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The effect of deterioration of nanofiltration membrane on retention of pharmaceuticals

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Abstract

The retention of 8 acidic and 2 neutral pharmaceuticals in nanofiltration (NF) was investigated by a loose NF membrane and a tight NF membrane. The retention change due to the exposure to chlorine was studied. The retention of pharmaceuticals was affected by the electric repulsion effect in addition to the size exclusion effect. In the case of the loose NF membrane, the retention of pharmaceuticals was more sensitive to the exposure to chlorine than salt retention because both the decrease in electric repulsion effect and the increase in pore size affected the permeation of pharmaceuticals. On the other hand, in the case of the tight NF membrane, the retention of acidic pharmaceuticals were maintained at higher range at neutral pH range even after exposure to chlorine, though the increase in the pore size was obvious judging from the decrease in the retention of pharmaceuticals in the acidic solution environment.

Keywords: Pharmaceuticals; Contact to chlorine; Nanofiltration; Reverse osmosis

1. Introduction

Pharmaceutical substances have been recognized since 1990s as new unregulated contaminants [1–3]. On the contrary to hydrophobic and persistent compounds such as dioxins, some of pharmaceutical compounds are relatively hydrophilic and biologically persistent [4]. Their hydrophilic characteristics make it difficult to be removed in biological processes and in adsorption processes because they tend to remain in the water phase due to their hydrophilic characters [5,6]. Biological processes and adsorption processes may not be efficient on the removal of this group of substances.

The separation mechanism of nanofiltration includes both electric repulsion and size sieving [7].

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Nanofiltration membranes can easily retain solutes with larger molecular size and with electric charge, including pharmaceutical compounds. A group of pharmaceutical substances is one of the target groups for removal in treatment process considering wastewater reclamation and reuse. One of the advantages using nanofiltration is the treatment of these hydrophilic and biologically persistent compounds.

Cellulose acetate and polyamides are widely used for the materials of nanofiltration and reverse osmosis membranes. Polyamide membranes easily loose their retention characteristics by the exposure to chlorine, which is often used for the cleaning of membrane processes [8,9]. In the long term use of membranes, the change in retention characteristics by the contact to oxidants is important. This paper focuses on the change in retention characteristics by the degradation of membranes due to the contact to chlorine with taking the example of retention of pharmaceuticals. It is emphasized which effect of electric repulsion or size sieving is damaged in the contact to chlorine.

2. Materials and method

2.1. Target compounds

The target compounds in this study were clofibric acid (CA), gemfibrozil (GFZ), ibuprofen (IBP), fenoprofen (FEP), ketoprofen (KEP), naproxen (NPX), diclofenac (DCF), indomethacin (IDM), propyphenazone (PPZ) and carbamazepine (CBZ). CA is a metabolite of a certain type of lipid regulators like clofibrate, etofibrate and etofyllinclofibrate. GFZ is a lipid regulator. IBP, FEP, KEP, NPX, DCF, IDM, PPZ are commonly used non-steroidal anti-inflammatory drugs. CBZ is an antiepileptic agent. Table 1 shows the physical and chemical properties of these compounds. Two size parameters, the molecular width and the molecular radius, were calculated by the Kiso's method [10], with the use of Chem-Office software. Molecular width is the half of square root of minimum square of the objected molecule to a plane perpendicular to the line between the most distant two atoms of the target compounds. Molecular radius is the minimum diameter of the circle which includes the objected molecule to the same plane. The dipole moment of the target compounds was calculated with the same software.

2.2. Nanofiltration membranes

Nanofiltration membranes used in this study are C-membrane (under development by Toray) with nominal salt retention of 85% and nominal glucose retention of 95%, and ES-20 (supplied by Nitto Denko) with nominal salt retention of 99.7%. C-10T membrane module (supplied by Nittodenko with effective surface area of 60 cm^2) was used for the retention experiments. Virgin membranes and membranes degraded by chlorine were used. The condition for the degradation is 6 h for C-membrane and 24 h for ES-20 in 1250 mg/L sodium hypochlorite solution without pH control.

2.3. Nanofiltration experiment

The feed solution was prepared to contain 100 μg each of pharmaceuticals in 1 litter with the addition of 5% landfill leachate at a solid waste disposal site to simulate artificial treated wastewater and to reduce adsorption of pharmaceuticals onto membrane surface. The solution pH was adjusted by sodium hydroxide or by hydrochloric acid at 3, 5, 7 and 9. The bulk samples and permeate samples were taken at 2 and 4 h after the start of experiment to confirm that the samples were taken at steady-state condition.

2.4. Chemical analysis

The water samples containing target pharmaceutical substances were mixed with internal standards, 2,3-dichlorophenoxyacetic acid and chrysene-d12, and pH was adjusted at 2 by adding hydrochloric acid. This solution was

Table 1
Physical and chemical properties of target compounds

S.No.	Chemical name	Abbrev.	Mol. formula	Mol. weight	log K_{ow}	Dipole [Debye]	pK_a	Mol. width (nm)	Mol. radius (m)
1	Clofibric acid	CA	$C_{10}H_{11}ClO_3$	214.65	2.57	1.862	3.00	0.262	0.274
2	Gemfibrozil	GFZ	$C_{15}H_{22}O_3$	250.34	4.77	0.833		0.315	0.379
3	Ibuprofen	IBP	$C_{13}H_{18}O_2$	206.29	3.97	2.089	4.91	0.276	0.295
4	Fenoprofen	FEP	$C_{15}H_{14}O_3$	242.28	3.9	1.991	7.3	0.293	0.299
5	Ketoprofen	KEP	$C_{16}H_{14}O_3$	254.29	3.12	3.604	4.45	0.295	0.337
6	Naproxen	NPX	$C_{14}H_{14}O_3$	230.27	3.18	3.168	4.15	0.284	0.297
7	Diclofenac	DCF	$C_{14}H_{11}C_{12}NO_2$	296.16	4.51	0.966	4.15	0.293	0.414
8	Indomethacin	IDM	$C_{19}H_{16}ClNO_4$	357.8	4.27	1.432	4.5	0.348	0.473
9	Propyphenazone	PPZ	$C_{14}H_{18}N_2O$	230.31	1.94	4.100		0.286	0.341
10	Carbamazepine	CBZ	$C_{15}H_{12}N_2O$	236.28	2.45	3.943		0.315	0.319

applied to 3M-ODS disk filter after it was rinsed with 10 mL of methanol and 10 mL of acidic pure water. The target substances were recovered from the disk filter by 5 mL of methanol. Pentafluorobenzyl derivatization was carried out before GC/MS analysis using DB-5 MS column, at the temperature range programmed from 100 to 260°C [11,12]. PPZ and CBZ, which require no derivatization in the analysis, were quantified in the same chromatogram, though CBZ have to be quantified by a peak derived from a thermally degraded product of CBZ. 2,4-Dichlorobenzoic acid was added to check the recovery in the derivatization step.

3. Results and discussion

Fig. 1 shows the salt retentions and volume flux measured at different pH by the virgin C-membrane and by degraded C-membrane. Volume flux was increased to the double by the degradation of the membrane. Chloride retention was decreased except in the case of pH of 3 and the dependence of salt retention upon pH became small after degradation of the membrane. The exposure of membrane to chlorine spoiled to a certain extent the electric exclusion characteristics of the membrane because chloride retention is affected mainly by the electric repulsion effect.

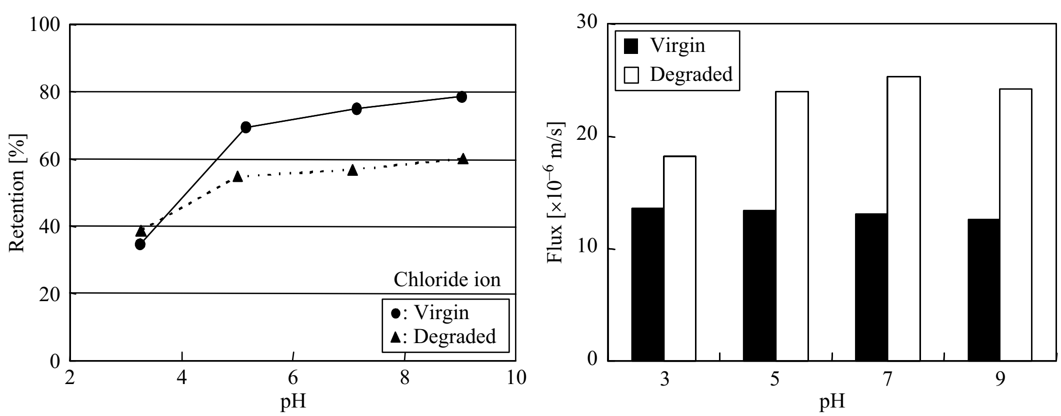

Fig. 1. Salt retentions and volume flux measured at different pH in the case of C-membrane.

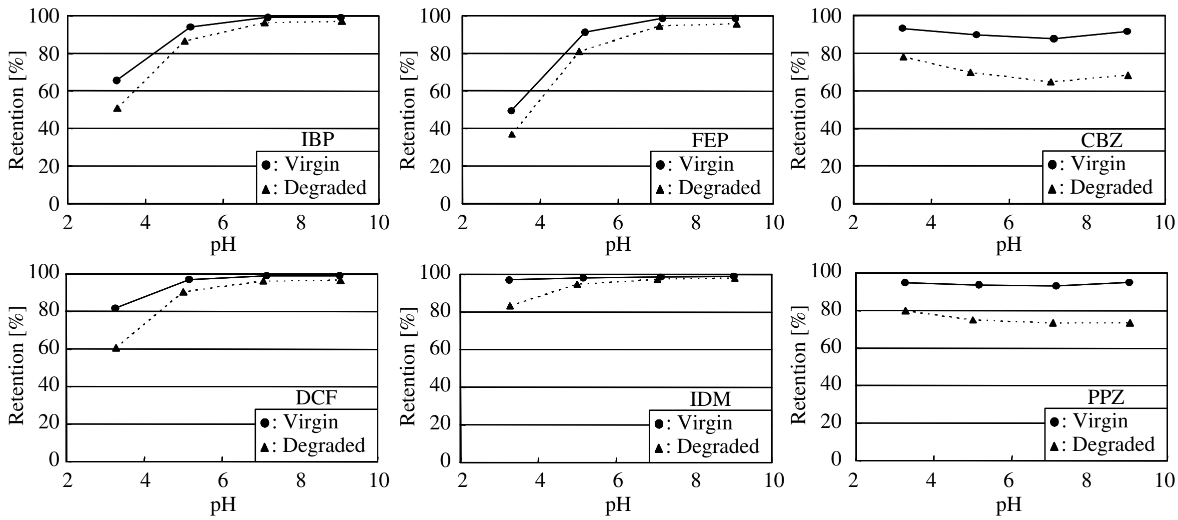

Fig. 2. The retention of pharmaceuticals measured at different pH by C-membrane.

Fig. 2 shows the retention of pharmaceuticals measured at different pH by the virgin C-membrane and by degraded C-membrane. The retention of PPZ and CBZ which has no acidic functional groups were not affected by pH of the solution, while retention of acidic pharmaceuticals, CA, GFZ, IBP, FEP, KEP, NPX, DCF, and IDM were affected by pH. These acidic pharmaceuticals are ions at neutral and alkali pH and they are neutral solutes in acidic pH judging from pK_a value. The retention dependence on pH can be explained by the ionization of the target solutes because the retention of ions is higher in nanofiltration than that of neutral solutes [7,13,14]. At lower pH range, where the acidic pharmaceuticals are neutral solutes, larger solute like IDM gave higher retention, because size parameter is the most important parameter in the retention of polyamide nanofiltration membranes [15,16], while in the neutral pH condition, the size parameter like molecular weight was not a dominant factor determining retention as shown in Fig. 3.

In the neutral pH condition, the retention of chloride was decreased from 75 to 57% by the

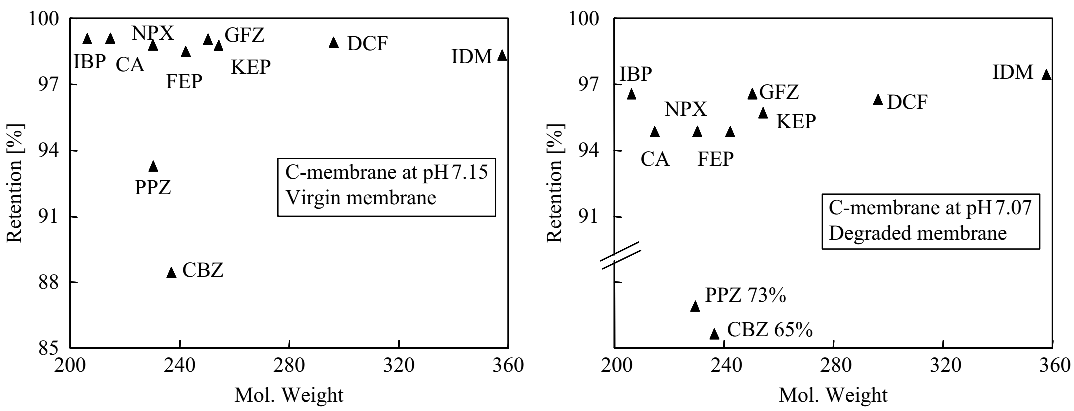

Fig. 3. The retention of pharmaceuticals by C-membrane before and after the degradation of the membrane.

degradation of the membrane as shown in Fig. 1. This decrease in retention corresponds to the increase in permeability by 72%. Judging from the increase in the salt permeability, the exposure to chlorine decreased the effective charge of the nanofiltration membrane. At the same time in the neutral pH condition, the permeability of pharmaceuticals increased by 60 to 600% depending on the species of pharmaceuticals as shown in Fig. 3. The permeation of pharmaceuticals was more sensitive to the degradation of the membrane than salt permeation. Judging from the permeation of PPZ and CBZ, and from the permeation of other pharmaceuticals in the acidic pH range, the pore size of the nanofiltration membrane was increased by the exposure to chlorine. The reason why the permeation of the pharmaceuticals was more sensitive to the degradation of the membrane than salt permeation is that both decrease in electric charge repulsion and increase in pore size affected the retention of the pharmaceuticals in the neutral pH range. Watters et al. reported that the size sieving characteristics can be maintained after degradation of a polyamide nanofiltration membrane [8]. However our study showed that the size sieving characteristics was affected by the exposure to chlorine and decrease in retention of both neutral solutes and ions was observed.

Fig. 4 shows the salt retentions and volume flux measured at different pH by the virgin ES-20 membrane and by degraded ES-20 membrane, which is a more tight membrane than C-membrane. Volume flux was increased to the double by the degradation of the membrane. Chloride retention was decreased except in the case of pH of 3 and the retention of salt at neutral pH was decreased from 99.2% to 96.2%, which corresponds to 390% increase in permeability.

Fig. 5 shows the retention of selected pharmaceuticals measured at different pH. The retention of the pharmaceuticals by the virgin membrane was very high. For example the retention of IBP was in the range of 99.88–99.95% regardless of pH by the virgin membrane and retention of pharmaceuticals at neutral pH was above 99.84% regardless of the pharmaceutical species. However, after degradation of the membrane, the retention of the pharmaceuticals decreased especially in the lower pH range, though the retention of acidic pharmaceuticals in the neutral pH was maintained above 99.55%.

The decrease in the retentionl of acidic pharmaceuticals at lower pH and the decrease in the

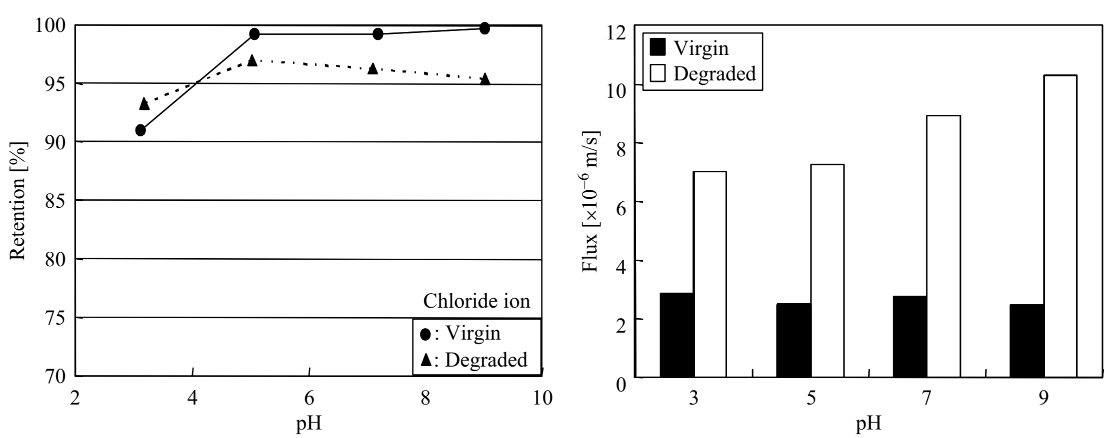

Fig. 4. Salt retentions and volume flux measured at different pH in the case of ES-20 membrane.

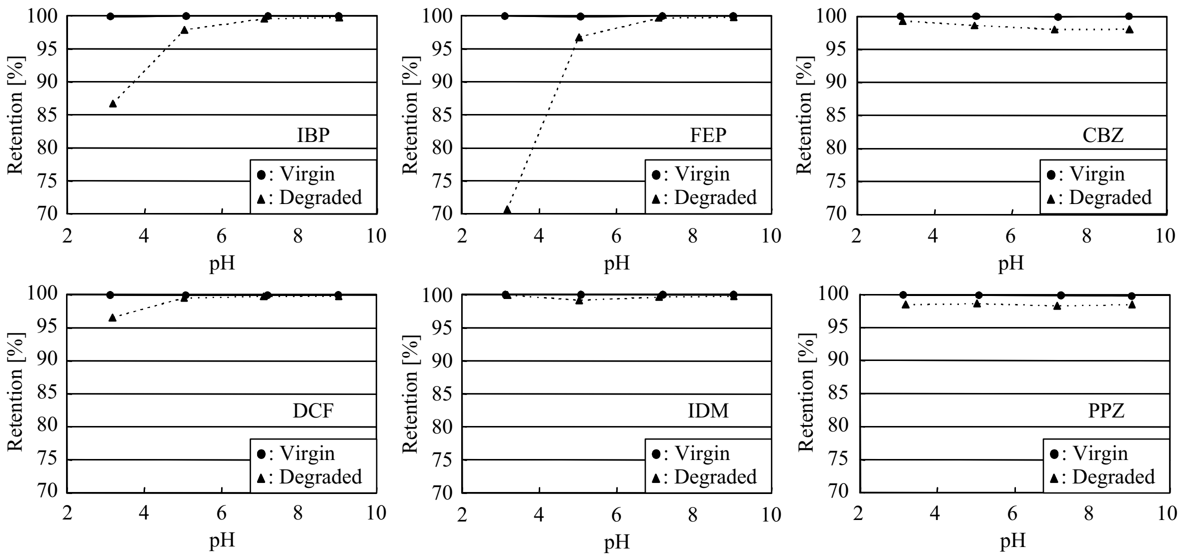

Fig. 5. The retention of selected pharmaceuticals measured at different pH by ES-20 membrane.

retention of neutral pharmaceuticals can be explained by the increase in the pore size of the ES-20 membrane. However, the electric charge decrease, as can be seen from the decrease in salt retention, did not affect the retention of pharmaceuticals in the neutral pH range, though the retention of neutral solutes PPZ and CBZ was decreased due to the pore size increase. Taniguchi et al. reported that permeation of boron, which is neutral solute in the neutral pH, was in proportional to salt permeation in the experiment of chlorine degradation in the case of seawater desalination by a reverse osmosis membrane [17]. However, our study shows more complicated relation between the salt retention and the retention of other solutes with dependence on pH.

4. Conclusion

The retention of 8 acidic and 2 neutral pharmaceuticals were investigated by a loose NF and a tight NF membranes and the retention change due to the exposure to chlorine was studied. The retention of pharmaceuticals was affected by the electric repulsion effect in addition to the size exclusion effect. The retention of acidic pharmaceuticals by the loose NF membrane was increased with increase in solution pH, as can be explained by the dissociation to ions of the pharmaceuticals. The retention of the pharmaceuticals by the tight NF membrane was kept high regardless of a species of the pharmaceuticals at all pH range. In the case of the loose type NF membrane, the retention of pharmaceuticals was more sensitive to the exposure to chlorine than salt retention because both the decrease in electric repulsion effect and the increase in pore size affected the permeation of pharmaceuticals. On the other hand, in the case of the tight NF membrane, the retention of acidic pharmaceuticals were maintained at higher range at neutral pH range even after exposure to chlorine, though the increase in the pore size was obvious judging from the decrease in the retention of pharmaceuticals in the acidic solution environment.

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