

# SELECTIVE ADSORPTION OF METAL IONS ON NOVEL CHITOSAN-SUPPORTED SULFONIC ACID RESIN

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**Key Words:** Ion Exchange, Chitosan, Sulfonic Acid Resin, Metal, Propane Sultone

A novel chitosan-supported sulfonic acid resin modified by propane sultone was prepared and the adsorption characteristics of metal ions are examined by using a crosslinked chitosan-supported sulfonic acid resin (PSC) and a crosslinked chitosan resin (CLC).

In the low acidity region, the metal selectivity of PSC is similar to that of CLC. This suggested that the selectivity of PSC was attributed not to the sulfonate group but to the chitosan matrix. The role of the sulfonate is believed to be enriching the metal concentration in the neighborhood of the chitosan matrix. At the same time, since the hydrogen ion is also enriched in a thin layer near the surface of the resin, the characteristic adsorption curves of PSC shift to the high pH region compared with those of CLC. The adsorption equilibrium constants of metal ion on PSC and CLC are evaluated. The maximum adsorption capacity for PSC in the case of adsorption of copper is 1.6 times that of CLC. On the other hand, in the high acidity region, the maximum adsorption capacity for PSC in the case of adsorption of palladium is lower than that for CLC because of steric hindrance.

## Introduction

Today, the most widely used cation exchange resin is polystyrene-supported sulfonic acid resin. The sodium salt of this resin is used in household and industrial water softening systems for the removal of metallic ions such as iron, manganese, calcium and magnesium (Alexandratos and Crick, 1996). While sulfonic acid resin is effective for removing cations, it is nonselective for various metal cations (Boyd *et al.*, 1964, 1967). Therefore, the resin cannot be used to separate a specific metal from a mixture.

Recently, it has been found that chitosan biopolymer, which consists of D-glucosamine with  $\beta$ -(1,4) bonds, is a superior metal adsorbent. Since chitosan can be dissolved in acidic media, crosslinking of chitosan is necessary for the purpose of insolubilization (Kurita *et al.*, 1986). The capacity of metal adsorption is known to become relatively small due to crosslinking between the polymer chains of chitosan (Inoue *et al.*, 1993) as metallic ions normally adsorb onto the amino and hydroxyl groups of chitosan. To overcome this disadvantage, Ohga *et al.* (1987) proposed to prepare resins by crosslinking a metal-complexed chitosan. In their method, a central metal ion of the complex is most likely to protect the amino group necessary for adsorption against attack by crosslinking agents. Inoue

*et al.* (1988, 1993) reported that the resin prepared by this method has a higher selectivity than conventional chelating resins. To enhance the capacity and selectivity for metal adsorption, on the other hand, many metal ligands were chemically introduced to the amino or hydroxyl groups in chitosan, and such resins with metal selectivity have been developed (Kurita, 1991). As mentioned above, though the polystyrene-supported sulfonic acid resin is nonselective, the metal selectivity of the sulfonic acid resin may be changed by replacing polystyrene by a chitosan matrix. Researchers were interested in the anticoagulant activity of sulfonated chitosan (Wolfrom and Han, 1959), but adsorption of metal on chitosan-supported sulfonic acid resin has not been examined so far.

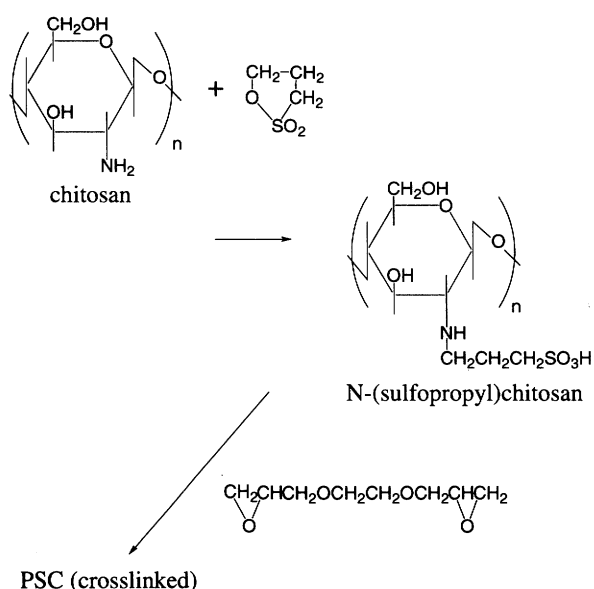
In the present work, we prepare a novel chitosan-supported sulfonic acid resin modified by propane sultone and the adsorption of metal ions is examined by using both the crosslinked chitosan-supported sulfonic acid resin (henceforth PSC) and a crosslinked chitosan resin (henceforth CLC). The metal selectivity of PSC is also discussed.

## 1. Experimental

### 1.1 Preparation of chitosan resin modified by propane sultone

Chitosan whose degree of deacetylation was 100% was purchased from Katokichi Co., Japan. Chitosan modified by propane sultone was prepared

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**Scheme 1** Preparation scheme of PSC

according to the method shown in **Scheme 1**. First, 3 g of chitosan powder was dissolved in a 1% acetic acid aqueous solution (90 ml), and then 15 ml of propane sultone was added to the solution. The mixture was allowed to react at 303 K for 6 hours. Then the resultant solution was poured into 2 dm<sup>3</sup> of acetone to precipitate the product. The product collected by filtration was washed sufficiently with methanol and acetone, and then it was ground by a homogenizer. The product obtained was water-soluble. The product was then crosslinked with 45 g of ethylene glycol diglycidyl ether in methanol (60 ml) at 333 K for 6 hours. After filtration, the yellowish solid was washed with methanol several times, and finally dried in vacuo. The average yield was about 85%. The final product PSC was identified by IR spectrum and NMR. In its IR spectrum, characteristic adsorption bands of the sulfonate group appeared at around 1200-1000 cm<sup>-1</sup>. In <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, the ring-opening of propane sultone was confirmed. From the results of elemental analysis, the degree of substitution of sulfonic acid group was estimated as 0.90 on the basis of the ratio of sulfur to nitrogen. Furthermore, because sulfonation of chitin by propane sultone did not proceed, the sulfonation was considered to occur at an amino moiety in the chitosan as shown in Scheme 1. A crosslinked chitosan was synthesized according to the same procedure as in crosslinking PSC.

## 1.2 Procedure of adsorption experiment

The resin was ground and sieved to 100-120 mesh size. The sieved resin, 50 mg, was placed in an Erlenmeyer flask, to which was added 20 ml of aqueous solution containing a metal chloride whose concentration was 1 x 10<sup>-3</sup> mol/dm<sup>3</sup> except for base metals (5 x 10<sup>-4</sup> mol/dm<sup>3</sup>). In the low acidity range, the

pH of the aqueous solution was adjusted by 1 mol/dm<sup>3</sup> NH<sub>4</sub>NO<sub>3</sub>-NH<sub>3</sub>-HNO<sub>3</sub> aqueous solution to form metal-amine complex preventing the metal ions from being hydrolyzed. In the high acidity range, hydrochloric acid solution was used to adjust the pH. The mixture was shaken at 303 K for 24 hours to attain equilibrium. The equilibrated mixture was centrifuged, and then the metal concentration in the supernatant was analyzed by atomic absorption spectrophotometry (Shimadzu AA 660) or inductively coupled plasma spectrophotometry (Shimadzu ICPS-8000). The quantity of metal ion adsorbed by the resin was calculated by subtracting the metal concentration in the supernatant from the initial concentration. The distribution ratio, *D*, is defined as the ratio of the concentration of the metal ion adsorbed on the dry adsorbent to its equilibrium concentration in an aqueous solution. The metal ions tested were Li, Na, Mg, Ca, Mn, Co, Ni, Cu, Zn, Sr, Pd, Ag, Ba, Sm, Eu, Gd, Pt and Au.

## 2. Results and Discussion

### 2.1 Metal adsorption in a low acidic range

**Figures 1 and 2** show the effect of pH on the adsorption of metal ions in the cases of PSC and CLC, respectively. In both figures, metal ions other than those indicated are not adsorbed on the resins. In the high pH region, the adsorption percentage decreases because of the decrease in free metal concentration due to the formation of metal-amine complex. From these figures, some interesting results are found. 1) Both resins have similar metal selectivity. It is very interesting that PSC including sulfonate does not adsorb alkali metal ions such as Li and Na. 2) PSC has a higher adsorption capacity than CLC. 3) The characteristic adsorption curves of the metals on PSC shift to the high pH region compared with those of CLC.

The p*K*<sub>a</sub> value of amino group in chitosan derivatives is reported to be about 4 (Muzzarelli *et al.*, 1982, Kishimoto and Yoshida, 1995), while the p*K*<sub>a</sub> value of sulfonate group is estimated to be very small. Under our experimental conditions, PSC may exist in the anionic state.

These facts suggest that the metal adsorption of PSC is attributed not to the sulfonate group but to the chitosan matrix. The role of the sulfonate is considered to be enriching metal concentration in the neighborhood of the chitosan matrix. At the same time, since hydrogen ion is also enriched in a thin layer near the surface of the resin, the pH of the surface region becomes lower than that of the bulk solution. Therefore, the characteristic adsorption curves of PSC shift to the high pH region compared with those of CLC.

The adsorption mechanism of metal ions on PSC is considered to be similar to that on CLC (Inoue *et al.*, 1993), that is, the metal ions are adsorbed to form a chelate coordinated by primary amino group nitrogen

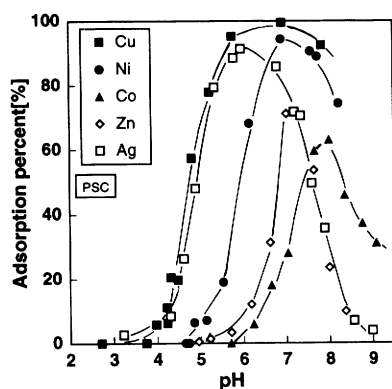


Fig. 1 Effect of pH on extent of adsorption of metal ions on PSC

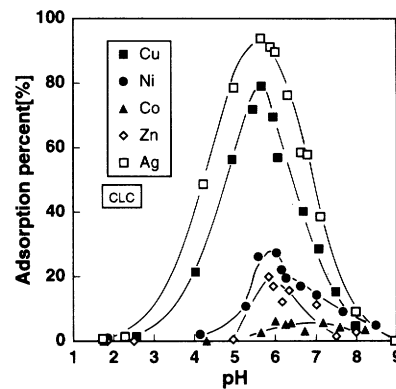


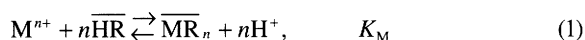
Fig. 2 Effect of pH on extent of adsorption of metal ions on CLC

Table 1 Stability constant of metal-amine complex\*

	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log \beta_5$	$\log \beta_6$
$\text{Cu}^{2+}$	4.27	7.82	10.72	12.90		
$\text{Ni}^{2+}$	2.36	4.26	5.81	7.04	7.89	8.31
$\text{Co}^{2+}$	2.11	3.76	4.79	5.55	5.73	5.11
$\text{Zn}^{2+}$	2.37	4.81	7.31	9.46		
$\text{Ag}^+$	3.32	7.31				

\*Data from Kagaku Binran (Nippon Kagaku Kai ed.1984)

atoms and alcoholic hydroxyl group oxygen atoms of chitosan.  $n$ -Valent metal ions, therefore, are considered to be adsorbed on the resin as metal chelates whose composition (metal: glucosamine unit ratio) is  $1:n$ . So the following adsorption equilibrium is assumed.



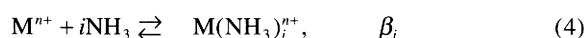
where,  $\overline{\text{HR}}$  represents the ligand moiety included in a glucosamine unit and  $K_M$  is the adsorption equilibrium constant.

The concentration of uncoordinated  $\overline{\text{HR}}$  is assumed to be approximated to its initial concentration. The logarithm of  $D$  can be expressed by Eq. (2).

$$\log D = npH + n \log [\overline{\text{HR}}]_0 + \log K_M \quad (2)$$

$$= npH + \log K'_M \quad (3)$$

where  $K'_M (= [\overline{\text{HR}}]^n K_M)$  represents the apparent adsorption equilibrium constant. As mentioned above, the concentration of the free metal ion decreases due to the formation of metal-amine complex in the high pH region. It is necessary to take into account formation of metal-amine complexes, as follows.



where  $\beta_i$  denotes the stability constants of metal-amine complexes. The values used are shown in Table 1. As the existence of hydrolyzed species can be negligible under the conditions of a large excess of ammonia, the free metal concentration can be expressed as follows.

$$[\text{M}^{n+}] = \frac{[\text{M}]_{aq,t}}{1 + \sum \beta_i [\text{NH}_3]^i} = \alpha_0 [\text{M}]_{aq,t}$$

$$\alpha_0 = \frac{1}{1 + \sum \beta_i ([\text{NH}_3])^i}, \quad [\text{NH}_3] = \frac{[\text{NH}_3]_t K_A}{[\text{H}^+] + K_A} \quad (5)$$

where  $K_A (= 5.5 \times 10^{-10} \text{ mol/dm}^3)$  is the acid dissociation constant of ammonium ion (Nippon Kagakukai, 1984). Accordingly, from Eqs. (3) and (5), Eq. (6) is derived.

$$\log D - \log \alpha_0 = npH + \log K'_M \quad (6)$$

Figures 3 and 4 show the relation between  $(\log D - \log \alpha_0)$  and pH for PSC and CLC, respectively. Because the amounts of nickel, cobalt and zinc adsorbed on CLC are small, plots of these metals are excluded. Linear relations with slopes equating to the valency of the metal ions are obtained except for copper ion. In the case of adsorption of copper ion on PSC, the experimental data deviate upwards from the straight line with a slope of two in the high pH region. In this region, the copper-amine complex is considered to also be

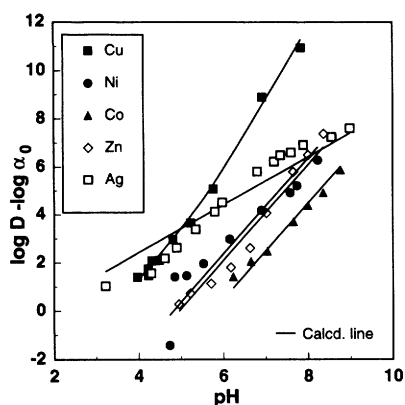


Fig. 3 Determination of adsorption equilibrium constants of metal ions on PSC

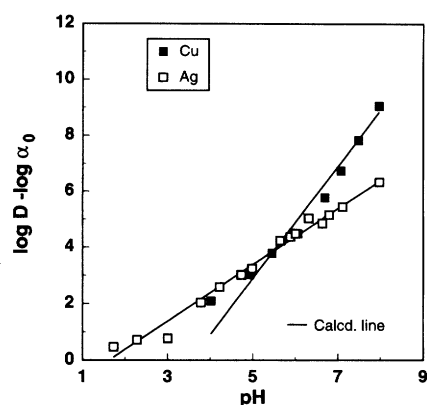


Fig. 4 Determination of adsorption equilibrium constants of metal ions on CLC

Table 2 Adsorption equilibrium constants (logarithmic values) and maximum adsorption capacities

$\log K_M'(\text{or } K_{M1}')$	$\text{Cu}^{2+}$	$\text{Cu}(\text{NH}_3)^{2+}$	$\text{Ni}^{2+}$	$\text{Co}^{2+}$	$\text{Zn}^{2+}$	$\text{Ag}^+$
PSC	-6.69	-7.24	-9.60	-11.51	-9.90	-1.58
CLC	-7.10	—	—	—	—	-1.62

$q_{\max}$ [mol/kg]	$\text{Cu}^{2+}$	$\text{PdCl}_4^{2-}$
PSC	1.48	1.72
CLC	0.95	2.79

$K_{\text{ad}}$ [ $\text{m}^3/\text{mol}$ ]	$\text{Cu}^{2+}$	$\text{PdCl}_4^{2-}$
PSC	1.44	0.58
CLC	0.84	5.67

adsorbed, as reported for copper adsorption on N-(2-hydroxybenzyl) chitosan (Baba *et al.*, 1994).



where  $K_{M1}$  represents the adsorption equilibrium constant of copper for Eq. (7).

From Eqs. (1) and (7), Eq. (8) is derived.

$$\log D - \log \alpha_0 = 2\text{pH} + \log(K_M' + K_{M1}'\beta_1[\text{NH}_3]) \quad (8)$$

where  $K_{M1}'(=[\overline{\text{HR}}]_0^n K_{M1})$  represents the apparent adsorption equilibrium constant. The values of  $K_M'$  and  $K_{M1}'$  were estimated by a nonlinear least squares method. The adsorption equilibrium constants obtained were listed in Table 2. The solid lines in Figs. 3 and 4 are the calculated ones using the estimated parameters.

Figure 5 shows the adsorption isotherms of copper ion on PSC and CLC. The experiments were carried out at pH = 7.0 for PSC and at pH = 5.7 for CLC. Using Langmuir adsorption isotherms, the maximum adsorption capacities,  $q_{\max}$ , and the

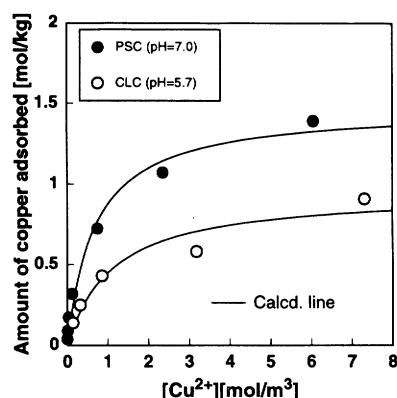


Fig. 5 Adsorption isotherms of copper ion on PSC and CLC in low acidic media

adsorption equilibrium constants,  $K_{\text{ad}}$ , were estimated and also listed in Table 2. These results indicate that  $q_{\max}$  for PSC is 1.6 times higher than that of CLC. Thus, Table 2 indicates clearly that PSC is an excellent resin with a high adsorption capacity and selectivity.

## 2.2 Metal adsorption in a high acidic range

Figures 6 and 7 show the metal adsorption on PSC and CLC in the high acidic range. The metal ions tested were Pd, Pt, Au, Cu and Co. Pd, Pt and Au were adsorbed on both resins. As is clear from Eqs. (1) and (7), the metal ions can not be adsorbed in a high acidic range. However, another adsorption mechanism according to anion-exchange was reported (Inoue *et al.*, 1993), in which chloro-metal complexes like  $\text{PdCl}_4^{2-}$ ,  $\text{PtCl}_6^{2-}$  and  $\text{AuCl}_4^-$  may be adsorbed. Figure 8 shows the adsorption isotherms of palladium from 0.02

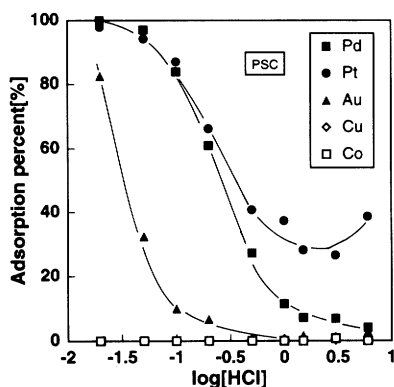


Fig. 6 Effect of hydrochloric acid concentration on extent of adsorption of metal ions on PSC

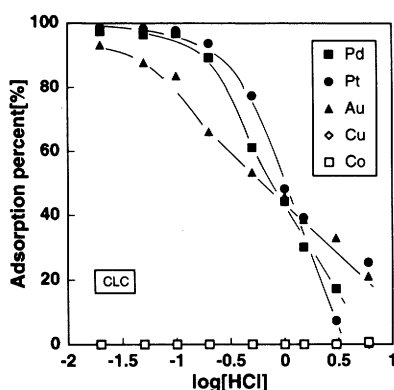


Fig. 7 Effect of hydrochloric acid concentration on extent of adsorption of metal ions on CLC

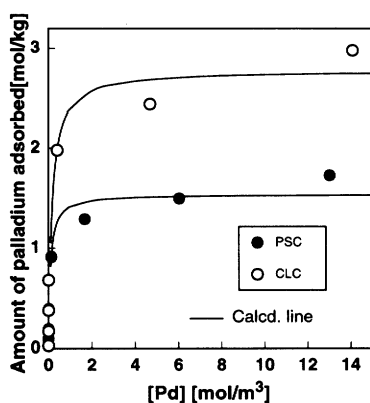


Fig. 8 Adsorption isotherms of palladium ion on PSC and CLC

mol/dm<sup>3</sup> hydrochloric acid solution on PSC and CLC. Using a Langmuir adsorption isotherm, the maximum adsorption capacities and the adsorption equilibrium constants were estimated and also listed in Table 2. These results indicate that  $q_{\max}$  for CLC is higher than that for PSC. This may be caused by the steric hindrance of sulfopropyl group. Thus, PSC is not suitable for the

adsorption of metal ion in a high acidic range.

## Conclusion

A novel chitosan-supported sulfonic acid resin using propane sultone was prepared and the adsorption of metal ions is examined by using crosslinked chitosan-supported sulfonic acid resin (PSC) and crosslinked chitosan resin (CLC). The following information is obtained.

(1) In the low acidic region, the metal selectivity of PSC is similar to that of CLC. This suggested that the metal selectivity of PSC is attributable not to the sulfonate group but to the chitosan matrix. The role of the sulfonate is considered to be enriching the metal concentration in the neighborhood of the chitosan matrix. At the same time, since hydrogen ion is also enriched in a thin layer near the surface of the resin, the characteristic adsorption curves of PSC shift to a higher pH region compared with those of CLC.

(2) The adsorption equilibrium constants of metal on PSC and CLC are evaluated taking into account formation of metal-amine complexes. The adsorbed species are free metal ions. In the case of copper,  $\text{CuNH}_3^{2+}$  is also adsorbed. The maximum adsorption capacity for PSC is 1.6 times higher than that of CLC.

(3) In the high acidic region, the maximum adsorption capacity for PSC is lower than that for CLC because of steric hindrance.

## Nomenclature

$D$	= distribution ratio of metal	[kg/dm <sup>3</sup> ]
$K_{\text{ad}}$	= Langmuir adsorption equilibrium constant	[m <sup>3</sup> /mol]
$K_{\text{A}}$	= acid dissociation constant of ammonia	[mol/dm <sup>3</sup> ]
$K_{\text{M}}$	= adsorption equilibrium constant of free metal ion	[(kg/dm <sup>3</sup> ) <sup>n-1</sup> ]
$K_{\text{M1}}$	= adsorption equilibrium constant of copper-amine complex	[(kg/dm <sup>3</sup> ) <sup>n-1</sup> ]
$K'_{\text{M}}$	= $[\text{HR}]_0^n K_{\text{M}}$	[mol <sup>n</sup> /(kg•dm <sup>3(n-1)</sup> )]
$K'_{\text{M1}}$	= $[\text{HR}]_0^n K_{\text{M1}}$	[mol <sup>n</sup> /(kg•dm <sup>3(n-1)</sup> )]
$q_{\max}$	= maximum adsorption capacity	[mol/kg]
$\alpha_0$	= $1/(1+\sum \beta_i [\text{NH}_3]^i)$	[—]
$\beta_i$	= stability constant	[(dm <sup>3</sup> /mol) <sup>i</sup> ]
[ ]	= concentration	[mol/dm <sup>3</sup> ]

## Literature Cited

- Alexandros, S. D. and D. W. Crick; "Polymer-Supported Reagents: Application to Separation Science," *Ind. Eng. Chem. Res.*, **35**, 635-644 (1996)
- Baba, Y., H. Hirakawa, K. Yoshizuka, K. Inoue and Y. Kawano; "Adsorption Equilibria of Silver(I) and Copper(II) Ions on N-(2-hydroxybenzyl)chitosan Derivative," *Anal. Sci.*, **10**, 601-605 (1994)
- Boyd, G. E., F. Vaslow and S. Lindenbaum; "Calorimetric Determinations of the Heats of Ion Exchange Reactions. I. Heats of Exchange of the Alkali Metal Cations in Various Cross-Linked Polystyrene Sulfonates," *J. Phys. Chem.*, **68**, 590-597 (1964)

- Boyd, G. E., F. Vaslow and S. Lindenbaum; "Thermodynamic Quantities in the Exchange of Zinc and Sodium Ions in Various Cross-Linked Polystyrene Sulfonates Cation Exchangers at 25°C," *J. Phys. Chem.*, **71**, 2214-2219 (1967)
- Inoue, K., Y. Baba, K. Yoshizuka, H. Noguchi and M. Yoshizaki; "Selectivity Series in the Adsorption of Metal Ions on a Resin Prepared by Crosslinking Copper(II)-Complexed Chitosan," *Chem. Lett.*, 1281-1284 (1988)
- Inoue, K., Y. Baba and K. Yoshizuka; "Adsorption of Metal Ions on Chitosan and Crosslinked Copper(II)-Complexed Chitosan," *Bull. Chem. Soc. Japan*, **66**, 2915-2921 (1993)
- Kishimoto, N. and H. Yoshida; "Adsorption of Glutamic Acid on Crosslinked Chitosan Fiber: Equilibria," *Separ. Sci. Technol.*, **30**, 3143-3163 (1995)
- Kurita, K., Y. Koyama and A. Taniguchi; "Studies on Chitin. IX. Crosslinking of Water-Soluble Chitin and Evaluation of the Products as Adsorbents for Cupric Ion," *J. Appl. Polym. Sci.*, **31**, 1169-1176 (1986)
- Kurita, K.; "Preparation of Chitin Derivatives," *Kagaku Kogyo*, **42**, 765-773 (1991)
- Muzzarelli, R.A.A., F. Tanfani, S. Mariotti and M. Emanuelli; "N-(o-Carboxybenzyl)chitosans: Novel Chelating Polyampholytes," *Carbohydrate Polym.*, **2**, 145-157 (1982)
- Nippon Kagakukai ed.; *Kagaku Binran Kisohe*, 3rd Ed., Maruzen, Tokyo, Japan (1984)
- Ohga, K., Y. Kurauchi and H. Yanase; "Adsorption of  $\text{Cu}^{2+}$  or  $\text{Hg}^{2+}$  Ion on Resins Prepared by Crosslinking Metal-Complexed Chitosans," *Bull. Chem. Soc. Japan*, **60**, 444-446 (1987)
- Wolfson, M. L. and T. M. S. Han; "The Sulfonation of Chitosan," *J. Am. Chem. Soc.*, **81**, 1764-1766 (1959)