

Pharmaceutical rejection by membranes for wastewater reclamation and reuse

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Abstract Various membranes, which have different materials and nominal molecular weight cut-offs (MWCO), were compared in terms of rejection of ibuprofen and removal of effluent organic matter (EfOM) from membrane bioreactor (MBR), because pharmaceutical compounds contain a potential risk and EfOM is the precursor of carcinogenic disinfection by-products when reusing for drinking water source. To provide equivalent comparison with respect to hydrodynamic condition, mass transfer parameter, J_0/k ratio, was used. A tight-UF membrane with a molecular weight cut off of 8,000 daltons exhibited 25–95% removal efficiencies of ibuprofen with a molecular weight of 206 with and without presence of EfOM_{MBR}. EfOM_{MBR} caused the reduction of ibuprofen removal efficiency for UF membrane. Rejection of EfOM_{MBR} by UF and NF membranes ranged 29–47% and 69–86%, respectively. UF membrane could successfully remove ibuprofen at lower J_0/k ratio range (≤ 1) in organic free water but could not efficiently reject ibuprofen with a relatively hydrophilic EfOM_{MBR} (SUVA ≤ 3).

Keywords J_0/k ratio; nanofiltration; pharmaceuticals; ultrafiltration; wastewater reuse

Introduction

Recently, pharmaceutically active compounds (PhACs) have become of great aquatic environmental concern, due to their biological activity. Pharmaceuticals used for human medical care are not entirely utilized in the human body, and they are excreted to wastewater treatment plants (WWTPs) after therapeutic use. Some of pharmaceutical compounds are not removed completely in the WWTP, thus they can be introduced into receiving water that is a potential drinking water source. Despite much research about the occurrence, fate, and removal of pharmaceuticals in the aquatic environment have been executed (Heberer, 2002; Stumpf *et al.*, 1999; Ternes, 1998)), there is still a lack of knowledge about their influence and treatability. PhACs can be a potential risk, especially if WWTP effluent is used for potable water production.

The pharmaceutical compound investigated in this study is ibuprofen, which is an analgesic/non-steroidal anti-inflammatory drug (NSAID). It is frequently used for human medical care and reported to exhibit higher concentrations than other PhACs in treated effluent. NSAIDs are not significantly adsorbed on soil and sediment, due to their polar structures (i.e., acetic and propionic forms), thus they can easily be transported into a surface water. In drinking water treatment plants, pharmaceuticals can be removed by several processes such as chemical precipitation, activated carbon adsorption, oxidation (Huber *et al.*, 2003), biofiltration, and membrane filtration (Yoon *et al.*, 2002). Since NSAIDs are acidic/polar compounds, thus membrane treatment is a promising process to be able to remove negative-charged NSAIDs from wastewater-effluent containing source waters due to the negative-charged membrane surface.

Methods and materials

Stock solution of ibuprofen was prepared with a nano pure water from NANOpure system (Barnstead). All chemicals used for experiments were reagent grade and were used without a further purification. EfOM containing effluent water was treated by a MBR process

Table 1 Membrane properties

Code (manufacturer)	Material	Nominal MWCO (datons)	Contact angle (°)	Zeta potential (mV) at pH 7.0	Lp (l/day-m ² -Pa)
PW (Desal)	Polyethersulfone	10,000	66	-30	50
GM (Desal)	Polyamide TFC	8,000	58	-45	3.5
HL (Desal)	Polyamide TFC	150-300	41	-30	3.7
Ceram (TAMI)	Titanium oxide	1k, 3k, 5k, 8k	-	-25	4-30

equipped with a MF membrane with a pore size of 0.05 μm . Membrane properties are listed in Table 1. Various membranes of different materials (polymeric vs. ceramic) and MWCO (UF vs. NF) were used.

Nominal MWCOs were provided by manufacturers. Contact angle and zeta potential values of membranes are measured by the sessile drop method (Tantec, Contact Angle meter) and electrophoresis method (Otsuka, ELS-8000), respectively. According to zeta potential results, all membranes have negative surface charge at a neutral pH. Two different types of commercialized bench-scale cross-flow membrane units were used for ceramic membrane (clover type), and for polymer membrane (flat sheet type). The active area and cross-flow velocity with a feed-flow of 500 ml/min are 78 cm², 9.3 cm/s (for ceramic membrane) and 55.8 cm², 21.7 cm/s (for polymer membrane), respectively. All membrane experiments are executed at the same feed flow rate (500 mL/min) and pressure intervals (0.5, 1, 1.5, 2, 2.5, 3 bar) by varying pump speed and backpressure to provide equivalent hydrodynamic conditions in terms of J_0/k ratio. J_0 is the initial pure water permeation flux and k is mass transfer coefficient solute properties diffusing away from membrane surface.

$$J_0 = \frac{Q_{\text{permeate}}}{A_{\text{active}}}, k = \alpha \left(\frac{vD^2}{d_h L} \right)^{0.33}; (\alpha_{\text{channel}} = 1.85, \alpha_{\text{tube}} = 1.62)$$

Here, Q_{permeate} is permeate flow rate, A_{active} is membrane surface area, v is average velocity of feed fluid, D is the solute diffusion, d_h is equivalent hydraulic diameter, L is the channel length. MBR effluent quality parameters are listed in Table 2.

Ibuprofen (IB: Sigma-Aldrich) was measured by a high-performance liquid chromatography (HPLC: Shimadzu LC-10AVP Series equipped with a UV-VIS detector) using an isocratic eluent consisting of 10 mM phosphoric acid and acetonitrile (5:5) with a Nova-Pak C-18 (Waters, 60 \AA , 4 μm , 3.9 \times 150 mm) at 220 nm. The sample injection volume was 200 μL .

Results and discussion

The results of ibuprofen rejection by various tight UF membranes (T-series, PW, and GM) and NF membrane (HL) are presented in Figure 1.

They can be categorized into three groups for rejection patterns; the first is T-1k, T-3k, and T-5k (see Figure 2a), the second is T-8k and PW (see Figure 2b), the third is GM and HL (see Figure 3a, diamond symbols). The molecular weight of ibuprofen is 206 daltons, thus is much lower than MWCOs of UF membranes (1,000–10,000 daltons) and similar as

Table 2 EfOM characteristics of source water (MBR effluent)

DOC (mg/L)	UVA ₂₅₄ (cm ⁻¹)	SUVA (m ⁻¹ mg ⁻¹ L)	Conductivity ($\mu\text{S/cm}$)	pH	Average molecular weight	
					Weight-average (Mw)	Number-average (Mn)
4.52	0.0756	1.67	298	5.48	1036	808

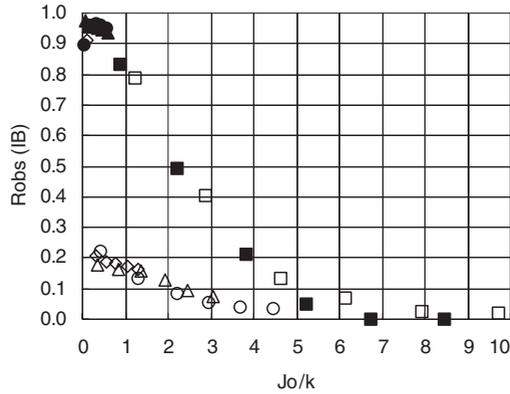


Figure 1 Rejection of ibuprofen by T-1k (◇), T-3k (△), T-5k (○), T-8k (□), PW (■), GM (▲) and HL (●)

the MWCO of NF membrane (150–300 daltons) tested in this study. Therefore, in the case of UF membranes, it is difficult to expect efficient removal of ibuprofen by “*size exclusion mechanism*”. The rejection efficiencies of ibuprofen by GM and HL membranes are remarkable high at a lower J_0/k (≤ 1). This phenomenon is rather explained by “*electrostatic repulsion mechanism*”; the pK of ibuprofen is 4.9, and zeta potentials of all of the tested membranes have negative values at a neutral pH, thus both solute and membranes have negative charge values at the operating pH.

Except for the first group (i.e., T-1k, T-3k, T3k), the rejection trends agree with our assumption (at a higher J_0/k , the lower rejection; as the J_0/k ratio increases, IB rejection by UF membranes decreases because of a relative decrease in diffusion transport compared to convective transport through the membrane pores). Moreover, the results of the each group are fully consistent with our hypothesis. These three groups are divided by observational removal rate, but membranes belonging to each group have similarity with respect to pure water permeability. Thus, the difference in rejection efficiencies can be resulted from their hydraulic resistances.

At the same feed side pressure (R_{obs} data of each membrane test have six points from the y-axis, its corresponding pressures are 0.5, 1, 1.5, 2, 2.5, 3 bar), T-8k and PW have higher permeability (larger J_0/k) than T-1k, T-3k, and T-5k. Furthermore, rejection efficiencies of T-8k and PW membranes are higher than three ceramic membranes.

Figure 3 illustrates the effects of ionic strength (see Figure 3a) and MBR effluent organic matter (EfOM_{MBR}) presence on membrane performance (Figure 3b). The GM and HL membranes have almost the same ibuprofen rejection even with different nominal

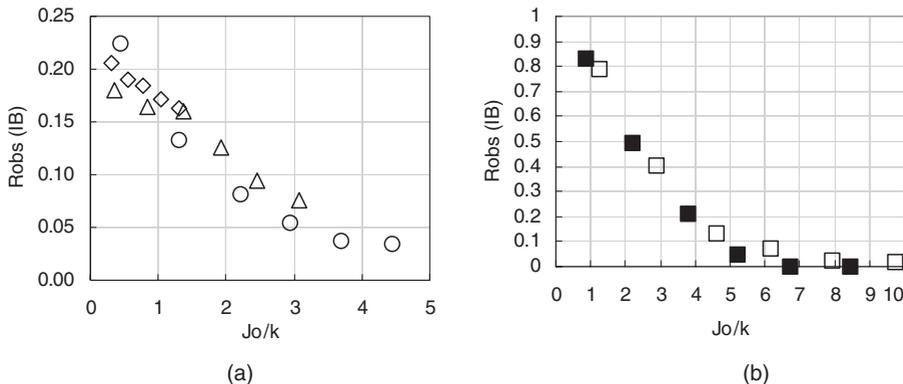


Figure 2 Rejection of ibuprofen: (a) T-1k (◇), T-3k (△), T-5k (○), (b) T-8k (□), PW (■)

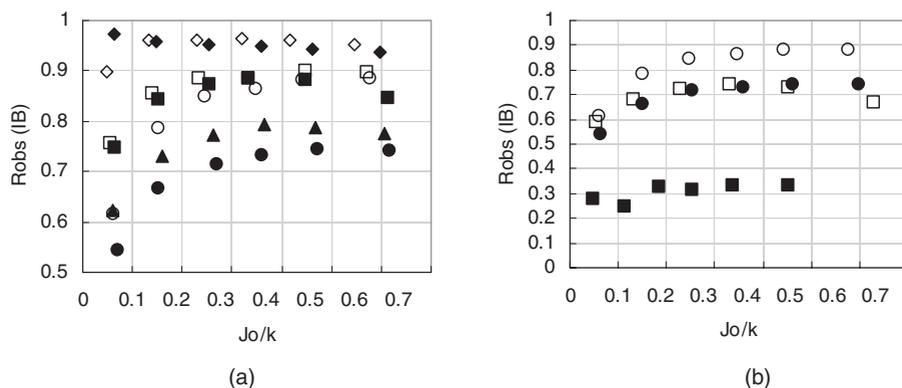


Figure 3 Rejection of ibuprofen by GM (filled symbols) and HL (open symbols) membranes: (a) pure water (◆,◇), 0.2 mM phosphate buffer (■,□), 1 mM NaCl (▲,△), 2 mM NaCl (●,○), 2 mM NaCl (●,○), (b) EfOM_{MBR} (■,□)

MWCOs, and required relatively similar TMP to achieve the corresponding J_0/k ratios at a different ionic strength (see Figure 3a). This suggests that J_0/k ratio is a powerful tool to reflect hydrodynamic condition in the cell, to enhance removal efficiency, and to overcome borderline of UF and NF in pure water test.

When the J_0/k ratio is less than 1 (defined as the *critical J_0/k ratio*), it can be hypothesized that solute moving due to back diffusion away from the membrane surface is higher than solute passing through the boundary along with fluid due to convection. For that reason, concentration polarization is very weak so the concentration of solute at the membrane surface approximates to the bulk concentration. In this diffusion dominant region, rejection efficiencies of ibuprofen by GM and HL membranes have reverse U-shape, and a maximum rejection will exist at the critical J_0/k ratio. The rejection trends are shifted to the lower part with increasing ionic strength. It is caused by reduction of charge repulsion forces (Shim *et al.*, 2002).

There was no significant flux decline during the membrane filtration without EfOM_{MBR}, however EfOM_{MBR} containing water caused the decrease of permeate flux due to development of resistance by EfOM_{MBR} for GM membrane at the same TMP. Furthermore, EfOM_{MBR} caused the severe reduction of ibuprofen removal behavior for GM rather than HL membrane. Excluding ibuprofen rejection in presence of EfOM_{MBR} by GM, the trend is still reverse U-shape.

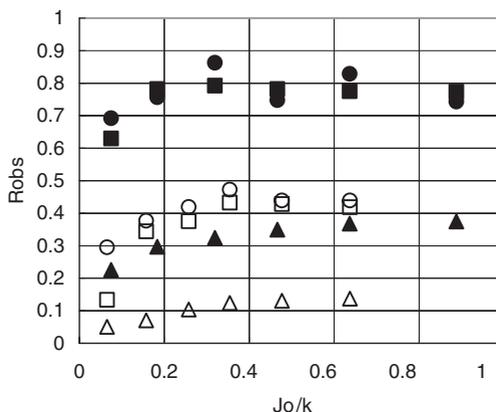


Figure 4 Rejection of EfOM_{MBR} in terms of DOC (●,○), UVA254 (■,□), conductivity (▲,△) by GM (filled symbols) and HL (open symbols) membranes

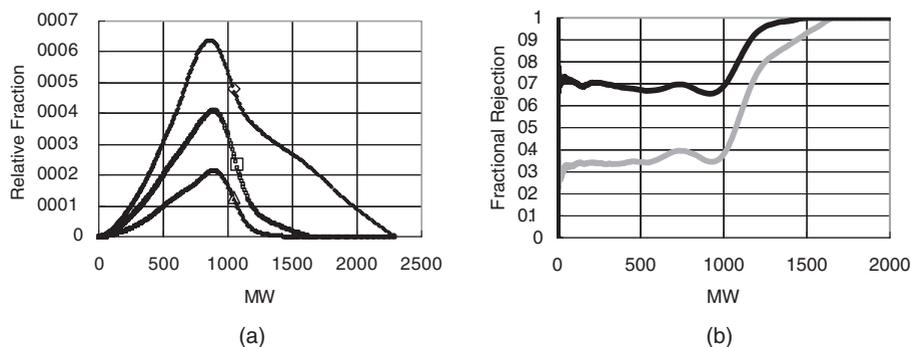


Figure 5 (a) Relative fractions and (b) fractional rejection of EfOM_{MBR}: (a) feed (◇, —) and permeate GM (□, —) and HL (△, —) membranes (b) GM (—; grey line) and HL (—; black line) membranes

The rejection trends of EfOM_{MBR} in terms of DOC and UVA₂₅₄ between GM and HL membranes are similar for ibuprofen in the absence of EfOM_{MBR}; NF and UF membranes can reject almost the same amount of ibuprofen in pure water at the same J_0/k ratio, even with different MWCO values (see Figure 3a). However, this did not accord with EfOM_{MBR}. Cho *et al.* (2002) suggested that UF membrane can be used as an alternate for the NF membrane with almost the same rejection of natural organic matter (NOM) when NOM has a high SUVA.

MW distributions of EfOM_{MBR} included in membrane permeate were compared with those of feed water. When a feed side pressure is 2 bar, M_w and M_n of EfOM_{MBR} in permeate were 793 and 657 daltons for GM membrane and 764 and 647 daltons for HL membrane, and effective MWCOs (Cho *et al.*, 2000; Lee *et al.*, 2002), which were determined by 90% rejection of EfOM_{MBR}, were 1,445 and 1,164 daltons for GM and HL membranes, respectively. Fractional rejection of EfOM_{MBR} is almost constant in the molecular range of 0–1,000 daltons and this value is similar to rejection of ibuprofen. Therefore, the same removal efficiency is expected for the most part of PhACs (200–600 daltons).

Conclusions

This study verified several hypotheses, including membrane MWCO and material effects, ionic strength and EfOM_{MBR} effect, in terms of membrane performance such as pharmaceutical compound and EfOM_{MBR} rejection either with different membranes at the same J_0/k ratio or with the same membrane at different J_0/k ratios. If different J_0/k ratios were used with the same membrane, the rejection of ibuprofen increased with increasing J_0/k , when it is lower than critical J_0/k ratio. Both NF and UF membranes exhibited similar ibuprofen rejection behaviors for EfOM_{MBR} free water at the same J_0/k ratio. Similar MW distributions of EfOM_{MBR} included in membrane permeates were found for different membranes with different MWCO values at the similar J_0/k . This indicates that the J_0/k ratio is an influencing factor to control organic matter rejection. Effective MWCO for negatively charged membranes was significantly reduced from a nominal MWCO. It confirms electrostatic repulsion mechanism between the negatively charged membrane surface and polar/acidic pharmaceutical (and/or EfOM_{MBR}). Effective MWCO can be concluded to reflect more practical information than nominal.

Acknowledgements

This research was supported by a grant (4-1-1) from Sustainable Water Resources Research Center (SWRRC) of 21st century frontier R&D program through the Water Reuse Technology center (WRTC) at Kwangju Institute of Science and Technology

(K-JIST) and by the K-JIST through the project “Remediation technology of acid mine drainage and contaminated soils in the metal mining areas”.

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