Desalination 274 (2011) 182–191

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

A combined pore blockage, osmotic pressure, and cake filtration model for crossflow nanofiltration of natural organic matter and inorganic salts

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

[a] Environmental Engineering Program, Department of Chemical Engineering, Faculty of Engineering, Ubon Ratchathani University, Ubonratchathani 34190, Thailand
[b] National Center of Excellence for Environmental and Hazardous Waste Management, Ubon Ratchathani University, Ubonratchathani 34190, Thailand
[c] Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
[d] Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

ARTICLE INFO

Article history:
Received 3 November 2010
Received in revised form 1 February 2011
Accepted 5 February 2011
Available online 4 March 2011

Keywords:
Cake filtration
Inorganic salt
Nanofiltration
Natural organic matter
Osmotic pressure
Pore blockage

ABSTRACT

The performance of nanofiltration (NF) process for water treatment is affected by flux decline due to membrane fouling. Many models have been applied to explain fouling mechanisms. In this work, a combined pore blockage, osmotic pressure, and cake filtration model was developed and successfully used to determine NF performance and model parameters for crossflow NF. NOM solutions containing sparingly soluble inorganic salts (i.e. $CaCO_3$, $CaSO_4$, and $Ca_3(PO_4)_2$), showed higher normalized flux decline than those containing soluble inorganic salts (i.e. NaCl and $CaCl_2$). The $\alpha_{blocked}$ and $R_{m,s}$ parameters for sparingly soluble inorganic salts exhibited higher values than those for soluble inorganic salts, while the $R_{m,s}$ and α_{cake} parameters were found to be significant for soluble inorganic salts due to increased salt concentration and NOM cake accumulation at the membrane surface. Increased ionic strengths from 0.01 M to 0.11 M resulted in more pronounced flux decline, thus increased model parameters (i.e. $\alpha_{blocked}$ and $R_{m,s}$). The membrane surface characteristics examined by the scanning electron microscopy (SEM) images evidently supported the precipitation of sparingly soluble inorganic salts. The flux decline was the most pronounced for phosphate species, corresponding to the lowest water flux recovery, thus increased non-recoverable resistance ($R_{non\text{-}rec}$) due to pore plugging from phosphate salt precipitation.

Introduction

Membrane processes have been increasingly used in the applications of drinking water treatment to meet more stringent water quality regulations [1]. Of particular interest is the use of nanofiltration (NF) to effectively remove dissolved natural organic matter (NOM) and simultaneously control disinfection by-products (DBPs) after chlorination process of drinking water treatment [2]. However, membrane fouling can significantly reduce membrane performance, thus increase operating costs due to higher operating pressures, and frequent chemical cleaning leading to shortened membrane life [3]. Fouling may be attributed to several mechanisms including concentration polarization of retained solutes, pore blocking by solutes adsorbed on the membrane surface and/or within pores, and cake layer formation, which presents an additional resistance to flow, and precipitation of inorganic, and organic solutes as a result of high concentration at the membrane surface [4,5].

Natural organic matter is considered as a major membrane foulant during NF [6]. NOM component comprises a heterogeneous mixture of organic materials with wide molecular size distribution and functional groups [7,8]. Membrane fouling caused by NOM can be dependent on molecular size distribution of feed solution components. Components smaller than membrane pores can penetrate the membrane pores, while larger components including aggregates can block membrane pores and contribute to cake formation [9]. Yuan and Zydney [10] indicated that both pore blockage and surface deposition can dominate fouling mechanisms of humic acid during ultrafiltration, when compared with adsorption and concentration polarization. The accumulation of retained dissolved organic matter (DOM) mass significantly affected membrane fouling, while larger pore membranes exhibited significant flux decline in comparison with smaller pore membranes [11]. Jurusuthirak et al. [12] exhibited that cake formation dominated permeate flux decline with increased NOM concentration.

Inorganic fouling is one of the major limitations of NF applications in drinking water treatment [13,14]. This fouling is induced by concentration polarization and scale formation (or precipitation fouling) during NF. An increased concentration of the scale-forming species in the bulk solution occurs due to permeate withdrawal, which is further enhanced in the region next to the membrane surface

---

* Corresponding author at: Department of Chemical Engineering, Faculty of Engineering, Ubon Ratchathani University, Warinchumrab, Ubonratchathani 34190, Thailand. Tel.: +66 45 353 344; fax. +66 45 353 333.
E-mail addresses: supatpong.m@hotmail.com, mattas@ubu.ac.th (S. Mattaraj).

0011-9164/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2011.02.010

by the superimposed effect of concentration polarization [15]. Flux decline caused by inorganic fouling is dependent on solution pH, ionic strength and solution types [16,17]. It was evident that an increase of NaCl concentration or the presence of divalent cations increased osmotic pressure due to high salt concentration [12] and enhanced membrane membrane fouling [17]. Multivalent cations can lead to more membrane fouling when combined with polyanions, such as carbonate (CO_3^{2-}), sulphate (SO_4^{2-}), and phosphate (PO_4^{3-}) ions, thus attributing to pore blockage of precipitated species formed and blocked membrane surface and/or pores [15,18]. However, the influence of combined inorganic salts and NOM with different solution chemistry during NF fouling is required to understand fouling mechanisms in order to mitigate membrane fouling.

In our previous work [19], a combined osmotic pressure and cake filtration model for crossflow nanofiltration of NOM was proposed. This model integrates the combined effects of osmotic pressure caused by retained salt concentration in the boundary layer of the membrane surface and cake formation caused by additional NOM cake resistance. The model can be used successfully to interpret membrane performances during crossflow NF of soluble inorganic salt with NOM. In addition, the model parameters due to the effect of operating conditions in crossflow reverse osmosis can be successfully evaluated [20]. However, we could not apply this model for solutions containing sparingly soluble inorganic salts with NOM due to different fouling mechanisms observed [18]. Therefore, this paper describes the modified mathematical fouling model, which combines pore blockage, osmotic pressure, and cake filtration model for crossflow NF of NOM with the presence of different inorganic salts. The objective of this study was to determine nanofiltration performance and model parameters of the modified mathematical fouling models. The results of this work also include the changes in the model parameters with different inorganic salts (i.e. Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}) and ionic strengths (I.S.) of different multivalent cations (i.e. calcium and magnesium). The membrane performance and model parameters were estimated to provide an insight of fouling phenomena during NF of NOM and salts. Membrane surface characteristics were examined by scanning electron microscope (SEM) in order to illustrate surface images of the fouled membrane surface.

2. Theory

2.1. Solution flux

Solution flux during membrane filtration can be determined in terms of membrane permeability and the net transmembrane pressure gradient ($\Delta P-\sigma\Delta\pi$)as follows [19]:

$$J_v = L_p(\Delta P-\sigma\Delta\pi) = \frac{\Delta P-\sigma\Delta\pi}{\mu(R_m + R_{non-rec})} \tag{1}$$

where J_v is the solution flux ($Lm^{-2}h^{-1}$, LMH); L_p is the membrane permeability (LMH kPa^{-1}), ΔP is the averaged transmembrane pressure (kPa); σ is the osmotic reflection coefficient (estimated by the intrinsic membrane rejection; ($R_{mem} = 1 - C_{perm}/C_{mem}$); C_{mem} and C_{perm} are the solute concentrations at the membrane surface and in the permeate (mol L^{-1}); $\Delta\pi$ is the difference in osmotic pressure of the solution at the membrane (π_{mem}) and in the permeate (π_{perm}), $\Delta\pi = \pi_{mem} - \pi_{perm}$ (kPa); μ is the dynamic viscosity (kg m^{-1} s^{-1}); R_m is the membrane hydraulic resistance (m^{-1}); $R_{non\text{-}rec}$ is the additional resistance due to the non-recoverable resistance (m^{-1}). For clean water flux (J_{vo}), solution flux can be evaluated for unfouled membrane, while the effects of osmotic pressure and non-recoverable resistance are relatively small and therefore neglected. Membrane hydraulic resistance can be described by the Hagen-Poiseuille equation for laminar flow in the assumption of a uniform membrane pore radius (r_p) (m), while clean water flux can be written as follows:

$$J_{vo} = \frac{\Delta P}{\mu R_m} = \frac{N\pi r_p^4 \Delta P}{8\mu\delta_m} \tag{2}$$

where N is the number of pores per unit membrane area (pores m^{-2}); and δ_m is the membrane thickness (m).

2.2. Pore blockage model

Pore blockage model illustrates the rate of change in the number of pores (or pore area,$A_{p,T} = NA_m\pi r_p^2$), which can be assumed to be proportional to the net transport of solute to the membrane surface [21].

$$\frac{dA_{p,T}}{dt} = \pi r_p^2 A_m \frac{dN}{dt} = -\alpha_{blocked} A_m C_{reten,NOM}(t)(J_{vo}-J^*) \tag{3}$$

where A_m is total active permeable membrane area (m^2); t is the operating period (min); $\alpha_{blocked}$ is the pore blockage efficiency ($m^2 kg^{-1}$); $C_{reten,NOM}$ is the NOM concentration in the retentate (kg m^{-3}), which can be determined based on the mass balance model [19]; J^* is the effective flux associated with back-transport resulting from crossflow (LMH). Eqs. (1), (2), and (3) can yield Eqs. (4) and (5), which describe the pore blockage model:

$$\frac{dJ_v}{J_{vo}dt} = \frac{dA_p}{A_m dt} \tag{4}$$

$$\frac{dJ_v}{dt} = -\alpha_{blocked} C_{reten,NOM}(t) J_{vo}(J_{vo}-J^*). \tag{5}$$

2.3. Combined osmotic pressure and cake filtration model

The combined osmotic pressure and cake filtration model was developed to evaluate nanofiltration performance of a solution containing both salt and NOM [19]. This model incorporates additional term of cake resistance (R_c), which is used to characterize flux in ultrafiltration and microfiltration [22,23]. The solution flux (J_v) can be determined by incorporating an additional term of cake resistance as follows:

$$J_v = \frac{(\Delta P-\sigma\Delta\pi)}{\mu\left(R_{m,s} + R_{non-rec} + R_c\right)} \tag{6}$$

where the subscript s refers to salt; $R_{m,s} = (R_m + (1-\eta)R_{non-rec})/\eta$ is the membrane hydraulic resistance with the presence of salt (m^{-1}); η is the permeability reduction factor (−) due to the effect of salt concentration at the membrane surface. The change in solution flux as a function of time can be written as follows [19]:

$$\begin{aligned}\frac{dJ_v}{dt} = &-\frac{\sigma_s \alpha_s R_{mem,s} \beta_s}{\mu\left(R_{m,s} + R_{non-rec} + R_c\right)}\left(\frac{dC_{reten,s}}{dt}\right)\\ &-\frac{J_v}{\left(R_{m,s} + R_{non-rec} + R_c\right)}\left(\frac{dR_c}{dt}\right)\end{aligned} \tag{7}$$

where α_s is the correlation between osmotic pressure and salt concentration (kPa L mol^{-1}); the ratio β_s ($= C_{mem,s}/C_{reten,s}$) is the salt concentration polarization (−). $R_{mem,s}$ is the intrinsic membrane rejection in the presence of salt (−). $C_{mem,s}$ and $C_{reten,s}$ are salt concentration at the membrane surface and in the retentate (mol L^{-1}). The change in salt concentration in the retentate ($dC_{reten,s}/dt$) as a function of time can be determined based on the mass balance model using a completely stirred tank reactor [24].