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# Effects of Chitosan Concentration and Precipitation Bath Concentration on the Material Properties of Porous Crosslinked Chitosan Beads

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# Effects of Chitosan Concentration and Precipitation Bath Concentration on the Material Properties of Porous Crosslinked Chitosan Beads

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## ABSTRACT

Flaked chitosan obtained by deacetylating 80% of chitin extracted from crab shell was dissolved in acetic acid aqueous solution, and highly porous chitosan beads were formed by dropping the chitosan solution into aqueous NaOH solution, followed by crosslinking with ethylene glycol diglycidyl ether. Fifteen different crosslinked chitosan beads (CRCS) were fabricated by controlling the concentration $C_{chitosan}$ of chitosan in the chitosan/acetic acid solution and the concentration $C_{NaOH}$ of NaOH in the precipitation bath. We presented the way in which the values of $C_{chitosan}$ and $C_{NaOH}$ were controlled to fabricate chitosan beads with any desired values of the apparent density, the solid phase concentration of amino group, the pore radius, the total porosity, and the specific surface area. In order to assess the possibility of using CRCS as a matrix of an adsorbent for the separation of metal ions, poly(ethylene imine) was introduced onto the CRCS which had a relatively high concentration of amino group. The polyaminated CRCS had a high capacity, and it had a high selectivity for the adsorption of Hg(II), Cu(II), Ni(II), Cd(II), and Zn(II). The results suggest that CRCS is a good matrix for introducing functional groups.

## INTRODUCTION

Chitin is a natural biopolymer obtained from crustaceans (such as lobsters, shrimps, and crabs), some invertebrates, and fungi. It is produced in a vast amount (about $1 \times 10^9$ to $1 \times 10^{11}$ ton/year), second only to cellulose on a worldwide basis (1). Chitosan is prepared by deacetylation of chitin. Chitosan is inexpensive, environmentally benign, harmless to humans, and a hugely obtainable biomass. It has potential as a separator of biochemical products, as an immobilization support of biocatalysts in food and pharmacy processes, as a coagulant in wastewater treatment, and for use in other industrial applications (2).

The ability of chitosan is improved remarkably by developing the way in which it is fabricated to porous beads. As the beads are dissolved in an aqueous acid solution, they are commonly crosslinked and modified chemically to enhance their performance. For instance, Tuchiyama et al. (3, 4) introduced affinity ligands for α- and β-cyclodextrin into crosslinked porous chitosan beads. They applied the specific adsorbents to the cyclodextrin producing process in which the production and the separation of cyclodextrin took place as one step. Yoshida et al. (5–9) introduced poly(ethylene imine) into crosslinked chitosan beads. They applied it for the removal of organic acids from wine (6), adsorption of strong acids (7), adsorption of glutamic acid (8), and chelation of metal ions (9). Hsien et al. (10) and Rorrer et al. (11) investigated the adsorption of cadmium ion by using crosslinked chitosan beads and crosslinked porous-magnetic chitosan beads, respectively.

In all of the applications mentioned above, the physical properties of crosslinked chitosan beads (such as particle diameter, porosity, pore distribution, average pore radius, concentration of ligands in the solid phase, specific surface area) are significant factors for the design of adsorbents. However, the relation between such physical properties and the precipitation conditions of crosslinked chitosan beads has not been studied systematically.

In this work, 15 different chitosan beads were systematically formed by dropping a chitosan/acetic acid solution into an aqueous NaOH solution, followed by crosslinking with ethylene glycol diglycidyl ether. We present the way in which the concentration of chitosan in the chitosan/acetic acid solution and the concentration of NaOH in the precipitation bath are controlled to fabricate chitosan beads with any desired value of the apparent density, the solid phase concentration of the amino group, the pore radius, the total porosity, and the specific surface area. Thereafter the experimental results for the adsorption of metal ions on a polyaminated CRCS fabricated by the same method that we presented elsewhere [Kawamura et al.

(5)] are shown. The selectivities for the adsorption of $Hg^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ on the crosslinked chitosan beads and polyaminated CRCS are given to show the possibility of using CRCS as a matrix on which functional groups are introduced for the separation of metal ions.

## EXPERIMENTAL

### Fabrication of Chitosan Beads

The molecular weight of commonly obtainable commercial chitosan is about 200,000. Since the viscosity of chitosan/acetic acid solution is too high, for it to flow through the tubes and the nozzles without difficulty, flaked chitosan (80% deacetylation) with a molecular weight of about 50,000 (purchased from Kyowa Technos Co., Japan) was used. The viscosity of its solution was much lower. Although the chitosan of MW 50,000



TABLE 1
Experimental Conditions for the Fabrication of Chitosan Beads. The Flaked Chitosan and Acetic Acid Were Dissolved in Water. The Obtained Acid Chitosan Solutions Were Dropped into Precipitation Baths Containing the Five Different Concentrations of NaOH Aqueous Solutions. The Diameters of the Obtained Chitosan Beads Were 1.0 to 1.5 mm

| | Chitosan/acetic acid/aq solution | | Precipitation bath (NaOH aq solution) | | Particle diameter of crosslinked chitosan beads | |
|---|---|---|---|---|---|---|
| Chitosan beads | Chitosan (wt%) | Acetic acid (wt%) | NaOH (wt%) | $C_{NaOH}$ ($kg/m^3$) | Mean diameter (mm) | Standard deviation |
| 5CS3N | 5 | 2.5 | 3 | 29.1 | 1.45 | 0.186 |
| 5N | 5 | 2.5 | 5 | 47.5 | 1.41 | 0.175 |
| 7N | 5 | 2.5 | 7 | 65.1 | 1.43 | 0.179 |
| 9N | 5 | 2.5 | 9 | 82.1 | 1.25 | 0.146 |
| 11N | 5 | 2.5 | 11 | 98.4 | 1.26 | 0.175 |
| 6CS3N | 6 | 3.0 | 3 | 29.1 | 1.22 | 0.153 |
| 5N | 6 | 3.0 | 5 | 47.5 | 1.16 | 0.106 |
| 7N | 6 | 3.0 | 7 | 65.1 | 1.14 | 0.077 |
| 9N | 6 | 3.0 | 9 | 82.1 | 1.11 | 0.108 |
| 11N | 6 | 3.0 | 11 | 98.4 | 1.02 | 0.105 |
| 7CS3N | 7 | 3.5 | 3 | 29.1 | 1.25 | 0.100 |
| 5N | 7 | 3.5 | 5 | 47.5 | 1.23 | 0.107 |
| 7N | 7 | 3.5 | 7 | 65.1 | 1.20 | 0.100 |
| 9N | 7 | 3.5 | 9 | 82.1 | 1.17 | 0.088 |
| 11N | 7 | 3.5 | 11 | 98.4 | 1.09 | 0.105 |

was made by decomposing the original chitosan, it retained the properties of the original chitosan except for the viscosity.

Table 1 shows the experimental conditions for the fabrication of porous beads. Figure 1 shows the apparatus used for the fabrication of chitosan beads. Chitosan solutions of 5, 6, and 7 wt% in the tank were supplied to the nozzle by using the gear pump at a constant flow rate. The chitosan solution was dropped into a precipitation bath containing 10 kg of sodium hydroxide aqueous solution. The concentrations of sodium hydroxide in the precipitation solution were 3, 5, 7, 9, and 11 wt% (see Table 1). The drops of chitosan solution precipitated within a few seconds after they contacted the precipitation solution. The precipitated chitosan beads were taken out from the bath and washed thoroughly with distilled deionized water.

The beads were crosslinked using ethylene glycol diglycidyl ether (special grade, Nagase Chemicals, Co., Japan) at 80°C for 3 hours, (Fig. 2). The degree of crosslinking, $\chi$ (%), was about 17%. It is defined by



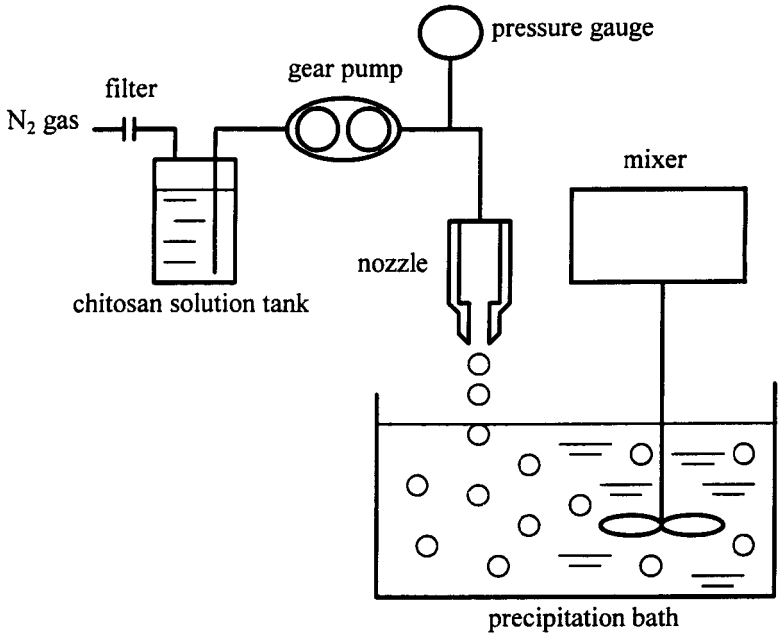


FIG. 1 Apparatus for preparation of chitosan beads.

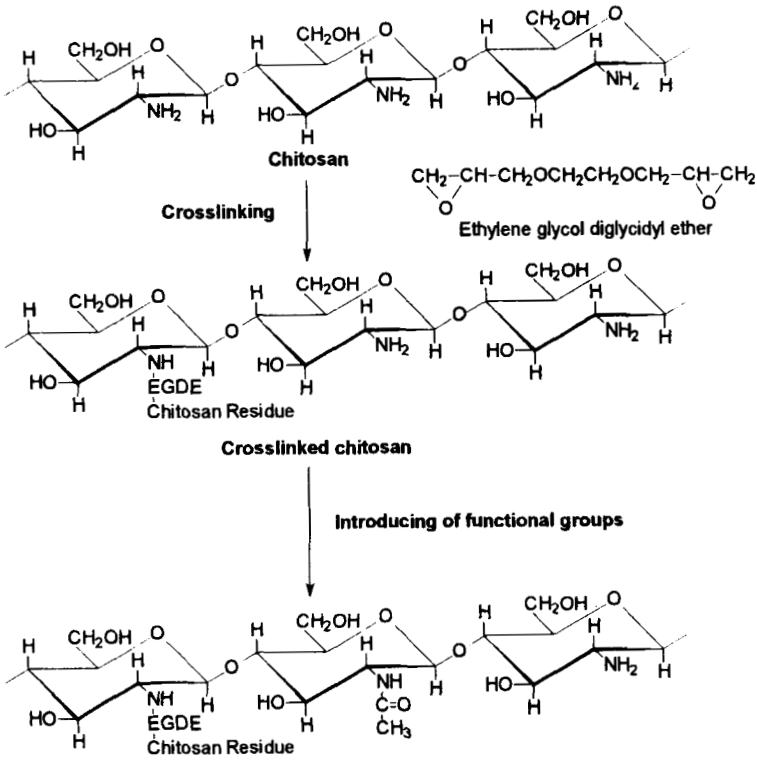


FIG. 2 Scheme of crosslinking with ethylene glycol diglycidyl ether and available different chemical modifications for the crosslinked chitosan beads.

$$\chi = \frac{\text{weight of crosslinking reagent}}{\text{weight of dry particles}} \times 100 \qquad (1)$$

This value was the lowest level which had durability in an acid solution. We consider the crosslinked chitosan beads to be the matrix on which functional groups are introduced for the separation of metal ions. In order to introduce functional groups onto chitosan beads, it is necessary that the degree of crosslinking be as small as possible, so we chose the smallest degree of crosslinking, 17%. The finished products were thoroughly washed with distilled and deionized water. The crosslinked chitosan beads (hereafter called CRCS) did not dissolve in acetic acid solution.

### Apparent Density and Total Porosity

Bulk densities were measured by the method proposed by Yoshida et al. (9). The wet CRCS were put in a nylon mesh bag and centrifuged at 4000 rpm for 1.5 minutes to remove any water from the surface of the beads. The weighed wet beads (about 2 g) were put into a pycnometer of 5 mL which was filled with water at 25°C to measure the volume of the wet beads. The wet beads were recovered from the pycnometer and freeze-dried to measure their dry weight. The apparent density was calculated according to Eq. (2), where $V_{wet}$ ($m^3$) and $W_{dry}$ (kg) are the volume of wet beads and the weight of dry beads, respectively, and $\rho_{app}$ ($kg/m^3$) denotes the apparent density.

$$\rho_{app} = W_{dry}/V_{wet} \tag{2}$$

The total porosity of wet CRCS, $\epsilon_P$, was determined by assuming that the pore volume was equal to the volume of water which filled the pores of the beads. The value of $\epsilon_P$ was calculated according to Eq. (3), where $V_{W,P}$ ($m^3$) is the volume of the water filling the pores of the beads.

$$\epsilon_P = V_{W,P}/V_{wet} \tag{3}$$

### Concentration of Amino Group

The solid phase concentration of the amino group of wet CRCS was determined by measuring its saturation capacity for the adsorption of HCl. The wet CRCS was prepared as mentioned above. The reaction between chitosan beads and HCl is [Yoshida et al. (9)]

$$R{\cdot}NH_2 + HCl \rightleftarrows R{\cdot}NH_3^+Cl \tag{4}$$

### Scanning Electron Microscope Observation

Water in the pores of CRCS was replaced with ethanol, and then ethanol was replaced with tertiary butanol. CRCS containing tertiary butanol in the pores were freeze-dried. This drying method is usually adopted for the preparation of electron microscope specimens. This method may be better than the critical point drying method because much more of the native structure of the chitosan beads in water was kept by this method. The dried beads were coated with gold by an ion spattering apparatus and observed with a scanning electron microscopy (SEM).

### Pore Radius Distribution (mercury intrusion method)

The pore radius distribution and the radius of the maximum peak of freeze-dried CRCS were measured by using a Porosimeter 2000 (Carlo

Erba Co., Italy), and they were calculated by a Milestone 200 Report generatory (Carlo Erba, Co., Italy).

### Specific Surface Area ($N_2$ gas adsorption method)

The BET specific surface area of freeze-dried CRCS was measured by using a Belsorp 28 (Bel Japan Co., Japan). The sample was dried in vacuo at 50°C for 14 hours using $P_2O_5$ as the drying agent.

### Adsorption of Metal Ions on Crosslinked Chitosan Beads (CRCS) and Polyaminated Crosslinked Chitosan Beads (PEI-CS)

Metal standard solutions for atomic adsorption analysis (Wako Junyaku Kogyo Co., Japan) were used for the experiments. The pH values of these metal solutions were adjusted with 100 mol/m$^3$ [bis(2-hydroxyethyl)amino]-tris(hydroxymethyl)methane and diluted with water to 100 ppm. One cubic centimeter of wet resin of CRCS and PEI-CS were individually stirred in 80 cm$^3$ of the metal solution at 25°C for 72 hours. The initial concentrations and equilibrium concentrations of metal ions were measured with ICP.



## RESULTS AND DISCUSSION

### Particle Diameters

Maruca et al. (12), Jha et al. (13), Udaybhasker et al. (14), and Rorrer et al. (11) reported that the metal adsorption capacity increases with decreasing particle size of chitosan. Rorrer et al. (11) proposed a pore blockage mechanism to explain this phenomenon: as metal ions penetrate the porous beads and are adsorbed on amine sites near the outer surface, the formation of adsorbed metal clusters may constrict or completely block pores, rendering amine sites deep within the interior of the bead inaccessible for adsorption with metal ions. Hence, particle diameter is an important factor when chitosan is applied to an adsorbent for metal ions.

It was possible to control the particle diameter range from about 0.5 mm to 1.5 mm by the method mentioned earlier. In this work the mean particle diameter of CRCS and the standard deviation of 100 particles in each lot were 1.0 to 1.5 mm and 0.073 to 0.186, respectively (see Table 1). Since the decrease in diameter caused by crosslinking was negligibly small, ethylene glycol diglycidyl ether may be a good crosslinking reagent. As shown in Table 1, the mean diameter decreased slightly with increasing sodium hydroxide concentration ($C_{NaOH}$) in the precipitation bath. The effect of chitosan concentration (5CS, 6CS, 7CS) was not clear.

## Scanning Electron Microscope Observation

Figure 3(a) shows crosslinked chitosan beads (6CS7N). The beads were almost spherical. The shapes of other beads (Table 1) were similar to those in Fig. 3(a). Figure 3(b), (c), (d), and (e) show cross-sectional views of 5CS3N, 5CS11N, 7CS3N, and 7CS11N, respectively. They have a honeycomb structure which has ultrahigh porosity. These beads does not have the so-called skin-core structure. As NaOH may diffuse into the center of the particles rapidly, macropores may be formed uniformly from the surface to the inside. The pore diameter decreases with increasing concentration of chitosan. The higher the concentration of NaOH was, the thicker the wall of a pore became.

## Apparent Density of CRCS

The relation between the apparent density $\rho_{app}$ (kg/m$^3$) of crosslinked chitosan beads (5CS, 6CS, and 7CS series) and the concentration of sodium hydroxide $C_{NaOH}$ (kg/m$^3$) in the precipitation bath is shown in Fig. 4. This relation was correlated with three different secondary polynomial expressions:

$$\rho_{app} = 106 - 0.614C_{NaOH} + 0.00902C_{NaOH}^2, \quad \text{for 5CS} \quad (5)$$

$$\rho_{app} = 125 - 1.14C_{NaOH} + 0.0147C_{NaOH}^2, \quad \text{for 6CS} \quad (6)$$

$$\rho_{app} = 167 - 1.62C_{NaOH} + 0.0185C_{NaOH}^2, \quad \text{for 7CS} \quad (7)$$

The solid, dashed, and point dash lines denote Eqs. (5) to (7), respectively. The value of $\rho_{app}$ ranged from 100 to 200 kg/m$^3$. $\rho_{app}$ was little affected by NaOH for 25 kg/m$^3$ $< C_{NaOH} <$ 70 kg/m$^3$. When $C_{NaOH} >$ 70 kg/m$^3$, $\rho_{app}$ increased with $C_{NaOH}$. When chitosan beads are fabricated using a high concentration of sodium hydroxide, it is important to maintain $C_{NaOH}$ constant in order to ensure homogeneous quality. The values of $\rho_{app}$ were also influenced by the concentration of chitosan, and the effect of the concentration of chitosan was more significant than $C_{NaOH}$.

## Concentration of Amino Group and Hydroxyl Group

The relation between the solid phase concentration of the amino group $Q_{NH_2}$ (kmol/m$^3$ of wet resin) and $\rho_{app}$ is shown in Fig. 5. The value of $Q_{NH_2}$ was determined by adsorption of HCl. $Q_{NH_2}$ increased linearly with $\rho_{app}$, and the empirical equation is

$$Q_{NH_2} = 0.00351\rho_{app} + 0.119$$

When chemical modifications are carried out on CRCS, the amino groups are the reactive sites. The amino group itself serves as a chelation site for metal ions and the adsorption ligand for proteins. Therefore, it is im-

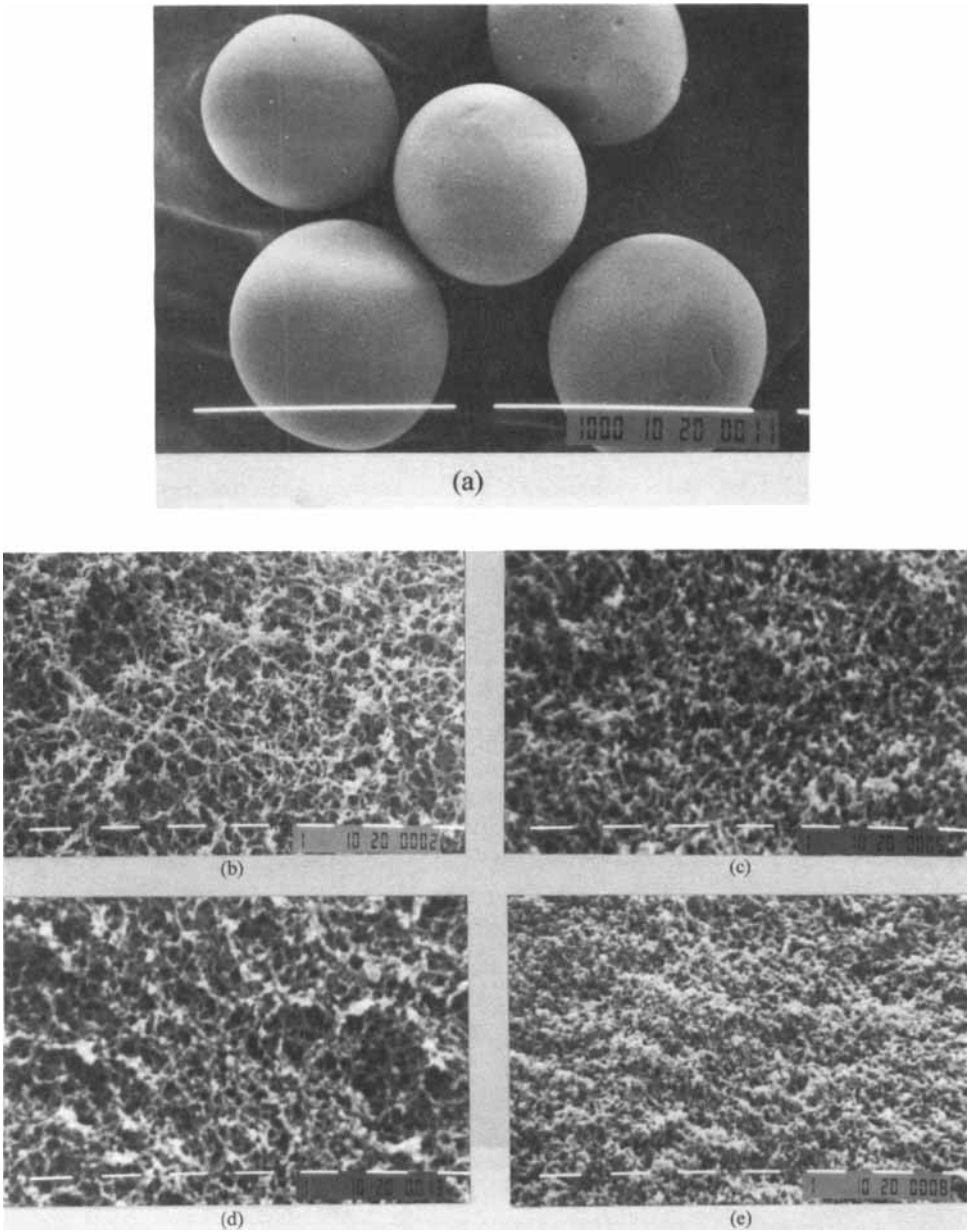


FIG. 3 Scanning electron micrographs of crosslinked chitosan beads. (a) Whole view of 6CS7N (bars denote 1000 μm). (b) Cross-section view of 5CS3N (bars denote 1 μm). (c) Cross-section view of 5CS11N (bars denote 1 μm). (d) Cross-section view of 7CS3N (bars denote 1 μm). (e) Cross-section view of 7CS11N (bars denote 1 μm).

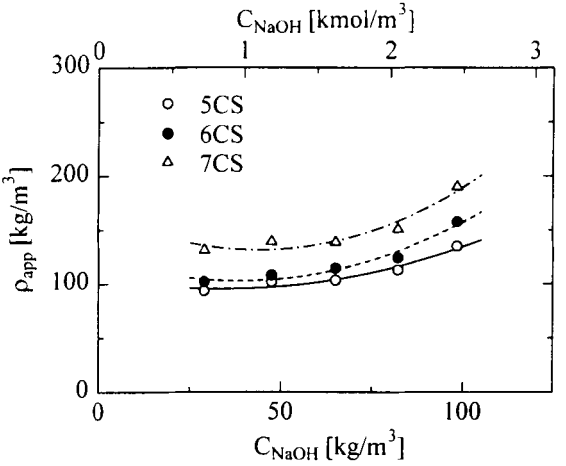


FIG. 4 Influence of NaOH concentration of precipitation bath on apparent density of fabricated chitosan beads. The order of concentrations of chitosan aqueous solutions were 5CS, 6CS, and 7CS. (——) Eq. (5); (- - -) Eq. (6); (–·–) Eq. (7).



portant to control the concentration of the amino group. The fabrication conditions of chitosan beads having the desired solid phase concentration of the amino group can be predicted from Eq. (8).

## Pore Radius Distribution

The pore radius distributions were measured by the mercury intrusion method for dried 5CS3N, 5CS11N, 7CS3N, and 7CS11N beads, they are

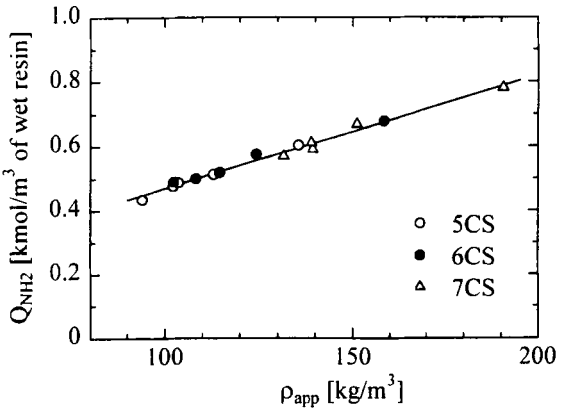


FIG. 5 Relation between amino group concentration of wet beads and apparent density.

shown in Fig. 6. The volume fractions of mercury intrusion $V_f$ (%) are plotted versus the pore radius $R_P$ (nm). The value of $R_P$ as related to the maximum peak of $V_f$ in each bead were 900, 200, 300, and 90 nm, respectively. $R_P$ increased with decreasing chitosan concentration and increased with decreasing sodium hydroxide concentration. The pore radii are large enough to permit diffusion of any macromolecule. Since the pore radius varies widely, these beads cannot be used for size separation chromatography.

The relation between the radius of the maximum peak $R_{P,mp}$ (nm) and the apparent density $\rho_{app}$ is shown in Fig. 7. The value of $R_{P,mp}$ ranged from 90 to 900 nm. A macromolecule such as protein can easily diffuse into the big pores. The following empirical equation was obtained:

$$\log R_{P,mp} = -2.87 \log \rho_{app} + 8.57 \quad (9)$$

Beads with the desired $R_{P,mp}$ can be fabricated by controlling $\rho_{app}$ only.

## Total Porosity

Fig. 8 shows the relation between $\epsilon_p$ and $\rho_{app}$. The data were correlated by

$$\epsilon_p = -6.96 \times 10^{-4} \rho_{app} + 1.002 \quad (10)$$

The value of $\epsilon_p$ ranged from 0.87 to 0.94. The results obtained by using a scanning electron microscope (Fig. 3) support the above values of $\epsilon_p$. The experimental values of $\epsilon_p$ of DEAE-Sepharose FF and CM-Sepharose FF (Pharmacia LKB Biotechnology, Sweden) were 0.92 and 0.94, respec-

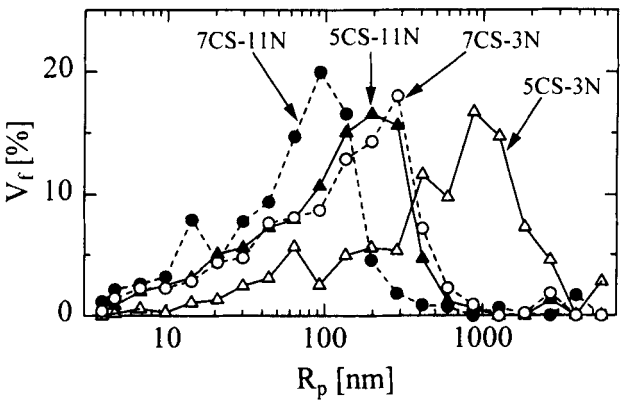


FIG. 6 Pore radius distributions by mercury intrusion method for dried chitosan beads. Volume fractions for three typical beads were plotted against pore radius.

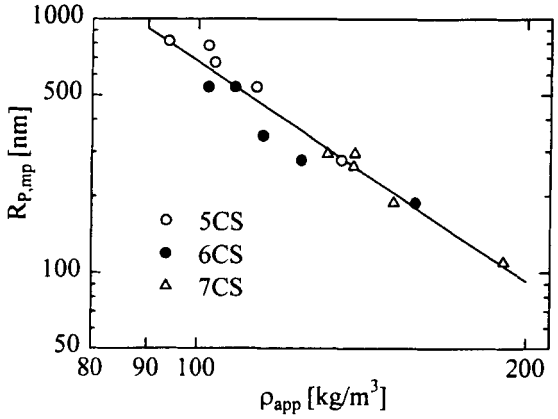


FIG. 7 Relation between pore radius of maximum peak of $V_f$ by mercury intrusion method for dried chitosan beads and apparent density.



tively. The chitosan beads have an ultrahigh porous structure comparable to Sepharose FF.

## Specific Surface Area

The relation between the BET specific surface area $S$ ($m^2/kg$) measured by $N_2$ adsorption for dried chitosan beads and the apparent density is shown in Fig. 9. The value of $S$ ranged from $1.0 \times 10^5$ to $1.5 \times 10^5$ $m^2/$

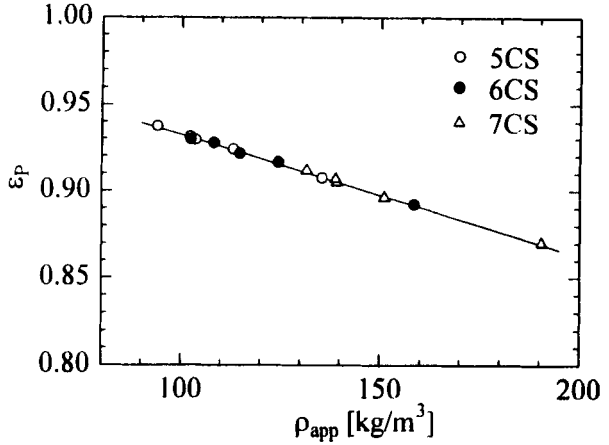


FIG. 8 Relation between total porosity for wet chitosan beads and apparent density.

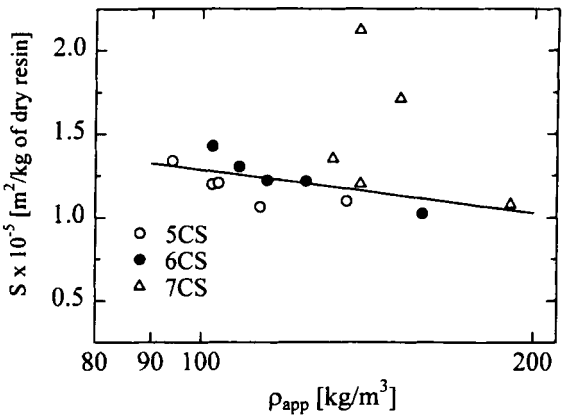


FIG. 9 Relation between specific surface area by $N_2$ adsorption method for dried chitosan beads and apparent density.



kg except for 7CS7N and 7CS9N which had values of $2.1 \times 10^5$ and $1.7 \times 10^5$ $m^2/kg$, respectively. As shown in Fig. 6, the pore radius distribution in crosslinked chitosan beads is broad. The beads must have not only the macro pores shown in SEM views but also micro and meso pores (10 to 200 nm). These micro and meso pores must be the true source of the high surface area. The relation between $S$ and $\rho_{app}$ (except for the data of 7CS7N and 7CS9N) was correlated by the straight line expressed as

$$S = -0.8544 \log \rho_{app} + 2.993 \quad (11)$$

The value of $S$ increases with decreasing $\rho_{app}$, but the relation is not as clear as that of $Q_{NH_2}$, $R_{P,mp}$, and $\epsilon_p$. Crosslinked porous chitosan beads are so soft that mercury may cause distortion. On the other hand, $N_2$ gas adsorption does not cause distortion. Therefore, analysis of the results of mercury intrusion and gas adsorption may not be discussed in the same way.

## Adsorption of Metal Ions on CRCS and PEI-CS

The degree of crosslinking was about 17% in all the CRCS fabricated. The cross-linking reagent consumed 20% of the amino group of chitosan, and the remaining 80% are available for chemical modification. In order to assess the possibility of using CRCS as a matrix for an adsorbent for the separation of metal ions, we fabricated polyaminated crosslinked chitosan beads (PEI-CS) by introducing poly(ethylene imine) onto the crosslinked

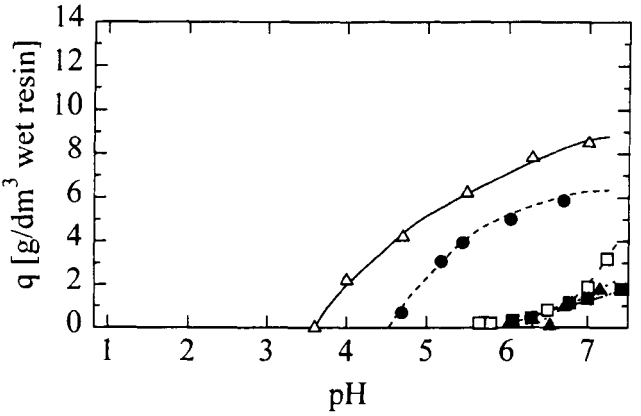


FIG. 10 Effect of pH on amount of metal ions adsorbed on crosslinked chitosan beads (7CS9N): (●) Cu(II); (□) Cd(II); (■) Zn(II); (△) Hg(II); (▲) Ni(II).



chitosan beads (7CS9N) according to a procedure presented elsewhere [Kawamura et al. (5)].

The concentrations of amino group in 7CS9N and PEI-CS were 669 and 2100 mol/m$^3$, respectively. Figs. 10 and 11 show the effect of pH on the adsorption of metal ions on 7CS9N and PEI-CS, respectively. The amount of ion adsorbed decreases with decreasing pH, but the effect of pH is

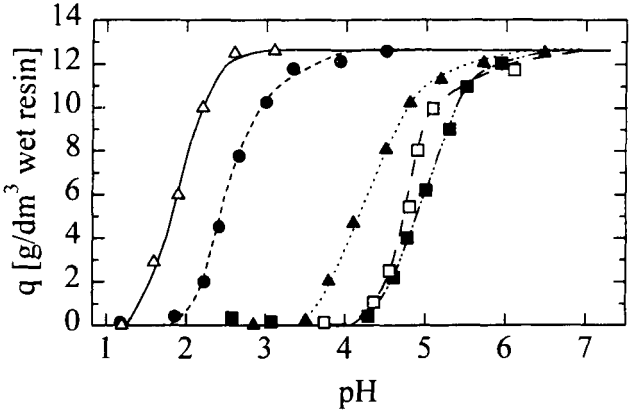


FIG. 11 Effect of pH on amount of metal ions adsorbed on polyaminated crosslinked chitosan beads. (●) Cu(II); (□) Cd(II); (■) Zn(II); (△) Hg(II); (▲) Ni(II).

different for each ion. The selectivities of the ions on 7CS9N are Hg(II) > Cu(II) > Ni(II) ≅ Cd(II) ≅ Zn(II). On the other hand, the selectivities of the ions on PEI-CS are Hg(II) > Cu(II) > Ni(II) > Cd(II) > Zn(II), which is similar to the selectivity of metal–ammonia complexes presented by Bjerrum (15). The amount of metal ions adsorbed on PEI-CS is larger than that on 7CS9N. These results suggest that CRCS is a good matrix for an adsorbent for the separation and recovery of metal ions through the introduction of functional groups.

## CONCLUSION

Fifteen different chitosan beads were fabricated by controlling the concentration of chitosan in the chitosan/acetic acid solution and the concentration of NaOH in the precipitation bath, followed by crosslinking with ethylene glycol diglycidyl ether. The physical properties of crosslinked chitosan beads (CRCS) were $100 < \rho_{app} < 200$ kg/m$^3$, $0.4 < Q_{NH_2} < 0.8$ kmol/m$^3$, $90 < R_{P,mp} < 900$ nm, $0.87 < \epsilon_p < 0.94$, and $1.0 < S < 1.5 \times 10^5$ m$^2$/kg.

The concentration of chitosan in the chitosan/acetic acid solution, $C_{chitosan}$, and the concentration of NaOH in the precipitation bath, $C_{NaOH}$, were important factors which affected the physical properties of the finished products of CRCS. The value of $\rho_{app}$ was given as a function of $C_{chitosan}$ and $C_{NaOH}$, and the estimating equations were expressed by Eqs. (4) to (6) at $100 < \rho_{app} < 200$ kg/m$^3$. The values of $Q_{NH_2}$, $R_{P,mp}$, $\epsilon_p$, and $S$ could be estimated by using the value of $\rho_{app}$ and Eqs. (7), (8), (9), and (10), respectively. The authors established a method by which CRCS with any desired properties can be fabricated.

We fabricated polyaminated crosslinked chitosan beads (PEI-CS) by introducing poly(ethylene imine) onto the crosslinked chitosan beads (7CS9N). The polyaminated CRCS had the high capacity, and it had high selectivity for the adsorption of Hg(II), Cu(II), Ni(II), Cd(II), and Zn(II). The results suggest that CRCS is a good matrix for an adsorbent for the separation and recovery of metal ions through the introduction of functional groups.

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## NOMENCLATURE

| | |
|---|---|
| $C_{NaOH}$ | concentration of sodium hydroxide in precipitation bath (kmol/m$^3$) |
| $Q_{NH_2}$ | adsorbed-phase concentration of amino group (kmol/m$^3$ of wet resin) |
| $R_P$ | pore radius (nm) |
| $R_{P,mp}$ | average pore radius (nm) |
| $S$ | specific surface area (m$^2$/kg) |
| $V_f$ | volume fraction of pore (%) |
| $V_{wet}$ | volume of wet beads (m$^3$) |
| $V_{W,P}$ | volume of water filling pore of beads (m$^3$) |
| $W_{dry}$ | weight of beads dry (kg) |
| $\epsilon_p$ | total porosity |
| $\rho_{app}$ | apparent density (kg/m$^3$) |
| $\chi$ | degree of crosslinking (wt%) |

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