Adsorption of Metal Ions on Chitosan and Crosslinked Copper(II)-Complexed Chitosan

Katsutoshi INOUE,* Yoshinari BABA,† and Kazuharu YOSHIZUKA
Department of Applied Chemistry, Faculty of Science & Engineering, Saga University, Saga 840
†Department of Material Engineering, Faculty of Engineering, Miyazaki University, Miyazaki 889-21

(Received May 17, 1993)

A fundamental investigation on the adsorption behavior of metal ions on chitosan from aqueous ammonium nitrate and hydrochloric acid solutions was conducted by batch-wise examining the effects by various factors: the pH, concentrations of ammonium nitrate and hydrochloric acid, and initial metal concentration on the amount of metals adsorbed. In order to prevent the dissolution loss of chitosan into an acidic aqueous solution, crosslinked copper(II)-complexed chitosan was prepared and its adsorption behavior was compared with that of the original chitosan. The amount of adsorption, not only of metal ions, but also of the hydrogen ion, was decreased by crosslinking in the adsorption from an ammonium nitrate solution. The decrease, however, was least for copper(II), compared with the other divalent metal ions examined: oxovanadium(II), zinc(II), nickel(II), and cobalt(II). It was considered that this result may be attributable to the "template" effect by the copper(II) ion, which was employed during crosslinking in order to protect the active adsorption site of chitosan from an attack by a crosslinking reagent. It was found that chitosan has an excellent loading capacity and a selectivity much greater than the commercial iminodiacetic acid type of chelating resin. A qualitative discussion is given concerning the excellent adsorption behavior. Contrary to the case of adsorption from an aqueous ammonium nitrate solution, no significant decreases in the distribution ratios were observed between the crosslinked copper(II)-complexed chitosan and the original chitosan regarding the adsorption of palladium(II) and platinum(IV) from hydrochloric acid.

In recent years, much attention has been paid to the adsorption of metals on various kinds of microorganisms or biomass, such as algae and fungi, as well as on their cell components: alginic acid, chitin, cellulose, and so on.[1] Among these, chitin is a main component existing in the shells of Crustaceans, such as crabs, shrimps, prawns, insects, and centipedes, and is easily prepared from their shells at cheap cost by removing other components, calcium and proteins, by treating with acids and alkalis, respectively. Consequently, it is one of the most abundant and cheap forms of bio-mass, as well as cellulose. Chitosan is also easily prepared from chitin by deacetylating its acetoamide groups with a strong alkaline solution. It is well known that chitosan as well as chitin exhibits an excellent adsorption behavior not only for metal ions, but also for a variety of organics, including polychlorinated biphenyls, and proteins, nucleic acid.[2] These properties are practically utilized in a wide range of fields: as an effective coagulating agent in activated sludge plants, for recovering proteins from food-processing factories, as carriers for immobilized enzymes, and for chromatographic separations.

In recent years, Fuji Spinning Co., Ltd. (Tokyo, Japan) has developed a variety of high-porous chitosan-based bead-type adsorbents under the trade name CHITOPEARL having different bead diameters, micropore sizes, specific surface areas as novel types of carriers for immobilized enzymes or gel matrix for affinity chromatography and so on.[3] These are highly crosslinked by hexamethylenediisocyanate or ethyleneglycol diglycydil ether and so on for the purpose of maintaining the mechanical strength of the bead carriers.

Although a considerable number of studies have so far been conducted concerning its application to chromatographic separations of metal ions, there have been only a few fundamental studies concerning its metal adsorption behavior; consequently, the mechanism of metal adsorption has not yet been elucidated. In the present work we conducted fundamental investigations on the metal adsorption on chitosan, carrying out batchwise experiments to examine various factors which affect the amount of adsorption of the metal ions.

Chitosan has some aqueous solubilities in some acidic media; that is, it is completely dissolved in organic acids, such as acetic acid and formic acid, and partially soluble in some mineral acids, nitric, hydrochloric, and perchloric acids, in the concentration range 0.05—0.5 $\mathrm{mol\,dm^{-3}}$. However, very surprisingly, it is quite insoluble in sulfuric acid solution over the entire concentration region at room temperature. In order to avoid dissolution in aqueous acid solutions, crosslinking between polymer chains has been proposed; however, the crosslinking results in a significant decrease in the adsorption capacity, due to the formation of chemical bonds at the adsorption sites. Ohga et al. successfully overcame this contradiction by crosslinking chitosan after complexation with metal ions to prepare chitosan-based adsorption gels that are insoluble in aqueous solutions without losing its high adsorption capacity.[4] This concept is similar to that proposed by Nishide and Tsuchida,[5] who prepared crosslinked poly(4-vinylpyridine) resins with high selectivity to the metal ion which was used as the template. It is consequently expected that the crosslinked metal-complexed chitosan exhibits not only a high loading capacity that is nearly equal to that of the original chitosan, but also high selectivity to the metal ion employed as the template.

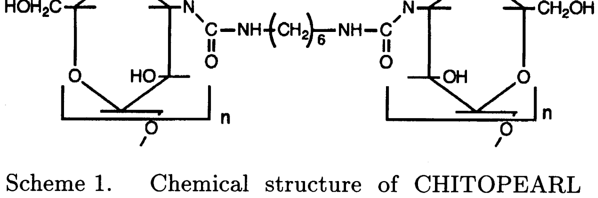
In the present work, from such a point of view, we examined the effect of crosslinking on the loading capacity and selectivity in the adsorption of various base metals from aqueous ammonium nitrate solution, the ionic strength of which was maintained constant and in that of palladium(II) and platinum(IV) from hydrochloric acid solution. In the latter case, we also examined adsorption on a commercial high-porous chitosan bead (CHITOPEARL BCW-3012) for a comparison, in order to again exemplify the effect of crosslinking.

Experimental

Reagents. Samples of chitosan powder prepared from shells of prawns were kindly donated from Katokichi Co., Ltd. (Kan-onji, Japan). The degree of deacetylation of the sample was greater than 95%, and it was used as delivered without further purification. The copper(II)-complexed chitosan crosslinked with (chloromethyl)oxirane according to a method partially modified to that proposed by Ohga et al. as follows: 5 g of the chitosan powder was mixed together with 400 ml of 0.3 mol dm^{-3} aqueous acetic acid solution containing 10 g of copper(II) chloride and stirred for about 12 h at 30 °C. The blue-colored solution was added dropwise from a burette into 1500 ml of a 0.2 mol dm^{-3} sodium hydroxide solution, and was further stirred for about 12 h to obtain a black-color gel. After filtration followed by several times washing with water, the gel was transferred into a flask where it was stirred together with 400 ml of water and 50 ml of (chloromethyl)oxyrane and refluxed for 1 h. After adding 300 ml of a 0.1 mol dm^{-3} aqueous sodium hydroxide solution, the mixture was further stirred and refluxed for 2 h. After filtration followed by water washing, the gel was washed with a 1.2 mol dm^{-3} hydrochloric acid solution to remove the copper(II) ion used as the template, and was then washed with water to neutral pH. It was further washed with a 0.2 mol dm^{-3} sodium hydroxide solution and then with water to convert it into the free amine form. After drying in vacuo, it was ground and sieved to smaller than 150 mesh size.

Sample of CHITOPEARL WBS-3012, supplied by Fuji Spinning Co., Ltd. (Tokyo, Japan) was also used after the usual conditioning. This adsorbent is a spherical bead of chitosan crosslinked by hexamethylenediisocyanate, the chemical structure of which is shown in Scheme 1.

In the cases of adsorption from an aqueous ammonium nitrate solution, aqueous metal solutions were prepared by dissolving the reagent grade of each corresponding metal nitrate, except for vanadium(IV) and molybdenum(VI), into a 1 mol dm^{-3} aqueous ammonium nitrate solution, except for in an experiment to examine the effect of the concentration of ammonium nitrate. In the cases of the adsorption of vanadium and molybdenum, reagent-grade oxovanadium(IV) nitrate and sodium molybdate were used, respectively. The pH of the aqueous metal solution was adjusted by adding a small amount of an aqueous ammonia or nitric acid solution. In the cases of the adsorption of palladium(II) and platinum(IV) from a hydrochloric acid solution, palladium(II) chloride, and hydrogen hexachloroplatinate(IV) hexahydrate (kindly donated by Tanaka Kikinzoku Kogyo K.K. (Tokyo, Japan)) were dissolved into hydrochloric acid.



Scheme 1. Chemical structure of CHITOPEARL BCW 3012.

Procedure. A weighed amount (around 50—100 mg) of dried crosslinked chitosan or original chitosan was shaken together with 20 ml of an aqueous metal solution in a stoppered glass flask using a water bath incubator maintained at 30±0.1°C for about 24 h. From the preliminary experiments, equilibrium was confirmed to have been attained within the period of shaking for all cases. The initial metal concentration was about 5 mmol dm^{-3} for all experiments, except for that carried out to examine the effect by the initial concentration of copper(II). The amount of adsorption was calculated based on the difference of the metal concentration in the aqueous solutions before and after adsorption, the volume of the aqueous solutions (20 ml) and the weight of the dry gel. The metal concentration in the aqueous solutions was measured by means of titration with EDTA or by using a Seiko (Hamamatsu, Japan) model SPS-7500 atomic absorption spectrophotometer, except for vanadium and molybdenum. The concentrations of vanadium and molybdenum were measured using a Shimadzu (Kyoto, Japan) ICPS-100 III ICP-AES spectrometer.

Results and Discussion

Adsorption from Aqueous Ammonium Nitrate Solution. Figure 1 is a plot of the distribution ratio of metal ions (D), which is defined as the ratio of the amount of metal ion adsorbed on a dry adsorbent (mol kg^{-1}) to its equilibrium concentration in an aqueous solution (mol dm^{-3}) against the equilibrium pH in the adsorption of molybdenum(VI), vanadium(IV), iron(III), indium(III), gallium(III), aluminum(III), copper(II), silver(I), nickel(II), cadmium(II), lead(II), zinc(II), and cobalt(II) on crosslinked copper(II)-complexed chitosan. Except for molybdenum(VI), the distribution ratio monotonously increases with increasing pH, and the plots appear to lie on a straight line with a slope equal to the valence of the adsorbed metal ion, except for vanadium(IV) and cobalt(II). That is, the plots for trivalent ions of iron(III), gallium(III), indium(III), and aluminum(III) lie on straight lines with a slope of 3, and that for monovalent silver on a straight line with a slope of unity, while those for divalent metal ions (copper(II), nickel(II), cadmium(II), lead(II), and zinc(II)) lie on lines with a slope of 2. These tendencies are analogous to those observed in the solvent extraction of cationic metal ions with acidic extractants, including chelating extractants; that is, this

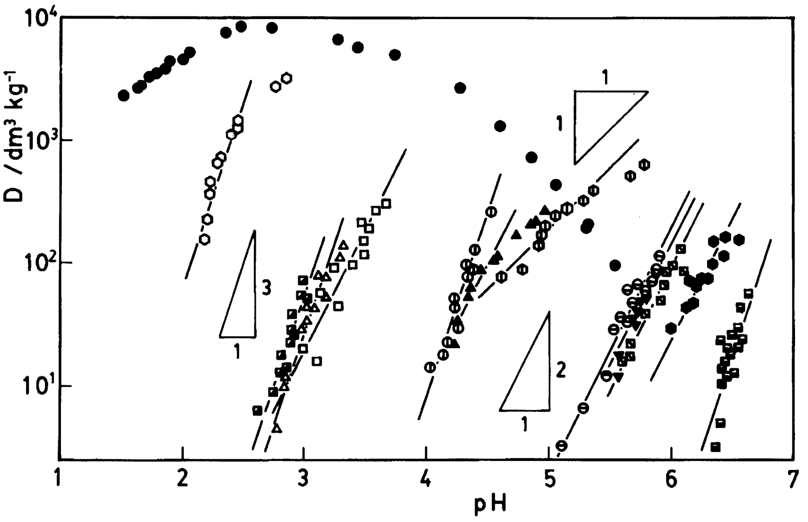


Fig. 1. Plots of the distribution ratio against the equilibrium pH in the adsorption of molybdenum(VI) (●), iron(III) (○), indium(III) (◪), gallium(III) (△), vanadium(IV) (□), aluminum(III) (⦶), copper(II) (▲), silver(I) (⦶), nickel(II) (⊖), cadmium(II) (▼), lead(II) (⧅), zinc(II) (⬢), and cobalt(II) (⬓) from a 1 mol dm^{-3} ammonium nitrate solution on crosslinked copper(II)-complexed chitosan.

result may be considered to suggest that metal ions are adsorbed according to the cation-exchange mechanism, which will be described in detail later. In the case of the adsorption of molybdenum(VI), the distribution ratio increases with increasing pH at low pH; after passing through the maximum at around pH= 2.5—3, it oppositely decreases with increasing pH at high pH, which is frequently observed in the solvent extraction of molybdenum(VI) with acidic extractants and is attributable to the formation of unadsorptive anionic species, such as $\mathrm{HMoO_4^-}$ and $\mathrm{MoO_4^{2-}}$. In the case of vanadium(IV), since it exists as the divalent oxovanadium ion, $\mathrm{VO^{2+}}$, it is very reasonable that the plots lie on a straight line with a slope of 2, similar to other divalent metal ions. In the case of cobalt(II), the plots appear to lie on a straight line with a slope of not 2, but 3, which might suggest that the divalent cobalt is oxidized to the trivalent state during adsorption as is frequently observed in solvent extraction with chelating extractants from aqueous ammoniacal solutions, as in the present case.

Figure 2 gives plots of the distribution ratio of copper(II) against the equilibrium pH from varying concentrations of ammonium nitrate solutions. The plots lie on a single straight line with a slope of 2, regardless of the large difference of ammonium nitrate concentrations at low pH, suggesting that the nitrate anion does not explicitly take part in the adsorption reaction, while they deviate downward at high pH, which may be attributable to the formation of copper(II)–ammine complexes in an aqueous solution, which are not (or less) adsorbed on chitosan. This is also the similar phenomenon commonly observed in solvent extraction with acidic extractants or in the ion-exchange adsorption on cation-exchangers, as is exemplified in Fig. 4.

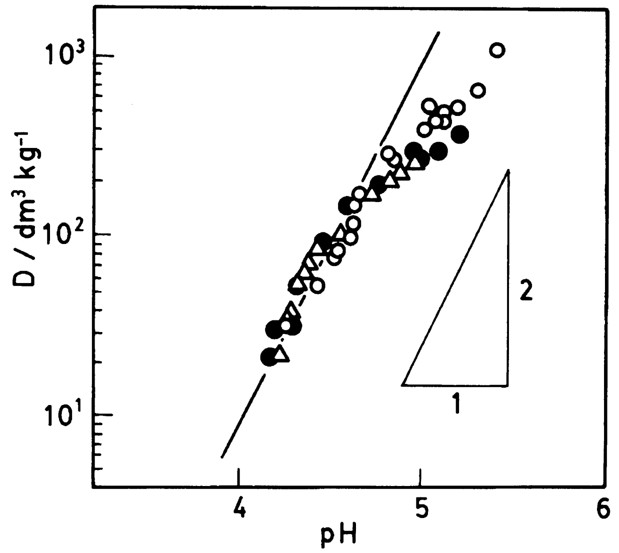


Fig. 2. Plot of the distribution ratio of copper(II) against the equilibrium pH in the adsorption on copper(II)-complexed chitosan from varying concentrations of ammonium nitrate solutions as follows: (○) 0.1 mol dm^{-3}, (△) 1.0 mol dm^{-3}, and (●) 3.0 mol dm^{-3}.

Figure 3 is a plot of the amount of adsorption of the hydrogen ion on original and crosslinked copper(II)-complexed chitosan from a 1 mol dm^{-3} aqueous ammonium nitrate solution against the equilibrium pH. From this figure, it can be seen that both are nearly saturated with hydrogen ion over the entire pH region less than 7, where the adsorption of all of the examined metal ions was observed, as shown in Fig. 1. It should therefore be concluded that the adsorption of metal ions takes place on the protonated chitosan.

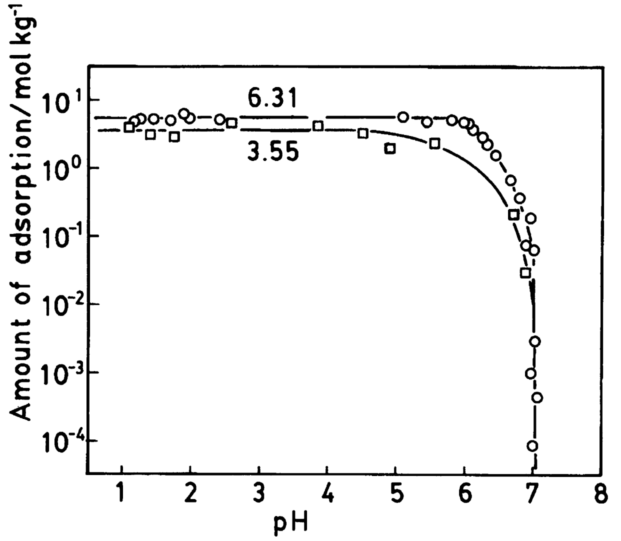


Fig. 3. Plot of amount of hydrogen ion adsorbed from a 1 mol dm^{-3} ammonium nitrate solution on original chitosan (○) and crosslinked copper(II)-complexed chitosan (□) against the equilibrium pH. The figures on each adsorption line denotes the maximum amount of adsorption on each adsorbent.

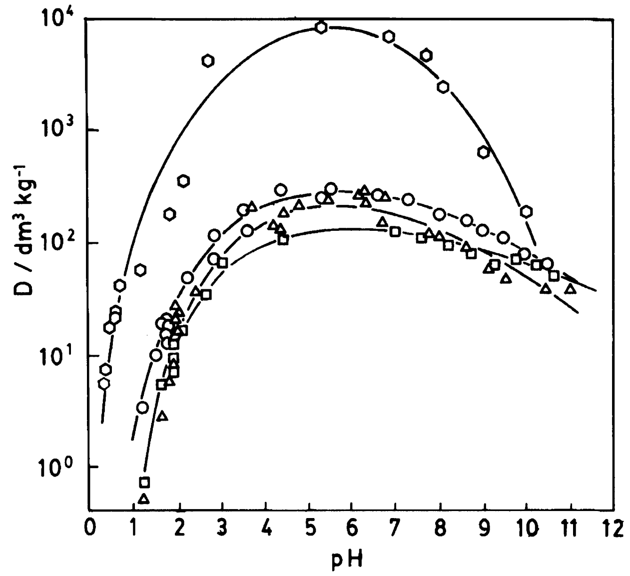


Fig. 4. Plot of the distribution ratio of divalent copper(II) (○), zinc(II) (△), nickel(II) (○), and cobalt(II) (□) against the equilibrium pH in the adsorption from a 1 mol dm^{-3} ammonium nitrate solution on a Lewaitit PT-207 chelating resin.

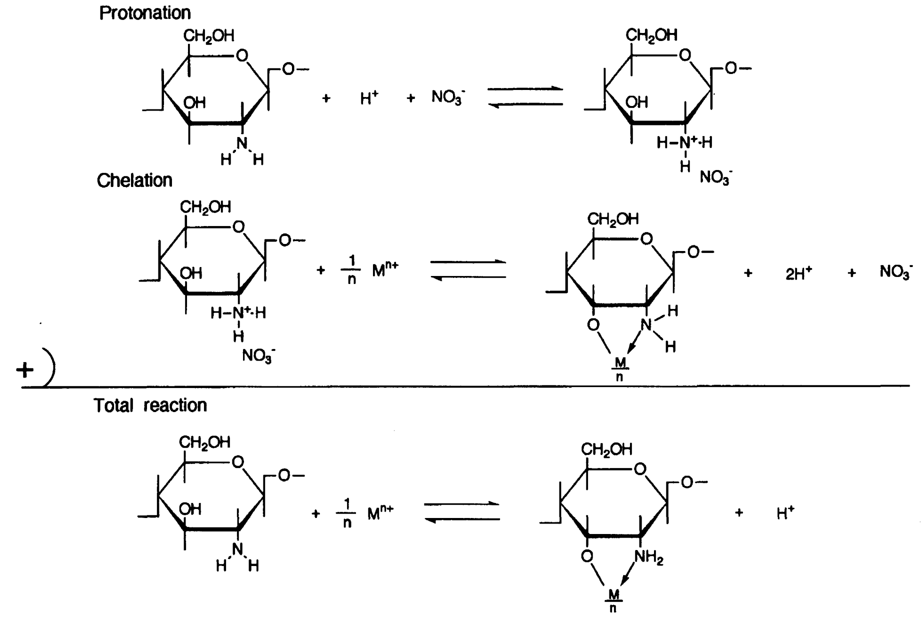
From these results it can be reasonably concluded that an n-valent metal ion is adsorbed according to the cation-exchange mechanism, releasing a total of n hydrogen ions, as shown in Scheme 2. Here, the adsorption reaction consists of two consecutive reactions: (1) protonation of the primary amino groups and (2) adsorption of the metal ions to form n stable five-membered chelate rings coordinated by free nitrogen atoms of primary amino groups and oxygen atoms of alcoholic hydroxy groups of chitosan.

Figure 4 is a similar plot of the distribution ratio of various divalent metal ions (copper(II), zinc(II), cobalt(II), and nickel(II)) against the equilibrium pH in the adsorption on a commercial iminodiacetic acid-type chelating resin (Lewatit TP-207, Bayer AG.) for a comparison of the selectivity to metal ions with the crosslinked copper(II)-complexed chitosan illustrated in Fig. 1. In this figure, although the adsorption line for copper(II) is much higher than those for other metal ions, suggesting that it is easy to selectively separate copper(II) by this chelating resin, those for nickel(II), zinc(II), and cobalt(II) are very contiguous to each other, suggesting difficulty of mutual separation among these three kinds of metal ions. In contrast to the poor selectivity of the commercial chelating resin, the selectivity exhibited by the crosslinked copper(II)-complexed chitosan (Fig. 1) is sufficiently high for the mutual separation of various pairs of metal ions to be effectively achieved; noticeable is the high selectivity to copper(II) over other divalent metals, to nickel(II) over cobalt(II), to iron(III) over other trivalent metals, to molybdenum(VI) over all of the other metals and so on. These remarkable features of metal adsorption on crosslinked copper(II)-complexed chitosan with excellently high selectivity may have a potential for extensive fields of application, not only for analytical purposes, but also for practical purposes in the metallurgical industry for the separation, concentration and purification of metals.

In Fig. 3, the amounts of hydrogen ion adsorbed from a 1 mol dm^{-3} acid solution are compared for crosslinked copper(II)-complexed chitosan and the original chitosan. This figure indicates that the maximum amount of hydrogen ion adsorbed is 3.55 and 6.31 mol kg^{-1}-dry gel, respectively, suggesting that the adsorption capacity significantly decreases by crosslinking, in spite of protecting the adsorption site of primary amino groups of chitosan by complexing with copper(II) ion against an attack by the crosslinking reagent.

Figure 5 illustrates the adsorption of various divalent metal ions (oxovanadium(II), copper(II), nickel(II), zinc(II), and cobalt(II)) on the crosslinked copper(II)-complexed chitosan and on the original chitosan for a comparison of the plot of the distribution ratio against the equilibrium pH. In this figure, the adsorption on the former decreases compared with the latter for all metal ions; the degree of the decrease is in the following order: oxovanadium(II) > zinc(II) > cobalt(II) = nickel(II) > copper(II). That is, the decrease in the amount of adsorption by crosslinking is least for copper(II), the metal ion employed for complexing with chitosan during crosslinking. This result might suggest a "template" effect by the copper(II) ion.

Figure 6 illustrates the relationship between the amount of copper(II) ion adsorbed on crosslinked copper(II)-complexed chitosan, the original chitosan and TP-207 chelating resin and the initial copper(II)



Scheme 2. Adsorption of *n*-valent metal ion on chitosan from ammonium nitrate solution.

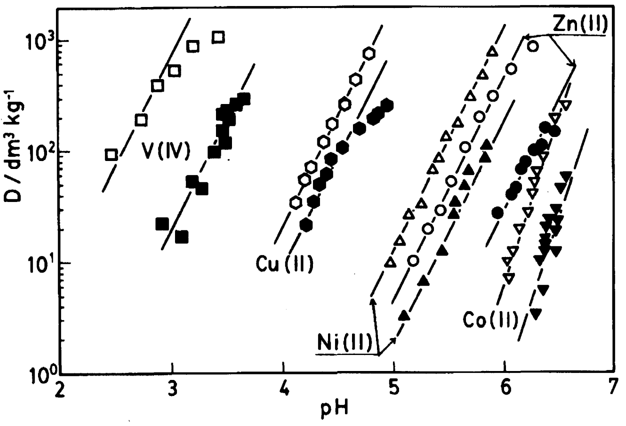


Fig. 5. Plot of the distribution ratio of oxovanadium(II), copper(II), nickel(II), zinc(II), and cobalt(II) against the equilibrium pH in the adsorption from a 1 mol dm^{-3} ammonium nitrate solution on original chitosan (open keys) and crosslinked copper(II)-complexed chitosan (closed keys).

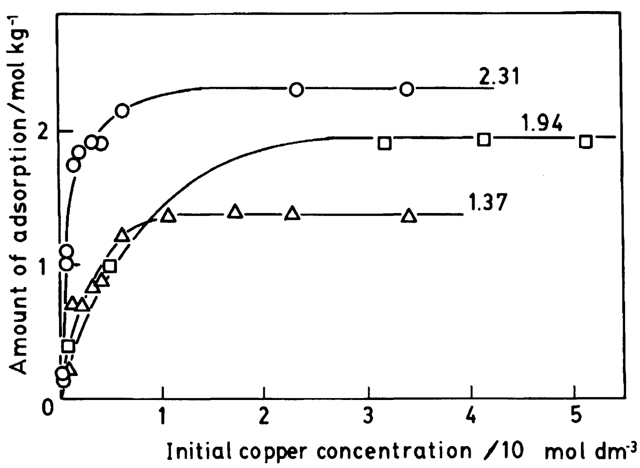


Fig. 6. Plot of the amount of copper(II) adsorbed against its initial concentration in a 1 mol dm^{-3} ammonium nitrate solution on original chitosan (○), PT-207 resin (□), and crosslinked copper(II)-complexed chitosan (△). The figures on each line denote the maximum amounts of adsorption on each adsorbent.

concentration in an aqueous solution. The amount of adsorption increases with increasing initial concentration, and approaches a constant value, which was found to be 2.31, 1.37, and 1.94 mol kg^{-1} for the original chitosan, crosslinked copper(II)-complexed chitosan and TP-207 resin, respectively. This result clearly demonstrates that the original chitosan has a greater adsorption capacity than that of the commercial chelating resin and, again, that the maximum adsorption capacity for copper(II) is also decreased by crosslinking as well as that for the hydrogen ion, as shown in Fig. 3.

The above-mentioned excellent adsorption behavior of chitosan for metal ions with high selectivity and high adsorption capacity are considered to be attributable to the following factors: (1) the high hydrophilicity of chitosan with a large number of hydroxyl groups; (2) the large number of primary amino groups with high activity; and (3) the flexible structure of the polymer chains of chitosan, which enables a suitable configuration for complexation with metal ions. The decrease in the amount of metal adsorbed and the template effect shown in Fig. 5 is attributable to only a loss in the flexibility of the polymer chain by cross-linking.

Adsorption from Hydrochloric Acid Solution. Figure 7 illustrates the relationship between the amount of hydrochloric acid adsorbed on crosslinked copper(II)-

complexed chitosan and the equilibrium acid concentration in an aqueous solution. From this figure, the maximum amount of hydrochloric acid adsorbed was evaluated as 2.96 mol kg^{-1}, slightly less than that of the hydrogen ion from a 1 mol dm^{-3} aqueous ammonium nitrate solution (3.55 mol dm^{-3}).

Figures 8 and 9 are plots of the distribution ratios of palladium(II) and platinum(IV), respectively, from varying concentrations of hydrochloric acid on crosslinked copper(II)-complexed chitosan and original chitosan as well as CHITOPEARL BCW 3000 for a comparison. Different from the adsorption from aqueous ammonium nitrate solution shown in Fig. 5, the difference in the adsorption behavior between the crosslinked copper(II)-complexed chitosan and the original chitosan appears to be comparatively little; that is, in the case of platinum(IV), the distribution ratio for the crosslinked copper(II)-complexed chitosan is only slightly less than that for the original chitosan, while for palladium(II) there appears to be no significant difference between the two adsorbents. However, the adsorption on the strongly crosslinked CHITOPEARL BCW 3000 is considerably less than that of other two adsorbents, not only for palladium, but also for platinum(IV).

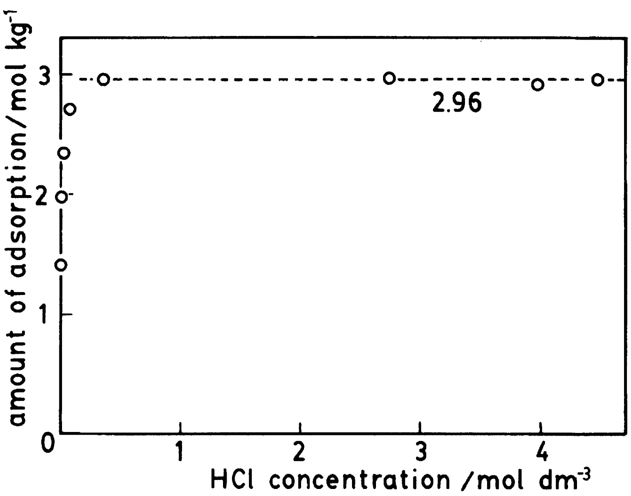


Fig. 7. Plot of the amount of hydrochloric acid adsorbed on crosslinked copper(II)-complexed chitosan against its equilibrium concentration.

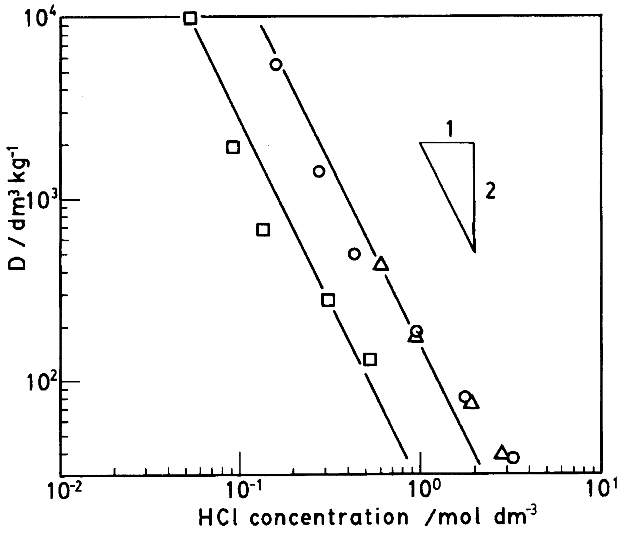


Fig. 8. Plot of the distribution ratio of palladium(II) against the hydrochloric acid concentration in the adsorption on original chitosan (△), crosslinked copper(II)-complexed chitosan (○), and CHITOPEARL BCW 3012 (□).

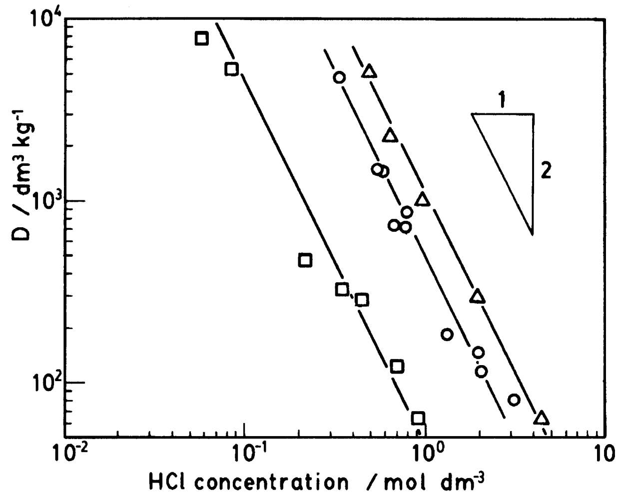
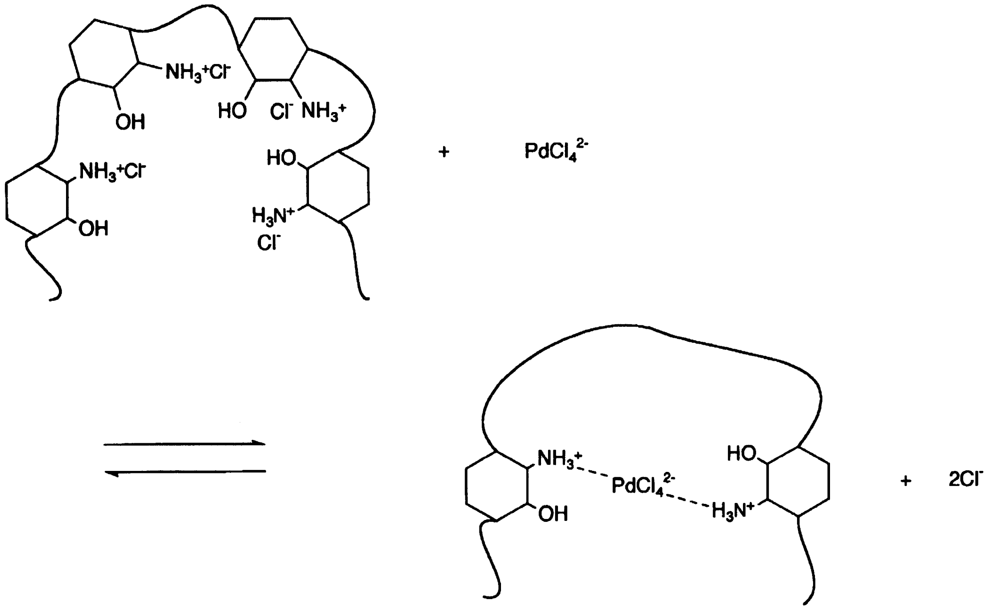


Fig. 9. Plot of the distribution ratio of platinum(IV) against the hydrochloric acid concentration in the adsorption on original chitosan (△), crosslinked copper(II)-complexed chitosan (○), and CHITOPEARL BCW 3012 (□).

In both figures, the plots lie on straight lines with a slope of −2 for both metals. These tendencies are similar to those observed in solvent extraction with high-molecular-weight amines and in adsorption on anion exchangers. Taking into consideration that palladium(II) and platinum(IV) exist as dianionic species, PdCl_4^{2-} and PtCl_6^{2-}, respectively, and that these adsorbents are completely saturated with hydrochloric acid, i.e., all of these adsorbents exist as the ammonium chloride type, both metals are considered to be adsorbed according to the anion-exchange mechanism, while releasing two chlorides per unit metal ion, as shown in Scheme 3 as an example for palladium. Different from the adsorption from ammonium nitrate solution, where metal ions are directly coordinated to the nitrogen atoms of the primary amino groups of chitosan, it is considered that crosslinking after complexation with the copper(II) ion does not significantly affect the adsorption of tetrachloropalladate(II) and hexachloroplatinate(IV) ions on protonated chitosan as ion pairs, since the bond distances between the ion pairs is greater than those of the coordination bonds and, consequently, the configuration of the ion pairs has a much greater flexibility than that of coordinated complexes. However, in CHI-



Scheme 3. Adsorption of palladium from hydrochloric acid solution.

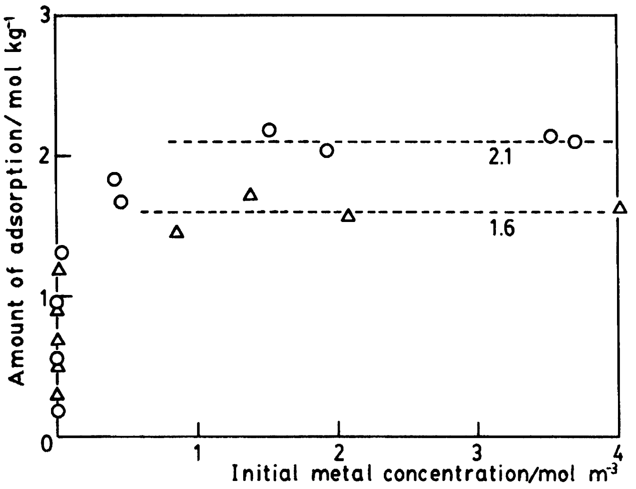


Fig. 10. Plot of the amount of palladium(II) (○) and platinum(IV) (△) adsorbed from a 0.01 mol dm^{-3} hydrochloric acid solution on crosslinked copper(II)-complexed chitosan against the initial metal concentration.

TOPEARL BCW 3012, the flexibility, as such, is considered to be deprived by the excess extent of crosslinking.

Figure 10 illustrates plots of the amount of adsorption of both metals on the cross-linked copper(II)-complexed chitosan from a 0.01 mol dm^{-3} hydrochloric acid solution. From this figure, the maximum amount of adsorption was evaluated as being 2.1 and 1.6 mol kg^{-1} for palladium(II) and platinum(IV), respectively. These values are slightly greater than the maximum adsorption capacity of copper(II) from the ammonium nitrate solution, shown in Fig. 6. This result is considered to reflect the fact that palladium(II) and platinum(IV) are adsorbed as ion-pairs while being sterically less restricted and having a comparatively more flexible configuration, while copper(II) is adsorbed as a chelate which is sterically strongly restricted and having a less flexible configuration coordinated by amino and hydroxyl groups of chitosan.

We are indebted to Katokichi Co., Ltd., Fuji Spinning Co., Ltd., and Tanaka Kikinzoku Kogyo K.K. for supplying samples of chitosan, CHITOPEARL BCW 3012 and palladium(II) chloride, and hydrogen hexachloroplatinate(IV) hexahydrate, respectively. This work was financially supported in part by a Grant-in-Aid for Scientific Research No. 01550578 from Ministry of Education, Science and Culture.

References

1) B. Volesky, *Trends Biotechnol.*, **5**, 96 (1987).

2) R. A. A. Muzzarelli, "Chitin," Pergamon, London (1977).

3) H. Tanibe, in "Application of Chitin and Chitosan," ed by Chitin, Chitosan Kenkyukai, Gihohdo Shuppan, Tokyo (1990), pp. 123—154.

4) K. Ohga, Y. Kurauchi, H. Yanase, *Bull. Chem. Soc. Jpn.*, **60**, 444 (1987).

5) H. Nishide, J. Deguchi, E. Tsuchida, *Chem. Lett.*, **1976**, 169.