Adsorption of Metal Ions on Polyaminated Highly Porous Chitosan Chelating Resin

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Adsorption of Metal Ions on Polyaminated Highly Porous Chitosan Chelating Resin

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Highly porous chelating resin was fabricated from the natural polysaccharide chitosan. The adsorption capacity was increased by polyamination with poly(ethylene imine) (MW = 10000). The capacity was about 1–2-times larger than that of commercial chelate resins. The selectivity for adsorption of metal ions on the resin, which was determined for a single solute at pH $\simeq$ 7, was Hg(II) > UO$_2$(II) > Cd(II) > Zn(II) > Cu(II) > Ni(II). Mg(II), Ca(II), Ga(III), As(III), and Sr(II) were not adsorbed on the resin at all. The selectivity depended on the pH of each metal solution. The equilibrium isotherms for adsorption of HgCl$_2$ were correlated by the Langmuir equation. The saturation capacities were close to the concentration of amino group fixed on the resin. When HCl or NaCl coexisted in HgCl$_2$ solution and their concentrations were lower than 100 mol/m^3, the saturation capacity of HgCl$_2$ was little affected by them. When 500 mol/m^3 H$_2$SO$_4$ coexisted in HgCl$_2$ solution, extremely low pH inhibited the adsorption of Hg(II) at all.

1. Introduction

Chitin, poly(*N*-acetyl-D-glucosamine) is produced in shells of crabs, shrimps, insects, fungal cell wall, etc. Chitin is virtually insoluble with water and organic solvents, so it has been considered to be an abundant biomass. Chitosan, poly(D-glucosamine) is obtained by deacetylation of chitin. Chitosan is soluble in acid solution and contains a reactive amino group, which is useful for chemical modifications. It has many useful features, for example, hydrophilicity, biocompatibility, biodegradability, antibacterial property, and remarkable affinity for many proteins. As it is harmless to humans and abundantly available, ion exchangers or adsorbents made from chitosan may also have potential as separators in food and pharmacy processes, medical and agricultural drugs, wastewater treatment, and other industrial applications.

Randall et al. (1979) reported that the high sodium content of the nickel waste did not prevent the adsorption of nickel ion onto chitosan flake. Yang and Zall (1984) reported that chitosan flake had the strongest chelating ability among some natural polymers generated from seafood processing wastes. Kobayashi and Nakayama (1985) and Shigeno et al. (1980) showed that chitosan flake or film adsorbed metal ions according to the complex formation reaction between the amino group of chitosan and metal ions. Inoue et al. (1991) and Baba et al. (1991) modified chitosan gel chemically and reported that the selectivity for adsorption of several ions depended on pH significantly. Kawamura (1991) reported that chitosan solution was effective as a coagulant aid in drinking water treatment, because it was biodegradable, nontoxic, and produced much less sludge than alum flocculation.

When we use chitosan as a separator in an industrial-scale column, flake and gel chitosan may cause a pressure drop, and they do not give a high efficiency. In the present work, we made spherical highly porous chitosan particles from chitosan. In order to make them inert to acid and chemicals, we cross-linked them. However, because of high porosity of the cross-linked chitosan particles (ϵ_p = 0.89), the concentration of amino group in the resin phase was smaller than in commercial synthesized chelating ion exchangers. In order to reduce this problem, we introduced poly(ethylene imine), which had primary, secondary, and tertiary amines, into the cross-linked chitosan particles.

Four different polyaminated chitosan particles were produced by introducing poly(ethylene imines) of MW = 300, 600, 1800, and 10000, respectively. We tested the selectivity for adsorption of 27 different metal ion species at pH = 7 on the polyaminated chitosan particles. The effect of pH of the solution on the selectivity was tested to show the possibility of using them as a separator of metal ions. Since Hg(II) was the most strongly adsorbed species, we presented the equilibrium isotherms for adsorption of HgCl$_2$ on the cross-linked chitosan particles and the four different polyaminated chitosan particles and discussed the adsorption mechanism.

## 2. Fabrication of Polyaminated Highly Porous Chitosan Beads

2.1. Preparation of Porous Chitosan Particles. We used a chitosan of which the molecular weight was about 50000 and the degree of deacetylated *N*-acetyl was 80%. Chitosan in the amount of 70 g was dissolved in 930 g of 3.5% acetic acid aqueous solution. The chitosan solution was sprayed into a diluted NaOH aqueous solution through a thin nozzle, and spherical porous chitosan particles were formed in the aqueous NaOH solution. The chitosan particles were washed with distilled water thoroughly. The mean diameter of the particles was 0.568 mm. Figure 1 shows scanning electron microscopy (SEM) views of the surface and cross section of a chitosan particle. Macropores are formed uniformly from the surface to inside. The diameters of the macropores were about 100 nm. The porous structure did not change after the cross-linking and polyamination reaction mentioned below. The porosity was 0.89 and the pore diameter was extremely large but the particles were hard.

2.2. Cross-Linking of Chitosan Particles. The chitosan particles were very stable in alkaline and neutral solutions. However, they dissolved easily in acid solution such as diluted acetic acid solution. In order to make them resistant to alkali, acid, and chemicals, we cross-linked them with a double functional compound as shown in Figure 2.

A sample of 500 cm^3 of chitosan particles was suspended in 500 cm^3 of distilled water. Thereafter, cross-linking reagent, ethylene glycol diglycidyl ether (Nagase Kasei Kogyo Co., Ltd., Japan), was added. The amount of the
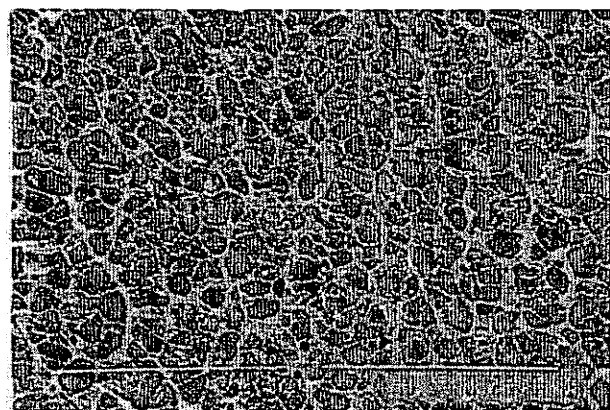
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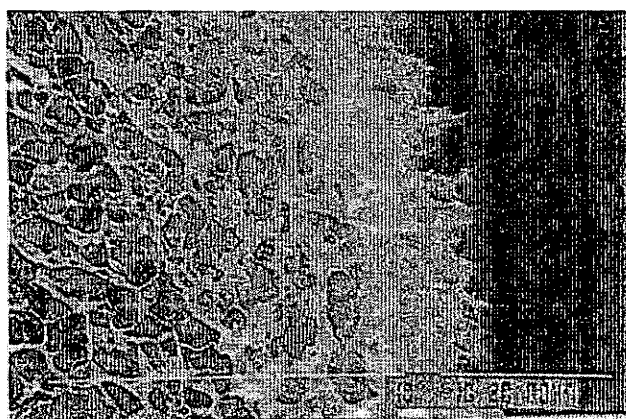
b

Figure 1. Scanning electron micrographics of PEI–chitosan: (a) surface structure; (b) cross-section structure.

reagent added was 8.0 g, which was 10% equivalent moles per glucosamine residue of the chitosan. The reaction was carried out at 70 °C for 3 h under gentle agitation. Since the chitosan particles were cross-linked successively, they did not dissolve in acetic acid solution. They had enough durability for acid solutions.

2.3. Polyamination of Cross-Linked Chitosan Particles. The cross-linked chitosan (hereafter called CRCH) particles adsorbed various metal ions, but because of the high porosity ($\epsilon_p = 0.89$), the adsorption capacities were about 3 times smaller than those of commercial chelating
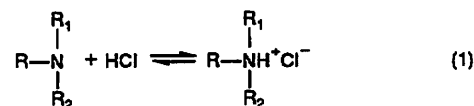
Table I. Concentration of Amino Groups Fixed in the Adsorbent Phase

chitosan resin	MW of PEI introduced	concn of amino groups fixed in ads phase (equiv/m^3 wet resin)
CRCH		670
PEI–CH-A	300	1490
PEI–CH-B	600	1770
PEI–CH-C	1800	2130
PEI–CH-D	10000	2260

ion exchangers. In order to increase the adsorption capacity, we introduced poly(ethylene imine) (hereafter called PEI) into CRCH particles. We used four different poly(ethylene imines), SP003, SP006, SP018, and SP200 (Nippon Shokubai Kagaku Co., Ltd., Japan), of which the molecular weights were 300, 600, 1800 and 10 000, respectively. The ratio of primary, secondary, and tertiary amines in PEI was 1:2:1 as shown in Figure 2.

The polyaminations were carried out as follows. CRCH particles suspended in water (total volume was 500 cm^3) was washed with 500 cm^3 of isopropyl alcohol four times and they were finally suspended in isopropyl alcohol of 500 cm^3. A sample of 8.5 g of epichlorohydrin (Wako Junyaku Kogyo Co., Ltd., Japan) was added to it. The amount of epichlorohydrin was 3 times equivalent moles per glucosamine residue of the chitosan. The reaction was carried out at 50 °C for 2 h. Thereafter, 100 cm^3 of chitosan beads was well mixed in 100 cm^3 of 30% PEI aqueous solution at 80 °C for 3 h. The finished product, PEI–chitosan particles, was washed with water thoroughly. We fabricated four different PEI–chitosans, PEI–CH-A, PEI–CH-B, PEI–CH-C and PEI–CH-D, by introducing PEI of molecular weights of 300, 600, 1800, and 10 000, into the CRCH particles, respectively.

2.4. Concentrations of Fixed Amino Group of CRCH and PEI–Chitosan. The concentrations of amino groups fixed in the adsorbent phase were determined by measuring the saturation capacities for adsorption of HCl. The reaction is shown by eq 1, where R denotes the net-

$$R-\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{N}} + HCl \rightleftharpoons R-\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{N}}H^+Cl^- \tag{1}$$

work of the resin; R_1 and R_2 show hydrogen or cross-linking reagent. Table I shows the results. The concentration of amino group of CRCH is the smallest, and it is even less than commercial chelating ion exchangers. This is because
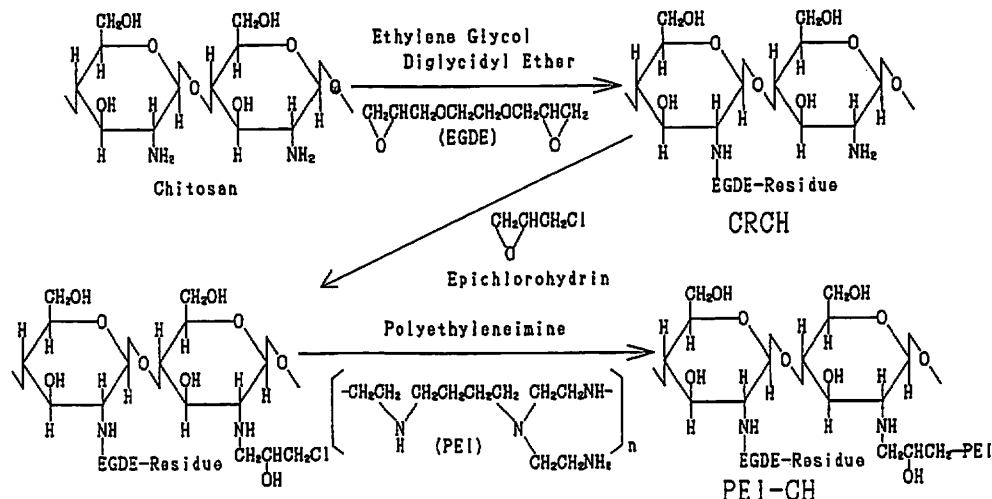

Figure 2. Scheme of cross-linking and polyamination reaction.

Table II. Selectivity for Adsorption of Metal Ions on PEI-CH-D^c

ion species	contents of metal std soln			final pH	final concn (ppm)
	solute	medium			
Al(III)	AlCl$_3$	1000 mol/m^3 HCl		7.05	98.3
As(III)	As$_2$O$_3$	1000 ppm NaCl		8.81	110.0
B(III)	H$_3$BO$_3$	water		7.55	96.3
Ba(II)	BaCl$_2$	1000 mol/m^3 HCl		7.05	99.2
Ca(II)	CaCl$_2$	1000 mol/m^3 HCl		7.27	100.2
Cd(II)	CdCl$_2$	1000 mol/m^3 HCl		7.21	0.2
Ce(III)	Ce(NO$_3$)$_3$	1000 mol/m^3 HNO$_3$		6.89	99.8
Co(II)	CoCl$_2$	1000 mol/m^3 HCl		7.15	33.3
Cr(III)	K$_2$Cr$_2$O$_7$	20 mol/m^3 HCl		8.85	30.1
Cu(II)	CuCl$_2$	100 mol/m^3 HCl		7.27	0.9
Ga(III)	Ga(NO$_3$)$_3$	1000 mol/m^3 HNO$_3$		6.88	102.0
Ge(IV)	K$_2$GeO$_3$	50 mol/m^3 K$_2$CO$_3$		7.84	67.4
Hg(II)	HgCl$_2$	20 mol/m^3 HCl		7.05	0.0
In(III)	In	500 mol/m^3 HNO$_3$		7.01	33.9
La(III)	La(NO$_3$)$_3$	1000 mol/m^3 HNO$_3$		7.02	96.1
Mg(II)	MgCl$_2$	20 mol/m^3 HCl		7.35	101.3
Mn(II)	MnCl$_2$	20 mol/m^3 HCl		7.32	85.1
Mo(III)	(NH$_4$)$_6$Mo$_7$O$_{24}$	water		8.85	29.0
Ni(II)	NiCl$_2$	100 mol/m^3 HCl		7.14	1.4
Pb(IV)	Pb(NO$_3$)$_2$	1000 mol/m^3 HNO$_3$		6.91	96.8
Si(IV)	Na$_2$SiO$_3$	200 mol/m^3 Na$_2$CO$_3$		9.26	53.2
Sn(IV)	SnCl$_2$	6000 mol/m^3 HCl		6.80	97.5
Sr(II)	Sr(NO$_3$)$_2$	1000 mol/m^3 HNO$_3$		6.92	100.0
Ti(III)	Ti(SO$_4$)$_2$	500 mol/m^3 H$_2$SO$_4$		6.95	97.8
UO$_2$(II)	UO$_2$SO$_4$	water		8.60	0.1
Y(III)	Y(NO$_3$)$_3$	1000 mol/m^3 HNO$_3$		7.02	90.5
Zn(II)	Zn(NO$_3$)$_2$	100 mol/m^3 HNO$_3$		7.19	0.5

^{a} Metal standard solution for atomic absorption analysis, which contained 1000 ppm solute in the medium, was neutralized with 100 mol/m^3 [bis(2-hydroxyethyl)amino]tris(hydroxymethyl)-methane to initial pH = 7.0 and diluted with water to initial concentration C_0 = 100 ppm. One milliliter of wet resin of PEI-CH-D was stirred in 80 mL of the metal solution at 25 °C for 72 h.

the amino groups are only those of chitosan as shown in Figure 2. On the other hand, the concentration of amino group increased with increasing the molecular weight of PEI introduced into CRCH. The concentration of amino group of PEI-CH-D is the highest. In spite of the high porosity (ϵ_p = 0.89), the amino group concentration is about 1–2 times larger than that of commercial chelating ion exchangers. These results may suggest that PEI-CH-D is feasible for recovery of metal ions.

3. Experimental Section

3.1. Selectivity for Adsorption of Metal Ions. The selectivity for adsorption of metal ions was determined by single-solute conditions. The solutes used are listed in Table II. Twenty-six different metal standard solutions for atomic absorption analysis (Wako Junyaku Kogyo Co., Ltd., Japan) were used for the experiments. Only UO$_2$(II)

was prepared by dissolving uranyl sulfate (99% purity) with water. The concentration and pH of each solution listed in Table II were adjusted to pH = 7.0 and 100 ppm using 100 mol/m^3 [bis(2-hydroxyethyl)amino]tris(hydroxymethyl)methane (Dohjin Kagaku Kenkyuhsyo Co., Ltd., Japan) and water. [Bis(2-hydroxyethyl)amino]tris-(hydroxymethyl)methane is a component of Good's buffer solution, which is supposed to be relatively inert for metal ions. One milliliter of wet resin of PEI-CH-D was stirred in 80 mL of the metal solution at 25 °C for 72 h. Initial concentration and equilibrium concentration of metal ion were measured with an inductively coupled plasma atomic emission spectrometer (SPS-7000; Seiko Denshi Kogyo Co., Ltd. Japan). We also tested the effect of pH on the amount of several ions, which appeared to be strongly adsorbed on PEI-CH-D. pH values of these metal solutions were also adjusted with 100 mol/m^3 [bis(2-hydroxyethyl)amino]tris(hydroxymethyl)methane and diluted with water to 100 ppm. The adsorbed-phase concentration was calculated according to eq 2, where C_0

$$q = \frac{V(C_0 - C)}{W} \qquad (2)$$

(mol/m^3) and C (mol/m^3) are initial concentration and equilibrium concentration of the ion in the liquid phase, respectively, q (mol/m^3 wet resin) denotes the adsorbed-phase concentration, and V (m^3) and W (m^3) are the volume of the solution and adsorbent particles, respectively.

3.2. Equilibrium Isotherm for Adsorption of HgCl$_2$. Equilibrium isotherms for adsorption of Hg(II) on CRCH and four different PEI–chitosans were measured by the batch method. HgCl$_2$ solutions were prepared by dissolving mercury(II) chloride (extra pure grade; Wako Junyaku Kogyo Co., Ltd., Japan) with water. In order to examine the effect of the accompanying salt or acid, NaCl, HCl, or H$_2$SO$_4$ was added to the HgCl$_2$ solution. The systems and conditions are given in Table III. The solution and the resin particles were well mixed. The equilibrium was fully reached in 4 days at 25 °C. The adsorbed-phase concentration of Hg(II) was calculated according to eq 2.

4 Results and Discussion

4.1. Selectivity for Adsorption of Metal Ions on PEI–CH-D. Since PEI–CH-D had the highest concentration of amino group in five chitosan chelating resins as shown in Table I, we considered the possibility of using PEI–CH-D for adsorption and separation of metal ions. Table II shows the final pH of the solution and the concentration of metal ion. The initial concentration of each metal ion was 100 ppm, and the initial pH of the solutions was 7.0. PEI–CH-D adsorbed Hg(II) completely and also

Table III. Experimental Conditions for Adsorption of Hg(II) on Cross-Linked Chitosan and PEI–Chitosan and Experimental Langmuir Coefficients

no.	chitosan resin	C_0 (mol/m^3)	$C_{0,NaCl}$ (mol/m^3)	$C_{0,HCl}$ (mol/m^3)	C_{0,H_2SO_4} (mol/m^3)	q_0 (mol/m^3)	K (m^3/mol)	q_0/Q
1	CRCH	1, 5, 10, 25, 50, 100	0	0	0	660	0.382	0.99
2	PEI-CH-A	1, 5, 10, 25, 50, 100	0	0	0	1420	0.384	0.95
3	PEI-CH-B	1, 5, 10, 25, 50, 100	0	0	0	1820	0.325	1.03
4	PEI-CH-C	1, 5, 10, 25, 50, 100	0	0	0	2040	0.354	0.96
5	PEI-CH-D	1, 5, 10, 25, 50, 100	0	0	0	2090	0.459	0.92
6	PEI-CH-D	1, 5, 10, 25, 50, 100	10	0	0	2020	0.776	0.89
7	PEI-CH-D	1, 5, 10, 25, 50, 100	100	0	0	1940	0.442	0.86
8	PEI-CH-D	1, 5, 10, 25, 50, 100	1000	0	0	770	0.484	0.34
9	PEI-CH-D	1, 5, 10, 25, 50, 100	0	10	0	1880	0.237	0.83
10	PEI-CH-D	1, 5, 10, 25, 50, 100	0	100	0	1540	0.223	0.68
11	PEI-CH-D	1, 5, 10, 25, 50, 100	0	1000	0	1010	0.190	0.45
12	PEI-CH-D	1, 5, 10, 25, 50, 100	0	0	500	0		
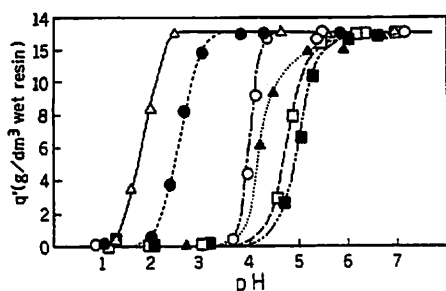
Figure 3. Effect of pH on amounts of metal ions adsorbed on PEI–CH–D: (○) $UO_2(II)$; (●) Cu(II); (□) Cd(II); (■) Zn(II); (▲) Hg-(II); (▲) Ni(II).

showed very high selectivity for $UO_2(II)$, Cd(II), Zn(II), Cu(II), and Ni(II). Mg(II), Ca(II), Ga(III), As(III), and Sr(II) were not adsorbed at all. B(III), Al(III), Ti(III), Sn(IV), Ba(II), Pb(IV), La(III), and Ce(III) were adsorbed little. The selectivity was Hg(II) > $UO_2(II)$ > Cd(II) > Zn(II) > Cu(II) > Ni(II) ≫ Mo(III) = In(III) ≫ Si(IV) ≫ Y(III). Bjerrum (1941) presented the formation constants of (K_n) of metal–ammonia complexes (eq 3) as below

$$[M(NH_3)_{n-1}]^{m+} + NH_3 \overset{K_n}{\rightleftharpoons} [M(NH_3)_n]^{m+} \quad (3)$$
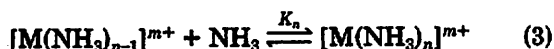
where M^{m+} is a metal ion.

Ag(I): $\quad K_1 = 2000, \quad K_2 = 7000$

Cd(II): $\quad K_1 = 500, \quad K_2 = 100, \quad K_3 = 20, \quad K_4 = 8,$
$$K_5 = 0.5, \quad K_6 = 0.02$$

Co(II): $\quad K_1 = 100, \quad K_2 = 40, \quad K_3 = 10, \quad K_4 = 5,$
$$K_5 = 1, \quad K_6 = 0.2$$

Cu(II): $\quad K_1 = 12000, \quad K_2 = 3000, \quad K_3 = 800,$
$$K_4 = 120, \quad K_5 = 0.3$$

Hg(II):
$$K_1 = 6 \times 10^8, \quad K_2 = 5 \times 10^8, \quad K_3 = 10, \quad K_4 = 6$$

Mg(II): $\quad K_1 = 1.7, \quad K_2 = 0.7, \quad K_3 = 0.4, \quad K_4 = 0.2,$
$$K_5 = 0.1, \quad K_6 = 0.05$$

Ni(II): $\quad K_1 = 500, \quad K_2 = 150, \quad K_3 = 50, \quad K_4 = 15,$
$$K_5 = 5, \quad K_6 = 1$$

Zn(II): $\quad K_1 = 200, \quad K_2 = 250, \quad K_3 = 300, \quad K_4 = 120$

Since the selectivities of the ions are Hg(II) > Cu(II) > Ni(II) > Cd(II) > Zn(II) and are similar to our results, the adsorption of metal ions on PEI–chitosan may be ligand sorption on amino groups fixed in the chitosan particle.

Since Hg(II), $UO_2(II)$, Cd(II), Zn(II), Cu(II), and Ni(II) appeared to be very strongly adsorbed species at pH ≃ 7.0, we tested the effect of pH on the amount of those ions adsorbed. Figure 3 shows the relation between equilibrium concentration of the ion in the resin phase and pH. The initial liquid-phase concentration of each ion was 100 ppm. The amount of ion adsorbed decreased with decreasing pH, but the effect of pH is different for each. The selectivities of the ions are Hg(II) > Cu(II) > $UO_2(II)$ > Ni(II) > Cd(II) > Zn(II), which are similar to eq 3. These results may suggest that PEI–CH–D is useful for separation and recovery of those ions.

4.2. Equilibrium Isotherm for Adsorption of $HgCl_2$.
We measured the equilibrium isotherms for adsorption of Hg(II), which was the most strongly adsorbed species, on the three different PEI–chitosan resins to confirm whether the adsorption capacities were enough or not. Figure 4 shows the experimental equilibrium isotherms for adsorption of $HgCl_2$ on CRCH, PEI–CH–A, and PEI–CH–D from pure aqueous $HgCl_2$ solution. The isotherms showed
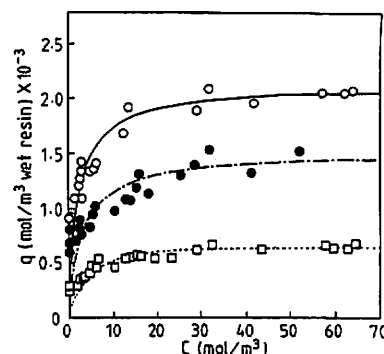

Figure 4. Equilibrium isotherms for adsorption of $HgCl_2$ on (□) CRCH, (●) PEI–CH–A, and (○) PEI–CH–D.

very favorable for adsorption of $HgCl_2$ on the resins. The lines show the Langmuir isotherm, eq 4, where K (m^3/mol)
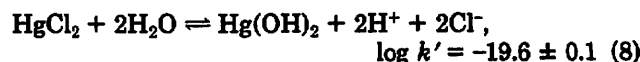
$$q = \frac{Kq_0C}{1 + KC} \quad (4)$$

and q_0 (mol/m^3 wet resin) are the equilibrium constant and saturation capacity, respectively. The experimental Langmuir coefficients are listed in Table III. The saturation capacity (q_0) for the CRCH was the smallest, and it increased with increasing molecular weight of PEI that had been introduced into CRCH. The equilibrium constant (K) for PEI–CH–D was higher than CRCH. That is, for PEI–CH–D, which was made by introducing PEI of molecular weight 10 000 into CRCH, both the saturation capacity and equilibrium constant became higher than those for CRCH.

Ciavatta and Grimaldi (1968a) discussed the ionization of $HgCl_2$ in the liquid phase and calculated the formation constants (k_1, k_1k_2) as below.

$$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+, \quad \log k_1 = 6.72 \pm 0.02 \quad (5)$$

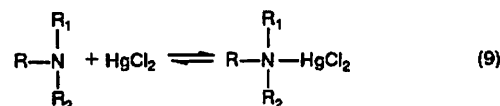$$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2, \quad \log k_1k_2 = 13.23 \pm 0.02 \quad (6)$$

The formation constants show that the concentration of Hg^{2+} is negligibly small. Ciavatta and Grimaldi (1968b) also showed the reactions, eqs 7 and 8. In the case of the $HgCl_2 + H_2O \rightleftharpoons HgClOH + H^+ + Cl^-$,

$$\log k = -9.56 \pm 0.05 \quad (7)$$

$HgCl_2 + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^+ + 2Cl^-$,

$$\log k' = -19.6 \pm 0.1 \quad (8)$$

single-solute system of $HgCl_2$, the dissociation constants (k, k') denote that $HgCl_2$ does not dissociate at all in the liquid phase. That is, the concentration of any ionized or dissociated species from $HgCl_2$ was negligibly small, and we can assume that only $HgCl_2$ existed in the experimental solution. Since the saturation capacity (q_0) was nearly equal to the concentration of amino group in the resin phase (Q) as shown in Table III, Hg(II) may be adsorbed on the resin not by ion exchange but by the following complex formation reaction:

$$\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{R-N}} + HgCl_2 \rightleftharpoons \underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{R-N}}-HgCl_2 \quad (9)$$

Applying the mass action law to eq 9, eq 4 is derived directly.

Supposing industrial use, we tested the effect of NaCl and HCl on the equilibrium isotherms for adsorption of Hg(II) on PEI–CH–D. When garbage containing mercury is burned, it vaporizes into flue gas, and the mercury is recovered by washing the flue gas with aqueous HCl so-
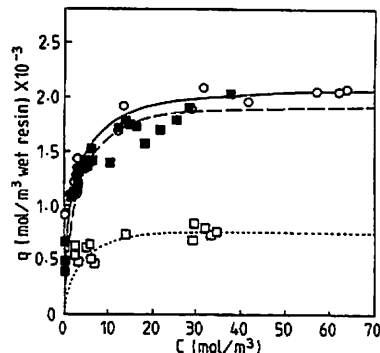
Figure 5. Effect of NaCl on equilibrium isotherms for adsorption of $HgCl_2$ on PEI–CH-D: (□) 1000 mol/m^3 NaCl; (■) 100 mol/m^3 NaCl; (O) 0 mol/m^3 NaCl.
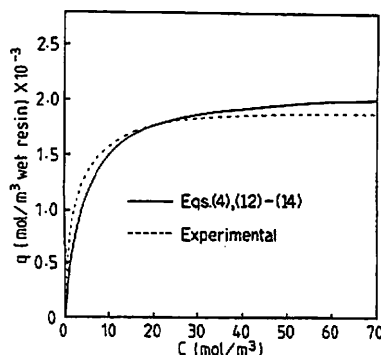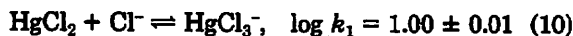

Figure 6. Langmuir isotherms for adsorption of $HgCl_2$ in 100 mol/m^3 NaCl solution.

lution in a scrubber. The solution is usually neutralized with NaOH, so it contains $HgCl_2$, NaCl, and/or HCl.

Figure 5 shows the effect of NaCl on the equilibrium isotherm for adsorption of $HgCl_2$ on PEI–CH-D. When the concentration of NaCl was 100 mol/m^3, NaCl affected the equilibrium little. However, when the concentration of NaCl was 1000 mol/m^3, the saturation capacity of $HgCl_2$ was reduced to 770 mol/m^3. This may be because the concentration of $HgCl_2$ decreases by ionization with Cl$^-$ ion. Ciavatta and Grimaldi (1968a) showed the following complex formation reactions in the liquid phase when concentrated NaCl and/or HCl coexisted in $HgCl_2$ solution.

$$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^-, \quad \log k_1 = 1.00 \pm 0.01 \quad (10)$$

$$HgCl_2 + 2Cl^- \rightleftharpoons HgCl_4^{2-}, \quad \log k_1k_2 = 1.97 \pm 0.025 \quad (11)$$

The reaction of eq 11 can be neglected in the case of low concentration of $HgCl_2$. Kataoka and Yoshida (1988) presented that the concentration of $HgCl_2$, C (mol/m^3), for the ($HgCl_2$ + NaCl + HCl) solution could be calculated from eqs 12–14, where, in mol/m^3, a_0, [H$^+$], and [Na$^+$] are

$$C = \frac{-\xi + (\xi^2 + 4\beta\gamma_{Cl}a_0)^{1/2}}{2\beta\gamma_{Cl}} \quad (12)$$

$$\xi = \gamma_{Cl}\beta([H^+] + [Na^+] - a_0) + 1 \quad (13)$$

$$-\log \gamma_{Cl} = \frac{0.51([H^+] + [Na^+])^{1/2}}{1 + 0.99([H^+] + [Na^+])^{1/2}} \quad (14)$$

the concentrations of ($HgCl_2$ + $HgCl_3^-$), H$^+$ ion, and Na$^+$ ion, respectively. β is the equilibrium coefficient for eq 10, and the value is 10 (Ciavatta and Grimaldi, 1968a,b). γ_{Cl} is the activity coefficient of Cl$^-$ ion. When a_0 = [$HgCl_2$ + $HgCl_3^-$] is 50 mol/m^3, eqs 12–14 give the value of C = [$HgCl_2$] = 50, 47.0, 31.0, and 7.92 mol/m^3 for [NaCl] = 0,

10, 100, and 1000 mol/m^3, respectively. The concentration of $HgCl_2$ decreases with increasing concentration of NaCl. Therefore, the amount of $HgCl_2$ adsorbed on the resin according to eq 9 may decrease with increasing concentration of NaCl. Figure 6 shows the Langmuir isotherms for adsorption of $HgCl_2$ in the case that 100 mol/m^3 of NaCl coexisted in the solution. The solid line represents the Langmuir isotherm (eq 4) using the C value calculated from eqs 12–14 and q_0 and K which were obtained from pure $HgCl_2$ solution. The dotted line represents the experimental isotherm. Since there is little difference between them, the reaction may be given by eq 9 when NaCl coexisted in $HgCl_2$ solution, too.

Figure 7 shows the effect of HCl on the equilibrium isotherm for adsorption of $HgCl_2$. The amount of $HgCl_2$ adsorbed decreased with increasing concentration of HCl. The saturation capacity of $HgCl_2$ was reduced to 1010 mol/m^3 wet resin when the concentration of HCl was 1000 mol/m^3. The saturation capacity is larger than that when the same concentration of NaCl coexisted in $HgCl_2$ solution as mentioned above. This may be caused by the different adsorption mechanism. When concentrated HCl coexisted in the solution, almost all amino groups of the resin adsorbed HCl according to eq 1. Therefore, Hg(II) is not adsorbed by eq 9 but is adsorbed by the following ion exchange reaction.
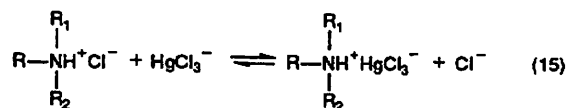
Therefore, even when concentrated HCl such as 1000 mol/m^3 coexists in $HgCl_2$ solution, PEI–CH-D can adsorb $HgCl_2$, although the amount of $HgCl_2$ adsorbed is smaller than that for pure $HgCl_2$ aqueous solution.

We also tested the effect of H_2SO_4 on the equilibrium isotherm for adsorption of $HgCl_2$. When 500 mol/m^3 H_2SO_4 coexisted in $HgCl_2$ solution, Hg(II) was not adsorbed on PEI–CH-D at all. This may be explained as follows. Hg(II) does not form any complex with SO_4^{2-}, so $HgCl_2$ is not ionized by SO_4^{2-} in the liquid phase like eq 10. On the other hand, almost all amino groups in the liquid phase adsorb H_2SO_4 by an acid/base neutralization reaction (eq 16). H$^+$ is adsorbed on the amino group strongly and SO_4^{2-} exists near amines.

Since when H_2SO_4 coexists in the solution anionic complex of $HgCl_2$ does not exist in the solution as mentioned
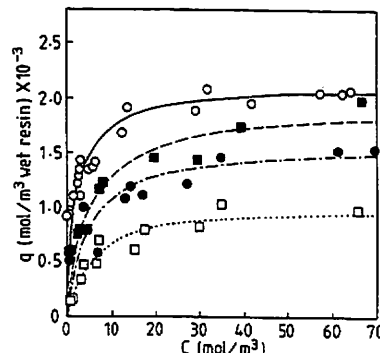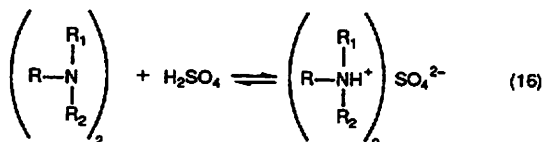
Figure 7. Effect of HCl on equilibrium isotherms for adsorption of $HgCl_2$ on PEI–CH-D: (□) 1000 mol/m^3 HCl; (●) 100 mol/m^3 HCl; (■) 10 mol/m^3 HCl; (O) 0 mol/m^3 HCl.

above, $HgCl_2$ is not adsorbed by the ion exchange reaction such as eq 15. Further, free amino group does not exist in the resin phase because of the reaction of eq 16, and $HgCl_2$ is not adsorbed by eq 9. This means that $HgCl_2$ adsorbed in the resin can be desorbed easily using 500 mol/m^3 aqueous H_2SO_4 solution. In fact, desorption of Hg(II) was perfectly performed with 500 mol/m^3 aqueous H_2SO_4 solution at room temperature without swelling of resin. The regeneration of the resin was performed by neutralization of adsorbed H_2SO_4 with NaOH aqueous solution and washing with excess of deionized water.

5. Conclusion

Highly porous PEI–chitosan resin (PEI–CH) appears feasible for separation and recovery of metal ions.

(i) The concentration of amino group fixed in the resin phase, Q, increased with increasing molecular weight of poly(ethylene imine) introduced into the highly porous cross-linked chitosan particles (CRCH). The value of Q was 2260 mol/m^3 when the poly(ethylene imine) of MW = 10 000 was introduced (PEI–CH-D). It is 1–2 times larger than that for the commercial synthesized chelating resin.

(ii) The selectivity for adsorption of metal ions on PEI–CH-D at pH $\simeq$ 7 was Hg(II) > UO_2(II) > Cd(II) > Zn(II) > Cu(II) > Ni(II) $\gg$ Mo(III) = In(III) $\gg$ Si(IV) $\gg$ Y(III). Mg(II), Ca(II), Ga(III), As(III), and Sr(II) were not adsorbed on the resin at all. B(III), Al(III), Ti(III), Sn(IV), Ba(II), Pb(II), La(III), and Ce(III) were adsorbed significantly.

(iii) Experimental equilibrium isotherms for adsorption of $HgCl_2$ were correlated by the Langmuir equation. The saturation capacity was almost the same as the concentration of amino group in the resin phase. Even when 1000

mol/m^3 HCl or NaCl coexisted in the solution, the saturation capacity of $HgCl_2$ was enough for recovery.

(iv) PEI–CH-D did not adsorb $HgCl_2$ at all when 500 mol/m^3 H_2SO_4 coexisted in the solution. This means that $HgCl_2$ adsorbed in the resin can be desorbed easily using 500 mol/m^3 aqueous H_2SO_4 solution.

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