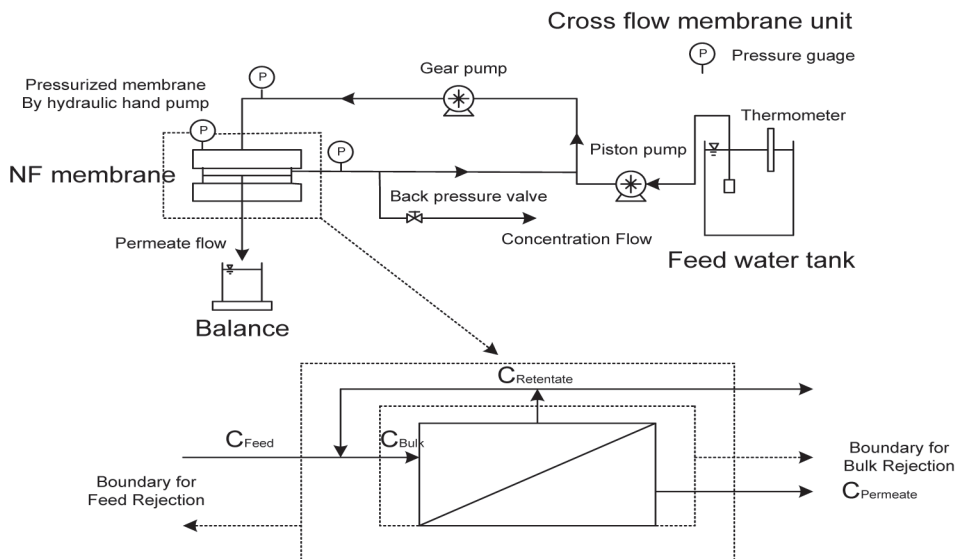
Figure 1. Schematic diagram of crossflow NF unit

Analytical methods

The concentrations of copper ion were analyzed using an atomic absorption spectrophotometer (AAs, Perkin Elmer), while the NOM concentration was analyzed using a total organic carbon analyzer (Shimazu Co., Japan). The permeate flux was measured gravimetrically by a balance (Mettler Toledo Monobloc model PB3002, USA) with a measurement error of 0.01%. The NaCl concentration was measured with a conductivity meter (inoLab Cond Level 2, Wissenschaftlich-Technische Werkstatten, Germany) at a constant temperature of 25 °C. All instrumental conditions were optimized for maximum sensitivity as described by the manufacturers.

Calculation

The parameters used to quantify the efficiency of NF membrane are solution flux, J_v (Lm^{-2}h^{-1} or LMH) and rejection (R). The membrane fluxes were evaluated using membrane permeability and the pressure difference between operating pressure and osmotic pressure as in Equation (1).

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

L_p is the membrane permeability (L m^{-2} h^{-1} KPa^{-1})

ΔP is the transmembrane pressure (kPa)

σ is the osmotic reflection coefficient (-)

π is the osmotic pressure (kPa)

Q_p is the flow rate of permeate (L h^{-1})

A is the membrane area (m^2).

The rejection was calculated as percentage removal (R) by comparing the concentrations between the permeate concentration (C_p) and the retentate concentration (C_r) as in Equation (2).

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

Total hydraulic resistance (R_T) due to the intrinsic membrane hydraulic resistance (R_m), and hydraulic resistance of the fouling layer due to a combination of concentration polarization, fouling, and resistant fouling (R_f). The equation can be written shown in Equation (3).

$$J_v = \frac{\Delta P}{\mu(R_T)} = \frac{\Delta P}{\mu(R_m + R_f + R_{non-rec})} = \frac{\Delta P}{\mu(R_m + R_{c1} + R_{c2} + R_{non-rec})} \qquad (3)$$

where R_f can be written as the sum of a polarization resistance and fouling (R_{C1}) recoverable with hydrodynamic cleaning (m^{-1}), and a reversibly adsorbed NOM layer resistance recoverable using chemical cleaning (R_{C2}) (m^{-1}), a non-recoverable resistance ($R_{rom-rec}$) can be determined after hydrodynamic and chemical cleaning (m^{-1}).

Results and Discussion

Effect of solution pH on NF performance

Solution pH during NF of NOM and copper(II) ion were carried out at pH 4, 5, and 6 with constant ionic strength 0.01 M as NaCl. Feed concentrations of copper(II) ion and NOM solution were kept at 20 mgL^{-1} and 10 mgL^{-1}, respectively. Figure 2 shows the effect of solution pH on flux decline. It was found that the solution flux decline increased with increased solution pH for copper (II) ion solution, while the addition of copper (II) ion to feed solutions containing NOM caused a decrease in solution flux. However, feed solutions containing NOM resulted in remarkably lower flux than the feed waters containing copper (II) ion. Membrane fouling of NOM and/or interaction between NOM and copper (II) ion was possibly due to strong adsorption, precipitation, or binding within the pore structure. The combination of NOM and copper (II) ion caused membrane fouling, possibly increased accumulation on the membrane surface. At solution pH of 4, an increased fixed charge of H$^+$ ion was suggested, which decreased electrical double layer thickness on the membrane surface, thus decreasing concentration of heavy metal ions at the membrane surface[20]. Therefore, the charge interaction between a positively charged H$^+$ and a negatively charged NF membrane caused

salt passage though the membrane surface, thus decreasing salt rejections. The flux decline was less as observed. At high solution pH of 6, the decreasing solution flux of copper (II) ion could be affected by increased salt rejection on the membrane surface. In general, the increase of water flux decline is possibly caused by accumulation, which increased the effect of removal. This was observed in Figure 2(b) by NOM accumulation at the membrane surface. However, the fouling characteristics of the membrane were tested at two different permeate fluxes; this variable did not have an effect on the overall amount of material deposited, but it significantly impacted the membrane fouling rate[21]. The different

behavior was most probably caused by the differences in the fouling layers and foulant characteristics as well as by the electroneutrality[6]. As a result, a high solution pH with NOM showed flux decline due to increase accumulation near the membrane surface, thus affecting flux reduction. Wang et al.[12] indicated that the permeate flux was minimum around the isoelectic points of the membranes. Zularisam et al.[4] reported that NOM and its components were the major membrane foulants that occurred during the water filtration process, possibly damaging the mechanisms and methods to control fouling such as feed properties, membrane characteristics, operational and solution conditions.

(a)   (b)   (c)
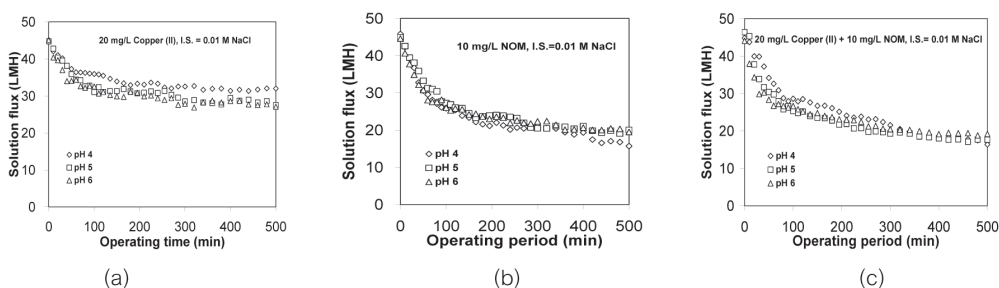
Figure 2 Effect of solution pH on flux decline; (a) copper (II) ions, (b) NOM and (c) combined NOM and copper (II) ions.

Figure 3 shows the effect of solution pH on conductivity rejection. The influence of solution pH on membrane characteristics was due to the charge effect on the membrane. The conductivity rejection showed the lowest rejection at solution pH

4 with NOM. This was possibly due to reduced charge repulsion, thus allowing salt passage at the membrane surface. High solution pH for NOM alone showed the highest conductivity rejections due to charge interaction between negatively

charged NOM and positively charged sodium ion from ionic strength. For combined NOM and copper (II) ions, the conductivity rejections were ranged from those of NOM and copper (II) ion alone. The decrease in the conductivity rejections for the combined NOM and copper (II) ion was possibly due to Donnan exclusion phenomena (between sodium ion and copper (II) ions) in order to keep electroneutrality in the permeate and concentrate stream. The experimental results were confirmed with TOC rejection and copper ion rejection as shown in Figure 4. Solutions containing copper (II) ion alone resulted in the lowest copper rejections, while the solutions containing NOM alone exhibited relatively high in TOC rejections. Solutions containing pH of 4 illustrated higher copper ion rejection than those of solutions containing pH of 5 and 6. The rejection of cations increases at pH values below the isoelectric points, in consequence of repelling interactions between cations and the membrane when positively charged at a lower pH[22]. From Figure 4C, the TOC and copper rejections shows relatively high rejections for combined NOM and copper (II) ions, pronouncing NOM-cation accumulation on the membrane surface.

However, the copper ion rejections were dependent on the effect of solution pH, possibly due to the effects of Donnan exclusion phenomena. Solution pH of 4 showed the highest copper ion rejections. In addition, Childress and Elimelech[23] suggested that divalent cations were more readily adsorbed by the membrane surface than divalent anions, especially in the higher pH range. Previous results indicated that the separation of copper (II) ion from an aqueous solution by NF was strongly influenced by the type and concentration of anion, solution pH, operating pressure, and the presence of surfactant and chelating agents[24, 25]. Jarusutthirak and co-workers[7] reported that increased solution pH from 4 to 10 exhibited greater flux decline caused by increased salt (only Na^+ ion) rejection and enhanced salt concentration on the membrane surface. Teixeira et al.[26] reported that the pH increase caused pore narrowing, larger NOM hydrodynamic radius and stronger repulsions between the negatively charged membrane and NOM functional groups, yielding higher rejections, which in turn, increased the osmotic gradient with a subsequent flux decline.
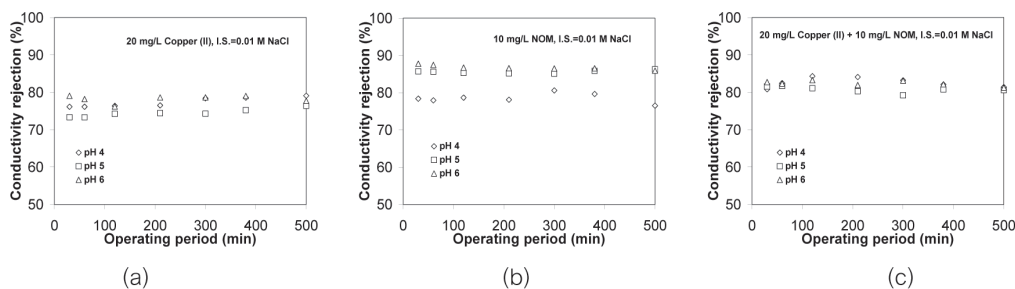
Figure 3 Effect of solution pH on conductivity rejection; (a) copper (II) ions, (b) NOM and (c) combined NOM and copper (II) ions
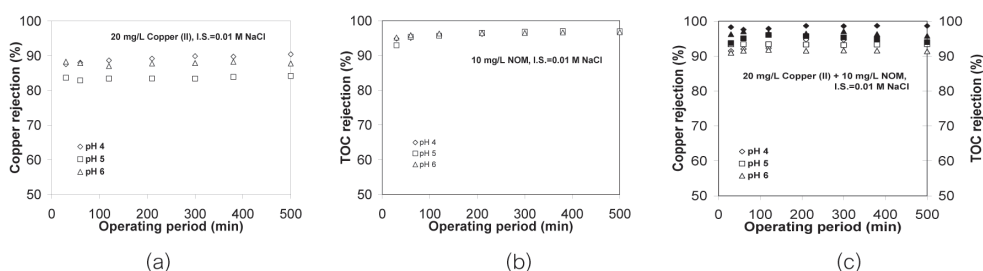

Figure 4 Effect of solution pH on TOC rejection and copper (II) ion; (a) copper (II) ions, (b) NOM and (c) combined NOM and copper (II) ions

Effect of ionic strength on NF performance

The effect of ionic strength on NF performance of NOM and copper (II) ion was investigated in this study. Figure 5 presents the effect of ionic strength on flux decline at ionic strength 0.005, 0.01 and 0.05 M as NaCl with constant solution pH of 4. The solution pH of 4 was selected in order to avoid metal precipitation. The results revealed that the solution flux decreased significantly by increasing ionic strengths, especially at high ionic strength of 0.05 M. Increased ionic strength could cause salt concentration on the membrane surface, suggesting high concentration polarization. This result showed an increased osmotic pressure, thus reducing electrostatic repulsion at the membrane surface. In addition, at high ionic strength, the charges of the membrane surface and NOM macromolecules could significantly be reduced, leading to a decrease on electrostatic repulsion between NOM and the membrane surface. Consequently, NOM deposition onto the membrane surface was greatly enhanced, which in turn leaded to a thick NOM deposit layer. Al-Abri et al.[8] reported that an increase in ionic strength

could reduce the area of electric double layer of the NF membrane and increased the area available for the transport of the heavy metals. Jarusutthirak et al.[7] found that solutions having divalent cation (calcium) exhibited greater flux decline than those having monovalent cation (sodium), while solution flux curves dominated the cake formation model, especially at high ionic strength. The flux decline of copper (II) ion increased with increasing ionic strength in feed solution. Nanda et al.[27] reported that the rejection of objectionable hardness producing magnesium ions decreased with increased ionic strength, due to the rejection of sodium chloride used to maintain the ionic strength of the solution. Al-Abri et al.[8] reported that the reduction in heavy metal

retention with increase in ionic strength was due to the effect of salinity on humic structure. Humic molecules coil up and their surface area is reduced when ionic strength is increased due to double layer compression. The rejection of copper chelate was markely influenced by the solution pH and the molecular weight of chelate [25]. Al-Abri et al.[8] reported that heavy metals interacted with the surface of the colloidal humic molecules. The reduction in humic colloidal surface area could reduce the number of humic binding sites available for heavy metal agglomeration. This can result in the quantity of non-associated metal ions, which pass though the membrane pores, thus decreasing their retention.
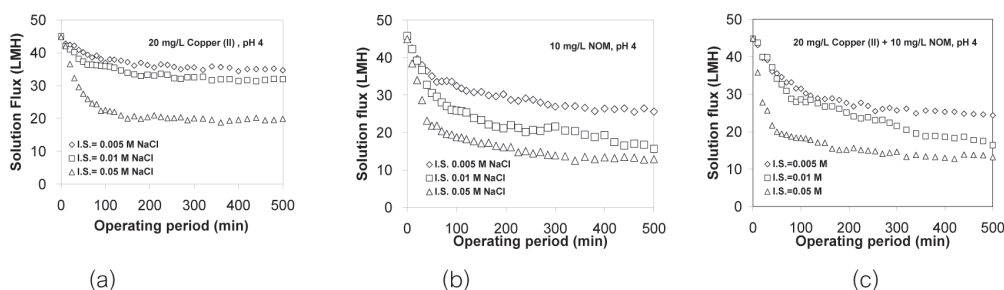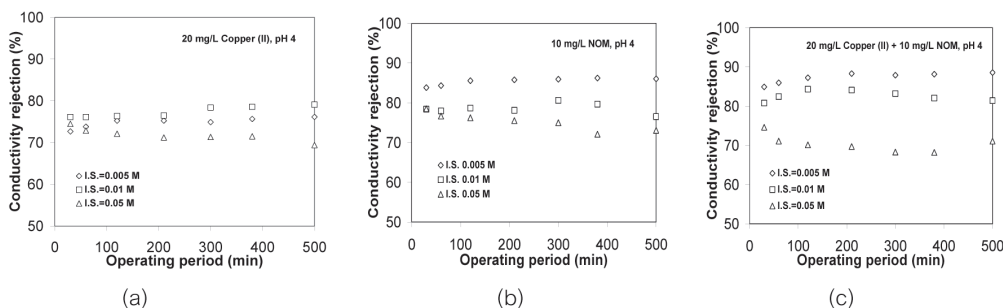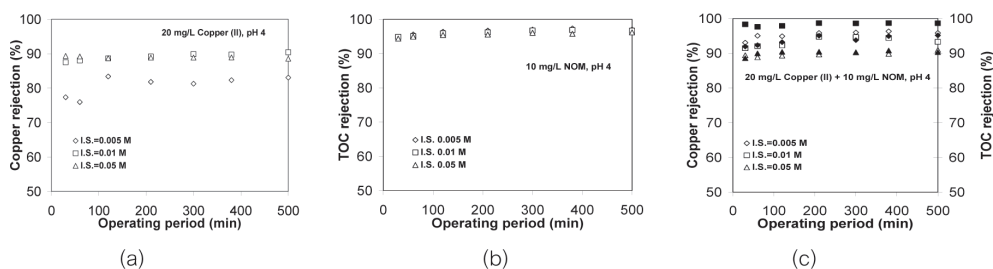

(a)   (b)   (c)

Figure 5 Effect of ionic strength on flux decline; (a) copper (II) ions, (b) NOM and (c) combined NOM and copper (II) ions

Figure 6 Effect of ionic strength on conductivity rejection; (a) copper (II) ions, (b) NOM and (c) combined NOM and copper (II) ion

Figure 7 Effect of ionic strength on rejections; (a) copper (II) ions, (b) NOM and (c) combined NOM and copper (II) ion

Figure 6 shows the effect of ionic strength on conductivity rejection. It was found that the conductivity rejections at 0.05 M as NaCl were lower than those at 0.005 M as NaCl, due to increased salt concentration affecting flux decline. Increased ionic strengths could increase osmotic pressure in the system, enhancing a decrease in flux decline and conductivity rejections. However, an ionic strength can be a significant factor that affects copper (II) ion and TOC rejection during filtration. Figure 7 presents the effect of ionic strength on copper (II) ion rejection and TOC rejection. Increased ionic strengths increased copper ion rejections, possibly due to charge effect in order to keep charge balance in both streams. For NOM solution (Figure 7b), high TOC rejections were observed with no significant effect of ionic strengths. For combined NOM and copper (II) ion (Figure 7c), the copper ion rejections increased at low ionic strength of 0.005 M. This was caused by the charge interaction between NOM and copper (II) ions. Moreover, increasing ionic strength, copper (II) ion can produce stable complexes with NOM in water. However, the accumulation of

NOM particles on the membrane surface was significantly increased by the combination of NOM and copper (II) ions. Cake formation of NOM could dominate fouling mechanism at the membrane surface. Lee et al.[3] found that NF membrane salt rejection increased noticeably in case of combined fouling compared to individual colloidal fouling due to the formation of an active rejecting layer by the accumulated NOM on the membrane surface.

Interaction between NOM and copper (II) ion

The impact of combined NOM and copper (II) ion at different concentrations was observed on the NF membrane performance. Figures 8 and 9 show the effect of NOM and copper (II) ion on solution flux and rejection at different concentrations. The concentrations of both NOM and copper (II) ion in the experiments were prepared from 10 to 20 mgL^{-1} with solution pH of 4 and ionic strength of 0.01 M NaCl. The various concentration ratios of NOM to copper (II) ion were adjusted to 1:1, 1:2, 2:1 and 2:2. The initial solution flux was adjusted at 45 LMH, while the recovery was operated at 85% during NF filtration. The results showed that solutions containing high NOM concentration of 20 mgL^{-1} caused lower flux reduction, while there were no significant difference in flux decline with copper ion concentrations between 10 and 20 mgL^{-1}. This indicated that NOM was considered as a major cause of membrane fouling. The fouling of the membrane was generally caused by rejected inorganic and organic species, thus producing the accumulation of solutes near the membrane surface, gradually non-recoverable changes in cake formation, and adsorption of solute on the membrane. The conductivity rejections were relatively low when compared with copper ion rejections and TOC rejections. This indicated that the lower conductivity rejections were observed due to monovalent sodium ion passing through the membrane surface, while the NOM (98.3% for 10 mgL^{-1} NOM) and copper ion rejections (93.3% for 20 mgL^{-1} copper ion) increased due to combined charge interaction between NOM and copper ion. In relation to the effect of NOM and heavy metals on solution flux and rejection, the apparently stronger binding sites were utilized at lower metal ion loading and progressively weaker sites contributed to metal complexation at higher loading[28, 29].
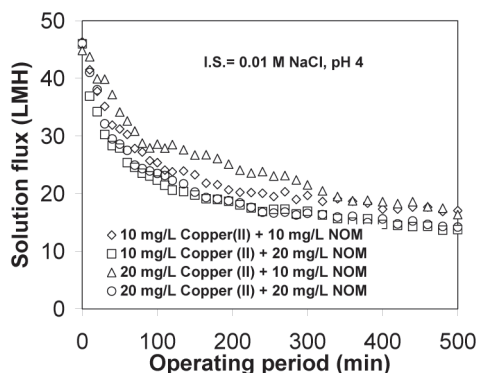
Figure 8 Effect of NOM and copper (II) ion on solution flux at different concentrations.
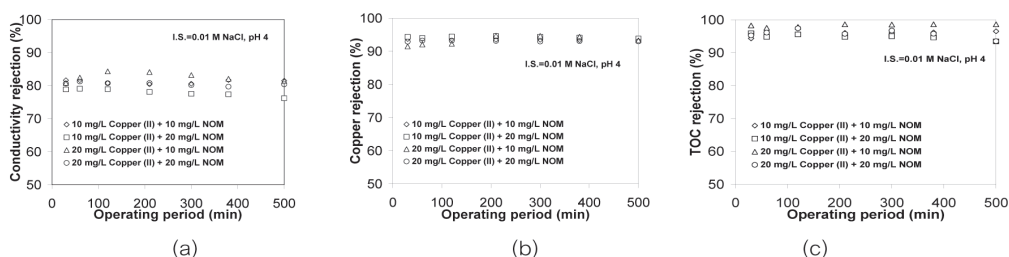

(a) (b) (c)

Figure 9 Effect of NOM and copper (II) ion on rejections; (a) conductivity rejection, (b) copper (II) ion rejection and (c) TOC rejection.

FT-IR spectrum analysis

The characteristics of NOM have generally different physical properties from different surface waters. The physical characteristics and NOM surrogate parameters of raw water were determined in order to gain an understanding of physical and chemical properties as well as the quantity of NOM in such water. FT-IR analysis was conducted on the membrane surface after complexation between NOM and copper (II) ion on NF membrane. A number of adsorption peaks were identified, depicting the complex nature of the NOM and copper (II) ions. A FT-IR spectroscope was used to investigate the effect of NOM and/or copper (II) ion on membrane fouling (Figure 10). It was seen that the FT-IR spectra displayed a number of absorption peaks, indicating the complex nature of the NOM examined. The FT-IR spectra of NOM and/or metal ion formation of the membrane surface in the range of 4,000-400 cm^{-1} were observed. The different functional groups absorbed energy at different specific wavelengths that could

later be translated into an intensity response[4]. The FT-IR spectra displayed a number of peaks, indicating the complex nature of the NF membrane. The experimental results revealed that the compositions of carboxylic acid (OH deformation, C-O stretching of phenolic OH) were observed at 1,295 and 1,318 cm^{-1}, while the composition of aliphatic (C-H) was observed at 1,489 cm^{-1}. The composition of N-H deformation (COO$^-$) was observed at 1,582 cm^{-1}. The composition of carbon double bond (carboxylic acid C = C) was found at wavelengths 1,665 1,901 1,986 and 2,047 cm^{-1}, while the composition of aliphatic C-H stretching was observed at 2,966 and 3,065 cm^{-1}, which were represented for the NF membrane.

(a)   (b)   (c)
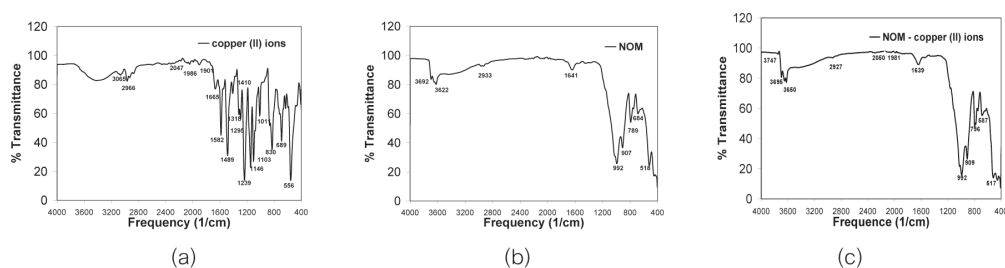
Figure 10 Transmittance of infrared spectrum of the membrane surface after system cleaning; (a) copper (II) ions, (b) NOM, and (c) combined NOM and copper (II) ions.

NOM in surface water is more hydrophobic in its nature, resulting in a more noticeable effect in increased copper release than did the more hydrophilic. This was contrary to what would be expected, as complexation was considered to be associated with the hydrophilic functional groups[30]. For the NF test (Figure 10a) of copper (II) ions, after cleaning the transmittance of infrared spectrum changed for the frequency range of 1,103 1,146 1,239 1,295 1,318 1,489 1,582 1,665 1,901 2,966 3,065 and 3,692 cm^{-1}. From Figure 10(b), the FT-IR spectra displayed the change number of peaks as following the frequency range of 517 587 796 909 992 1,639 1,981 2,050 2,927 3,650 and 3,695 cm^{-1}. From Figures 10(b) and 10(c) of NOM and combination between NOM and copper (II) ions, the results showed that the transmittance of infrared spectrum was found for 1,239 1,318 1,489 and 1,582 cm^{-1}, indicating that a hydrophobic fraction of NOM presented on the membrane surface. Other frequency ranges found that the functional group could cause cake formation at the membrane surface, generating non-recoverable resistance. The results could possibly

cause NOM adsorption on the membrane surface and/or membrane pores. Thus, it was suggested that these functional groups were likely to participate in binding between NOM and the membrane surface.

Resistance-in-series analysis

The resistance-in-series analysis was used to explain permeate flux decline in crossflow operation during filtration. Increasing the resistance on the membrane may possibly come from NOM and copper (II) ions, due to cake formation. Membrane fouling caused permeate flux decline, resulting in an increase in resistance. However, increasing hydraulic resistances occurred from non-recoverable fouling and strongly adsorbed at the membrane surface. Figure 11 shows the fouling resistance for NOM and copper (II) ions. The membrane resistance (R_m) was equal to 5.61×10^{13} m^{-1}.

Su et al.[31] reported that the pure water permeability of ESNA was measured to be 1.18×10^5 ms^{-1}. MPa^{-1}and the average pore radii of ESNA membrane was estimated to be 0.3 nm. Membrane fouling was caused by inorganic and organic species, inducing accumulation layer at the membrane surface. This was possibly due to strong adsorption on the membrane surface, which increased the resistance of the membrane. Ku et al.[25] indicated that the rejections of copper (II) ion and salt concentration decreased with increasing values of solute transport parameters, while the mass transfer coefficients of copper (II) ion decreased with the presence of surfactants, indicating that the formation of the secondary filtration layer led to the increase of resistance of solutes permeated though the membrane surface.
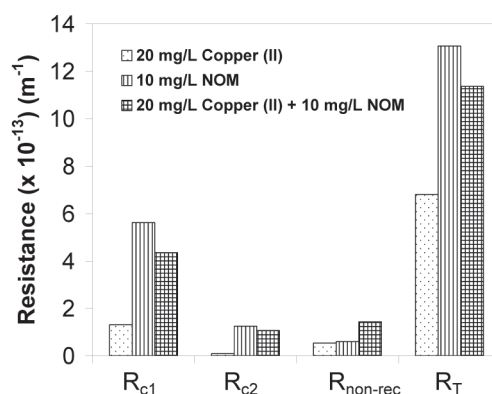

Figure 11 Fouling resistances for NOM and copper (II) ions.

From Figure 11, the NOM and combined NOM and copper (II) showed relatively high in R_{C1} and R_T. The resistant value of copper (II) ion yielded low fouling resistant for R_{c1}, indicating the loose cake formation at the membrane surface. It was found that non-recoverable fouling resistance ($R_{non-rec}$) after chemical cleaning increased for combined NOM and copper (II) ions. Previous study illustrated that the interaction between membrane and inorganic pollutants (i.e. SiO_2, NO_3^-, Mn (II) and humic acid) caused membrane fouling. The interaction of metal-NOM caused a flux reduction due to increased permeate resistance at the membrane surface. The removal of NOM and heavy metals tended to increase, possibly due to reduced charge repulsion between positively charged metal ions and negatively charged NOM, thus causing complete pore fouling and/or accumulation at the membrane surface [32].

Conclusions

The NF process can be a good alternative in treating solutions containing NOM and copper (II) ion. Flux decline and rejection from aqueous solution on NF performance were influenced by solution pH and ionic strength. For copper (II) ion, increased solution pHs from 4 to 6 exhibited greater flux decline, while there were no significant difference in flux for solutions containing NOM. The rejections of conductivity were relatively low when compared with those of copper ion, possibly due to Donnon exclusion phenomena. For combined NOM and copper (II) ion, the rejections of copper ion tended to increase, thus enhancing NOM-copper accumulation at the membrane surface. Solutions containing high ionic strength showed greater flux decline than those having low ionic strength. A FT-IR spectroscope was successfully used to investigate the binding between NOM and the membrane surface, thus enhancing non-recoverable resistance. This was significantly affected by the combined effect of NOM and copper (II) ion, possibly causing cake formation at the membrane surface and/or membrane pores.

Acknowledgements

References

(1) Gong, R., Guan, R., Zhao, J., Liu, X. and Ni, S. 2008. Citric acid functionalizing wheat straw as sorbent for copper removal from aqueous solution. J. Health Sci. 54: 174-178.

(2) Takács, M. and Alberts, J.J. 1999. Characterization of natural organic matter from eight Norwegian surface water: proton and copper binding. Environ. Inter. 25: 315-323.

(3) Lee, S. Cho, J. and Elimelech, M. 2005. Combined influence of natural organic matter (NOM) and colloidal particles on nanofiltration membrane fouling. J. Membr. Sci. 262: 27-41.

(4) Zularisam, A.W., Ismail, A.F. and Salim, R. 2006. Behaviours of natural organic matter in membrane filtration for surface water treatment-a review. Desalination 194: 211-231.

(5) Lee, S. and Lee, C.-H. 2007. Effect of membrane properties and pretreatment on flux and NOM rejection in surface water nanofiltration. Sep. Purif. Technol. 56: 1-8.

(6) Liikanen, R., Kiuru, H., Peuravuori, J. and Nyström, M. 2005. Nanofiltration flux, fouling and retention in fouling dilute model waters. Desalination. 175: 97-109.

(7) Jarusutthirak, C., Mattaraj, S. and Jiraratananon, R. 2007. Influence of inorganic scalants and natural organic matter on nanofiltration membrane fouling. J. Membr. Sci. 287: 138-145.

(8) Al-Abri, M. Da, A. kheel, Tizaoui, C.and Hilal, N. 2010. Combined humic substance and heavy metals coagulation, and membrane filtration under saline conditions. Desalination. 253: 46-50.

(9) Murthy, Z.V.P. and Chaudhari, L. B. 2009. Separation of binary heavy metals from aqueous solutions by nanofiltration and characterization of the membrane using Spiegler–Kedem model, Chem. Eng. J. 150: 181-187.

(10) Mattaraj, S., Phimpha, W., Hongthong, P. and Jiraratananon, R. 2010. Effect of operating conditions and solution chemistry on model parameters in crossflow reverse osmosis of natural organic matter. Desalination. 253: 38-45.

(11) Amy, G. 2008. Fundamental understanding of organic fouling of membranes. Desalination. 231: 44-51.

(12) Wang, Z., Liu, G., Fan, Z., Yang, X., Wang, J.and Wang, S. 2007. Experimental study on treatment of electroplating wastewater by nanofiltration. Desalination. 305: 185-195.

(13) Rubia, Ă.D.L., Rodǐguez, M., Leǒn, V. M. and Prats, D. 2008. Removal of natural organic matter and THM formation potential by ultra- and nanofiltration of surface water. Water Res. 42: 714-722.

(14) Murthy, Z.V.P. and Chaudhari, L.B. 2008. Application of nanofiltration for the rejection of nickel ions from aqueous solutions and estimation of membrane transport parameters. J. Hazard. Mater. 160: 70-77.

(15) Qdais, H. A. and Moussa, H. 2004. Removal of heavy metals from wastewater by membrane processes: a comparative study. Desalination. 164: 105-110.

(16) Sarathy, V. and Allen, H. E. 2005. Copper complexation by dissolved organic matter from surface water and wastewater effluent. Ecotoxicology and Environmental Safety. 61: 337–344.

(17) Schmitt, D. and Frimmel, F. H. 2003. Ligand Exchange Rate of Metal-NOM Complexes by EDTA. ESPR - Environ Sci. & Pollut Res. 10: 9 – 12.

(18) Smith, D.S., Bell, R.A. and Kramer, J.R. 2002. Metal speciation in natural waters with

emphasis on reduced sulfur groups as strong metal binding sites. Comparative Biochemistry and Physiology Part C. 133, 65-74.

(19) Wang, D.-X., Su, M., Yu, Z.-Y., Wang, X.-L., Ando, M.and Shintani, T. 2005. Separation performance of a nanofiltration membrane influenced by species and concentration of ions. Desalination. 175: 219-225.

(20) Saikaew, W., Mattaraj, S. and Jiraratananon, R. 2010. Nanofiltration performance of lead solutions: effects of solution pH and ionic strength. Water Sci. & Technol.: water supply-WSTWS. 10.2: 193-200,

(21) Mosqueda-Jimenez, D. B., Huck, P. M. and Basu, O. D. 2008. Fouling characteristics of an ultrafiltration membrane used in drinking water treatment. Desalination. 230: 79-91.

(22) Chilyumova, E. and Thöming, J. 2008. Nanofiltration of bivalent nickel cations-model parameter determination and process simulation. Desalination. 224: 12-17.

(23) Childress A.E. and Elimelech, M. 1996. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membrane. J. Membr. Sci. 119: 253-268.

(24) 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 modeling. Sep. Purif. Technol. 15: 181-187.

(25) 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.

(26) Teixeira, M.R. and Rosa, M.J. 2006. The impact of the water background inorganic matrix on the natural organic matter removal by nanofiltration. J. Membr. Sci. 279: 513-520.

(27) Nanda, D., Tung, K-L., Hsiung, C-C., Chuang, C-J., Ruaan, R-C., Chiang, Y-C., Chen, C-S. and Wu, T-H. 2008. Effect of solution chemistry on water softening using charged nanofiltration membrane, Desalination. 234: 344-353.

(28) Town, R.M. and Filella, M. 2002. Implications of natural organic matter binding heterogeneity on understanding lead(II) complexation in aquatic systems. Sci. Tot. Environ. 300: 143-154.

(29) Wutthasathien, N. 2005. Industrial water conditioning, Five edition, Bangkok; Technology Promotion Association (Thailand-Japan).

(30) Broo, A.E., Berghult, B. and Hedberg, T. 1998. Copper corrosion in water distribution systems-the influence of natural organic matter (NOM) on the solubility of copper corrosion products. Corros. Sci. 40: 1479-1489.

(31) Su, M., Wang, D.-X., Wang, X.-L., Ando, M. and Shintani, T. 2006. Rejection of ions by NF membranes for binary electrolyte solutions of NaCl, NaNO$_3$, CaCl$_2$ and Ca(NO$_3$)$_2$. Desalination. 191: 303-308.

(32) 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.