Rejection of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) by low pressure reverse osmosis membranes

H. Ozaki, N. Ikejima, Y. Shimizu, K. Fukami, S. Taniguchi, R. Takanami, R. R. Giri and S. Matsui

ABSTRACT

This paper aims to elucidate retention characteristics of some pharmaceuticals and personal care products (PPCPs), and endocrine disrupting chemicals (EDCs), by two polyamide low pressure reverse osmosis (LPRO) membranes. Feed solution pH did not have an influence on rejections of undissociated solutes, which was most likely governed by adsorption, size exclusion and diffusion simultaneously. Size exclusion was presumably dominant, especially with tight membranes (UTC-70U). Rejections of the solutes with low dipole moment (<1.0 debye) decreased with increasing octanol–water partition coefficient (K_{ow}). The solutes with large K_{ow} values were most likely adsorbed on membrane and subsequently passed through it resulting in larger diffusion coefficient (D_p). The rejections decreased with increasing D_p values irrespective of their dipole moments. Rejections of solutes with comparatively larger dipole moments might be dominated by diffusion and/or convection rather than their hydrophobicity. However, rejections of solutes with hydroxyl and carboxyl functional groups by UTC-60 increased with solution pH. More than 80% rejections were obtained for degree of dissociation (α) > 0.5. Electrostatic repulsion played a key role for rejection of dissociated solutes, especially by loose LPRO membranes. Therefore, assessing the dissociation degree at desired pH values can be a key step to obtain an insight of rejection mechanisms by polyamide membranes.

Key words | diffusion coefficient, dissociation degree, EDCs, hydrophobicity, LPRO membrane, PPCPs

H. Ozaki
K. Fukami
Department of Civil Engineering,
Osaka Sangyo University,
3-1-1 Nakagaito, Daito City,
574-8530 Osaka,
Japan
E-mail: *ozaki@ce.osaka-sandai.ac.jp*

N. Ikejima
S. Matsui
Graduate School of Global Environmental Studies,
Kyoto University,
Yoshida-Honmachi, Sakyo-Ku, 606-8501 Kyoto,
Japan
E-mail: *nori@eden.env.kyoto-u.ac.jp*;
matsui@eden.env.kyoto-u.ac.jp

Y. Shimizu
R. R. Giri
RCEQM, Graduate School of Engineering,
Kyoto University,
1-2 Yumihama, Otsu, 520-0811
Japan
E-mail: *shimizu@biwa.eqc.kyoto-u.ac.jp*

S. Taniguchi
R. Takanami
New Industrial R & D Center,
Osaka Sangyo University, 3-1-1 Nakagaito,
Daito City, 574-8530 Osaka,
Japan
E-mail: *r-nami@cnt.osaka-sandai.ac.jp*;
taniguch@cnt.osaka-sandai.ac.jp;
rabindra@cnt.osaka-sandai.ac.jp

INTRODUCTION

Ever increasing urbanisation, industrial activities and pharmaceutical uses have posed significant threats to water resources and reuse of treated wastewaters. Reports of pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) in water have raised substantial concern among the public and regulatory agencies recently. The majority of PPCPs and EDCs are more polar with acidic or basic functional groups than conventional contaminants. These properties coupled with their occurrence at trace levels create unique challenges for their removal processes and analytical detection (Snyder *et al.* 2003).

Reverse osmosis (RO) membrane filtration has been accepted as a proven technology for the effective removal of low molecular weight organics at low concentration levels in water and wastewater. However, its applications are limited due to the requirement for extensive pretreatment along with the high operational and maintenance costs associated with

doi: 10.2166/wst.2008.607

it. Low pressure reverse osmosis (LPRO) membrane filtration is emerging as an alternative to the conventional RO method to separate a wide range of organic pollutants in contaminated water and wastewaters due to its low operating pressure range (0.2–0.9 MPa).

The retention of organic pollutants in membrane separation processes depends on the characteristics of both membrane and the pollutants. Key membrane properties include molecular weight cut-off value, surface charge, hydrophobicity and surface morphology, while molecular weight, molecular size, dissociation constant (pK_a), hydrophobicity (log K_{ow}) and diffusion coefficient (D_p) are key characteristics of pollutants (Bellona *et al.* 2004). Kimura *et al.* (2004) found that size exclusion and electrostatic exclusion were dominant criteria for the retention of EDCs and pharmaceutically active compounds by polyamide and cellulose acetate membranes, respectively. Feed solution pH is noted as one of the important parameters influencing electrostatic exclusion of micropollutants in membrane filtration (Ozaki & Li 2002; Urase & Sato 2007). On the other hand, Agenson *et al.* (2003) predicted higher retentions of more hydrophobic organic molecules with larger molecular width and length. Hydrophobicity is shown to be a dominant factor affecting the adsorption of organic compounds on nanofiltration membranes (Van der Bruggen *et al.* 2002). In addition, solution pH is found to influence adsorption of oestrogen by RO membranes (Nghiem *et al.* 2006). Yoon *et al.* (2006) concluded that the retention of several EDCs and pharmaceuticals was governed by both hydrophobic adsorption and size exclusion in nanofiltration (NF), while the retention was typically governed by hydrophobic adsorption only in the case of ultrafiltration (UF). Braeken *et al.* (2006) noted that both convective and diffusive transports of dissolved organic compounds in water were influenced by electrostatic repulsion and molecular weight. Convection was the dominant mechanism involved in solute transport in nanofiltration, while the contribution of diffusion increased when convective transport was hindered by electrostatic repulsion or steric hindrance.

Retention mechanisms of organic micropollutants in membrane separations are quite complex (Pronk *et al.* 2006), because some may loose their importance while others play dominant roles among the several influencing factors involved. Dissociation of organic solutes in water plays a very important role on their retention by electrostatic repulsion in membrane filtration. Also, the degree of dissociation (α) of the organics may influence their diffusion and hydrophobicity, and hence transport associated with them. This paper aims to elucidate rejection characteristics of some common PPCPs and EDCs at their different levels of dissociation by two LPRO membranes (UTC-60 and UTC-70 U) in laboratory experiments. Adsorption of the selected PPCPs and EDCs on membranes and D_p values at different pH conditions were measured by laboratory experiments. Their octanol–water partition coefficient (K_{ow}) values were calculated using Advanced Chemistry Development Software (version 8.14), while all other parameters, including pK_a and dipole moment (D) values, were cited from literatures and scientific database (SciFinder Scholar).

MATERIALS AND METHODS

Membranes and solutes

Two types (UTC-60 and UTC-70U) of flat-sheet LPRO membranes (TORAY Industry Inc., Japan) were employed in this investigation. Other details of the membranes are given in Table 1. Thirteen PPCPs and five EDCs (bottom five), as listed in Table 2, were selected as target chemicals in this investigation. All the chemicals and reagents were obtained from Wako Pure Chemicals, Japan.

Membrane efficiency tests

A cross-flow module (C-10T: 210 mm × 110 mm × 82 mm, Nitto Denko Corporation, Japan) was used in continuous

Table 1 | Membrane properties

Membrane	Manufacturing company	Material	Surface area (cm^2)	Ref. 0.05% NaCl rejection (%)	Operating pressure (MPa)
UTC-60	Toray Industry Inc., Japan	Aromatic polyamide	60.0	55.0	0.30
UTC-70U	Toray Industry Inc., Japan	Aromatic polyamide	60.0	99.5	0.30

Table 2 | Target PPCPs and EDCs

No.	Compounds	Abbrev.	Mol. formula	Mol. weight	pK_a	log K_{ow} (pH 3.0)	Dipole moment (D)
1	Crotamiton	CTT	$C_{13}H_{17}NO$	203.28	–	3.1	–
2	Phenacetin	PCN	$C_{10}C_{16}NO_2$	179.22	–	1.63	1.67*
3	Naproxen	NPX	$C_{14}H_{14}O_3$	230.26	4.84†	4.84	3.16‡
4	Clofibric acid	CA	$C_{10}H_{11}ClO_3$	214.65	3.18†	3.18	1.86‡
5	Diclofenac	DCF	$C_{14}H_{11}Cl_2NO_2$	296.15	4.18†	2.57	0.97‡
6	Carbamazepine	CBZ	$C_{15}H_{12}N_2O$	236.27	2.30†	2.45	3.94[1]
7	Gemfibrozil	GFZ	$C_{15}H_{22}O_3$	250.33	4.75†	4.75	0.83‡
8	Ibuprofen	IBP	$C_{13}H_{18}O_2$	206.28	4.41†	3.97	2.09‡
9	Indomethacin	IDM	$C_{19}H_{16}ClNO_4$	357.79	3.96†	4.27	1.43‡
10	Ketoprofen	KEP	$C_{16}H_{14}O_3$	254.28	4.23†	3.12	3.60‡
11	Propyphenazone	PPZ	$C_{14}H_{18}N_2O$	230.31	–	2.05	4.10*
12	Triclosan	TCS	$C_{12}H_7C_{13}O_2$	289.54	8.14†	5.11	–
13	N,N-diethy1-3-methylbenzamide	DEET	$C_{12}H_{17}NO$	191.28	–	1.96	–
14	17β-estradiol	E2	$C_{18}H_{24}O_2$	272.38	10.27†	4.13	0.99§
15	Bisphenol A	BPA	$C_{15}H_{16}O_2$	228.29	9.73†	3.43	1.00§
16	Nonylphenol	NP	$C_{15}H_{24}O$	220.35	10.14†	5.59	1.40§
17	Diethyl phthalate	DEP	$C_{12}H_{14}O_4$	222.24	–	3.51	–
18	2,4-dichlorophenol	2,4-DCP	$C_6H_4Cl_2O$	163.0	8.05†	2.99	–

*Nghiem & Schafer (2005).
†Juan *et al.* (2004).
‡Urase & Sato (2007).
§Kimura *et al.* (2004).

laboratory experiments to examine retentions of PPCPs and EDCs. Figure 1 shows a schematic diagram of experimental set-up. A flat-sheet membrane with the effective surface area of 60 cm^2 was mounted in a cross-flow module, and feed solution was pumped through the membrane at 1.20 l min^{-1} cross flow rate with 0.30 MPa operating pressure. Concentrations of 17β-estradiol (E2), nonylphenol (NP), naproxen (NPX) and tricrosan (TCS) in feed solutions were 1.0 mg L^{-1}, while those of remaining solutes were 10.0 mg L^{-1}. The purpose of relatively larger solute concentrations in feed solution was to avoid difficulties in measuring their concentrations in permeate solutions due to larger rejections by the membranes. The solutes were first dissolved in a small amount of methanol, and then diluted with distilled-deionised water. Solution pH values in separation experiments were adjusted using standard HCl and NaOH solutions. The membrane efficiency tests were conducted at 25°C for 3 to 7 hours until the permeate became stable. The permeate samples were taken at 30 minute intervals for analysis.

Measurement of membrane zeta-potential

Membrane zeta-potential was measured with Zeta-CAD (CAD Instruments Ltd., France) using streaming potential method in 1×10^{-3} mole l^{-1} NaCl solution. The details of the method can be found elsewhere (Ozaki *et al.* 2002).

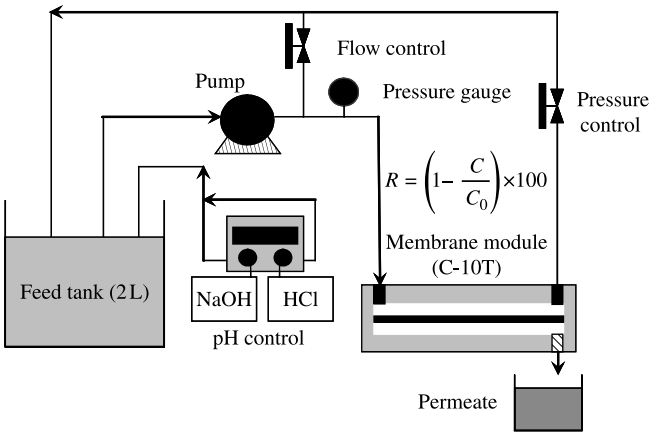

Figure 1 | Schematic diagram of experimental setup for membrane efficiency tests.

Solute adsorption tests

The amounts of PPCPs/EDCs adsorbed onto a membrane in equilibrium were determined using a laboratory scale batch test cell (C70-B, Nitto Denko Corporation, Japan) with flat sheet membranes. The cell volume was 350 mL and the effective surface area of membrane was 32.0 cm^2. Methoxalen (MX, MW: 216.2, log K_{ow}: 1.93), sulpiride (SPD, MW: 341.4, log K_{ow}: 0.57) and metoclopramide (MCP, MW: 299.8, log K_{ow}: 2.62) were also tested in addition to the solutes listed in Table 2. Solution of a PPCP (or EDC) adjusted to pH3, at which most of compounds tested were undissociated, was poured into the cell and a small amount of samples were taken for analysis at the specified time interval during 24 hours experiments. Magnetic bars and stirrers were used for mixing the solution in the cell for preventing concentration polarisation. Initial solute concentrations in these experiments were the same as those in membrane efficiency tests.

Measurement of diffusion coefficient

Diffusion experiments were carried out using cylindrical diffusion cells (Figure 2) made of quartz-glass (length: 28 cm, internal diameter: 8 cm and volume: 1.25 L) to evaluate diffusion coefficients of the PPCPs and EDCs. Each cell consisted of two compartments. A flat-sheet membrane with an effective membrane surface area of 50.3 cm^2 was placed between the two compartments and clamped tightly. One compartment contained solution of a PPCP (or EDC) while an equal volume of distilled-deionised water was poured into another compartment. The solute concentrations employed in diffusion experiments were the same as those in membrane efficiency tests. The solutions in both the compartments were continuously mixed using magnetic stirrers and bars. The experiments were carried out at a fixed pH for 7 to 14 days, and samples were taken every 24 hours for analysis.

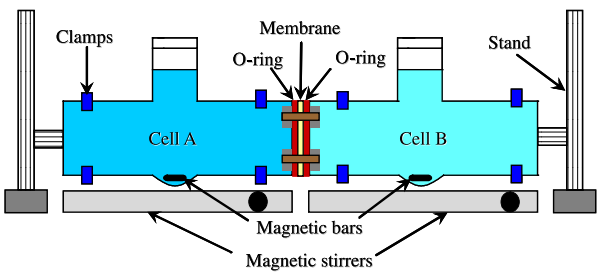

Figure 2 | Schematic diagram of experimental setup for diffusion tests.

Analyses

Concentrations of BPA, E2, NP, DEP, NPX and CA in permeate, feed solutions and other samples were measured using a spectroflurometer (FP-6300, JASCO Corporation). Concentrations of other chemicals used were measured by a spectrophotometer (UV-160A, Shimazdu, Japan). Rejections of the PPCPs and EDCs by the membranes were calculated as mentioned elsewhere (Ozaki & Li 2002).

RESULTS AND DISCUSSION

Effects of solute dissociation on rejection

The pH dependency of rejections of compounds with hydroxyl functional group by UTC-60 is illustrated in Figure 3. The rejections greatly increased with pH in the region over their pK_a values. The pK_a values of 2,4 DCP and TCS are 8.05 and 8.14 respectively, and those of other compounds are around 10 (Table 2). Dissociation of the compounds with large pK_a values was greatly enhanced with increasing solution pH. On the other hand, their rejections in neutral and acidic regions were almost constant and lower than the values in alkaline region. Similarly increased dissociation of pharmaceuticals with carboxyl functional group greatly enhanced their rejections by UTC-60 in acidic region (Figure 4). The pK_a values of

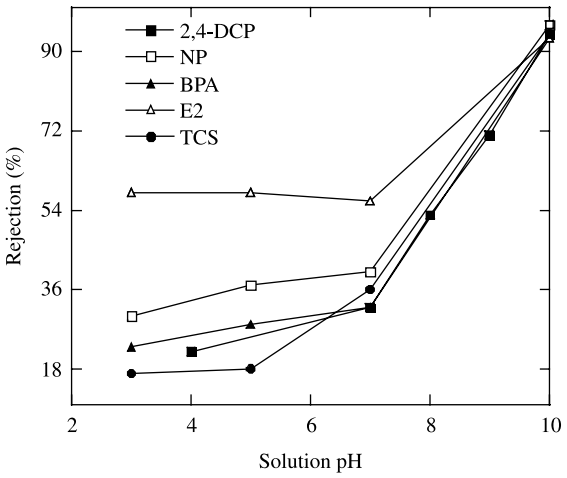

Figure 3 | Rejection of PPCPs with hydroxyl functional group (UTC-60) functional.

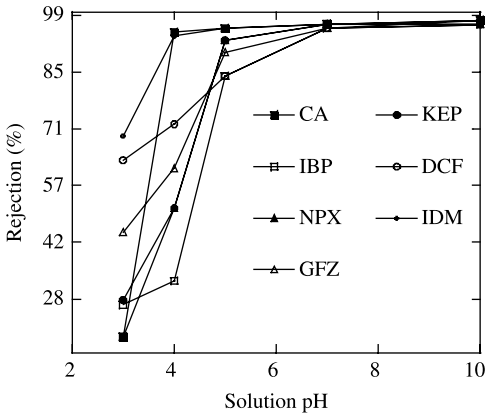

Figure 4 | Rejection of PPCPs with carboxyl group (UTC-60).

those compounds vary between 3 and 5. Rejections of the compounds at pH3, which is less than their pK_a values, were the lowest ones.

Membrane zeta potential values for UTC-60 and UTC-70U changed from positive to negative almost in similar fashions, with increasing solution pH as illustrated in Figure 5. The increase in negative potential values for both the membranes was drastic up to pH 6 to 7, but the rates of increase were rather slow from neutral to alkaline pH regions.

It is apparent from the experimental results presented so far that electrostatic repulsion between charged membrane surface and dissociated pharmaceutical molecules was presumably a dominant force for their rejections by relatively loose membranes such as UTC-60, which was consistent with the findings of previous investigations (Bellona *et al.* 2004). However, rejections of the same pharmaceuticals by UTC-70U were larger (Figure 6) than those by UTC-60 (Figure 4), especially at pH 3.0.

The rejections varied between 85 and 98% for UTC-70U and between 20 and 70% for UTC-60. Rejections of the PPCPs with hydroxyl functional group excluding 2,4-DCP by UTC-70U (not shown) were similar to those of the PPCPs with carboxyl functional group by the membrane. The comparatively lower rejections for 2,4-DCP by UTC-70U may be the result of its smaller pK_a value and molecular weight.

It is evident from the results and discussion presented so far that solution pH is a key parameter for separation of PPCPs/EDCs by LPRO membranes. Since solution pH greatly influences the dissociation of compounds, it would be interesting to correlate the dissociation of the PPCPs/EDCs with their rejections. Such a relationship for the tested PPCPs/EDCs with UTC-60 and UTC-70U is illustrated in Figure 7. The degree of dissociation (α) values for the compounds were calculated using a non-modified form of the Henderson–Hassselbach Equation (Braeken *et al.* 2006).

$$\alpha = \frac{100}{1 + 10^{(\mathrm{p}K_a - \mathrm{pH})}} \quad (1)$$

Unlike with solution pH, rejections by the membranes were not directly correlated with α (Figure 7). However, more than 80% of rejections by UTC-60 were obtained in the region for $\alpha > 0.5$, that is, in the solution pH region over solute pK_a values, presumably due to electrostatic repulsion

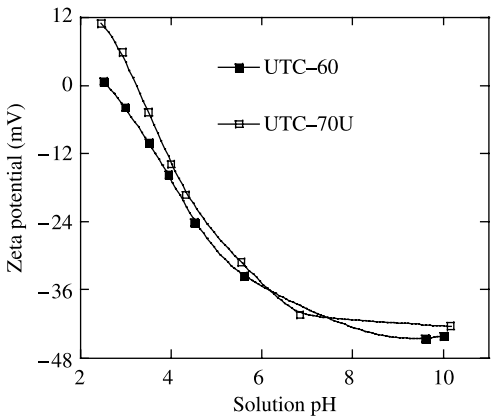

Figure 5 | Dependence of membrane zeta potential on solution pH functional.

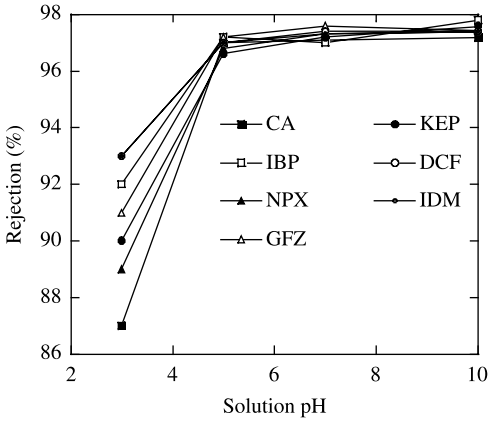

Figure 6 | Rejection of PPCPs with carboxyl group (UTC-70U).

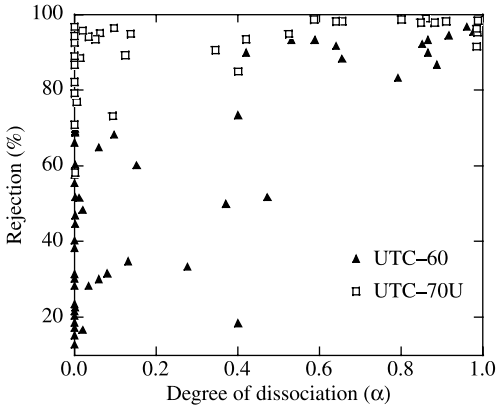

Figure 7 | Relationship between rejection and degree of dissociation.

between charged membrane surface and dissociated molecules. Over 90% of rejections by UTC-70U for the majority of the tested compounds suggested that molecular sieving rather than electrostatic repulsion was a dominant factor associated with relatively tight membranes (e.g. UTC-70U), and dissociation did not play a major role on the rejections.

Rejection of undissociated solutes

Rejections of undissociated pharmaceuticals at different solution pH values by UTC-60 and UTC-70U are illustrated in Figures 8 and 9, respectively. The rejection of each compound was almost constant in the pH range studied, as their rejections were not governed by electrostatic repulsion. UTC-60, being a relatively looser membrane than UTC-70U, there was presumably a larger size

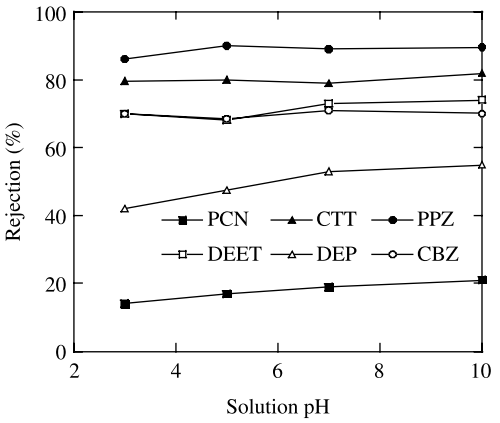

Figure 8 | Rejection of undissociated PPCPs by UTC-60.

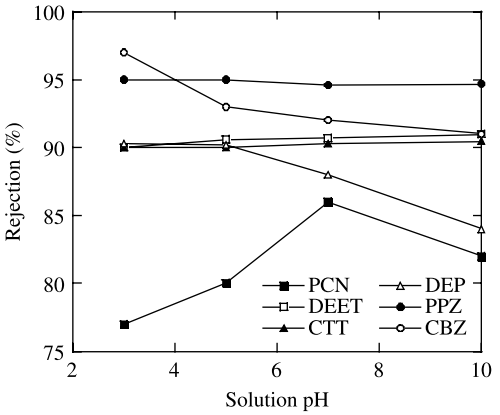

Figure 9 | Rejection of undissociated PPCPs by UTC-70U.

exclusion effect in the case of UTC-70U for the same compounds. The rejections of six compounds by UTC-60 (Figure 9) increased in the rough order of their molecular weight, but the rejection order was not always in agreement with the order of their molecular weights. For instance, CBZ molecules are larger in terms of molecular weight among the pharmaceuticals studied, but its rejection was similar to that of DEET. In this investigation, molecular width values of PPCPs/EDCs (Kiso *et al.* 1992) did not have good correlations with their rejections (UTC-60, $\alpha < 0.5$).

Based on the results and discussion presented so far, the size exclusion effect presumably resulted in a drastic increase in rejections of the pharmaceuticals by relatively tight membranes such as UTC-70U. In addition, size exclusion might play an important role on the rejections, even with a relatively loose membrane such as UTC-60. To some extent, molecular weight could be a simple and useful parameter to describe the rejection performance of PPCPs/EDCs by LPRO membranes. The results of this investigation are consistent with the results of earlier investigations (Kimura *et al.* 2004). However, other factors should also be taken into consideration for a more precise understanding on solute retention mechanisms of LPRO membranes.

Relation between log K_{ow}/log K_{mw} and rejection

The amounts of PPCPs/EDCs adsorbed on a UTC-60 membrane surface and experimentally determined distribution coefficients (K_{mw}) for the solutes at pH3 in equilibrium condition are presented in Table 3. The K_{mw} values were calculated using the equation: $K_{mw} = Q/C$,

Table 3 | Adsorbed PPCPs/EDCs and log K_{mw}

Abbrev.	Q (μg/cm^2)	log K_{mw}
NPX	1.07	0.13
CA	1.12	−0.92
DCF	–	–
CBZ	1.11	−0.95
GFZ	20.63	0.41
IBP	14.66	−0.02
IDM	–	–
KEP	11.24	0.09
PPZ	0	–
CTT	0.80	−1.09
DEET	1.34	−2.37
PCN	2.62	−2.07
MX	2.05	0.38
TCS	73.54	1.35
SPD	2.70	−0.54
MCP	9.72	0.05
E2	2.60	0.40
BPA	5.40	−0.24
NP	9.04	2.27
DEP	5.88	−0.21
2,4-DCP	31.82	0.65

where Q is the amount of solute adsorbed per unit surface area (μg cm^{-2}) of a membrane, and C is the solute concentration in equilibrium (mg L^{-1}).

Relatively large amounts of NP and TCS, which are characterised by high hydrophobicity values (i.e. large octanol–water partition coefficient (K_{ow})), were adsorbed to the membrane surface resulting to their greater K_{mw} values, while PPZ showed no adsorption at all. The K_{ow} values of E2 and GFZ were also high (>0.4), while K_{mw} values for hydrophilic, polar and undissociated compounds, such as CBZ, PPZ, DEET and PCN, were very small.

K_{ow} is accepted as a measure of hydrophobicity of organic micropollutants, and also regarded as a key parameter in membrane filtration (Bellona *et al.* 2004). Almost a linear relationship was observed between log K_{ow} and log K_{mw} values for the solutes employed in this investigation (Figure 10). The dipole moment may influence solute retention in membrane filtration (Kimura *et al.* 2004).

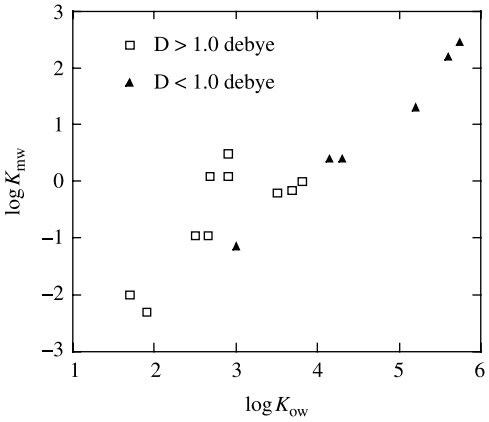

Figure 10 | Relationship between log K_{ow} and log K_{mw} (pH 3.0, UTC-60) and log K_{ow}.

However, no satisfactory research data are available on this aspect. It may be apparent from Figure 10 that the compounds with $D < 1.0$ had a higher tendency to partition to the organic phase than those with $D > 1.0$. Rejections of the compounds were also plotted against their log K_{ow} values considering their dipole moment values (Figure 11). Rejection of the solutes with comparatively low D (<1.0 debye) decreased with increasing log K_{ow} values, presumably due to increased hydrophobicity. After their adsorption to membrane, the solutes with larger K_{ow} (K_{mw}) values might be transported through the membrane. On the other hand, no clear trend was observed in the rejection of compounds with comparatively high D values (> 1.0 debye). With log K_{ow} values roughly in the range of 3.0 to 6.0, rejections of the solutes with D values larger than 1.0 debye seemed to be lower than those with D values smaller than 1.0 debye. This data might support the result of

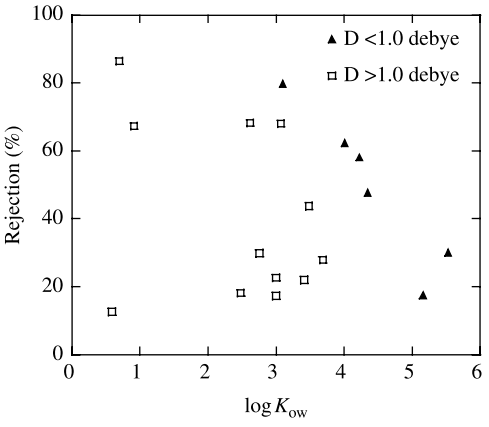

Figure 11 | Relationship between rejection (pH 3.0, UTC-60).

Van der Bruggen *et al.* (2002) that higher D results in lower retention of pesticides by NF. However, PPZ and CBZ with small K_{ow} and comparatively high D values were efficiently rejected by the membrane, probably due to their high polarity resulting in their reduced adsorption to the membrane. The poor rejection of PCN with small K_{mw} may be attributed to it smaller molecular weight.

Significance of diffusion in rejection

Diffusion coefficient (D_p) values of the PPCPs and EDCs were measured in laboratory experiments. The values were calculated using the following equation:

$$C_{B(t)} - C_{A(t)} = (C_{B(t=0)} - C_{A(t=0)})\exp\left[-\frac{AD_p}{L}\left(\frac{1}{V_B}+\frac{1}{V_A}\right)t\right] \quad (2)$$

where, C_A and C_B are the solute concentrations (mol. m^{-3}) in cell A and B, respectively, A is the effective surface area of membrane (m^2), L is the membrane thickness (m), and V_A and V_B are the volume of cells A and B (m^3), respectively (Figure 2). Since real D_p values in membrane filtration cannot be measured, the values obtained in this investigation are the apparent ones that includes the influences of electrostatic repulsion, molecular sieving, adsorption and so on.

The D_p values with the membrane in this investigation are smaller than the values in normal cases (10^{-8} to $10^{-10}\,m^2\,s^{-1}$), presumably due to several influencing factors such as electrostatic repulsion, adsorption and molecular sieving. Rejections of the solutes by UTC-70U decreased with increasing D_p values, as illustrated in Figure 12. The rejections with comparatively low dipole moment values (<1.0 debye) are understandable as molecules with large K_{ow} value were most likely adsorbed on membrane surface and/or pores, and passed through the pores by diffusion resulting in larger D_p values. However, the rejections of solutes with comparatively high D values (>1.0 debye) also decreased with increasing D_p values in this investigation. This result may indicate that diffusion and/or convection through the membrane, rather than hydrophobicity/hydrophilicity of the solutes, could have been the dominant factors in their rejections.

The results once again pointed out that adsorption, size exclusion, diffusion and/or convection and electrostatic exclusion simultaneously played roles on rejections of the PPCPs and EDCs at their low dissociated states, while electrostatic exclusion dominated other mechanisms at their higher dissociation.

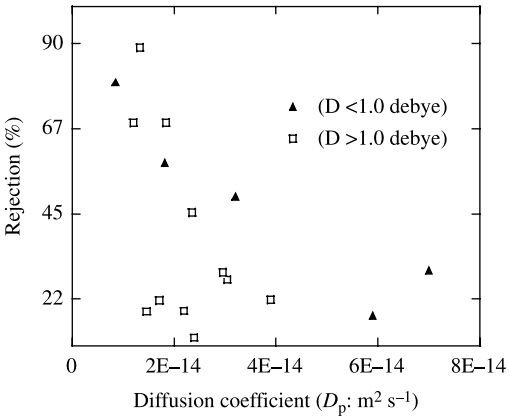

Figure 12 | Relation between rejection and D_p (UTC-70U).

CONCLUSIONS

The rejections of the undissociated PPCPs and EDCs selected in this investigation were most likely governed by adsorption, size exclusion and diffusion simultaneously. Size exclusion was presumably dominant, especially with the tight membrane (UTC-70U). In addition, parameters expressing hydrophobicity of the PPCPs/EDCs such as K_{ow} influenced the rejections. For instance, rejections of the solutes with comparatively low dipole moment (<1.0 debye) decreased with increasing K_{ow}. The molecules with a large K_{ow} value were most likely adsorbed on membrane surface and/or pores, and passed through the pores by diffusion resulting in larger D_p values. The solute rejections decreased with D_p values irrespective of their dipole moment values in this investigation. Rejections of the PPCPs and EDCs with hydroxyl and carboxyl functional groups by UTC-60 increased with pH. Over 80% rejections were obtained with $\alpha > 0.5$, that is, in solution pH region over solute pK_a values. Electrostatic repulsion between charged membrane surface and dissociated pharmaceuticals presumably played a key role on their rejections. especially by relatively loose RO membrane. Therefore, assessing dissociation degrees of organic micropollutants at desired

pH values can be the first and key step to obtain an insight of their rejection mechanisms by polyamide membranes.

ACKNOWLEDGEMENTS

This research was carried out under the project "Collaboration with Local Communities" for private universities: matching fund subsidy, and funded by the Ministry of Education, Culture, Sports, Science and Technology, Japan (2007–2011).

REFERENCES

Agenson, K. O., Oh, J. & Urase, T. 2003 Retention of a wide variety of organic pollutants by different nanofiltration/reverse osmosis membranes: controlling parameters of process. *J. Membr. Sci.* **225**(1–2), 91–103.

Bellona, C., Drewes, J. E. & Amy, G. 2004 Factors affecting the rejection of organic solutes during NF/RO treatment: a literature review. *Water Res.* **38**(12), 2795–2809.

Braeken, L., Bettens, B., Boussu, K., Meeren, P. V., Cocquyt, J., Vermant, J. & Bruggen, B. V. 2006 Transport mechanisms of dissolved organic compounds in aqueous solution during nanofiltration. *J. Membr. Sci.* **279**(1-2), 311–319.

Juan, J. M., Laura, E., Salbador, S., Rosa, M. V. & Maria, J. M. 2004 Chromatographic estimation of apparent acid dissociation constant (pK_a) in physiological resembling conditions. A case study: Ionizable non-steroidal anti-inflammatory drugs. http://www.biochempress.com/iecmd_2004_05.html (accessed on September 13th 2007).

Kimura, K., Toshima, S., Amy, G. & Watanabe, Y. 2004 Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes. *J. Membr. Sci.* **245**(1–2), 71–78.

Kiso, Y., Kitano, T., Jinno, K. & Miyagi, M. 1992 The effects of molecular width on permeation of organic solute through cellulose acetate reverse osmosis membranes. *J. Membr. Sci.* **74**, 95–103.

Nghiem, L. D. & Schafer, A. I. 2005 Nanofiltration of hormone mimicking trace organic compounds. *Sep. Sci. Technol.* **40**, 2633–2649.

Nghiem, L. D., Shaefer, A. I. & Elimelech, M. 2006 Role of electrostatic interactions in the retention of pharmaceutically active contaminants by a loose nanofiltration membrane. *J. Membr. Sci.* **286**, 52–59.

Ozaki, H. & Li, H. 2002 Rejection of organic compounds by ultra-low pressure reverse osmosis membrane. *Water Res.* **36**, 123–130.

Ozaki, H., Ikejima, N., Matsui, S., Terashima, Y., Takeda, S., Tari, I. & Li, H. 2002 The role of membrane (-potential in solute rejection by low pressure reverse osmosis. *Water Sci. Technol. Water Supply* **2**(5–6), 321–328.

Pronk, W., Palmquist, H., Biebow, M. & Boller, M. 2006 Nanofiltration for the separation of pharmaceuticals from nutrients in source-separated urine. *Water Res.* **40**(7), 1405–1412.

Snyder, S. A., Westerhoff, P., Yoon, Y. & Sedlak, D. L. 2003 Pharmaceuticals, personal care products and endocrine disruptors in water: implications for the water industry. *Environ. Eng. Sci.* **20**(5), 449–469.

Urase, T. & Sato, K. 2007 The effect of deterioration of nanofiltration membrane on retention of pharmaceuticals. *Desalination* **202**, 385–391.

Van der Bruggen, B., Braeken, L. & Vandecasteele, C. 2002 Evaluation of parameters describing flux decline in nanofiltration of aqueous solutions containing organic compounds. *Desalination* **147**, 281–288.

Yoon, Y., Westerhoff, P., Snyder, S. A. & Wert, E. C. 2006 Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. *J. Membr. Sci.* **270**, 88–100.