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A combined osmotic pressure and cake filtration model for crossflow nanofiltration of natural organic matter

Supatpong Mattaraj[a,*], Chalor Jarusutthirak[b], Ratana Jiraratananon[c]

[a] Department of Chemical Engineering, Faculty of Engineering, Ubon Ratchathani University, Ubon Ratchathani 34190, Thailand
[b] Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
[c] Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

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ABSTRACT

A combined osmotic pressure and cake filtration model for crossflow nanofiltration of natural organic matter (NOM) was developed and successfully used to determine model parameters (i.e. permeability reduction factor (η) and specific cake resistance (α_{cake})) for salt concentrations, NOM concentrations, and ionic strength of salt species (Na^+ and Ca^{++}). In the absence of NOM, with increasing salt concentration from 0.004 to 0.1 M, permeability reduction factor (η)) decreased from 0.99 to 0.72 and 0.94 to 0.44 for monovalent cation (Na^+) and divalent cation (Ca^{++}), respectively. This reduced membrane permeability was due to salt concentrations and salt species. In the presence of NOM, specific cake resistance tended to increase with increasing NOM concentration and ionic strength in the range of 0.85×10^{15}–3.66×10^{15} m kg^{-1}. Solutions containing divalent cation exhibited higher normalized flux decline ($J_v/J_{vo} = 0.685$–0.632) and specific cake resistance ($\alpha_{\text{cake}} = 2.89 \times 10^{15}$–$6.24 \times 10^{15}$ m kg^{-1}) than those containing monovalent cation, indicating a highly compacted NOM accumulation, thus increased permeate flow resistance during NF filtration experiments. After membrane cleaning, divalent cation exhibited lower water flux recovery than monovalent cation, suggesting higher non-recoverable ($R_{\text{non-rec}}$) resistance than monovalent cation.

1. Introduction

Nanofiltration (NF) is widely increasing in the application of drinking water treatment due to high removal efficiency in natural organic matter (NOM), the disinfection by-product (DBP) precursors during chlorination process, and in water softening for removing divalent cations from natural waters [1]. Nanofiltration membranes have molecular weight cut-offs (MWCO) ranging between 300 and 1000 Da [2], while the performances of NF membranes lie between reverse osmosis (RO) membranes (high operating pressure from 1400 to 6800 kPa) and ultrafiltration (UF) membranes (low operating pressure from <70 to 500 kPa) [3]. The separation mechanism of NF membranes is described in terms of charge and sieving effect [4]. Sieving effect is related to solute size responsible for the rejection of uncharged solutes by NF membranes, while charge effect is influenced by the electrostatic interactions between the ion species/valence types and membrane charges, as explained by the Donnan exclusion phenomena [5].

Natural organic matter is considered as a major cause of membrane fouling during NF [6]. NOM components consist of a heterogeneous mixture of complex organic materials, including humic substances, low molecular weight (hydrophilic) acids, proteins, carbohydrates, carboxylic acids, amino acids, and hydrocarbons [7]. Humic substances, the predominant compounds of NOM in surface waters, are amorphous, acidic, yellow-to-brown in color, hydrophilic, and chemically complex polyelectrolytes with the molecular weights ranging from a few hundreds to tens of thousands [8]. They comprise a large fraction of the dissolved organic matter (DOM), typically 30–80% of dissolved organic carbon (DOC) [9]. Molecular weight ranges of aquatic humic substances are from 500 to 5000 [10]. The major functional groups include carboxylic acids, phenolic hydroxyl, carbonyl, and hydroxyl groups [9].

Solution chemistry (i.e. ionic strength, mono- and divalent cations) can influence membrane performance (i.e. solution flux decline and rejection [11]). Increased ionic strength can increase solution flux decline, while divalent cation has a greater flux decline than monovalent cation in membrane fouling [12]. Concentration of salt solutions by NF membranes can result in enhanced rejections depending on ion species [13]. Divalent cations have significant effects on membrane surface charge [14], thus affecting membrane performance. The rejections of divalent cation (calcium) and

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* Corresponding author. Tel.: +66 45 353 344; fax: +66 45 353 333.
E-mail addresses: mattas@ubu.ac.th, supatpong.m@hotmail.com (S. Mattaraj), kjchalor@kmitl.ac.th (C. Jarusutthirak), ratana.jir@kmutt.ac.th (R. Jiraratananon).

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monovalent cation (sodium) were reported to range approximately 13–96% and 10–87%, respectively [15].

In our previous work [16], we investigated different factors affecting crossflow nanofiltration performances in natural organic matter rejection and flux decline. Four mathematical models (i.e. pore blocking, pore constriction, intermediate, and cake formation) were used to interpret membrane performances of NF membrane. However, we could not apply those mathematical models for solutions having salt alone. This was possibly affected by osmotic pressure caused by high salt concentration at the membrane surface. In addition, solutions having NOM were significantly affected by cake formation, especially at high NOM concentration and ionic strength, while model parameters were not characterized for specific cake resistance. Therefore, this paper integrates mathematical models for osmotic pressure caused by salt solution and cake filtration model obtained from NOM solution during crossflow nanofiltration. The objective of this study was to determine model parameters, i.e. permeability reduction factor (η) based on osmotic pressure effect and specific cake resistance (α_{cake}) using a combined osmotic pressure and cake filtration model. The results of this work could provide an evidence for changes in the model parameters as a function of salt concentrations, NOM concentrations, and ionic strength of salt species (sodium and calcium). The model parameters corresponded to the combination effects of osmotic pressure by salts/ion species that changed membrane permeability and cake formation caused by NOM accumulation at the membrane surface. The model parameters could give an insight interpretation of flux decline and rejection characteristics during crossflow NF of NOM with the presence of salts. The effects of ion species/valence types were investigated to compare solution flux curves with different solution chemistry.

2. Theory

2.1. Mass balance

The overall system mass balance model can be determined based on the bench-scale crossflow NF test cell with a recycle loop [16]. It is described as a completely stirred tank reactor (CSTR). The mass balance can be written as follows:

$$V_{\text{sys}}\frac{\mathrm{d}C_{\text{reten}}}{\mathrm{d}t} = Q_{\text{feed}}C_{\text{feed}} - Q_{\text{reten}}C_{\text{reten}} - Q_{\text{perm}}C_{\text{perm}} - k_{\text{a}}(C_{\text{ss}} - C_{\text{reten}}) \times V_{\text{sys}} \tag{1}$$

where V_{sys} is the system volume (about 72 mL); Q and C are the subscriptions for flow and concentration in the feed line (feed), in the retentate line (reten), and in the permeate line (perm); C_{ss} is the steady-state concentration in the retentate line; k_{a} is the overall mass transfer coefficient (min^{-1}) ($= k_1 a_{\text{s}}$); k_1 is the mass transfer coefficient (m s^{-1}) equaling to the ratio between salt diffusion coefficient (D) and boundary layer thickness (δ); a_{s} is the volumetric specific surface area ($\text{m}^2\,\text{m}^{-3}$) that equals to the ratio between the effective membrane surface area and the system volume; t is the operating time (min). The units of flow and concentration are mL min^{-1} and mg L^{-1} or mol L^{-1}, respectively, depending on solution types. Using a fourth-order Runge–Kutta routine, the overall mass transfer coefficient and the steady-state concentration were varied to minimize the sum of squared error (SSE) for each feed solution.

2.2. Solution flux

Solution flux can be determined as a function of membrane permeability, L_{p} (LMH kPa^{-1}), and the net transmembrane pressure gradient ($\Delta P - \sigma\Delta\pi$) (kPa), while the non-recoverable fouling occurs in many instances during filtration, imparting an additional resistance to solution flux [3]:

$$J_{\text{v}} = L_{\text{p}}(\Delta P - \sigma\Delta\pi) = \frac{(\Delta P - \sigma\Delta\pi)}{\mu(R_{\text{m}} + R_{\text{non-rec}})} \tag{2}$$

where J_{v} is the solution flux ($\text{L m}^{-2}\,\text{h}^{-1}$, LMH); ΔP is the averaged transmembrane pressure (kPa); σ is the osmotic reflection coefficient (estimated by the intrinsic membrane rejection, $R_{\text{mem}} = 1 - C_{\text{perm}}/C_{\text{mem}}$); C_{mem} is the concentration at the membrane surface; $\Delta\pi$ is the difference in osmotic pressure of the solution at the membrane and in permeate line, $\Delta\pi = \pi_{\text{mem}} - \pi_{\text{perm}}$ (kPa); R_{m} is the membrane hydraulic resistance (m^{-1}); and $R_{\text{non-rec}}$ is the non-recoverable resistance occurring during filtration (m^{-1}); and μ is the dynamic viscosity ($\text{kg m}^{-1}\,\text{s}^{-1}$).

Under constant-pressure operation, and assuming constant membrane permeability and in the absence of NOM cake on membrane surface, the change in solution flux is related to the change in osmotic pressure as a result of solute accumulation at the membrane surface:

$$\frac{\mathrm{d}J_{\text{v}}}{\mathrm{d}t} = -\frac{\sigma}{\mu(R_{\text{m}} + R_{\text{non-rec}})}\frac{\mathrm{d}\Delta\pi}{\mathrm{d}t} \tag{3}$$

The osmotic pressure is directly related to salt concentration, with π (kPa) = αC (mol L^{-1}), where $\alpha = 4814.5$ (NaCl) [3] and $\alpha = 7418.8$ (CaCl_2) at 25 °C (calculated using Van't Hoff equation). The permeate concentration is correlated to the concentration at the membrane surface by the rejection, $C_{\text{perm}} = (1 - R_{\text{mem}})C_{\text{mem}}$. Making these substitutions,

$$\begin{aligned}\frac{\mathrm{d}J_{\text{v}}}{\mathrm{d}t} &= -\frac{\sigma\alpha}{\mu(R_{\text{m}} + R_{\text{non-rec}})}\left(\frac{\mathrm{d}C_{\text{mem}}}{\mathrm{d}t} - \frac{\mathrm{d}C_{\text{perm}}}{\mathrm{d}t}\right)\\ &= -\frac{\sigma\alpha R_{\text{mem}}}{\mu(R_{\text{m}} + R_{\text{non-rec}})}\left(\frac{\mathrm{d}C_{\text{mem}}}{\mathrm{d}t}\right)\end{aligned} \tag{4}$$

The interface concentration (C_{mem}) is calculated from $\sigma\Delta\pi = \sigma(\pi_{\text{mem}} - \pi_{\text{perm}})$ under steady-state condition. The value of σ is assumed to be equal to the intrinsic rejection for each salt concentration. From the experiments, the ratio $\beta = C_{\text{mem}}/C_{\text{reten}}$ (salt concentration polarization) is related to salt concentration. Taking this parameter in the above equation and having an additional term of permeability reduction factor due to the effect of salt (η), the change in solution flux with time can be rewritten as follows:

$$\frac{\mathrm{d}J_{\text{v}}}{\mathrm{d}t} = -\eta\frac{\sigma\alpha R_{\text{mem}}\beta}{\mu(R_{\text{m}} + R_{\text{non-rec}})}\left(\frac{\mathrm{d}C_{\text{reten}}}{\mathrm{d}t}\right) \tag{5}$$

where $\eta(1/\mu(R_{\text{m}} + R_{\text{non-rec}})) = \eta L_{\text{p}} = L_{\text{p,s}} = (1/\mu(R_{\text{m,s}} + R_{\text{non-rec}}))$ ($L_{\text{p,s}}$ is the membrane permeability in the presence of salt solution). The membrane resistance in the presence of salt ($R_{\text{m,s}}$) including the permeability reduction factor can be determined as follows:

$$R_{\text{m,s}} = \frac{R_{\text{m}} + (1 - \eta)R_{\text{non-rec}}}{\eta} \tag{6}$$

In Eq. (5), the change in the retentate concentration with time can be calculated from the mass balance as described in Eq. (1).

2.3. Combined osmotic pressure and cake filtration model

A combined osmotic pressure and cake filtration model can be developed to describe the nanofiltration performance of a solution containing both salt and NOM. From the previous work, the fouling of nanofiltration membranes can be described by cake filtration model [17,18]. The model has also been used to describe flux in