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Adsorption of Cu^{2+} or Hg^{2+} Ion on Resins Prepared by Crosslinking Metal-Complexed Chitosans

Kazuya Ohga* Yoshiaki Kurauchi, and Hiroshi Yanase
Department of Environmental Chemistry and Engineering, Faculty of Engineering, Oita University,
Dannoharu, Oita 870-11

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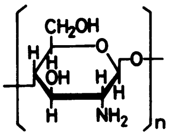
Synopsis. Crosslinking metal-complexed chitosans (metal ions=Cu(II), Cd(II), Zn(II), Ni(II), and Fe(III)) with (chloromethyl)oxirane yields resins having higher abilities to adsorb Cu^{2+} than a resin obtained from chitosan in the absence of metal ion. Resins from Cd(II)-chitosan complex can act as effective adsorbents for Hg^{2+}; their Langmuir's adsorption parameters depend on the quantity of (chloromethyl)oxirane used.

Chitosan has been used as an effective coagulating agent in activated sludge plants and for recovering proteins from food processing factories. This inexpensive polysaccharide can also act as an adsorbent for transition metal ions through chelation,[1—7] in which the amino group of the 2-amino-2-deoxy-D-glucose (glucosamine) unit plays an important role. The amino group is also responsible for dissolution of chitosan in acidic media.[2,3,5,7] This is one serious disadvantage from the practical viewpoint; thus, we attempted to crosslink chitosan with (chloromethyl)oxirane.[8] However, the crosslinking resulted in significant lowering of adsorptive activity, as will be described later. In the present paper, we describe that this problem can be largely overcome by crosslinking metal-complexed chitosan. Central metal ions of complexes are most likely to protect the amino group effective for the adsorption against the attack of the crosslinking agent and, at the same time, to preserve adsorption domains.



Chitosan

Experimental

Chitosan (Tokyo Kasei) was purified through gelation of its aqueous acetic acid solution with KOH, lyophilized, and sufficiently dried in vacuo (<0.13 Pa) for 2 d. The other reagents were of reagent or higher grade and used without further purification. All solutions were prepared with distilled, deionized water.

Preparation of Crosslinked Chitosan. Chitosan (5 g) was crosslinked with (chloromethyl)oxirane (2.9 g, equimolar to the glucosamine unit on the assumption that the chitosan is deacetylated completely[9]) accoding to the procedure reported by Noguchi et al.[10] The resin (NM-R) obtained was dried in vacuo (<0.13 Pa) to a constant weight 6.5 g.

Crosslinking of Metal-Complexed Chitosans. A 0.2 mol dm^{-3} NaOH solution was added dropwise to a 0.3 mol dm^{-3} acetic acid solution (40 cm^3) containing chitosan (500 mg) and a metal chloride ($CuCl_2$, $CdCl_2$, $ZnCl_2$, $NiCl_2$, or $FeCl_3$, equimolar to the glucosamine unit) with vigorous stirring to get a gelatinous metal-complexed chitosan.[5] The addition of the NaOH solution was stopped just before the solution pH got abruptly increased. The gel isolated after centrifugation was crosslinked with (chloromethyl)oxirane (2.9 g, ten times the molar quantity of the glucosamine unit) by the above method. The resin obtained was washed with 1.2 mol dm^{-3} HCl and 0.3 mol dm^{-3} acetic acid repeatedly to remove the metal ion and uncrosslinked chitosan, except for the Fe(III) complex which required conc. HCl to get rid of Fe^{3+} ion completely. The metal-free resin was washed subsequently with 0.2 mol dm^{-3} NaOH and with deionized water to neutral pH, and then dried similarly to the chitosan resin prepared in the absence of metal ion. The yields of the resins from the Cu(II)-, Cd(II)-, Ni(II)-, Zn(II)-, or Fe(III)-complex (abbreviated as Cu-R, Cd-R, Ni-R, Zn-R, or Fe-R, respectively) were 479, 477, 489, 487, and 250 mg, respectively. Likewise, crosslinking of the Cd(II) complex at (chloromethyl)oxirane/glucosamine unit molar ratios of 0.5, 1.0, 4.0, and 6.0 gave resins Cd-R$_{0.5}$, Cd-R$_1$, Cd-R$_4$, and Cd-R$_6$ in yields of 368, 394, 432, and 456 mg, respectively.

Equilibrium Adsorption Test. The resin was ground and sieved to 100—200 mesh size. After having been dried to constant weight, the sieved resin (10 mg) was placed in glass test tubes (16.5×165 mm), to which were added 0.05 mol dm^{-3} acetic acid/sodium acetate buffer solution (pH 5.0, 5 cm^3) containing a metal chloride (0.500—5.00 mmol dm^{-3} for Cu^{2+} or 1.00—8.00 mmol dm^{-3} for Hg^{2+}). The mixture was shaken at a shaking rate of ca. 110 strokes/min at 30.0±0.1 °C for 24 h. The equilibrated mixture was centrifuged, and then the supernatant solution was analyzed for the metal ion by atomic absorption spectrophotometry (Shimadzu AA-640-12). Hg^{2+} ion was determined by the cold vapor technique (Shimadzu mercury vaporizer unit MVU-1A). The quantity of metal ion adsorbed by the resin was obtained by subtracting the concentration in the supernatant solution from the initial concentration. A commercially available chelate resin, Chelex 100 (100—200 mesh; water content 68.8%), was also used for comparison.

Results and Discussion

Adsorption of Cu^{2+}. The ability of NM-R (the chitosan resin obtained in the absence of metal ion) to adsorb Cu^{2+} was first examined but no appreciable adsorption was observed. The resins prepared by crosslinking the metal-complexed chitosans adsorbed Cu^{2+} effectively. As Fig. 1 shows, the experimental isotherms obey the Langmuir equation, $C_{eq}/X=1/X_mb+C_{eq}/X_m$, where C_{eq} and X represent the equilibrium concentration of Cu^{2+} and the quantity of Cu^{2+} adsorbed, respectively. Adsorption parameters, binding constants b, and the quantities, X_m, of adsorbed Cu^{2+} ion with which the resins are saturated, are evaluated from the intercepts and slopes. The numerical data are summarized in Table 1, together

Table 1. Parameters for Cu^{2+} Adsorption

Adsorption parameters	Resins[a)]					
	Cu–R	Cd–R	Zn–R	Ni–R	Fe–R	Chelex 100
X_m/mmol g^{-1}	1.4	1.2	0.92	0.78	0.67	2.3
b/mmol^{-1} dm^3	1.1	1.1	1.0	0.51	0.73	1.9

a) Chitosan resins were prepared by crosslinking at a (chloromethyl)oxirane/glucosamine unit molar ratio of 10.

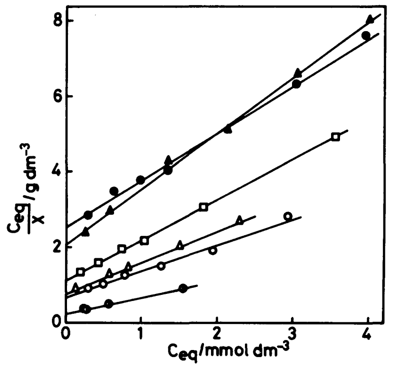


Fig. 1. Adsorption isotherms of Cu^{2+} on Cu–R(○), Cd–R(△), Zn–R(□), Ni–R(●), Fe–R(▲), and Chelex 100(◐) at 30.0 °C.

Table 2. Parameters for Hg^{2+} Adsorption

Adsorption parameters	Resins					
	Cd–R	Cu–R	Fe–R	Ni–R	NM–R[a)]	Chelex 100
X_m/mmol g^{-1}	1.6	1.5	1.3	1.1	0.85	1.5
b/mmol^{-1} dm^3	2.6	0.98	0.51	0.56	1.6	2.4

a) Prepared by crosslinking with (chloromethyl)oxirane of equimolar quantity to the glucosamine unit. For the other chitosan resins, see the footnote in Table 1.

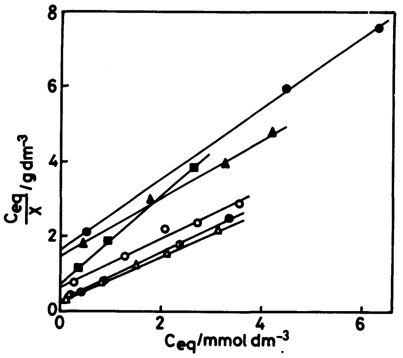


Fig. 2. Adsorption isotherms of Hg^{2+} on Cu–R(○), Cd–R(△), Ni–R(●), Fe–R(▲), NM–R(■), and Chelex 100(◐) at 30.0 °C. C_{eq} and X represent the equilibrium concentration of Hg^{2+} and the quantity of Hg^{2+} adsorbed, respectively.

with those for the commercial resin, Chelex 100. The quantities of Cu^{2+} uptake on the chitosan resins steeply decrease below pH 3, probably due to the protonation of the amino gourp of the glucosamine unit prevailing over its coordination to Cu^{2+}. The adsorption behavior was thus investigated at pH 5.0 where the precipitate of copper(II) hydroxide is not formed.

It is important to note here that lowering of the adsorption ability of parent chitosan by crosslinking was so small when the Cu(II)-chitosan complex (for resin (Cu–R), which of the chitosan resins has the largest adsorption parameters) was used; the uptake of Cu^{2+} from 5 cm^3 of an unbuffered solution ($[Cu^{2+}]$=1.17 mmol dm^{-3}) onto Cu–R or chitosan powder (10 mg) were 52 and 62%, respectively, at adsorption equilibrium. Thus, the central metal ions of the chitosan complexes serve to retain the adsorption ability of chitosan. This suggests that the metal ions can successfully leave domains available for the adsorption upon the removal of the ions from the resins. It is probable that the coordination of the amino groups to the metal ions leads to crosslinking between the hydroxyl groups so that the amino groups survive in the adsorption domains. Moreover, the fact that Cu–R has the largest adsorption parameters of the chitosan resins used, supports the idea that the Cu^{2+} ion in the complex serves, to some extent, as a template ion.[11)] The parameters for Cd–R, comparable to those for Cu–R, can be explained in terms of the large ionic radius of Cd^{2+}.

Table 1 also demonstrates that the abilities of the chitosan resins to adsorb Cu^{2+} are lower than that of Chelex 100. However, it should be emphasized that, for the adsorption of Hg^{2+}, Cd–R was found to possess a high ability comparable to that of Chelex 100 known as an excellent chelating resin for Hg^{2+},[6)] as will be mentioned in the following subsection.

Adsorption of Hg^{2+}. The isotherms for Hg^{2+} adsorption are also of Langmuir's type as shown in Fig. 2. The parameters obtained are summarized in Table 2.

Of the metal ions used for complexing with chitosan, Cd^{2+} has the largest ionic radius, so that Cd–R could be expected to have the greatest advantage for the adsorption of Hg^{2+} having a large ionic radius. This anticipation has been embodied by the large adsorption parameters of Cd–R, especially by its quite large binding constant comparable to that of Chelex 100.

NM–R has a moderate ability to adsorb Hg^{2+}. This adsorption behavior, different from the case of the Cu^{2+} adsorption, seems due to the coordination to Hg^{2+} of the hydroxyl groups and the ethereal oxygen atoms originating from the parent chitosan and (chloromethyl)oxirane. Thus, in the case of the resins from the metal-chitosan complexes also it is necessary to take into account the participation of these oxygen atoms.

Figure 3 and Table 3 are for the resins prepared by crosslinking the Cd(II)-chitosan complex with reduced quantities of (chloromethyl)oxirane. As Fig. 3

Table 3. Parameters for the Adsorption of Hg^{2+} on Resins Prepared by Crosslinking the Cd(II)-Chitosan Complex with Different Quantities of (Chloromethyl)oxirane

Adsorption parameters	Resins[a)]			
	Cd-R_6	Cd-R_4	Cd-R_1	Cd-$R_{0.5}$
X_m/mmol g^{-1}	1.8	1.9	2.5	2.6
b/mmol^{-1} dm^3	1.8	1.7	1.5	1.2

a) The numbers appearing after Cd-R denote the molar ratio of the (chloromethyl)oxirane used for crosslinking to the glucosamine unit.

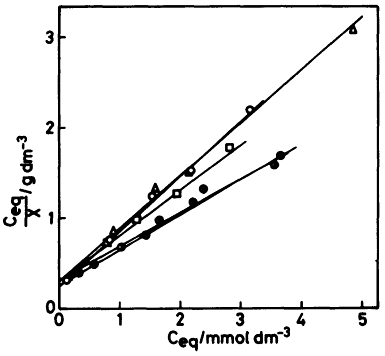


Fig. 3. Adsorption isotherms of Hg^{2+} on Cd-R_6(△), Cd-R_4(□), Cd-R_1(●), and Cd-$R_{0.5}$(◑) at 30.0 °C. For comparison, the isotherm for Cd-R(○) was plotted again. For C_{eq} and X, see the footnote in Fig. 2.

shows, Cd-R_4, Cd-R_1, and Cd-$R_{0.5}$ adsorb Hg^{2+} in larger quantities than Cd-R_6 and Cd-R do. Table 3 indicates that the X_m value progressively increases with decrease in the amount of (chloromethyl)oxirane used. The b value, on the contrary, tends to decrease. Thus, the above improvement of the adsorption ability by use of reduced quantities of oxirane, for which the resulting reduced degree of crosslinking is most probably responsible, is due to the increment in the X_m value prevailing over the decrement in the b value. The X_m value of Cd-R_1 is three times as large as that of NM-R (Table 2), which was crosslinked with the same molar quantity of (chloromethyl)oxirane as Cd-R_1. This again verifies the effectiveness of the central ion, Cd^{2+}, for leaving the domains available for the adsorption of Hg^{2+}.

Separation of Cu^{2+}, Hg^{2+}, and Cd^{2+} Ions. A great difference in the b value was observed between the adsorptions of Cu^{2+} and Hg^{2+} on the Cd-R resin (Tables 1 and 2). Moreover, Cd^{2+} was not adsorbed appreciably on Cd-R or Cd-R_6 under the same conditions as those for the Cu^{2+} or Hg^{2+} adsorption. These findings suggest that a selective separation of Cu^{2+}, Hg^{2+}, and Cd^{2+} ions is feasible by using an appropriate resin obtainable from the Cd(II)-complexed chitosan. Figure 4 illustrates that this separation may be achieved with 95—100% recovery by using a small column (8.0 cm×0.4 cm i.d.) containing 40 mg of Cd-R_6. The following solutions were successively used as eluents: 0.05 mol dm^{-3} acetate buffer, 1.00 mmol dm^{-3} HNO_3, and 0.5 mol dm^{-3} HNO_3. In addition, almost the same chromatograms were obtained when the metal ions were loaded into the column again after complete washing with deionized water, which indicates an effective durability in repeated use.

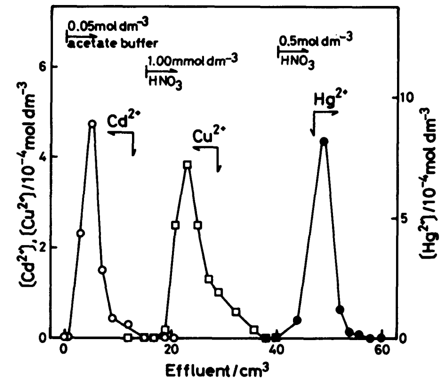


Fig. 4. Separation of Cd^{2+}, Cu^{2+}, and Hg^{2+} ions with a Cd-R_6 column (8.0 cm×0.4 cm i.d., 40 mg of Cd-R_6). The quantities of the metal ions loaded were 2 μmol for Cd^{2+}, 3 μmol for Cu^{2+}, and 4 μmol for Hg^{2+}. The flow rate was 2 cm^3/h.

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