B－33 REJECTION OF POLLUTANTS FREQUENTLY FOUND IN LANDFILL LEACHATES BY NANOFILTRATION IN LOW PRESSURE RANGE

(廃棄物処分場浸出水中に見出される微量汚染物質のナノろ過による低圧域での除去特性)

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1.0 INTRODUCTION

Waste plastics including plastic additives and potentially toxic wastes (e.g. incinerator ash or sewage sludge) are disposed on landfill sites. Many organic compounds have been detected at concentrations greater than 1000 ng/l and several endocrine disruptors including pesticides and plastic additives (e.g. phthalates, bisphenol A) are also found at some of these landfills (Yasuhara et al., 1999).

Among various technologies available for removing these compounds, nanofiltration (NF) which displays separation characteristics between ultrafiltration (UF) and reverse osmosis (RO) are able to reject small organic molecules having Molecular Weight Cut-off (MWCO) of 200-300 Da. Rejection characteristics of pollutants by RO or NF are a useful information for advanced water treatment technology. This study is an investigation on the performance of NF or RO membranes in leachate treatment with low concentration of frequently found pollutants of landfill leachate using laboratory scale test unit cell in low pressure condition.

2.0 MATERIALS AND METHOD

2.1 Membranes

Ten kinds of flat sheet type membranes were selected for use in this study. Seven of the membranes were obtained from Nitto Denko Corporation (Osaka, Japan) and the remaining from Toray Industries. Table 1 shows membrane properties.

2.2 Prepared Solution

The solution applied to the membrane separation experiment was prepared by dissolving organic compounds including organic phosphoric acid esters and phthalate esters in acetone to produce a 1000ppm (1 gram/litre) standard solution. These compounds have molecular size between 130 Da - 290 Da and within the nominal MWCO range (200 - 400) of the selected NF membranes. These were tested at 1ppm concentration with the exception of the organic phosphoric acid esters, which have 3 times concentration and Bisphenol A with 10 times concentration. In order to reduce adsorption, suspended solid free leachate taken from a municipal landfill site was added in a volume equal to 1/20th of the prepared solution.

2.3 Experimental Setup

Membrane retention and fluxes were determined using a Nitto Denko bench-top laboratory test cell-C-10T with surface area of 60cm^2 (Figure 1).

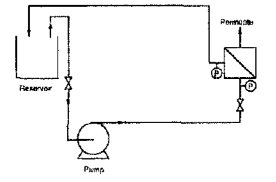

Figure 1: Schematic diagram of Membrane Test Apparatus

The process pumps the bulk solution from the reservoir to the test cell where filtration occurs and the retentate recirculated through the system. The pure water flux J_w was measured before solute separation experiment commenced.

2.4 Analytical Procedure

For each membrane test experiment the prepared solution (100 µl of standard solution mixed with 100 ml leachate with milliQ added to a 2 l mark) was applied to the cell at low pressures of 0.1 to 0.3 MPa. Generally samples were taken after 4 hours from the introduction of the bulk solution to further minimize the effect of adsorption and steady state rejections were evaluated. Extraction of organic pollutants was made using dichloromethane from 100 ml of each collected sample (of the permeate and retentate). 1 µl of solute was injected into the port of the Gas Chromatography/ Mass Spectrometer (GC/MS) with the selected ion monitoring quantification. Salt and Colour rejections were measured using collected samples of permeate and bulk by ion-chromatograph and light adsorption at 390 nm respectively. The rejection, R (%), was calculated using the expression

$$R = (1 - \frac{C_p}{C_r}) \times 100$$

where C_p and C_r are the concentrations for the permeate and the retentate.

Table 1: Properties of Membranes used

ID	MEMBRANE TYPE	MANUFACTURER	MEMBRANE PROPERTY	ELECTRIC CHARGE	SKIN LAYER-MATERIAL	NOMINAL DESALINATION OF NACL (%)
a.	NTR-7410	Nitto Denko Corporation	Hydrophobic	Negative	sulfonated polysulfonate	15
b.	UTC 20	Toray Industries	Hydrophilic	Positive	Aromatic polyamides	60
c.	NTR 7250	Nitto Denko Corporation	Hydrophobic	Negative	polyvinylalcohol/polyamides	60
d.	UTC 60	Toray Industries	Hydrophobic	Negative	Aromatic polyamides	55
e	NTR 729HF	Nitto Denko Corporation	Hydrophobic	Negative	polyvinylalcohol/polyamides	92
f	ES 10C	Nitto Denko Corporation	Hydrophobic	Negative	polyamides	99 5
g.	LES 90	Nitto Denko Corporation	Hydrophobic	Negative	polyamides	95
h.	UTC 70	Toray Industries	Hydrophobic	Negative	Aromatic polyamides	99
i.	ES 10	Nitto Denko Corporation	Hydrophobic	Negative	polyamides	99.5
j.	LF 10	Nitto Denko Corporation	Hydrophilic	Neutral	polyvinylalcohol/polyamides	99.5

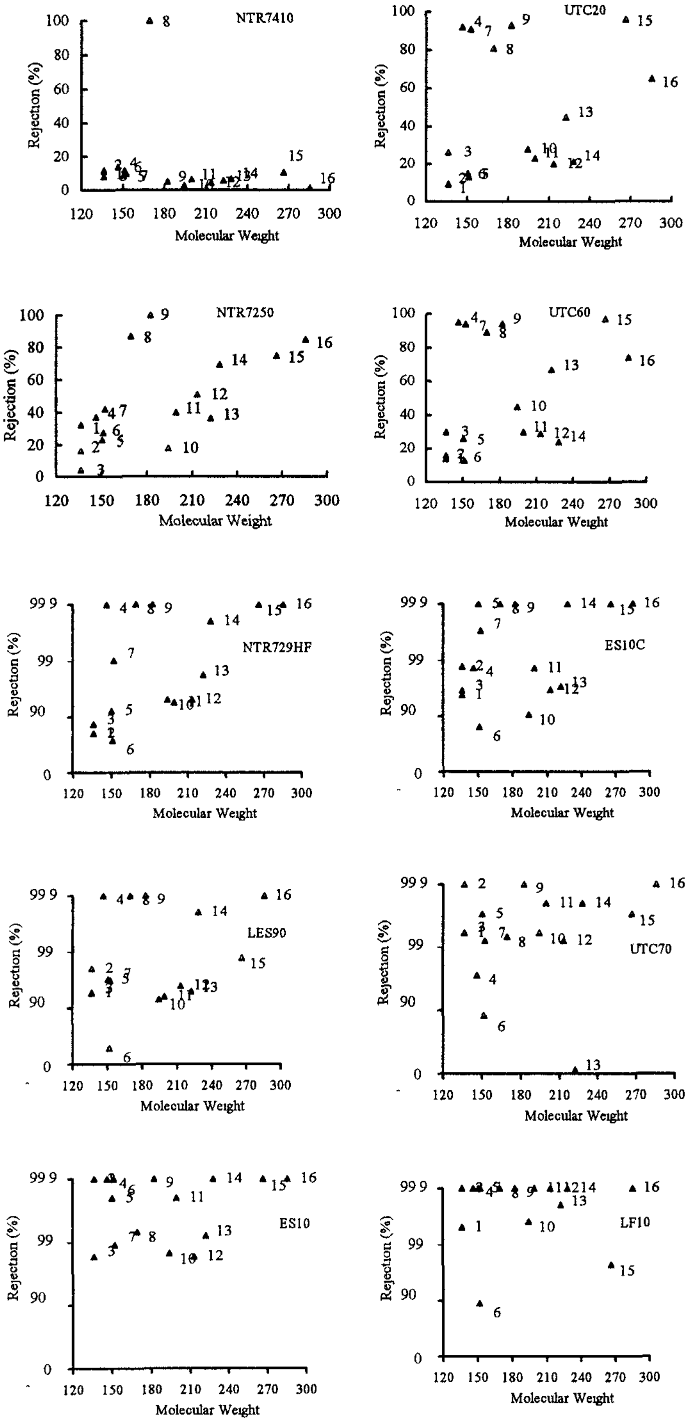

Figure 2: Effect of molecular weight on the rejection of solutes

* The numbers on figures correspond to solute number as indicated in Table 2

3.0 RESULTS AND DISCUSSION

3.1 Effect of molecular weight on rejection

The plots of the steady state rejection of organic solutes with molecular weight are shown in Figure 2. These values have been tabulated along with steady state rejection of chloride and colour in Table 2. The low rejection membranes were NTR7410, UTC60, NTR7250, and UTC20. All solutes were porous to NTR7410 except Diphenyl Amine which was rejected at >99.9%. UTC60, NTR7250, and UTC20 rejected the solutes in a pattern roughly consistent with the molecular weights of solutes (i.e. low weight solutes have low rejection and high weight solutes have high rejection) except for 2,2,4 Trimethyl 1,3 pentanediol, Camphor, Diphenyl Amine and Triethyl Phosphate which weren't consistent with the trend in most cases. The high rejection membranes were NTR729HF, ES10C, LES90, UTC70, ES10 and LF10. Triethyl Phosphate and Tri (2-chloroethyl) Phosphate were rejected at >99.9%. 2-H-Benzothiazol and Triethyl Phosphate from the fore going could be indicated as uniquely permeable solute and uniquely rejected solute respectively. However, the rejection of solutes increased with increase in salt rejection of the different types of membranes. This is in agreement with a similar work conducted by Kiso et al. (2001).

3.2 Effect of volume flux

Flux increased with applied pressure as shown in Figure 3. Figure 4 shows the relationship between chloride rejection and volume flux of all the membranes examined. The high rejection membranes have lower volume flux than the low rejection types.

3.3 Effect of salt rejection of membranes on organic solute rejection

The dependence in rejection between selected organic solutes (using 4 or 3-isopropyl phenol, dimethyl phthalate and bisphenol A) and the inorganic salt as chloride is shown in Figure 5. The result shows a strong dependence in the rejection of solutes and chloride. The high salt rejecting membranes rejected most of the organic solutes.

Table 2: Steady state rejection of organic solutes, chloride and colour by membrane at 0.3 MPa pressure

S/N	Substance/Molecular Formula	Mol. Wt.	NTR 7410[a]	UTC 20[b]	NTR 7250[c]	UTC 60[d]	NTR 729HF[e]	ES 10C[f]	LES90[g]	UTC 70[h]	ES10[i]	LF10[j]
1	2-isopropyl phenol ($C_9H_{12}O$)	136.19	11.0	9	32.2	16	80.2	98.7	98.0	>99.9	>99.9	>99.9
2	4 or 3-isopropyl phenol ($C_9H_{12}O$)	136.19	11.9	9.4	16.1	14	80.5	95.8	94.6	99.4	99.9	99.5
3	2-phenyl-2-propanol ($C_9H_{12}O$)	136.20	7.7	26.2	4.2	30	86.5	96.5	94.4	99.4	98.3	>99.9
4	2,2,4 Trimethyl 1,3 pentanediol ($C_8H_{18}O$)	146.23	13 5	92	36 9	95	>99.9	98.6	>99.9	97.2	>99.9	>99.9
5	p-t-butylphenol ($C_{10}H_{14}O$)	150.22	8.6	15	22.8	26	92.2	>99.9	96.6	99.7	99.8	>99.9
6	2-H-Benzothiazol (C_6H_4NSCOH)	151.19	11.5	13	27.5	13	73.6	84.4	48.2	88	>99.9	88.7
7	Camphor ($C_{10}H_{16}O$)	152.26	9.3	91	41.9	94	99.0	99.7	96.7	99.2	98.9	>99.9
8	Diphenyl Amine ($C_{12}H_{11}N$)	169.22	>99.9	81	86.9	89	>99.9	>99.9	>99.9	99.3	99.3	>99.9
9	Triethyl Phosphate ($C_6H_{15}O_4P$)	182.16	4.9	93.1	>99.9	94	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
10	Dimethyl Phthalate ($C_{10}H_{10}O$)	194.20	2.6	28	17.9	45	95.1	90.7	92.9	99.4	98.5	99.6
11	N-ethyl-p-toluensulfonamide ($C_9H_{13}NO_2S$)	199.27	6.2	23	39.8	30	94.4	98.6	93.7	99.8	99.8	99.9
12	n-Buthyl Benzenesulfoneamide ($C_{10}H_{15}SO_2N$)	213 30	4.1	20	50.7	29	95.0	96.6	95.9	99.2	98.3	>99.9
13	Diethyl Phthalate ($C_{12}H_{14}O$)	222.20	5.6	45	36.5	67	98.2	97.0	94.8	13.1	99.2	99.8
14	Bis Phenol A ($C_{15}H_{16}O_2$)	228.00	6.5	21	69.4	24	99.8	99.9	99.8	99.8	>99.9	>99.9
15	Tributyl Phosphate ($C_{12}H_{27}O_4P$)	266 32	10.6	96	75.0	97	>99.9	99.9	98.7	99.7	>99.9	97.7
16	Tri(2-chloroethyl) Phosphate($C_6H_{12}C_{13}O_4P$)	285.50	1.2	65	84.9	74	>99.9	>99.9	>99.9	>99.9	>99.9	>99 9
17	Chloride		10.9	28.4	38.2	42.8	71.0	91.1	98.2	98.4	99.0	99.2
18	Colour		88.1	99.3	99.7	99.6	99.8	99.6	99.8	99.8	99.6	99.8

* Numbers and alphabets correspond to solute number and membrane type respectively as indicated on tables and figures

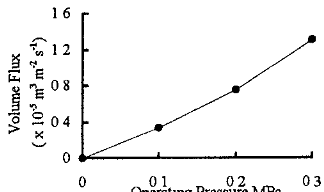

Figure 3: Change in volume flux at low pressure for UTC60

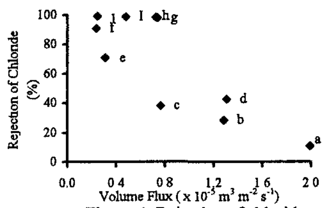

Figure 4: Rejection of chloride with permeate volume flux

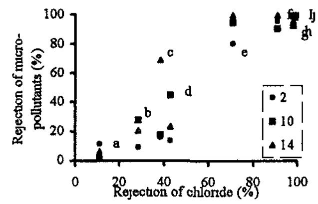

Figure 5: Rejection of chloride with rejection of micro-pollutants

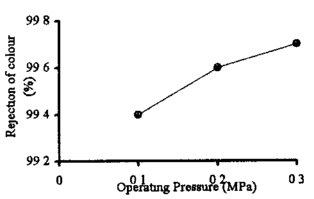

Figure 6: Rejection of colour in low pressure for UTC60

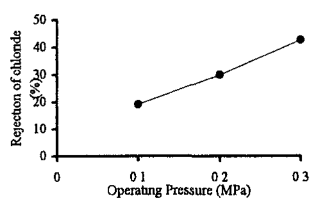

Figure 7: Rejection of chloride in low pressure for UTC60

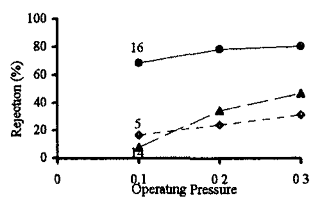

Figure 8: Solute rejection in low pressure for UTC60

3.4 Effect of operating pressure on rejection

The effect of operating pressure on colour, chloride and solute rejection are shown in Figures 6, 7 and 8 respectively. Rejections of these substances are lowest at 0.1 MPa and highest at 0.3 MPa pressure. The differences in solute rejection shown can be understood using the concept of the solution diffusion model. Lowering the operating pressures also decreased volume flux with relatively constant solute flux resulting in lower rejection.

4.0 CONCLUSION

The rejection of some frequently found pollutants in lecheate from landfill sites have been investigated in low-pressure range with low desalting reverse osmosis RO and NF membranes. Only the highest desalting membranes could effectively reject almost all the micro-pollutants. The molecular sieving effect of membrane on solutes is important especially in the low desalting membranes where the lower molecular weight substances had lower rejection than the higher molecular weight substances.

5.0 REFERENCES

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2. **Kiso, Y., Kon, T., Kitao, T., Nishimura, K.,** (2001). Rejection properties of alkyl phthalates with nanofiltration membranes, *J. Membr. Sci.* **182**, 205-214.