TRANSPORT OF PHARMACEUTICAL AND NOM IN NF AND TIGHT UF MEMBRANES

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Abstract

Membrane processes with NF and tight-UF membranes were proven to be very effective in removing organic electrolytes such as acidic pharmaceuticals and/or natural organic matter (NOM). This high efficiency is resulted from both back-diffusion and electrostatic repulsion in the concentration polarization layer: moreover, hindered transport of pharmaceuticals and NOM in membrane pores. In the transport equation for charged membranes, membrane physicochemical structures, solution chemistries, and solute characteristics may be important transport parameters. The filtration of aqueous mixtures containing charged solutes (acidic pharmaceuticals), NOM, and/or strong electrolyte was conducted. This study verified several hypotheses: effect of membrane molecular weight cut-off (MWCO) and NOM, with respect to membrane performance such as ibuprofen and NOM rejections.

1. INTRODUCTION

Pharmaceuticals used for human medical care are not eliminated in the human body, and they are excreted to the wastewater treatment plants (WWTPs) after therapeutic use. Some of pharmaceutical compounds were not removed completely in the WWTP, thus they can be introduced into the receiving water that is a potential drinking water source. Pharmaceuticals can be potential risk of potable water contamination; especially WWTP effluent is used directly for potable water production. Many pharmaceuticals have been detected in surface water, a few of which have been detected in finished drinking water.

Membrane process with NF and tight UF membranes were proven to be very effective in removing organic electrolytes. This high efficiency is resulted from both back-diffusion (away from membrane surface) and electrostatic repulsion (between pharmaceuticals/NOM and negative-charged membrane) in concentration polarization layer, moreover, hindered transport of pharmaceuticals and NOM in membrane pores. In the transport equation for charged membranes, membrane physicochemical structures (pore size, zeta potential, solvent permeability), solution chemistries (pH, ion strength), and solute characteristics (molecular size,

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pKa, Kow) may be important transport parameters.

Transport of pharmaceuticals through the membrane is generally governed by diffusion at low permeate flux, and convection is the dominant mechanism at high permeate flux.

2. EXPERIMENTAL MATERIALS AND METHODS

Membrane properties are listed in Table 1. Various membranes having different materials and MWCO (tight UF vs. NF) were used. Nominal MWCO of each membrane was provided by manufacturers. Contact angle and zeta potential values of membranes were 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.

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	10k	66	-30	50
PES5k, PES10k (Milipore)	Polyethersulfone	5k, 10k	-	-	20, 42
GM (Desal)	Polyamide TFC	8k	58	-45	3.5
RF (Saehan)	Polyamide TFC	200~500	43	-20	2.7

Two different types of commercialized bench-scale cross-flow membrane units with low and high-pressure pump were used for polymer membrane (flat sheet type). The active area and cross-flow velocity with a feed-flow of 500 ml/min are 55.8 cm^2, 21.7 cm/s, respectively. All membrane experiments are executed at the same feed flow rate (500mL/min) and the same pressure segments (high-permeable membrane was tested by 3 bars using low pressure pump, and low-permeable membrane was tested by 30 bars with high pressure) 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 representing solute diffusion away from membrane surface in concentration polarization layer.

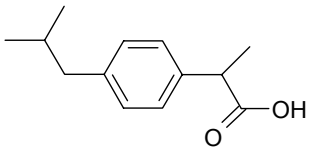
$$k = \alpha \left(\frac{vD^2}{d_h L}\right)^{0.33}; \quad (\alpha_{channel} = 1.85)$$

Here, v is average velocity of feed fluid, D is the solute diffusion, d_h is equivalent hydraulic

diameter, and *L* is the channel length.

Characteristics of ibuprofen are listed in Table 2. Ibuprofen (Sigma-Aldrich) was measured by a high-performance liquid chromatography (Shimadzu LC-10AVP Series equipped with a UV-VIS detector) using an isocratic mode consisting of 10 mM phosphoric acid and acetonitrile (5:5) with a Nova-Pak C-18 (Waters, 60 Å, 4 μm, 3.9×150 mm) at 220 nm. The sample injection volume was 200 μL. Feed concentration of membrane tests was 1 μM.

Table 2 Characteristics of tested pharmaceutical

Pharmaceuticals	Molecular weight	pKa	Kow (log)	Molecular structure
Ibuprofen	206	4.91	4.13~4.91	

Characteristics of Suwannee River NOM (SRNOM) are listed in Table 3. SRNOM purchased from International Humic Substances Society (IHSS) was used to investigate the effect of NOM on membrane performance.

Table 3 Characteristics of SRNOM in the source water

DOC (mg/L)	UVA_{254} (cm^{-1})	SUVA ($m^{-1}mg^{-1}L$)	Conductivity (μS/cm)	pH	Average Molecular Weight	
					Mw	Mn
3.53	0.1278	3.62	5.8	5.79	2360	1760

Weight-average (Mw) Number-average (Mn)

3. RESULTS AND DISCUSSIONS

The molecular weight of ibuprofen (acidic pharmaceutical) is 206 dalton, and thus is much lower than the MWCO of tight UF membranes (1,000~10,000) and similar to the MWCO of NF membranes (200~500). By means of steric hindrance pore model and Stokes-Einstein relation, Stokes radii of ibuprofen and NOM are 0.38 and 1 nm, respectively, and pore radii of NF (MWCO=200~500) and tight UF (MWCO=8,000) are 0.8~1.4 nm and 2.4~3.8 nm, respectively. Therefore, it is difficult to expect efficient removal of ibuprofen through only steric exclusion mechanism in the case of tight UF membrane.

The results of ibuprofen rejection by tight UF membrane (GM) and various NF membranes (HL,

NF90, RF) are presented in Fig. 1.

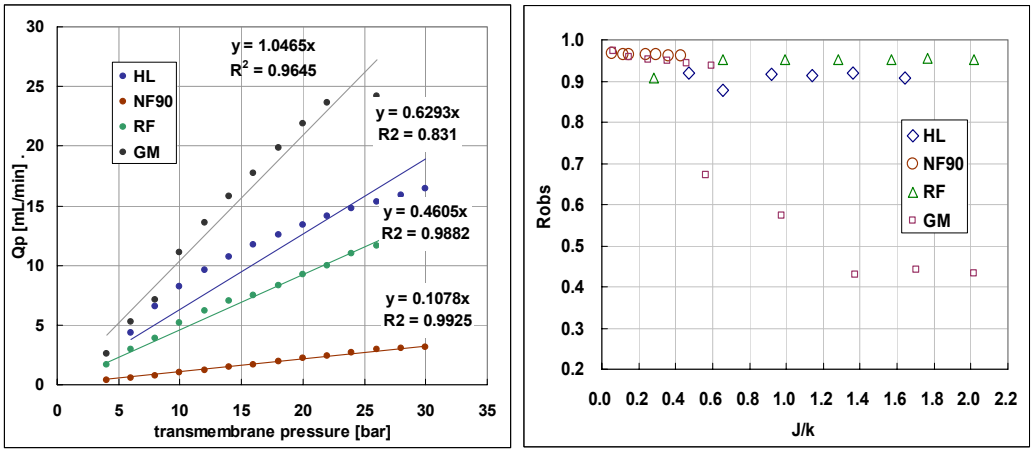


Figure 1. Pure water permeability and rejection of ibuprofen by NF (HL, NF90, and RF) and tight UF (GM) membranes in NOM free water

The rejection efficiencies of ibuprofen by GM membrane are remarkably high at a lower J/k (≤ 0.5) with low-pressure pump. This phenomenon can be explained by electrostatic repulsion rather than hydrodynamics; the pK of ibuprofen is 4.9, and zeta potentials of all tested membranes have negative values at a neutral pH, and thus both solute and membranes have negative charge values at the operating pH. But, the rejection rate by GM membrane is dramatically dropped with increase of pressure inducing the increase of water permeation flux J at the high-pressure mode. NF membranes successfully reject ibuprofen over 90%. The less permeable membrane was used, the higher rejection efficiency was exhibited.

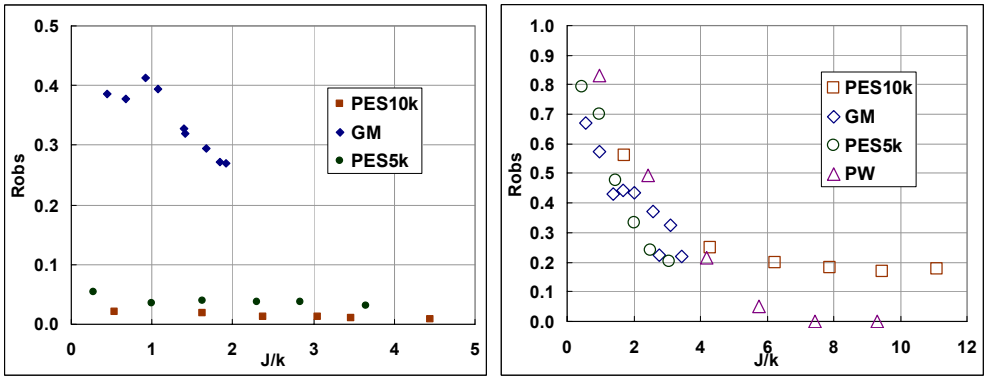


Figure 2. Rejection of NaCl (left) and ibuprofen (right) by tight UF membranes (MWCO; 5k~10k)

Fig. 2 shows rejection of NaCl and ibuprofen by tight UF membranes. The rejection of NaCl in GM membrane was the highest among 3 tight UF membranes (GM, PES 5k, and PES 10k), even though the MWCO of GM is between those of PES 5k and PES 10k. Thus, it can be expected that ibuprofen rejection rate by GM is higher than that of other UF membranes at the same J/k ratio due to electrostatic repulsion. However, the rejections of ibuprofen by tight UF membranes have same pattern. This phenomenon may be explained by the hydrodynamic force due to high permeate flux rather than the repulsion between negatively charged membrane surface and ibuprofen ion. The ratio of the molecular size of ibuprofen to the pore size of UF membranes is 0.09~0.19. Therefore, steric hindrance effect of ibuprofen on UF membrane is lower than that on NF membranes (0.3~0.5).

The effect of NOM on NF and tight UF membranes are illustrated with Fig. 3. NOM caused decrease of the permeate flux due to development of resistance by NOM for both two membranes with the same transmembrane pressure. In the previous study, both NF (HL) and tight UF (GM) membranes exhibited similar ibuprofen rejection behaviors without NOM in the feed water at the same J/k ratio (<0.5), even though the reduction of ibuprofen removal behavior was resulted from the feed water containing effluent organic matter (EfOM) for both two membranes. However, ibuprofen rejection increases due to SRNOM at the high-pressure mode.

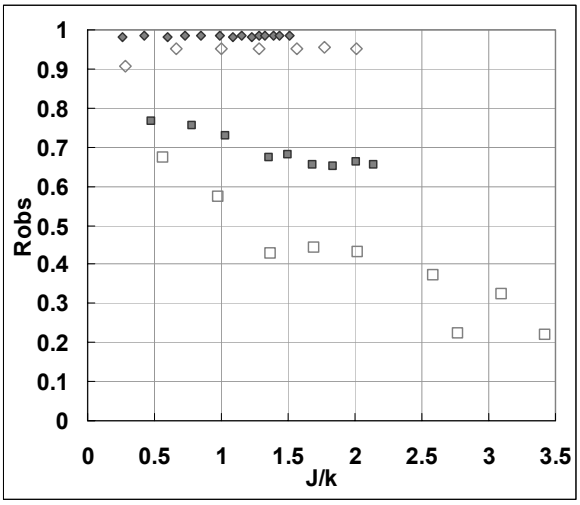


Figure 3. Rejection of ibuprofen by RF (◇) and GM (□) membranes with SRNOM (filled symbols) and without SRNOM (open symbols) in the feed water

Average hydrodynamic diameter of SRNOM was somewhat larger than pore diameter of NF

membrane. So, the rejection rates of SRNOM and ibuprofen by RF membrane are slightly increased with permeate flux. In the case of GM, the rejection rates of SRNOM are decreased with permeate rate (Fig. 4). But, the ratio of molecular size of SRNOM to pore size of GM membrane is 0.4~0.6 corresponding to the ratio of molecular size of ibuprofen to pore size of NF membranes. Therefore, rejections of SRNOM are not considerably affected by increase of J/k ratio describing convective transport, but affected by the steric hindrance.

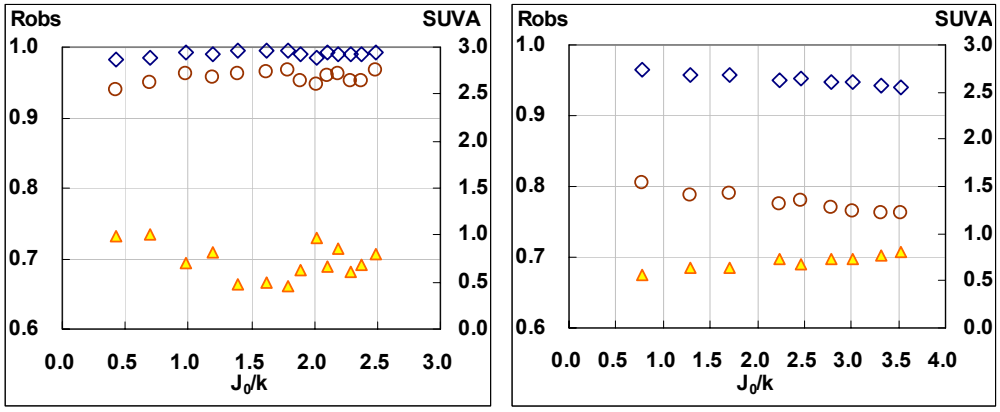


Figure 4. Rejection of SRNOM by RF (left) and GM (right) membranes and SUVA value of permeate: UVA254 (◇), DOC (○), SUVA (Δ)

4. CONCLUSIONS

This study verified several hypotheses, including membrane MWCO, water permeability, and NOM effect, in terms of membrane performance such as pharmaceutical compound and SRNOM rejection either with different membranes at the same J/k ratio or with the same membrane at different J/k ratios. If different J/k ratios were used with the same membrane, the rejection of ibuprofen decreased with increasing J/k in tight UF membranes, when it is higher than critical J/k. Tight UF membranes exhibited similar ibuprofen rejection behaviors for NOM free water at the same J/k ratio.

Hydrodynamic operating condition (J/k ratio) and SRNOM did not influence the performances of NF membranes. But, tight UF membranes were significantly affected by J/k ratio and SRNOM. This indicates that the J/k ratio is an influencing factor to determine whether convection force overcomes electrostatic repulsion force or not. It confirms steric hindrance effect (the ratio of molecule and membrane pore size) and electrostatic repulsion mechanism between the negatively charged membrane and polar/acidic pharmaceutical (and/or

NOM).

ACKNOWLEDGEMENTS

This research was supported by a grant (4-1-2) from Sustainable Water Resources Research Center (SWRRC) of 21st century frontier R&D program through the Water Reuse Technology Center (WRTC) at Gwangju Institute of Science & Technology (GIST).

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