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Effect of pH on the rejection of inorganic salts and organic compound using nanofiltration membrane

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Abstract−Nanofiltration (NF) has recently received increased attention as a possible tertiary treatment process providing high rejection of solutes and high water flux rate. In this research, solute separation experiments using NF membranes were made with inorganic salts including heavy metal and organic compounds in different pH levels. The rejection of inorganics from feed solution was found to be dependent on the electric charge of membrane as well as the ionic radius and valence of ion. The divalent cation appeared to reduce the potential of negatively charged membrane to lower the rejection of ion. The results of organic compounds showed that the rejection could be estimated from the pKa value and molecular weight of organics, and the pH of the feed solution.

Key words: Nanofiltration (NF), Inorganic Salts, Heavy Metal, Organic Compound, Zero Point of Charge, Wastewater Treatment

INTRODUCTION

The rejection of inorganic and organic pollutants from wastewater effluent, lake and river water for water supply, and ground water by using NF (nanofiltration) has recently become a subject of considerable research and application interest [Mulder, 1997; Itoh et al., 2000; Trebouet et al., 1999; Jung and Kang, 2003]. The main reason is that NF provides high rejection of solutes and high water flux rate under extremely low operating pressure. Reverse osmosis (RO) membranes generally separate materials less than 10 angstroms in size, while newly developed NF membranes are reported to retain organic substances more than 10 angstroms (one nanometer) or 200 MW (molecular weight) as well as a significant amount of inorganic substances, especially divalent cations [Cartwright, 1989; Croll, 1992].

In Germany, the NF was examined for its treatability in an actual leachate treatment plant including biological pretreatment. It was reported that by simply replacing the RO membranes with NF, an operational capacity of ca. 280 m^3/day could easily be achieved at the existing physical-post treatment stage [Baumgarten et al., 1996]. In a separate study, the authors have combined the process of MBR (membrane bioreactor) with NF for leachate treatment [Kim et al., 1996]. In addition, research on the rejection of anionic pollutants using nanofiltration membrane for water supply and water reuse showed that a high rejection of phosphate and sulfate ions could be maintained at very low operating pressure range [Ratanatamskul et al., 1996].

NF membranes have been known to have the attractive characteristic of rejecting organics and polyvalent ions while allowing a part of monovalent ions to pass into the product water. Furthermore, the experimental results presented in this paper will show that the monovalent ions are also rejected to a large extent in an alkaline region. A membrane with a cut-off molecular weight of about 200 MW (molecular weight) might be very useful for water treatment, as most of the environmental organic pollutants are above this value. In situations where water pollution caused by hazardous organic substances is a serious problem, NF may have a considerable potential in rejecting organics of comparatively large MW such as most of pesticides.

However, little is known of the solutes separation mechanism and optimum operating conditions of NF membranes. Generally, solutes rejection by an NF membrane is expected to be dependent on the electrical interaction between solutes and the membrane surfaces. It also depends on the pH level of solution, as NF membranes have charges which normally decrease gradually from positive to negative with an increase of the pH level. The objective of the present research is to study the effect of pH of the feed solution and MW of solutes on the solute separation by using NF membranes.

METHODS

1. Nanofiltration Membrane

The NF membranes used in this research were NTR-729HF (Nitto Denko, Japan) and UTC 60 (Toray Industries, Japan), whose thin layers are made of polyvinyl alcohol and aromatic polyamide, respec-

Table 1. Normal solutes rejection of NF membranes

	NTR-729HF[a]	UTC60[b]
NaCl	92%	63.6%
Na_2SO_4	-	99.6%
Ethyl alcohol	25%	10.0%
Glucose	97%	95.4%

[a] Catalog values at 1.5 Mpa, 0.15% solute
[b] Catalog values at 1.5 Mpa, 0.15% solute except for NaCl (0.05%)

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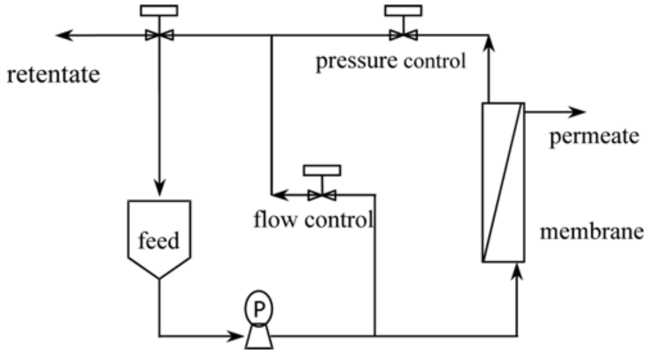

Fig. 1. A schematic diagram of membrane set-up.

Table 2. Inorganic salts used in this study

Solute	Concentration
NaCl	5 mM
$NaNO_3$	5 mM
NaF	5 mM
KCl	2.5 mM
Na_2SO_4	5 mM
$CaCl_2$	2.5 mM
$Ca(NO_3)_2$	2.5 mM
$CaSO_4$	2.5 mM
$MgCl_2$	2.5 mM
NaH_2PO_4	5 mM
$CdCl_2$	10 mg/L
$ZnCl_2$	10 mg/L
$CuCl_2$	10 mg/L
$Pb(NO_3)_2$	10 mg/L
$Cr(NO_3)_2$	10 mg/L

Table 3. Organic compounds used in this study

Compound	Fomula	M.W.	pKa
Methyl alcohol	CH_3OH	32	-
Ethyl alcohol	C_2H_5OH	46	-
Benzyl alcohol	$C_6H_5CH_2OH$	108	-
Acetic acid	CH_3COOH	60	4.7
Phenol	C_6H_5OH	94	9.9
Ethylene glycol	$HOCH_2CCH_2OH$	62	-
Triethylene glycol	$H[OCH_2CH_2]_3OH$	150	-
Urea	$[NH_2]_2CO$	60	-
Glucose	$C_6H_{12}O_6$	180	-
4-Cholorophenol	C_6H_4OCl	128	9.4
2,3-Cholorophenol	$C_6H_4OCl_6$	163	7.7
2,4-Cholorophenol	$C_6H_4OCl_6$	163	7.9
2,6-Cholorophenol[a]	$C_6H_4OCl_6$	163	6.8
2,4,5-Tricholorophenol[a]	$C_6H_4OCl_3Na$	219	6.7
Pentachlorophenol	C_6OCl_5Na	288	4.7
o-Nitrophenol	$C_6H_5O_3N$	107	7.2
p-Nitrophenol[a]	$C_6H_5O_3NNa$	129	7.1
2,4-Dinitrophenol	$C_6H_4O_5N_2$	183	4.1
Aniline	C_6H_7N	93	4.7
2,4-D[b]	$C_8H_6Cl_{12}O_3$	221	3.8
MCPA[c]	C_9H_9ClO	200	3.1
Metolachlor[d]	$C_5H_{22}ClNO_2$	284	-
DNOC[a,e]	$C_7H_5N_2O_5Na$	220	3.3
2,4,5-T[f]	$C_8H_5Cl_3O_3$	225	-
Propanil[g]	$C_9H_9Cl_2NO$	218	-

[a] Na salts
[b] 2,4-dichlorophenoxy acetic acid
[c] 4-chloro-2-methylphenoxy acetic acid
[d] 2-chloro-6′-ethyl-N-(2-methoxy-1-methylethy) aceto-o-toluidide
[e] 2-methyl-4,6-dinitrophenol
[f] 2,4,5-trichlorophenoxy acid
[g] 3′,4′-dichloropropionanilide

tively. The normal values of solute rejection of the membranes are listed in Table 1. A direct comparison between the corresponding values of a solute rejection of both membranes in Table 1 is not valid, as the values were obtained under different operating conditions. A schematic diagram of the membrane test unit is shown Fig. 1. The membrane modules used here were of the flat sheet type, effective surface areas of 60 cm^2 for NTR-729HF and 33 cm^2 of UTC 60, respectively.

2. Experimental Method

A feed solution including a sole solute was pumped to the membrane module in a continuous cross flow mode at a trans-membrane pressure of 0.3 MPa and at 20 °C. The retentate from the membrane module was recirculated to the feed tank in a closed loop. Tables 2 and 3 list the inorganic and organic substrates used in this research. The organic solute concentration in feed was set at 10 mg/L. In case of the organics being slightly soluble like that of pentachlorophenol, the sodium salts of organics were employed in each run. The concentrations of inorganic solutes used are indicated in Table 2. The pH of the feed solution in each run varying from 3 to 9 was controlled by a pH controller with 0.01 N HCl and 0.01 N NaOH. The UTC 60 membrane was mainly used for the experimental runs of inorganic substances, whereas NTR-729HF membrane was for both inorganic and organic substances. The efficiency of the membrane used was regularly checked with the NaCl rejection before each run started, and only membrane that had the same efficiency as that in initial usage was reused. Membrane cleaning was performed with 0.01 N HCl solution or distilled water for 60 to 120 minutes. The permeate samples from the membrane module were collected and analyzed after two hours of operation.

All the cations and anions in the permeate and feed solution were analyzed by using atomic absorption spectrometry (Nippon Jarrel Ash, AA-11) and ion chromatography (DIONEX 2000i), respectively. An analysis of heavy metals the spectrophotometry (UV-2500 PC, shimazu) at 220 nm was carried out after the sample solutions were acidified with HCl. The propanil concentration was measured by high performance liquid chromatography (HPLC, YANACO L-5000). The concentrations of other organics were determined by measuring total organic carbon (TOC) (TOC 5000, Shimazu) in the solutions.

RESULTS AND DISCUSSION

1. Effect of pH on the Rejection of Inorganic Ions

1-1. Monovalent Ions

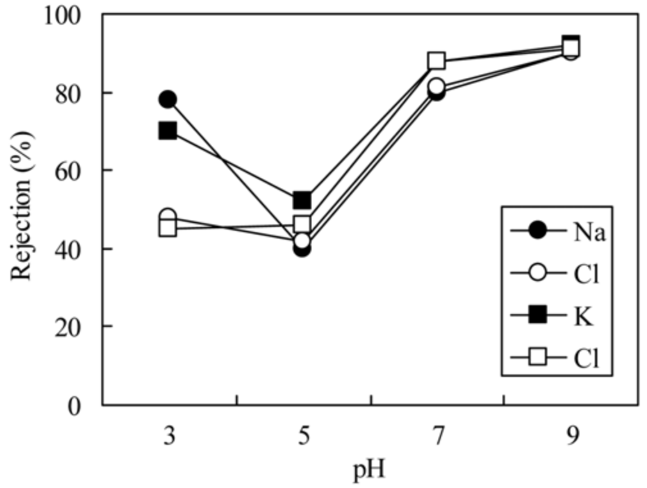

Fig. 2. Effect of pH on the rejection of monovalent cations (Na$^+$, K$^+$) using UTC-60 membrane.

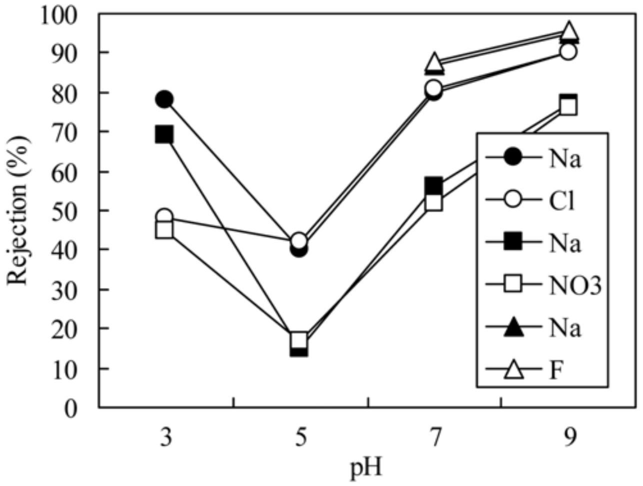

Fig. 4. Effect of pH on the rejection of monovalent anions (Cl$^-$, NO$_3^-$, F$^-$) using UTC-60 membrane.

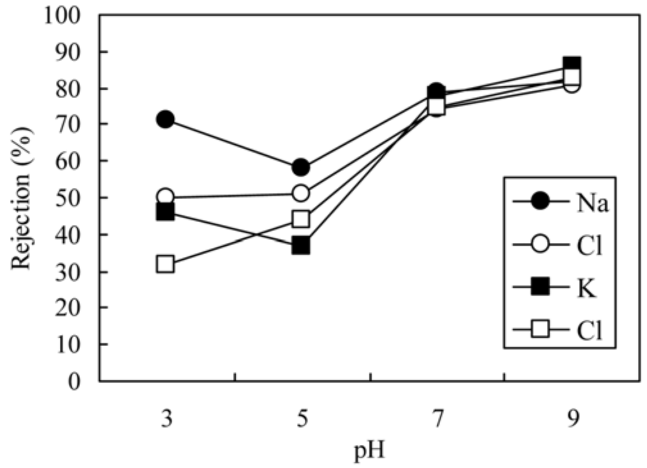

Fig. 3. Effect of pH on the rejection of monovalent cations (Na$^+$, K$^+$) using NTR-729HF membrane.

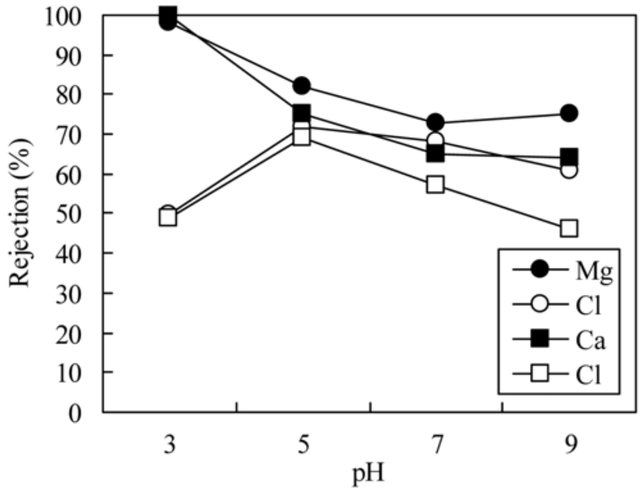

Fig. 5. Effect of pH on the rejection of divalent cations (Mg^{2+}, Ca^{2+}) using UTC-60 membrane.

Figs. 2 and 3 show the effect of pH of the feed solution on the rejection of Na$^+$, K$^+$, and Cl$^-$ by the NTR-729HF and UTC 60 membranes, respectively. The rejection of monovalent cations was found to decrease with the feed pH and then increased after a minimum point was reached. In addition, the rejection performance of anion (Cl$^-$) was similar to that of the monovalent cations. It has been reported on composite NF membranes that in general the membranes are negatively charged in a neutral and alkaline aqueous solution, positively charged in an acidic aqueous solution, and have a zero point of charge (zpc) in the pH range of 5 to 6 [Kamiyama, 1993; Childress et al., 2000].

The effect of feed pH on the rejections for three types of monovalent anions, F$^-$, Cl$^-$, NO$_3^-$, is illustrated in Fig. 4 (UTC 60). The counter ion of each anion in solution was Na$^+$. The variation of Cl$^-$ rejection with pH was similar to that of NO$_3^-$. In the alkaline region, the rejection of F$^-$ was better among the anions used and the order of rejection was F$^-$, Cl$^-$, NO$_3^-$. This result is compatible with the order of hydrated ion radius: F$^-$>Cl$^-$>NO$_3^-$.

1-2. Monovalent Ions and Heavy Metals

Figs. 5 and 6 display the effects of pH on the rejection of divalent cations (Ca^{2+} and Mg^{2+}) by the UTC 60 and NTR-729HF membranes, respectively. The results obtained in Fig. 5 were almost similar to those in Fig. 6, which were coincidentally different from those of the monovalent cations, particularly in the pH region above 5, i.e., the rejection of divalent cations decreased with an increase in the feed pH. This phenomenon might be explained in terms of the reduction of surface charge of membrane, which was caused by the adsorption of divalent cations on the surface of negatively charged membrane in the pH region. In fact, it has been occasionally observed that the ζ potential of sand on the surface without impurities is reduced when the sand is immersed in a solution of divalent cation [Terashima et al., 1982]. It is probable that the reduction of negative surface charge of membrane facilitated the permeation of anions through it, while divalent cations permeated through membrane easily. The rejection of Mg^{2+} was higher than that of Ca^{2+} over a wide pH range. This is probably because the hydrated ion radius of Mg^{2+} is larger than that of Ca^{2+}, as opposed to those atomic radii.

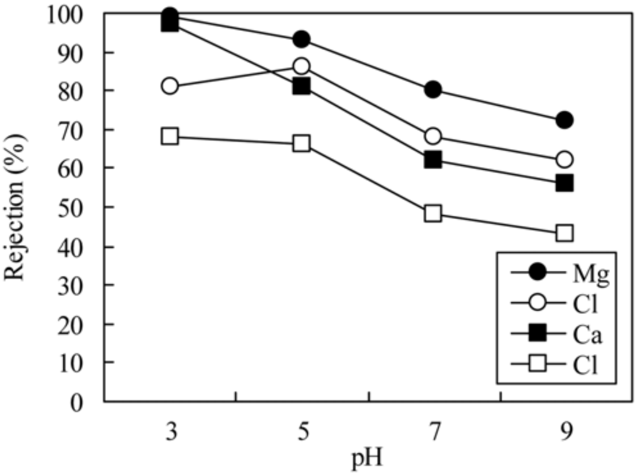

Fig. 6. Effect of pH on the rejection of divalent cations (Mg^{2+}, Ca^{2+}) using NTR-729HF membrane.

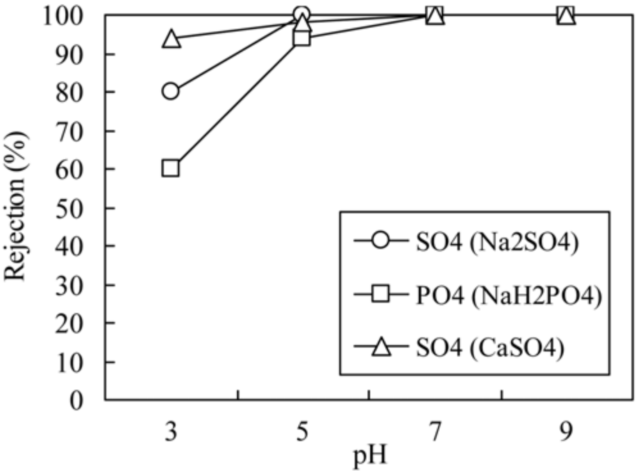

Fig. 7. Effect of pH on the rejection of divalent anions (SO_4^{2-}, PO_4^{3-}) using UTC-60 membrane.

As shown in Fig. 7, the rejection of divalent anions, whose counter ion is divalent or other, was observed almost above 90% except for the data at pH 3 and higher than that of monovalent ions. The RO membrane operated under a high pressure has also been reported to give a higher rejection of divalent anion than that of monovalent anion: $NO_3^-<Na^+<Cl^-$, $NO_3^-<NH_4^+<SO_4^{2-}$ [Hodgson, 1970].

Fig. 8 exhibits that the variations of rejection of divalent heavy metals Cu^{2+}, Zn^{2+}, Cd^{2+} and trivalent heavy metal (Cr^{3+}) with pH, are similar to those of Ca^{2+} and Mg^{2+} as shown in Fig. 5. The feed solution of Cr $(NO_3)_3$ showed a high rejection for Cr^{3+} up to 99% in the region of low pH, probably due to the mutual strong repulsion between the positively charged membrane and the trivalent cation. The reason for the rejection of anions different from that of divalent heavy metal ions has yet to be elucidated.

It can be deduced that the rejection of inorganics by NF membranes is dependent on the electric charge of the membrane, and the ionic radius and valence of ion in the feed solution. In a mixed solution system, divalent cations lower the rejection of coexistent cations than that of cation in a single solution system, although the details are not given here.

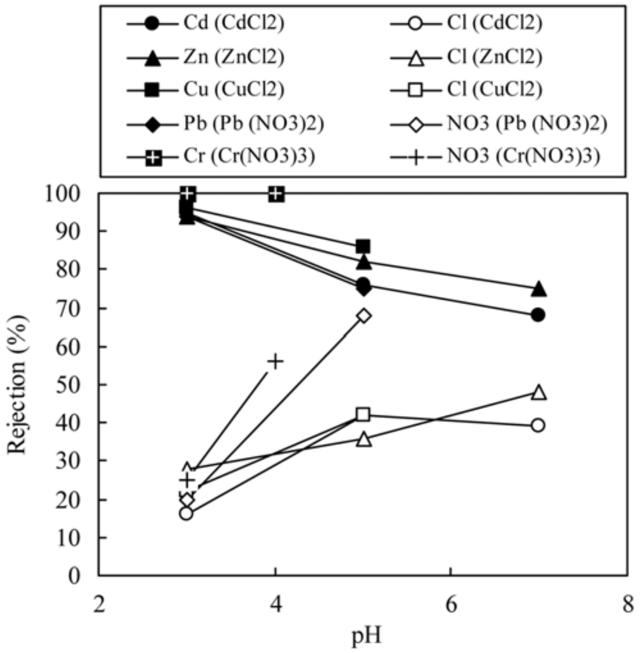

Fig. 8. Effect of pH on the rejection of heavy metals using UTC-60 membrane.

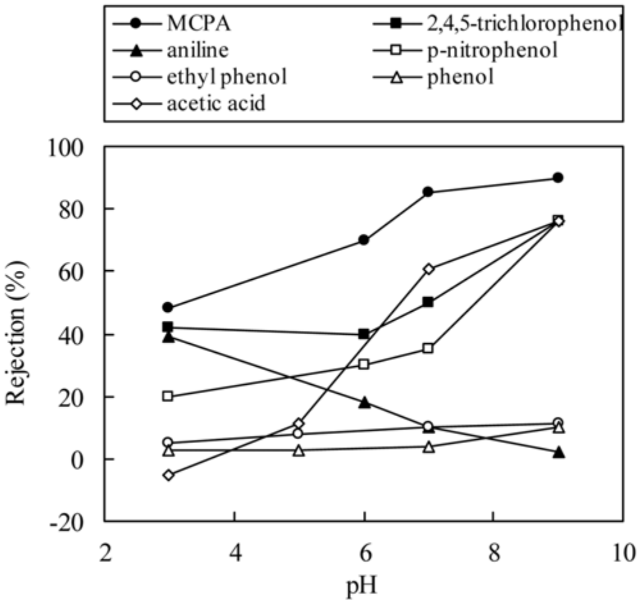

Fig. 9. Effect of pH on the rejection of organic compounds using NTR-729HF membrane.

2. Effect of pH on the Rejection of Organics

Fig. 9 shows the effect of pH of the feed solution on the rejection of typical organics as listed in Table 3. The NTR-729HF membrane was used for a series of experiments. The rejection of MCPA, whose pKa value is 3.1, increased with an increase of pH value of feed solution. In addition, the rejections of *p*-nitrophenol (pKa=7.1) and 2,4,5-trichlorophenol (pKa=6.7) increased markedly with pH when pH was roughly above pKa. Theoretically, almost all dissociated organic compounds are in a state of ionic form when the solution pH is more than pKa. In the case of MCPA, *p*-nitrophenol and 2,4,5-trichlorophenol, the fraction in the state of negatively charged ions of those compounds increases with pH. On the other hand, the membrane used is negatively charged when the pH of the solution is more than the isoelectric point value of the membrane, and is positively charged when less than the isoelectric point value. Hence, it is considered that the increase of rejections of those compounds with pH, especially in the alkaline region, resulted from an increase of mutual repulsion between the compounds dissociated into ions and membrane. Furthermore, the decrease of rejection of MCPA below pH 5 would be caused by the attraction between the dissociated MCPA and the membrane. The rejection of acetic acid (pKa=4.7) was similar to those of compounds such as MCPA, although the MW of acetic acid is comparatively small. As for aniline, the rejection was opposite to that of MCPA. Phenol rejection was extremely low over the range of pH tested, probably because phenol was in a state of molecular form derived from its large pKa and the MW is not so large. Low rejection was also obtained for ethyl alcohol of undissociated compounds. However, glucose of large MW was rejected at a higher efficiency. From these results, it appears that the rejection of organic compounds by NF membrane is dependent on both the pKa value and MW.

Fig. 10 shows the relationship between pKa and the rejection of organic compounds. The plot of pKa versus rejection at pH 6 gave approximately a straight line (line A) with a negative slope (correlation coefficient (r)=0.87). For the case of pH 9, the plot gave two straight lines (lines B and C) across the pKa value of approximately 7. Their correlation coefficients are 0.74 and 0.99, respectively. As exhibited in Fig. 11, the rejection of organics seems to increase with MW and reaches 90% around MW 200, except for some exceptional data. Further studies are required to investigate the factors that take place in the separation of organics by NF membranes.

CONCLUSIONS

The effect of pH of feed solution on the rejection of inorganic salts and organic compounds using NF were investigated and the main findings were presented.

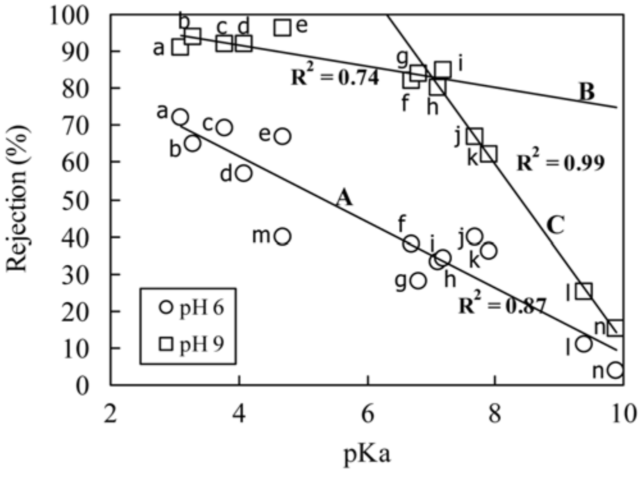

Fig. 10. The relationship between pKa and rejection (NTR-729HF).
a, MCPA; b, DNOC; c, 2,4-D; d, 2,4dichlorophenol; e, pentachlorophenol; f, 2,4,5-trichlorophenol; g, 2,6-dichloropheol; h, *p*-nitropheol; i, *o*-nitrophenol; j, 2,3-dichlorophenol; k, 2,4-dichlorophenol; *l*, 4-chlorophenol; m, acetic acid; n, phenol

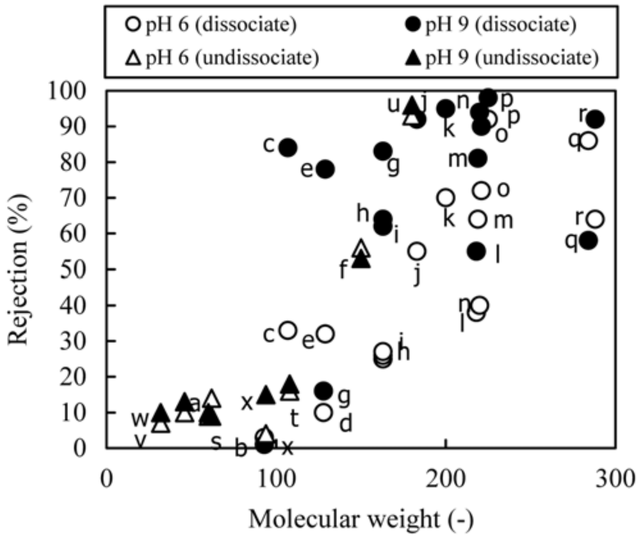

Fig. 11. The relationship between molecular weight and rejection (NTR-729HF).
a, ethylene glycol; b, aniline; c, *o*-nitrophenol; d, 4-chlorophenol; e, *p*-nitropheol f, triethylene glycol; g, 2,6-dichlorophenol; h, 2,4-dichlorophenol; i, 2,3-dichlorophenol; j, 2,4-dinitrophenol; k, MCPA; *l*, propanil; m, 2,4,5-trichlorophenol; n, DNOC; o, 2,4-D; p, 2,4,5-T; q, metolachlor; r, pentachlorophenol; s, urea; t, benzyl phenol; u, glucose; v, methyl alcohol; w, ethyl alcohol; x, phenol

The rejection of monovalent cations was found to decrease with the feed pH, which then increased after passing through a minimum point, according to the decrease or increase of mutual repulsion between the charged membrane and ions. On the other hand, the higher the pH of feed solution, the lower was the rejection of divalent cations including heavy metals. These phenomena could be explained by the reduction of surface charge of membrane caused by divalent cations, as well as the electric interaction between the charged membrane and ions in solution. The rejection of divalent anions was observed almost above 90% over the range of pH 3 to 9, higher than that of monovalent anions. In addition, it appears that the hydrated ion radius also affects the rejection of inorganic ions. As for organic compounds, the rejection was dependent on the pKa value of feed solution. For solutions with a higher fraction of ionic state in the compound, a higher rejection for the solute was obtained. There was also a strong correlation between molecular weight (MW) and the rejection. Most of the compounds whose MW were more than approximately 200 were rejected up to 90%.

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