Rejection of micropollutants by membrane filtration

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Abstract

There is currently great interest in the removal of hazardous micropollutants to concentrations in the lower level than microgram per litter. For example, endocrine disrupting chemicals (EDCs) are exogenous substances which interfere with the normal function of hormones at very low concentration in human body. Many people and animals have been contaminated with EDCs taken in through water and food. Membrane technology is to be expected for one of the best way to concentrate the micro-pollutants in water and wastewater prior to the degradation of them. The effort to reduce the cost of energy required for reverse osmosis (RO) operation have led to the development of low pressure reverse osmosis (LPRO) membranes, categorically nanofiltration, for operation under very low pressure (below 0.5 MPa). Furthermore, the ultra-low pressure reverse osmosis (ULPRO) membranes, which are a new type of nanofiltration membrane, have received attention especially for their application in the field of water purification and wastewater treatment. Nanofiltration and ULPRO remove not only inorganic pollutants but also organics under lower pressure. In addition, the application of those membrane technologies to water and wastewater has widened their potentials to reject micro-pollutants in dissolved form such chemicals as endocrine disrupting chemicals (EDCs). In this study, we found that six types of EDCs: Bisphenol A (BPA), 17β-estradiol (E2), Nonylphenol (NP), Diethylphthalate (DEP), 2,4-Dichlorophenol (2,4-DCP), and Pentachlorephenol (PCP) could be rejected very effectively by the ULPRO membrane. Although the rejection of EDCs by using a relatively loose membrane (LPRO) showed lower values in a single solution system, the E2 rejection in mixture system of humic acid and E2 was almost 100%. In addition, it was found that the rejection properties of EDCs by LPRO membranes were affected by coexisting substances in water or wastewater. This paper also presents the data on the membrane rejection performance of dioxins, the most hazardous substance of EDCs, in the liquid of river sediment.

Keywords : Membrane separation, low pressure reverse osmosis (LPRO), endocrine disrupting chemicals, membrane ζ-potential

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1. Introduction

Membrane technology has played an important role in controlling water pollution control as well as in the production of clean water. The major membrane processes used in water and wastewater treatment fall into four major categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). These processes are classified in terms of the range of materials separated and the applied pressure as listed in Table 1. MF and UF separate suspended matter, organic particles, and biological particles such as algae, bacteria, and viruses, while NF and RO can reject dissolved organic matter and ions. In particular, in addition to its role in brackish and sea water desalination, the application of RO to water pollution control has become more widespread with the introduction of a range of membrane materials which could offer better characteristics such as high water flux rates, high salt rejection, tolerance to chlorine and other oxidants, resistance to biological attack, relatively low cost, ease of formation into thin films or hollow fibres, chemical stability, and ability to withstand high temperatures (Brandt et al. 1993).

Table 1

General description of RO,NF,UF and MF membranes

Particulars	*Raverse osmsis (RO)*	*Nanofiltration (NF)*	*Ultrafiltation (UF)*	*Microfiltration (MF)*
Pore size	No detectable pore size	2~5nm	3~10nm	10nm~1μ m
Retain Particules (MW)	<350	>150	1,000~300,000	>300,000
Applied pressure	1~10 MPa	0.3~1.5MPa	0.01-0.3MPa	0.005－0.2Mpa
Material	aromatic palyamide cellulose acetate	aromatic palyamide Polyvinyl-alcohol	Polysulfon polyimide polyacrynitrile ceramics	polyethylene polyplopylene polyvinylidenfluoride ceramics
Main usage	-Desalination of brackish and seawater -Production of ultra pure water	-Removal of micro pollutants -Desalination of brackish water -concentration of chemicals	-drimking water production -clarification of fruit juice -membarance bioreactor -home water purifiers	-Removal of fine paticles and bacteria Pretreatment for RO and UF -Membrane bioreactor

Being pressure-driven systems, the results of the application of RO membranes have led to the development of low-pressure RO membranes, which are preferably categorized as nanofiltration (NF) membranes. The basic differences of NF and RO membranes concern their pressure requirements and salt rejection. As the name implies, NF membranes reject pollutants which have molecular weights greater than 100 and are of nanometer size. As NF membranes allow low molecular-weight salts to pass through the membrane element, the osmotic pressure difference is much less than that for an RO membrane. Thus, NF membranes require lower pressure (in the range of 500 to 2000 kPa) than do RO membranes, which require more than 4 MPa. Salt rejection is lower in NF than in RO; however, NF has been reported to successfully reject divalent cations (Ujang and Anderson 1998).

In addition, an ultra-low pressure reverse osmosis (ULPRO) membrane with a lower pressure requirement has been developed. The membranes are an improvement over commercial low-pressure nanofiltration membranes in regard to solute rejection and flux production. At a lower operating pressure (0.2-0.9 MPa), ULPRO produces a specific flux of more than 60 L/m^{2}hMPa (flux per membrane area and per net driving pressure). This flux rate is about double the flux of previous generations of composite reverse osmosis membrane. ULPRO membranes have been shown as energy saving membranes (Gerard et al. 1998) that can effectively reject salts, trihalomethane formation potential, heavy metals, colour, and all viruses, bacteria, and parasites from water and wastewater.

Nanofiltration and ULPRO not only remove cationic pollutants but also remove anionic ones under lower pressure. In addition, the application of those membrane technologies to water and wastewater widened their potentials to reject micro-pollutants in dissolved form, such as endocrine disrupting chemicals (EDCs). These chemicals are exogenous substances which interfere with the normal function of hormones in the human body. Many people and animals have been contaminated with EDCs taken in through water and food.

The objective of this paper is to discuss the performance efficacy of NF and ULPRO membranes in the treatment of water which contains micropollutants. The effect of coexisting chemicals on rejection of EDCs was investigated.

2. Performance and characteristics of LPRO membranes

2.1. Rejection performance of solutes by LPRO membrane

In our previous research, we reported that the rejection of organic compounds by LPRO membranes is controlled mainly by molecular weight. Figure 1 shows the rejection trends of organic compounds by an ULPRO membrane (ES-20). The organic compounds used in the experiment and the characteristics of membranes are listed in Table 2 and 3, respectively. In Table 3, the characteristics of membranes used in other experiments are also listed. The figure 1 indicates a positive correlation between rejection and molecular weight. In particular, a rejection of over 90% was obtained when the molecular weight is almost greater than 150. In addition, the figure shows that the rejections of organic compounds are dependent on the dissociation potential of compounds in the aqueous solution (the pKa values listed in Table2), as well as on molecular weight. Actually, the rejection of dissociated chemicals is higher than that of undissociated chemicals, depending on the pH of the bulk solution. These results indicate that the membrane ζ-potential also may be a main factor of solute rejection.

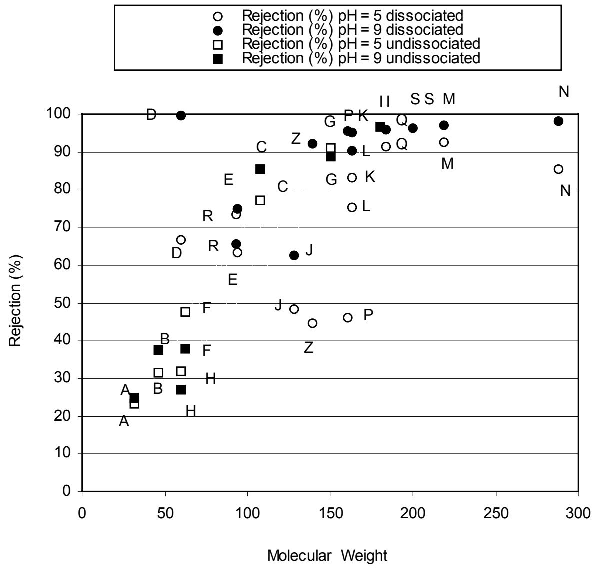

Figure 1 : Rejection of organic compounds with molecular weight in ULPRO membrane (ES-20)

Table 2

Organic compounds used in this study

Compound	Formula	M.weight	M.width	p*Ka*	Symbol
Methyl alcohol	CH_3OH	32	2.3884	—	A
Ethyl alcohol	C_2H_5OH	46	2.5419	—	B
Benzyl alcohol	$C_6H_5CH_2OH$	108	3.0842	—	C
Acetic acid	CH_3COOH	60	2.7316	4.7	D
Phenol	C_6H_5OH	94	2.6682	9.9	E
Ethylene glycol	$HOCH_2\ CH_2OH$	62	2.5500	—	F
Tri(ethylene glycol)	$H[OCH_2\ CH_2]_3OH$	150	2.6462	—	G
Urea	$[NH_2]_2CO$	60	2.3201	—	H
Glucose	$C_6H_{12}O_6$	180	3.5384	—	I
4-Chlorophenol	C_6H_5OCl	128	2.7279	9.4	J
2,3-Dichlorophenol	$C_6H_4OCl_2$	163	3.0800	7.7	K
2,4- Dichlorophenol	$C_6H_4OCl_2$	163	2.9260	7.9	L
2,4,5-Trichlorophenol[a]	$C_6H_4OCl_3Na$	219	3.0577	6.7	M
Pentachlorophenol[a]	C_6OCl_5Na	288	3.1198	4.7	N
o -Nitriphenol	$C_6H_5O_3N$	139	2.7548	7.2	Z
p -Nitriphenol	$C_6H_5O_3NNa$	161	2.7548	7.1	P
2,4-Dinitrophenol	$C_6H_4O_5N_2$	184	2.8852	4.1	Q
Aniline	C_6H_7N	93	2.6726	4.7	R
MCPA	$C_9H_9ClO_3$	200	3.5965	3.1	S

2.2. Measurement of ζ-potential by using the streaming potential method

A schematic diagram of the apparatus for measuring the membrane ζ-potential is shown in Figure 2. In this device, a micro-voltmeter detected the potential difference across each end of the silver chloride electrodes in the cell with the membrane, in which the electrolyte (10^{-3}M NaCl solution) was streamed by using pressurized N_2 gas. The cell was made of quartz glass, and the size of

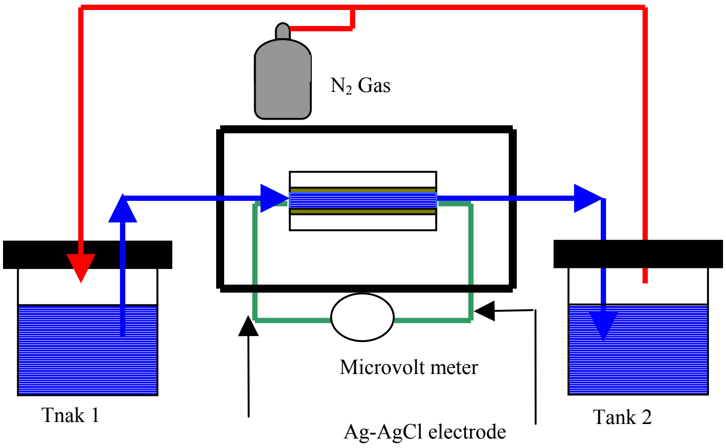

Figure 2 : A schematic diagram of experimental set-up for measuring ζ-potential of membrane

cell was 21mm width and 41mm length. The surface of the membrane mentioned below was exposed to the electrolyte. The electrolyte used in this research was 10^{-3}M NaCl solution, because this is the solution used to test membrane efficiency. The pH of the electrolyte solution was adjusted by 1M HCl and NaOH solutions.

The membrane ζ -potential (ζ) was calculated by the following equation according to the Helmholtz-Smoluchowski formula:

$$\zeta = 1.06 \times 10^5 \times (1/\rho) \times (E/P)$$

where ρ is the specific resistance of the solution and E/P is the gradient of potential difference to operating pressure.

Figure 3 shows the ζ-potential dependencies of three membranes (ES20, VTC-70U, andUTC-10) on pH by using 10^{-3}M NaCl for the electrolyte. For all membranes, the ζ-potential showed positive values under a strong acidic condition, decreasing from positive to negative values as the pH increased in the acidic region and further in the neutral and alkaline regions.

A good example showing the effects of membrane ζ-potential on solute rejection can be seen in Figure 4. The rejection of acetic acid increased with pH, whereas the rejection of aniline decreased with pH. The main reason for this trend may be that the dissociated aniline has a positive charge contrary to other dissociated compounds including acetic acid. The rejection trends of urea and acetic acid with pH were quite different, although they have the same molecular weight (60). Urea cannot dissociate in a pH range of 3 to 9, but acetic acid can take on an anion form in the pH region above the pKa value (pH 4.7). Acetic acid and urea were rejected at the same level, around 34% at pH 3, where both compounds should be in an undissociated state.

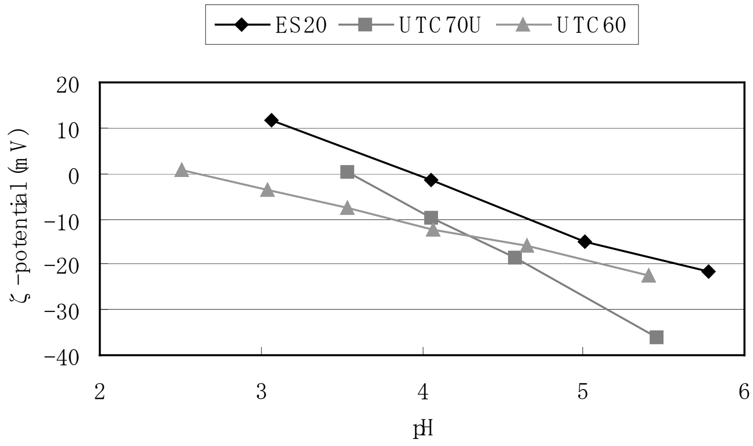

Figure 3 : Zeta-potentials of the membranes (NaCl 10^{-10}M)

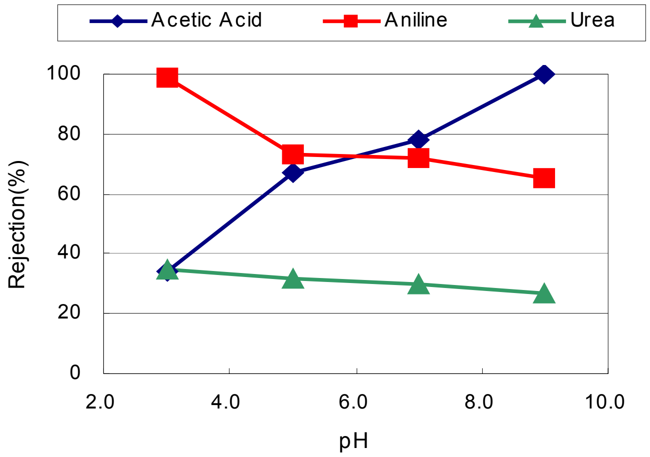

Figure 4 : Rejection of acetic acid, aniline and urea

The rejection of acetic acid increased to 99.7% when the pH was at least 5. These results indicate that molecular weight may be a main factor in the rejection of organic compounds in an undissociated state, and that the electrostatic repulsion between the negatively charged membrane and acetic acid at a dissociated state may cause the overall rejection of acetic acid depending on pH.

2.3. Rejection of endocrine disrupting chemicals by ulpro membraness

Table 4

Endocrine disrupting chemicals used in this study

Compound name	Formula	Molecular Weight	Dissociation Constant(pKa)
2,4-Dichlorophenol (2,4-DCP)	$C_6H_4O_5Cl_2$	163	7.9
Pentachlorophenol* (PCP)	C_6OCl_5Na	288	4.7
Bisphenol A (BPA)	$C_{15}H_{16}O_2$	228	9.59~10.56
17β-estradiol (E2)	$C_{18}H_{24}O_2$	272	10.08
Nonylphenol (NP)	$C_{15}H_{24}O$	220.36	10.3
Diethyphthalate (DEP)	$C_{12}H_{14}O_4$	222.24	-

*Sodium salt

3. Material and method

Two types of membrane, ES20 and UTC-60U manufactured by Nitto Denko Corp. and Toray Industries Inc., respectively, were used for EDCs separation. The characteristics of the ULPRO membrane are listed in Table 2, which is indicated in the preceding chapter. The six kinds of EDCs, Nonylphenol (NP), Bisphenol A (BPA), 17β-estradiol (E2), Diethylphthalate (DEP), 2,4-Dichlorophenol (2,4-DCP), and Pentachlorephenol (PCP) in Table 4 were used to examine the rejection of each chemical by the ULPRO membrane at a concentration of 1mg/L. Each membrane was supplied in flat sheet form and mounted in a cross-flow module (C10-T, Nitto Denko Corp.) The schematic diagram of experimental set-up is shown in Figure 5. The membrane module was 110mm wide, 210mm long, and 82mm high. The effective membrane surface area of the module was 60 cm^2 with a 46 mm width and an 180 mm length. The set-up was operated at 0.3Mpa. In addition, rejections of EDCs (E2 and BPA) were examined in the

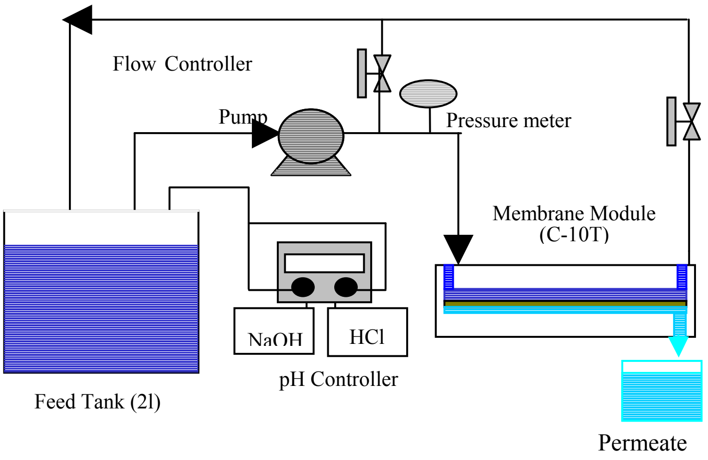

Figure 5 : Schematic diagram of the experimental set up for membrane separation

mixed solution including an effluent from secondary treatment, fulvic acid, and humic acid, respectively. As an example of EDCs treatment, separation of dioxins (a kind of EDCs) in a liquid of river sediment in Osaka, Japan was tested by using a batch test cell with MF membrane (pore size of 0.2 μm). The liquid sample was provided after sedimentation and filtration by an empore disk (1 μm).

4. Analysis

The concentrations of chlirophenols were analyzed by means of a diode array UV spectrophotometer (HP89532A) at 222nm. Nonylphenol, DEP, BPA, and E2 in single solution system were analyzed by using a fluorescence photometer. The EDCs in the effluent from a sewage treatment plant cannot be detected by a fluorescence photometer due to interference from co-existing substances. In this study, GC-MS and Enzyme Linked Immunosorbent Assay (ELISA) test kits (Japan EnviroChemicals Ltd.) were used for detecting BPA and E2 in the mixture solution of EDC and other organics.

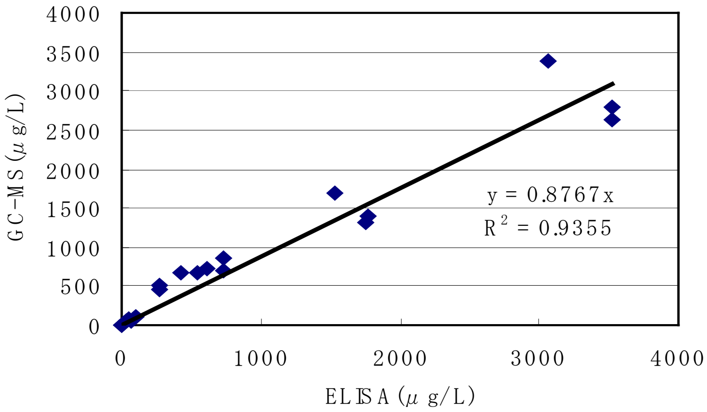

Figure 6 : Concentration of Bisphenol A measured by ELISA and GC-MS

Figure 6 shows the comparison of BPA concentration measured by ELISA with that measured by GC-MS. A close correlation between the results by ELISA and GC-MS can be seen in the complete range between high and low concentrations. ELISA, a measuring technique routinely employed for clinical diagnosis, is a simple and sensitive method which is available for determining minute quantities of ECDs .

Dioxins contents were determined by HRGC/HRMS (JEOL JMS-700D) analysis after the pre-treatment of samples, according to the official method by Environment Agency in Japan.

5. Results and discussion

Figure 7 shows the rejection levels of six EDCs by using ES20. The rejection of BPA, E2, and DEP were almost 100%, probably because the compounds have enough high molecules to be rejected by a ULPRO membrane. The rejection of chlorophenols, 2,4-DCP and PCP, decreased with pH in the region below the pKa value of each compound, although PCP has a high molecular weight. The rejection of compounds containing Cl substitute might change, being dependent on the pH of the solution and membrane ζ-potential. The rejection of NP also decreased with pH, depending on membrane ζ-potential.

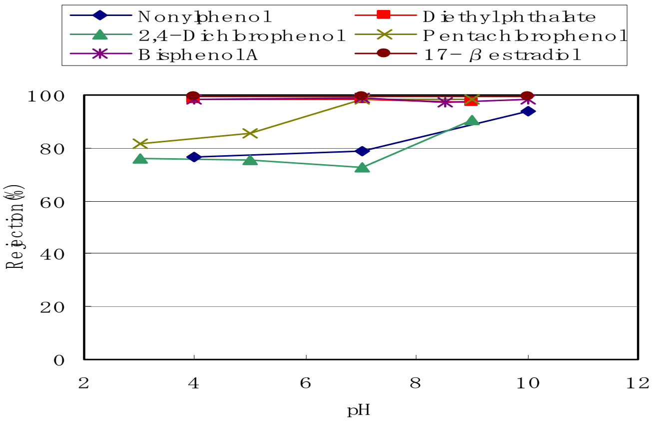

Figure 7 : Rejection of endocrine disrupting chemicals

The reason for the difference between the rejection of BPA and NP is not clear. Actually, we can see that the NP concentration in the permeate decreases gradually with time in an experimental run using a single NP solution. This trend indicates that NP easily detaches from membrane surface after adhering to it.

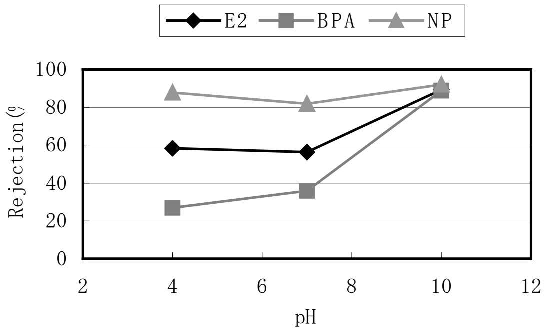

Figure 8 : The pH dependency of EDCs rejection
(UTC60, BPA:10mg/L, E2,NP:1mg/L)

The effects of pH on EDCs rejection using a relatively loose NF membrane (UTC-60) are shown in Figure 8. The rejection of E2 and BPA typically decreased with an decrease of pH, that is, with an decrease of absolute membrane ζ-potential shown in Figure 3. The rejections of E2 and BPA in each single solution are shown in Figure 9, with the rejections of the EDCs which had been spiked into an effluent from secondary treatment (+DWE) , into a solution of fulvic acid (+FA) , and into a solution of humic acid (+HA), respectively. It can be seen in the figure that the rejection of E2 in humic acid solution is almost 100 % which is higher than that in a single solution. The molecular weight of humic acid was found to range from about 10,000 to 30,000 by GPC measurement. Therefore, a possible explanation for the high E2 rejection is that the E2 was rejected after adhering to humic acid. On the other hand, the molecular weight of organic carbon in DWE ranged from about 200 to 15,000, and that of fulvic acid was around 300. These

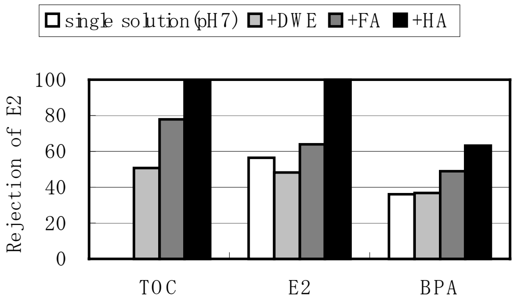

Figure 9 :The rejection of endocrine disrupting chemicals with organic coexisting substances (UTC60, EDCs:1mg/L, DWE, HA: 10mgTOC/L, FA: 2.5mgTOC/L)

results suggest that some amounts of E2 in DWE and FA solution might pass through the membrane together with comparatively low molecular organics which can easily associate with E2. Although BPA showed the same rejection trends, the rejection of BPA was about 60 %. This is probably because BPA is adsorbed by organics less than E2.

Table 5 indicate the rejection of dioxins (a kind of EDCs) in a liquid of river sediment by using a batch test cell with MF membrane (pore size of 0.2 μm). Almost all the dioxins, which are consist of PCDDs, PCDFs, and Co-PCB, were rejected by the membrane. This result suggests that dioxins are adsorbed by small particles larger than 0.2 μm.

Table 5

Rejection of Dioxins by MF membrane

	Measned volues				Toxicity Eguivalency Quantity			
	Total-PCDD$_s$ (Pg/L)	Total-PCDF$_s$ (Pg/L)	Co-PCB$_s$ (Pg/L)	Total (Pg/L)	Total-PCDD$_s$ (Pg-TEQ/L)	Total-PCDF$_s$ (Pg-TEQ/L)	Co-PCB$_s$ (Pg-TEQ/L)	Total (Pg-TEQ/L)
Supernatant of river sediment	3,300	3,900	30,000	34,000	16	22	14	52
Sample filtered by MF	9.2	1	21	23	0.0053	0.0027	0.0029	0.0028

6. Conclusion

1. When the molecular weight of organic compound is more than 150, the compound was very effectively rejected by ULPRO membrane, multi-layer thin film composites of aromatic polyamide, at the efficiency of over 90% In this case, undissociated organic compounds were rejected mainly by a "sieving effect".
2. The EDCs are also rejected effectively by the ULPRO membrane. The EDCs rejection by a relatively loose NF membrane (NaCl rejection of about 50 %) was lower than that by ULPRO membrane. However, the co-existing organic substance like humic substances enhanced the rejection of EDCs by a NF membrane.
3. The membrane ζ-potential as well as the ion size or molecular weight of organic compounds can be considered a key factor in the rejection of EDCs.
4. Almost all the dioxins, which are consist of PCDDs, PCDFs, and Co-PCB, in a liquid of river sediment were rejected by a MF membrane whose pore size is 0.2 μm.

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