Transport characteristics of wastewater effluent organic matter in nanofiltration and ultrafiltration membranes

Sangyoup Lee, Young-Gwan Cho, Yangseok Song, In S. Kim and Jaeweon Cho

ABSTRACT

This study demonstrates the transport characteristics of wastewater effluent organic matter (EfOM) through membrane pores using a four-parameter (intrinsic mass transfer coefficient (k_i), solute concentration near the membrane surface (C_m), solute permeability (P_m), and reflection coefficient (σ) model based on thermodynamics, concentration polarization (CP) and hydrodynamic operating conditions represented by a J_0/k ratio (the ratio of initial permeate flux (J_0) to a back diffusional mass transfer coefficient (k)). EfOM transport characteristics through the pores of four different membranes (a nanofiltration (NF)/ultrafiltration (UF) polymeric pair and two ceramic UF membranes with different molecular weight cutoffs (MWCOs)) were different; the NF polymeric membrane exhibited either convection- or diffusion-dominant conditions, while the UF membranes exhibited convection-dominant conditions in terms of EfOM transport through membrane pores. A critical J_0/k ratio (representing a transitional condition between diffusion- and convection-dominant transport of solute) was found for the examined NF membrane with a MWCO of 250 Daltons. Four different parameters (k_i, C_m, P_m, and σ) were determined by the model to be informative to elucidate the various interactions between EfOM and the tested membranes. EfOM characteristics (size, structure, and functionality) and membrane properties (MWCO, surface/pore charge in terms of zeta potential, and module configurations) were revealed to play a major role in EfOM rejection and flux decline under convection-dominant conditions, as compared to diffusion-dominant conditions.

Key words | convection/diffusion, critical J_0/k ratio, effluent organic matter (EfOM), flux decline, four-parameter model

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INTRODUCTION

Wastewater reclamation using membranes has become a widely accepted process in some areas suffering from water shortages. The concentration of wastewater effluent organic matter (EfOM) in secondary-treated effluent is relatively high, with large dissolved organic carbon (DOC) values compared with natural organic matter (NOM) in drinking water sources such as rivers, lakes and groundwater. EfOM serves as an organic precursor to disinfection by-products (DBPs) during chlorination in drinking water treatment plants. Filtration with ultrafiltration (UF) and nanofiltration (NF) membranes can be a potential candidate to minimize the formation of such DBPs as haloacetic acids (HAAs), by the efficient removal of EfOM prior to chlorination. EfOM also serves as an organic foulant for membranes which may be used for wastewater reclamation. Therefore, the transport characteristics of EfOM through membrane pores need to be rigorously investigated to maximize the performance of membrane filtration in terms of solute rejection and membrane fouling (flux decline).

A four-parameter model was applied in this study to determine quantitatively EfOM transport characteristics through membrane pores in terms of the intrinsic mass transfer coefficient (k_i), EfOM concentration near the membrane surface (C_m), EfOM diffusive permeability through membrane pores (P_m), and reflection coefficient (σ). The three major concepts included in the four-parameter model are as follows: (1) the Kedem–Katchalsky model (K–K model) based on irreversible thermodynamics (Kedem & Katchalsky 1958; Muler 1996); (2) the concentration polarization (CP) relationship obtained by performing a mass balance across the CP layer (Blatt 1976); and (3) the J_0/k ratio representing hydrodynamic operating conditions (Cho *et al.* 2000). The intrinsic mass transfer coefficient (k_i) defined in this study could be an indication not only of molecular diffusivity (related to solute molecular size), diffusivity facilitated by bulk motion (related to cross-flow velocity), and diffusivity dependent on filtration module configurations (i.e. module length and hydraulic diameter), but also various interactions between solute and membrane surface/pores including steric exclusion, electrostatic repulsion, and hydrophobic interactions. Hydrodynamic operating conditions represented by the J_0/k ratio play a major role in determining the dominant transport condition (either convection or diffusion) for a given solute with a particular membrane. In the case of convection-dominant conditions, observed EfOM rejection ($R_{obs} = (C_b - C_p)/C_b$, where C_b and C_p represent EfOM concentrations in the feed and permeate side, respectively) has been observed to decrease as permeate flux (J_v) increases, while R_{obs} increases as permeate flux decreases in the case of diffusion-dominant conditions (Tandon *et al.* 1994). In a similar fashion to this relationship under varying transport conditions, R_{obs} decreases as the J_0/k ratio increases when EfOM transport is dominated by convection, while R_{obs} increases as the J_0/k ratio increases under diffusion-dominant conditions. A transitional J_0/k ratio was found in this study, which was defined as the critical J_0/k ratio, below which R_{obs} increased as the J_0/k ratio increased (assumed to be a diffusion-dominant condition), and above which R_{obs} decreased as the J_0/k ratio increased (assumed to be a convection-dominant conditon), even with the same membrane. This is consistent with the general observation by Tandon *et al.* (1994) for the measurements of protein filtrations with UF membranes. The critical J_0/k ratio can be observed phenomenologically for a particular solute with a membrane in which transport may be dominated by both convection and diffusion depending on the applied J_0/k ratio.

Three hypotheses were tested in this study: (1) that four parameters (k_i, C_m, P_m, and σ) determined with EfOM and four different membranes could indicate not only transport characteristics but also various interactions between EfOM and the membranes (such as steric exclusion and electrostatic repulsion); (2) that the critical J_0/k ratio could be observed for an EfOM-NF membrane pair and possibly for an EfOM-tight UF membrane pair, while not for EfOM-loose UF membrane pairs (EfOM-NF: both diffusion and convection, EfOM-tight UF: more convection and less diffusion than EfOM-NF but both diffusion and convection still involved, and EfOM-polymeric/ceramic UF: mainly convection); and (3) that C_m increases significantly as J_0/k increases under a convection-dominant condition, but only increases slightly as J_0/k increases under a diffusion-dominant condition because concentration polarization with EfOM can be formed mainly under a convection-dominated condition (i.e. at a relatively high J_0/k ratio).

THEORY

In the theoretical foundation of this study, four different parameters were determined by combining the linear estimation of k_i and C_m using the concentration polarization relationship with the non-linear estimation of P_m and σ using the K–K model. The effects of different types of membrane in terms of MWCO on the four different parameters were demonstrated for EfOM.

Linear estimation of k_i and C_m using the concentration polarization (CP) concept

The following Equation (1) is transformed from the CP relationship in order to linearly estimate the intrinsic mass transfer coefficient (k_i) and the corresponding solute concentration near the membrane surface (C_m). In this equation, it can be envisioned that k_i represents all the types of diffusivities involved in an actual membrane filtration including molecular diffusivity, diffusivity induced by bulk motion (i.e. shear-induced diffusivity), diffusivity dependent on module configurations (hydraulic diffusivity), diffusivity induced by electrostatic interaction (electrostatic diffusivity), as well as other intrinsic diffusivities which might be facilitated by the individual or combined motions of solute and water near and through the membrane surface/pores. This assumption and the consequent study limitations should be kept in mind in the reading of this paper.

$$\ln(C_b - C_p) = -\frac{1}{k_i} \cdot J_v + \ln(C_m - C_p) \quad (1)$$

Here, J_v, C_b, and C_p represent solvent flux and solute concentrations of the feed and permeate side, respectively. These values can be determined experimentally for each EfOM-membrane pair at varying J_0/k ratios. By plotting $\ln(C_b - C_p)$ versus J_v, values for k_i and C_m can be estimated from the slope and intercept of the straight line, respectively.

Non-linear estimation of P_m and σ using the K–K model based on irreversible thermodynamics

The equation related to the solute flux (J_s) derived by Kedem & Katchalsky (1958) was transformed into the following equation to determine P_m and σ, having already determined C_m using Equation 1 (Tandon *et al*. 1994).

$$J_s = P_m(C_m - C_p) + J_v(1 - \sigma) \cdot C^* \quad (2)$$

Here, J_s, P_m, σ, and C^* represent the solute flux, the solute permeability (which represents the diffusive transport of solute through the membrane pores), the reflection coefficient (which is a measure of the selectivity of a membrane for a particular solute), and the logarithmic average concentration ($C^* = (C_m - C_p)/\ln(C_m/C_p)$), respectively. The values of C_m and J_v can be obtained from Equation 1, and J_s equals the product of J_v and C_p. Then, using experimentally determined parameters at different J_0/k ratios including $(C_m - C_p)$, J_s, J_v, and C^*, P_m and σ can be determined by non-linear estimation with a three-dimensional plot of J_s versus J_v versus C^*.

Hydrodynamic operating conditions and critical J_0/k ratio

The J_0/k ratio can be used to evaluate the effect of hydrodynamic operating conditions on transport characteristics. J_0 (initial pure water permeation flux (Equation 3) and k (back-diffusional mass transfer coefficient (Equations 4 & 5) are calculated by the following equations. Using the relationships between the applied J_0/k ratio and experimentally determined R_{obs}, a critical J_0/k ratio can be determined for each EfOM-membrane pair if a transitional point from diffusion (as J_0/k ratio increases, R_{obs} increases) to convection (as J_0/k ratio increases, R_{obs} decreases) can be shown to exist.

$$J_0 = \frac{Q_p}{A_m} \quad (3)$$

$$k = 1.62\left(\frac{UD^2}{d_h L}\right)^{0.33} \text{ (thin-channel-type module)} \quad (4)$$

$$k = \frac{1.62D}{d_h}\left(\frac{Re \cdot Sc \cdot d_h}{L}\right)^{0.33} \text{ (tubular-type module)} \quad (5)$$

Here, Q_p and A_m are permeate flow rate (cm^3/sec) and membrane surface area (cm^2), respectively. Equations 4 & 5 are derived from the Sherwood number ($S_h = kd_h/D$) with consideration of module configuration (flow regime), where U is the average velocity of the feed fluid (cross-flow velocity (cm/sec)), D is the diffusion coefficient of the solute (cm^2/sec) estimated by the Stokes–Einstein relationship, d_h is the equivalent hydraulic diameter (cm), L is the channel tube length (cm), Re is the Reynolds number ($d_h U/\upsilon$), and Sc is the Schmidt number (υ/D) (υ is the kinematic viscosity of water (cm^2/sec)).

MATERIALS AND METHODS

Membrane properties and EfOM characteristics

MWCO values (provided by manufacturer), zeta potentials (measured in the laboratory using the electrophoretic method), pure water permeabilities (PWP) (experimentally determined), and test module types used in this study

Table 1 | Membrane properties

Code	Material	MWCO (Daltons)	Zeta potential (mV) at pH 7.0	PWP (l/day-m^2-kPa)	Test module configuration
GM	Polyamide TFC	8,000	– 41.5	4.21	Thin channel
ESNA	Polyamide TFC	250	– 9.90	2.35	Thin channel
T-1000	Titania	1,000	– 21.2	6.07	Tubular
T-8000	Titania	8,000	– 21.4	8.57	Tubular

Table 2 | Water qualities of wastewater effluent containing EfOM[a]

DOC (mg/l)	UVA254 (cm^{-1})	pH	Cond. (μS/cm)	SUVA (l/m-mg)	Humic content (% mass)	Acidity (meq/g C) XAD-8 isolate (-COOH, -OH) XAD-4 isolate (-COOH, -OH)	MW (Daltons) (M_w, M_n)
7.86	0.136	7.27	646	1.73	44	11.0, 23.1, 11.3, 23.3	1,250, 1,030

[a]All measurements were performed after 0.45 μm prefiltration.

are listed in Table 1. All the tested membranes have a negatively charged surface at neutral pH, as based on zeta potential values. Thin channel and tubular modules are different in terms of both hydraulic diameter (d_h) and channel (or tube) length (L): a flat-sheet polymeric membrane with an active surface area of 58.9 cm^2, a flow channel thickness of 0.04 cm, an equivalent hydraulic diameter of 0.08 cm, a cross-flow velocity of 3.09 cm/sec, and a corresponding Reynolds number of approx. 100; and a tubular ceramic membrane with an active surface area of 95.2 cm^2, a channel diameter of 0.36 cm, a cross-flow velocity of 10.1 cm/sec, and a corresponding Reynolds number of approx. 110.

The water qualities of wastewater effluent containing EfOM are summarized in Table 2, along with EfOM properties (SUVA, humic content, acidity, weight-averaged (M_w) and number-averaged (M_n) molecular weight). Wastewater effluent was obtained from secondary treatment processes (including primary settling, activated sludge process, and secondary settling) of the Gwangju Wastewater Treatment Plant in Korea. Humic content (mass based) was determined by XAD-8/4 resin fractionation along with DOC measurement after pH adjustment to ambient pH. Acidity (measurement of ionisable functional groups of EfOM including carboxylic and phenolic groups) was determined using a micro titration for both XAD-8 and XAD-4 isolates. All of these characterization methods for EfOM have been described in detail in previous papers (Cho *et al*. 1999, 2000).

Determination of four characteristic parameters (k_i, C_m, P_m, and σ) and critical J_0/k ratio: experimental and analytic procedures

First, using bench-scale membrane filtration apparatus, initial J_0/k ratio tests were performed with de-ionised (DI) water, prior to the actual tests with sample feed waters containing EfOM, for four membranes (GM, ESNA, T-1000 and T-8000). A particular J_0/k ratio was adjusted by controlling J_0 (controllable by a trans-membrane pressure valve) and k (changeable by a cross-flow velocity control). Based on these predetermined J_0/k ratios, the actual tests were performed with four EfOM-membrane pairs. R_{obs} was then calculated at different J_0/k ratios to determine the critical J_0/k ratio if it existed. All filtration experiments were conducted in the recycle mode, as shown in Figure 1.

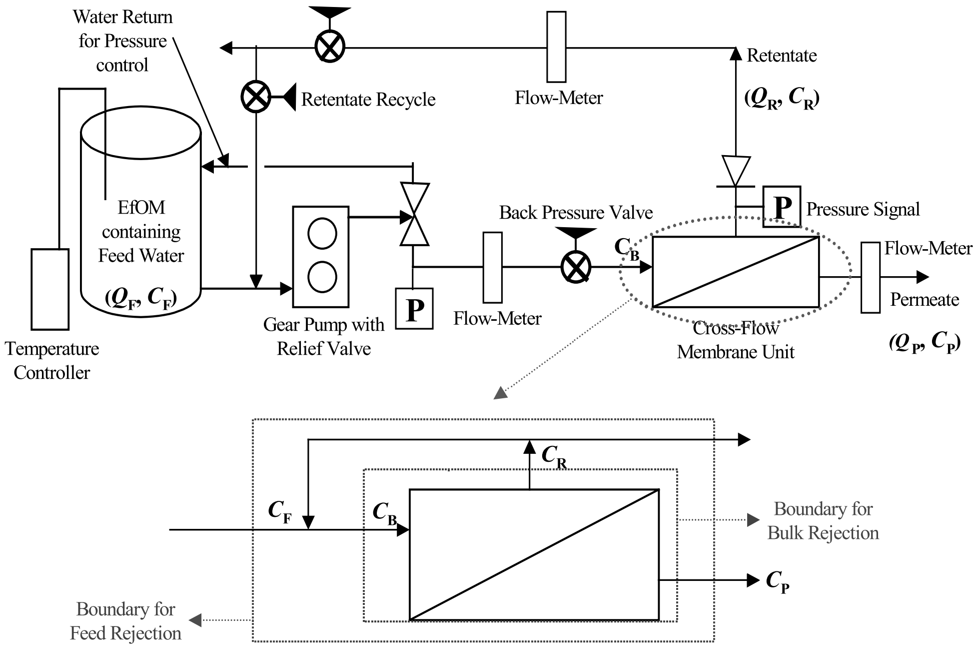


Figure 1 | Schematic diagram of the membrane filtration unit.

Secondly, using the CP relationship along with predetermined J_v, C_b, and C_p values at different J_0/k ratios, two characteristic parameters, k_i and C_m, were estimated by the linear estimation as described previously (Equation 1) for each EfOM-membrane pair. Finally, using the K–K model based on irreversible thermodynamics with the experimentally determined values of $(C_m - C_p)$, J_s, J_v, and C^* at different J_0/k ratios, the other two characteristic parameters, P_m and σ, were estimated by non-linear estimation as previously described in the Theory section (Equation 2) for four different EfOM-membrane pairs. For the non-linear estimations of P_m and σ with Equation 2, STATISTICA (99th Edition, StatSoft Inc., USA) was used to determine P_m and σ by plotting J_s as functions of $C_m - C_p$, J_v and C^*.

RESULTS AND DISCUSSION

R_{obs} at various J_0/k ratios (decision of dominant transport characteristics)

The effects of hydrodynamic operating conditions (J_0/k ratio) on observed EfOM rejections (R_{obs}) by GM, T-8000, T-1000 and ESNA membranes are depicted in Figure 2a, b, c and d, respectively. R_{obs} trends which corresponded to the respective J_0/k ratios, were estimated in terms of dissolved organic carbon (DOC) immediately following commencement of EfOM filtration. On the other hand, R_{obs} at a particular J_v/k ratio was determined by measuring the DOC values after EfOM filtration was performed for a designated period of time. No significant change in R_{obs} resulted from flux decline (which occurred for the duration of the filtration period) in terms of the J_0/k ratio. However, all of the UF membranes showed declining trends of R_{obs} with increasing J_0/k ratios. The NF membrane, however, exhibited different trends, which can provide a critical J_0/k ratio.

As hypothesized, EfOM transport through the ESNA membrane pores (MWCO = 250 Daltons) was dominated by either diffusion or convection with respect to the applied hydrodynamic operating conditions represented by the J_0/k ratio. EfOM rejection by the NF membrane increased as J_0/k increased below a critical J_0/k ratio of 1.12, and decreased as the J_0/k ratio increased above this critical J_0/k ratio (see Figure 2d). However, in the case of the other EfOM-membrane pairs, even for EfOM-tight UF (T-1000), the critical J_0/k ratio could not be observed.

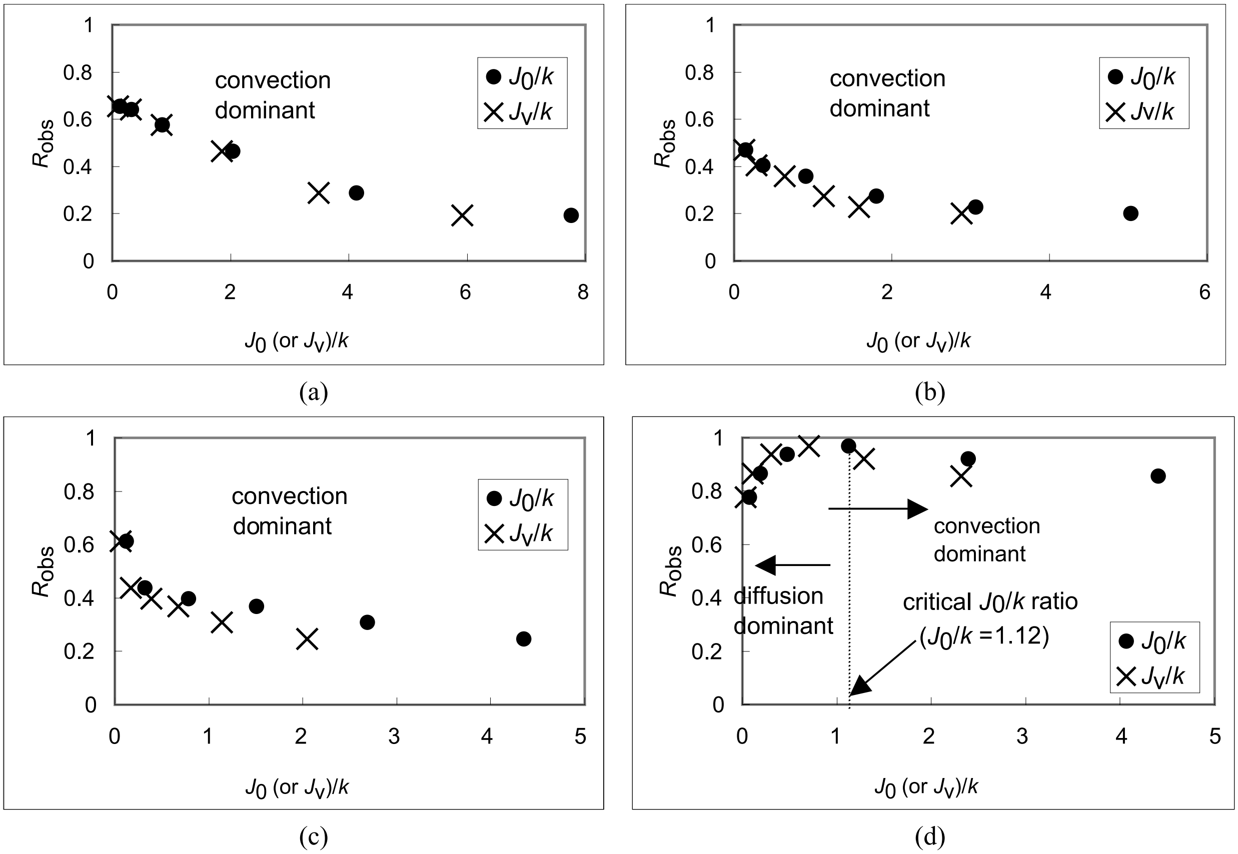


Figure 2 | Effect of J_0/k ratio on EfOM rejection by four membranes: (a) GM, (b) T-8000, (c) T-1000, and (d) ESNA.

Therefore, it can be assumed that the critical J_0/k ratio is a key value to describe EfOM transport through NF membrane pores. This means that the NF membrane can be operated under either convection- or diffusion-dominant conditions depending on the applied J_0/k ratio, in order to maximize filtration performance in terms of solute rejection and fouling. It was also observed that flux decline became more severe as the J_0/k ratio increased in all cases (see the comparisons between the J_0/k and J_v/k ratios in Figure 2). However, apparently the flux declined due to either the resistance which resulted from the CP or the gel layer near the membrane surface in the feed side for a convection-dominant condition, or that which resulted from EfOM adsorption in the membrane pores for a diffusion-dominant condition. These interpretations will be discussed more deeply later in this paper using estimated C_m, along with the effect of the J_0/k ratio on the C_m concentration under either convection- or diffusion-dominant conditions.

Estimation of four characteristic parameters (k_i, C_m, P_m and σ)

Estimation procedures for the four characteristic parameters, reflecting EfOM transport through membrane pores, are summarized in Figure 3. In the case of the EfOM-ESNA (NF) membrane pair, as shown in Figure 2d, a critical J_0/k ratio was observed, which means that the model can be applied for both convection- and diffusion-dominant conditions. Thus, two sets of k_i and P_m values (one set for convection- and the other set for diffusion-dominant conditions) could be obtained (Steps 4 and 5 in Figure 3).

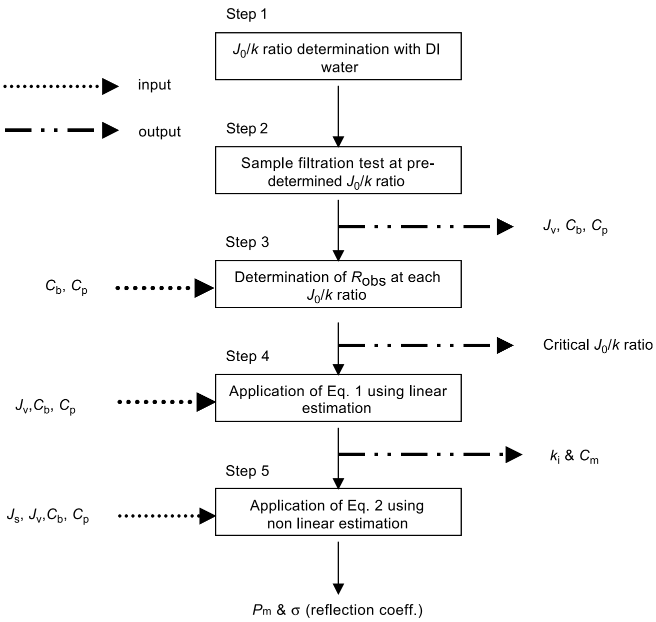
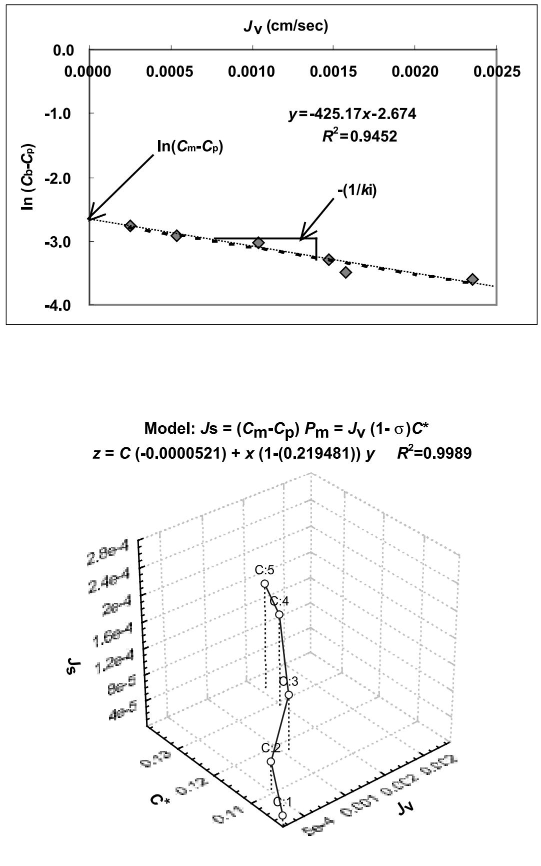


Figure 3 | Procedure for estimating four characteristic parameters (k_i, C_m, P_m and σ).



(a)

(b)

Figure 4 | Four-parameter model application for EfOM-T8000 pair: (a) linear estimation for k_i and C_m using Equation 1 and (b) non-linear estimation for P_m and σ using Equation 2.

The results (estimations for three different parameters (k_i, P_m and σ) for each EfOM-membrane pair) are summarized in Table 3 in order to compare the EfOM transport characteristics of different membranes in terms of the convective and diffusive transport of EfOM through the membrane pores, and to compare the selectivity of each membrane for EfOM as well. An example of the linear (Step 4 in Figure 3) and non-linear (Step 5 in Figure 3) estimation procedure for the EfOM and T-8000 pairs is shown in Figure 4. Three different parameters of EfOM with GM, T-1000 and ESNA are listed in Table 3, which were estimated using the procedures illustrated above in Figure 3. The estimation of C_m in terms of the relationship between the CP modulus (defined as C_m/C_b) (Muler 1996) and the J_0/k ratio will be discussed in another section of this paper.

Table 3 | The transport characteristics of EfOM through various membrane pores

Membranes tested	k_i (10^{-3} cm/sec)	P_m (10^{-5} cm/sec)	σ
T-8000	2.35	−5.2	0.31
GM	3.48	−2.5	0.50
T-1000	2.52	−4.0	0.52
ESNA*	−2.45 (4.61)	1.4 (−3.0)	0.89 (0.71)

*Values estimated under convection-dominant conditions (i.e. at a higher J_0/k ratio than the critical J_0/k ratio), are shown in parentheses.

Reflection coefficient (σ)

This is a measure of the membrane selectivity for a particular solute, which ranges between 0 (no selectivity) and 1 (no solute transport) (see Table 3) (Muler 1996). It

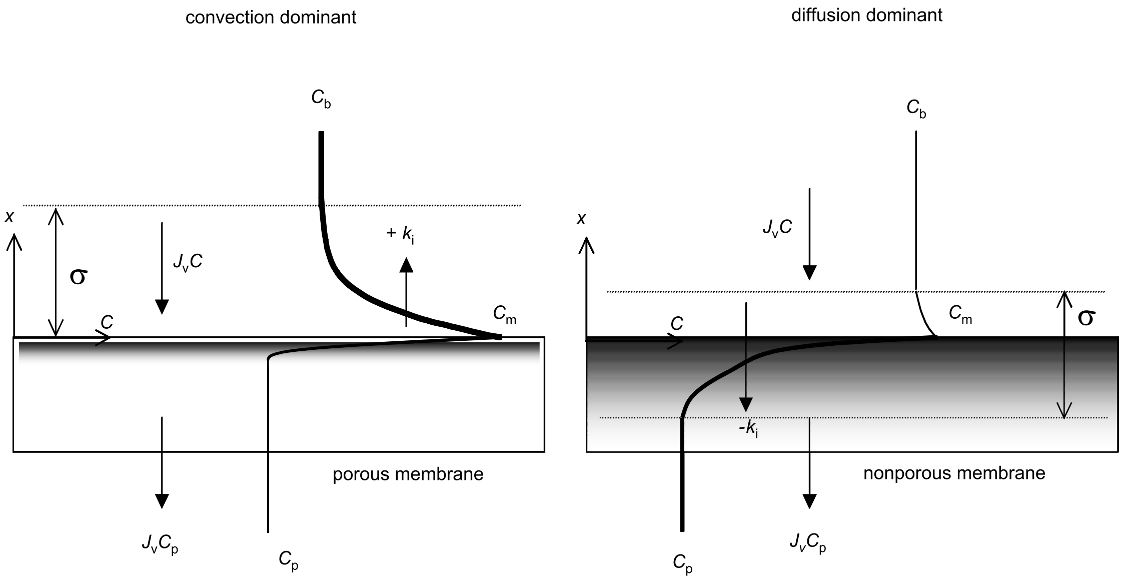


Figure 5 | Conceptual CP layer under convection- and diffusion-dominant conditions.

can also reflect the interactions between solute and membrane, which are involved in membrane filtration in addition to size exclusion. When the same solute (with respect to EfOM) was used for different membranes, the differences in σ are suggested to result from the different membrane properties including MWCO and surface/pore charge of membrane. The NF membrane shows a higher σ value than UF membranes due to the smaller pores (see Table 3). The effect of MWCO was also observed in the comparison between T-1000 and T-8000 membranes, as they manifested almost the same properties in terms of material, zeta potential, and module configuration (d_h and L). However, the GM membrane exhibited a higher σ value than the T-8000 membrane even though it has the same nominal MWCO value of 8000 Daltons. This is probably due to the negatively higher surface charge of the GM membrane than the T-8000 membrane (see Table 1). This difference in σ values is also possibly a result of the differences in material and surface charge between the two membranes. Interestingly, σ for T-1000 is similar to that of GM, even though T-1000 has a much lower MWCO value than GM. Possible explanations for these results are: (1) surface charge can significantly influence membrane selectivity unless there is significant difference in pore size (notice that both T-1000 and GM are UF membranes with relatively small pores), and (2) membrane material (here, ceramic versus polymeric) can be an influencing factor when considering membrane selectivity for a particular solute.

Intrinsic mass transfer coefficient (k_i) and solute permeability (P_m)

It was found that k_i exhibited a positive sign under convection-dominant conditions and a negative sign under diffusion-dominant conditions (a negative sign for P_m resulted from the mathematical relationship of the model with respect to k_i). The interpretation of this result is illustrated conceptually in Figure 5. Recalling that the intrinsic mass transfer coefficient (k_i) defined in this paper differs from k in the original CP model, in the sense that k_i reflects an overall diffusivity which is involved in actual membrane filtration (see the conceptual illustration, Figure 5), the molar diffusivity, resulting from the concentration gradient either on the membrane surface or inside the membrane pores, could then be estimated. The results are attributed to the following two suppositions. First, that the concentration gradient between the bulk phase and the membrane surface causes k_i to be directed upward (see left side of Figure 5) because C_m is much higher than C_b under convection-dominant conditions. This is consistent with the results reported previously in which the major resistance for flux decline is the CP layer under convection-dominant conditions (i.e. EfOM accumulates severely on the membrane surface). Secondly, that when a more significant concentration gradient occurred inside the membrane pores than in the CP layer, k_i was directed downwards under diffusion-dominant conditions (see the right side of Figure 5) because the main resistance for flux decline in this case was the adsorption of EfOM inside the membrane rather than on the membrane surface, resulting in almost the same C_b and C_m values. Therefore, it could be concluded that the model used in this paper reflects the overall transport characteristics of solute both near the membrane surface and through the membrane pores under either convection- (direction of k_i: from membrane surface to the bulk phase) or diffusion- (direction of k_i: to the permeate side inside the membrane) dominant conditions.

CP modulus based on estimated C_m

The ratio of C_m/C_b (CP modulus) increases (i.e. the concentration C_m at the membrane surface increases) with increasing flux J_v and with decreasing back-diffusional mass transfer coefficient k (Muler 1996). Therefore, the effect of the J_0/k ratio applied on C_m was investigated in terms of the CP modulus to determine whether EfOM was accumulated or adsorbed preferentially with respect to the dominant transport conditions (convection or diffusion) (see Figure 6).

The relationship between the CP modulus and the J_0/k ratio lead to two results. First, when EfOM transport through the membrane pores was dominated by convection, the CP modulus was always greater than 1.0 and increased as the applied J_0/k ratio increased, which is consistent with the previous results (i.e. the main resistance for flux decline is the CP layer on the membrane surface rather than adsorption inside the pores under convection-dominant conditions) (see Figure 6a, b & c). Moreover, in all cases (Figure 2a, b & c), CP increased rapidly at relatively lower J_0/k ratios, then increased slowly at higher J_0/k ratios, regardless of examined membrane types, which means that the maximum C_m estimated using this method can be used as an informative index to determine the fouling potential for a given solute with a membrane under convection-dominant conditions. Secondly, in the case of the EfOM-ESNA pair, the CP modulus was slightly greater than 1.0 (see Figure 6d) and did not change significantly as the J_0/k ratio increased. This observation ($C_m = C_b$) is also in accordance with the previous results (i.e. EfOM adsorption inside the membrane pores plays an important role for flux decline under diffusion-dominant conditions). Recall that flux decline (due to any type of resistance) occurred to a similar extent under both convection- and diffusion-dominant conditions (see the comparison between J_0 and J_v in Figure 2). Therefore, it may be difficult to determine the fouling potential which resulted under diffusion-dominant conditions due to lack of information inside the membrane pores. Similar trends were observed between EfOM-ESNA and EfOM-UF pairs when the applied J_0/k ratio was above the critical J_0/k ratio, which means that a transition from a diffusion- to a convection-dominant trend occurred for the NF membrane.

CONCLUSIONS

EfOM transport through UF membranes was primarily controlled by convection regardless of the applied J_0/k ratio (R_{obs} decreased as the J_0/k ratio increased), while EfOM transport through a NF membrane was primarily controlled by either convection or diffusion depending on the applied J_0/k ratio (diffusion- or convection-dominant at a J_0/k ratio below or above the critical J_0/k ratio, respectively). Therefore, hydrodynamic operating conditions, represented by the J_0/k ratio, can be an informative index to determine the transport characteristics for a given solute with a particular membrane. In addition, the critical J_0/k ratio can be a characteristic phenomenon for NF membranes.

The estimation of four parameters was identified as being useful to elucidate EfOM transport phenomena through both UF and NF membranes. These phenomena included: (1) overall transport condition as well as either

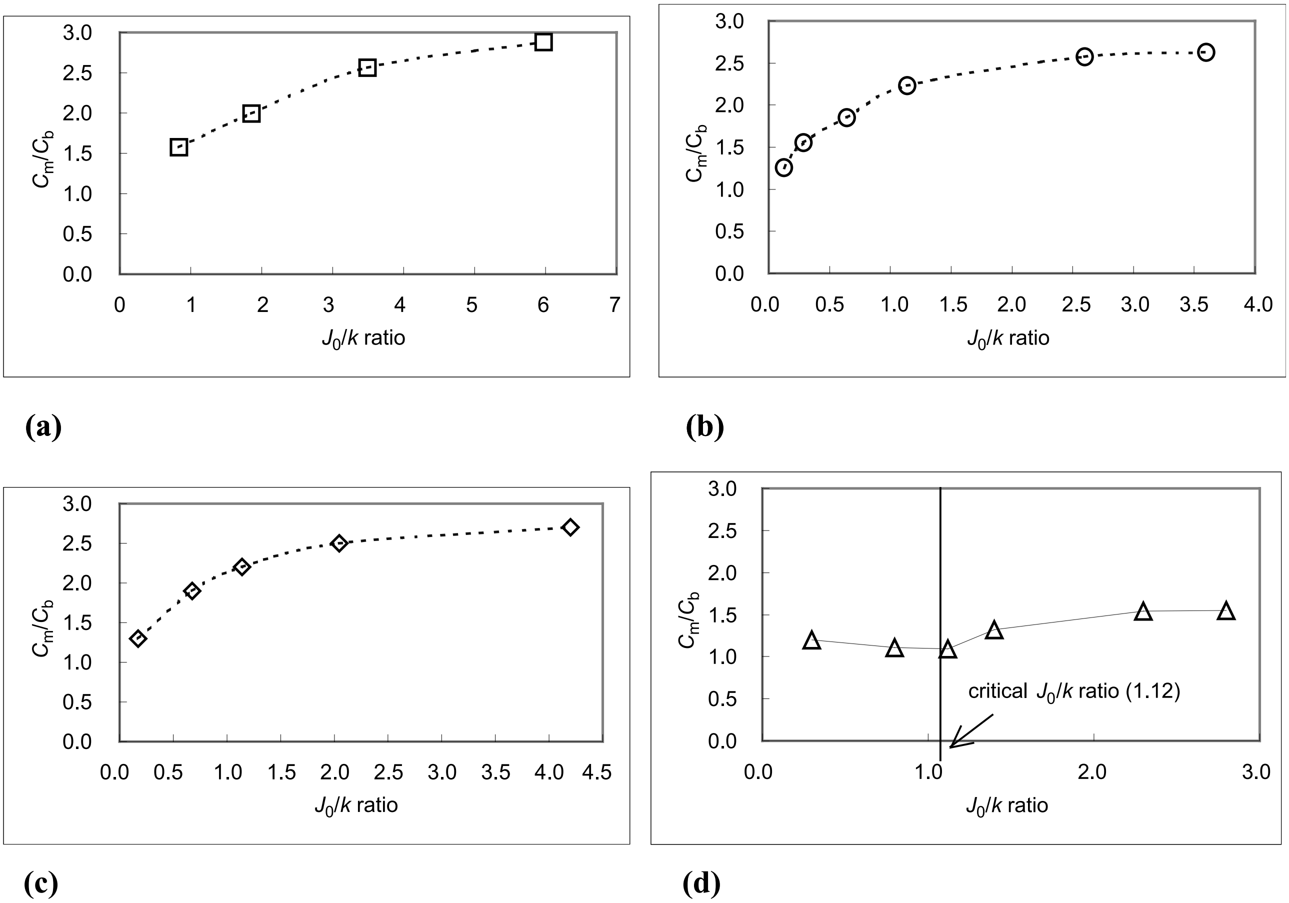


Figure 6 | CP modulus at varying J_0/k ratios: (a) EfOM-T 8000, (b) EfOM-GM, (c) EfOM-T 1000, and (d) EfOM-ESNA.

diffusive or convective transport of EfOM through the membrane pores under a certain condition (k_i and P_m); (2) interactions between EfOM and membrane surface/pores, resulting from different membrane properties (MWCO, zeta potential, module configuration and material) influencing membrane selectivity for EfOM; and (3) major resistance for flux decline under either convection- (resulting in severe CP) or diffusion- (resulting in relatively greater adsorption) dominant conditions. This confirms that interrelated mechanisms involved in membrane filtration could be identified by the four-parameter model, along with rigorous characterizations of EfOM (such as molecular size, structure and functionality) and membrane (such as MWCO, zeta potential and hydrophobicity). The most desirable condition (in terms of hydrodynamic operating conditions and EfOM transport characteristics determined with the estimated four parameters) can then be selected for EfOM removal, irrespective of the different properties for wastewater reclamation of various membranes, with both rejection maximization and fouling minimization being accomplished.

The experimental results of this study produced three interesting observations about these parameters (critical J_0/k ratio, negative k_i, and constant or slightly decreased CP modulus) with the EfOM-NF membrane pair examined under diffusion-dominant conditions. Hence, it may be envisioned that *negative concentration polarization* (or *intrinsic concentration polarization*) can occur under diffusion-dominant conditions, especially for the NF membrane. This hypothesis is now being studied more rigorously by considering the complex solute-membrane interactions of different solutes such as natural organic matter (NOM) and charged ions (such as bromate) with polymeric NF and tight ceramic UF membranes.

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