

A Study on the Synthesis of *N*-Acylchitosan Porous Beads and Their Metal Ion Adsorption Characteristics

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N-Acylchitosan Porous Bead들의 제조 및 금속이온 흡착특성에 관한 연구

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Abstract : Chitin was isolated from crab shell. Chitosan, which was prepared by the deacetylation of chitin, was acylated to obtain *N*-acetyl(regenerated chitin), *N*-propionyl, *N*-butyryl, *N*-hexanoyl, *N*-decanoyl and *N*-maleated chitosans and their metal ion adsorption characteristics of *N*-acylchitosans were investigated.

In order to enhance the adsorptivity, their porous beads were prepared and their adsorptivity with respect to the porosity and the adsorptivities for metal ions(Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Ag^{+}) were investigated. Their metal ion adsorptivities were remarkably improved compared to those of chitin.

As the larger acyl groups were introduced, adsorptivity increased, but that of *N*-decanoyl chitosan showed some decrease because of steric hindrance of the bulky *N*-decanoyl group. *N*-Maleated chitosan containing carboxyl group showed highly improved adsorptivity, and *N*-acylchitosans showed the good selective adsorption in the mixed metal ions(Cu^{+2} , Ni^{+2} , Co^{+2} , Mn^{+2} and Ag^{+}). They also showed excellent adsorption characteristics as chelating polymers.

1. INTRODUCTION

Chitin is a well-known natural chelate polymer. In the case of chitosan, the adsorptivity of metal ions is highly improved compared with chitin because of the primary amino group formed by deacetylation of chitin[1-3]. Many attempts have been made to use them as the adsorbent of heavy metal ions, coagulant for wastewater treatment, fillers for chro-

matographic columns and so on[4-10]. To enhance and extend the applicability of chitin and chitosan, various chemical modifications were attempted to prepare the derivatives of chitin and chitosan[11-20].

Several attempts for the *N*-acylation of chitosan have been reported using drastic conditions such as, with acetic anhydride at elevated temperatures[21], and in the presence of concentrated hydrochloric acid as catalysts

[22]. Selective *N*-acylation of chitosan under mild conditions has recently been reported[23-27] by treatment of a solution in aqueous methanolic acetic acid with carboxylic anhydrides at room temperature. Moore, Roberts [28-30] and Hirano[31-30] are representative researchers. Several patents regarding the novel processes for preparing a porous shaped material of acylated chitin derivative have been reported[40-42] to use as fillers for chromatographic columns, a base material for immobilizing enzymes and so on. In addition, many applications of acyl chitosans have been studied[43-49].

In this study, *N*-acylchitosan porous beads were prepared to investigate the selective adsorptivity as materials for separation. The adsorptivity of chitin and chitosan are due to acetyl amino group and free primary amino group, respectively. These ligands were changed to synthesize several derivatives of *N*-acylchitosan and their chelate forming abilities were also investigated for selective adsorbent of valuable metal ions such as Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} and Ag^+ .

2. EXPERIMENTS

2. 1. Materials and reagents

Chitin was isolated from crab shell according to the modified Hackman method[50].

Hydrochloric acid, sodium hydroxide, acetic acid, ethanol, diethyl ether, toluene, sorbitan monooleate and ammonia water were provided by Samchun Pure Chem. Ind. Ltd. Acetic anhydride, propionic anhydride, *n*-butyric anhydride, *n*-hexanoic anhydride, *n*-decanoic anhydride and maleic anhydride were provided by Tokyo Kasei Kogyo Co. Ltd., and metal nitrates were supplied from Kanto Chem. Co.

2. 2. Preparation of chitosan

Chitin was deacetylated with sodium hydro-

oxide solution to obtain chitosan, according to Mima's method[1]. The deacetylation degree of chitosan obtained was measured by the titration method[51].

2. 3. Preparation of *N*-acylchitosan porous beads

N-Acylchitosan porous beads were prepared by the method of Koshugi[40] with a little modification as follows. Chitosan(2g) was dissolved in 2% aqueous acetic acid to give 2.5% chitosan solution(80g). A liquid mixture prepared by dissolving sorbitan monooleate as the surfactant and 8g of toluene as the porosity-regulating agent into 40g of ethanol as the diluent was added to the above prepared chitosan solution with agitation to emulsify. The amounts of surfactant used were 0.05, 0.1, 0.15, 0.2, 0.3, 0.5, and 1 mol respectively per 1 mol toluene. On the other hand, 12g of sorbitan monooleate and excess of carboxylic anhydride were dissolved in 1.2 liters of toluene in a vessel and then the above mentioned emulsified chitosan solution was added into the reaction vessel stirring at 1,000rpm at 25°C in a constant temperature water bath. Acylating agents and *N*-acylated chitosans were shown in Table 1.

After reacting for about 20 hours for completion of acylation, 800ml of ethanol/aqueous solution of ammonia(7/3, v/v) was poured into the solution in the reaction vessel to make spherical gels.

Table 1. Acylating Agents and *N*-Acylchitosans Used

Acylating agents	<i>N</i> -Acylchitosans	DS.*	R**
Acetic anhydride	<i>N</i> -Acetylchitosan	0.96	-CH ₃
Propionic anhydride	<i>N</i> -Propionylchitosan	0.95	-CH ₂ CH ₃
<i>n</i> -Butyric anhydride	<i>N</i> -Butyrylchitosan	0.79	-(CH ₂) ₂ CH ₃
<i>n</i> -Hexanoic anhydride	<i>N</i> -Hexanoylchitosan	0.71	-(CH ₂) ₄ CH ₃
<i>n</i> -Decanoic anhydride	<i>N</i> -Decanoylchitosan	0.65	-(CH ₂) ₈ CH ₃
Maleic anhydride	<i>N</i> -Maleated chitosan	0.80	-CH=CHCOOH

* Degree of substitution of *N*-acyl group.

** R of *N*-acyl group in scheme.

After filtration, the gels were washed with ethanol several times at room temperature to extract any remaining reagents(carboxylic acid, anhydride, so on.) and separated by filtering.

Then, the products were suspended in distilled water and freeze-dried, or soaked into acetones several times, filtered, washed with diethyl ether, and dried in vacuo at 80°C.

In order to remove any O-acyl groups, the products were treated overnight in 0.5M potassium hydroxide in ethanol with shaking at room temperature[31-35].

The product was collected, washed well with ethanol, then with diethyl ether, and dried to prepare the *N*-acylchitosan porous beads. The structures of the products were confirmed by IR spectra.

2. 4. Adsorption experiment

Metal ion adsorption characteristics of *N*-acylchitosan porous beads were tested by the batch method. Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Ag^+ ion and their mixed ion solutions were made. The concentrations of each metal ions were 100ppm. After the pH of solutions were adjusted, 0.1g of each *N*-acylchitosan bead was added into the solution of each metal ion (25ml), and shaken occasionally for 24 hours at room temperature.

After filtration, the final concentration of metal ions was measured to determine the amount of metal ions adsorbed.

2. 5. Characterization of the products

For structure confirmation, the infrared spectroscopy was carried out by the KBr pellet method using a FT-IR(Nicolet Model 5-DX), and X-ray diffractometer(Rigaku Denki Model RAD-C) and elemental analyser(Perkin Elmer Model 240) were also used. Scanning electron microscope(SEM, Jeol Model JSM-35 CF) was used to observe the

morphology of the beads. The concentration of metal ions was measured using atomic absorption spectrophotometer(GBC Model 903).

3. RESULTS AND DISCUSSION

3. 1. Degree of deacetylation

The titration curve of chitosan(0.5g) dissolved in 20ml of 0.3 N HCl is shown in Fig. 1. The amount of consumption of NaOH between the two inflection points corresponds to the amount of free amino groups present in the chitosan solution. From this calculation, degree of deacetylation of chitin was found to be about 91%.

3. 2. *N*-Acylchitosan porous beads

Chitosan was dissolved in 2% aqueous acetic acid solution to prepare 'chitosan solution'. A liquid mixture prepared by dissolving the surfactant and the porosity-regulating agent into the diluent was added to the above

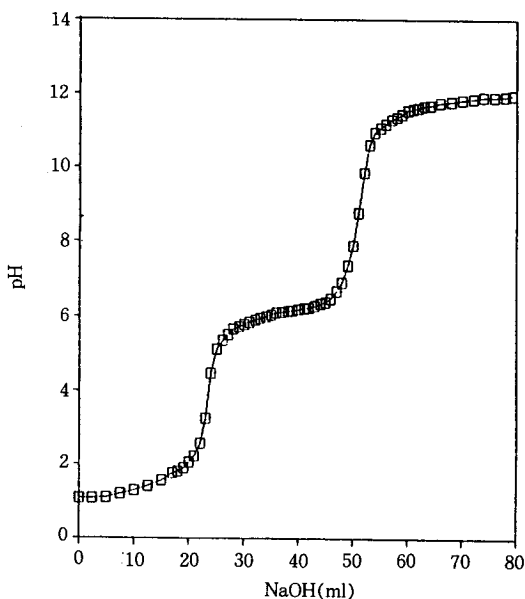


Fig. 1. Titration curve of chitosan sample dissolved in HCl with NaOH solution.

'chitosan solution' with agitation to emulsify. This 'chitosan emulsion' was added into the toluene dissolving the surfactant and acylating 1 mol with agitation at 1,000rpm to carry out the acylation of chitosan.

Ethanol was used as the diluent. The amount of the ethanol was 0.5 part by weight to one part by weight of the chitosan solution.

Toluene, the porosity-regulating agent, was used to obtain the highly porous and strong bead. In this case, 0.1 part to one part by weight of the chitosan solution was adequate.

Sorbitan monooleate was used as the surfactant and its amount was controlled to be 0.05, 0.1, 0.15, 0.2, 0.3, 0.5 and 1 mol per 1mol toluene as the porosity-regulating agent.

The size of the bead depends on the mixing speed of the stirrer. After agitation at 1,000 rpm, the bead of about 100microns in diameter was obtained. The amount of the carboxylic anhydride used as the acylating agent was 5 times to one equivalent of amino group of the chitosan.

The degree of *N*-acetylation was determined by IR spectroscopy according to Moore and Robert's method[28-30]. The rates of *N*-acetylation were followed by measuring the increase in absorption intensity of the amide I band at 1660cm^{-1} as a function of time, using the absorbance of the hydroxyl band at 3450cm^{-1} as an internal standard(Fig. 2). *N*-Acylation was completed after three hours of reaction time, and the ratio of these two bands of the *N*-acetylchitosan was almost identical to that of chitin. But the acylation of the larger carboxylic anhydrides were completed after 10~12 hours.

Two acylated chitosans are consisted of *N*-acetylation and *O*-acylation. *N*-Acylation and *O*-acylation are carried out in the primary amino group of chitosan(C-2) and the hydroxyl groups of chitosan(C-3 and C-6), respectively. However, reactivity of the primary amino

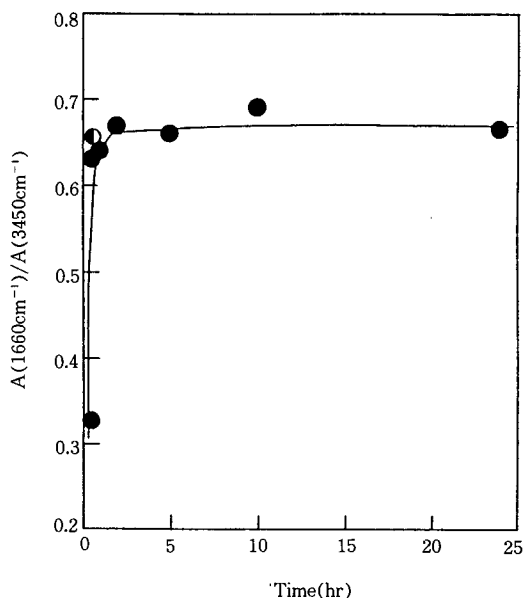


Fig. 2. Effect of reaction time in 1 molylation of chitosan. (●) *N*-acetylchitosan, (○) chitin.

group with carboxylic anhydride is much higher than that of the hydroxyl group. The reaction is carried out at relatively lower temperature(25°C). It assumes that *N*-acetylation is occurred exclusively at lower temperature.

Fig. 3 shows the IR spectra of chitosan and acylchitosans in the $1800\sim 1200\text{cm}^{-1}$ region. The carbonyl stretching vibration (amide I) in chitosan was observed at 1660cm^{-1} , and N-H bending vibration (amide II) of the primary amino group was observed at 1595cm^{-1} (Fig. 3 (a)). The amide II band at 1595cm^{-1} shifted to 1550cm^{-1} . As *N*-acetylation proceeds, this shift to lower frequencies indicates a gradual disruption of hydrogen bonding involving the amino group that was present in the chitosan. But this acylchitosan showed small shoulders due to *O*-acyl groups at 1750cm^{-1} (C=O) and 1240cm^{-1} (C-O), in addition to IR absorptions of *N*-acyl groups at 1660cm^{-1} (C=O) and 1500cm^{-1} (N-H) (Fig. 3(b)). From these

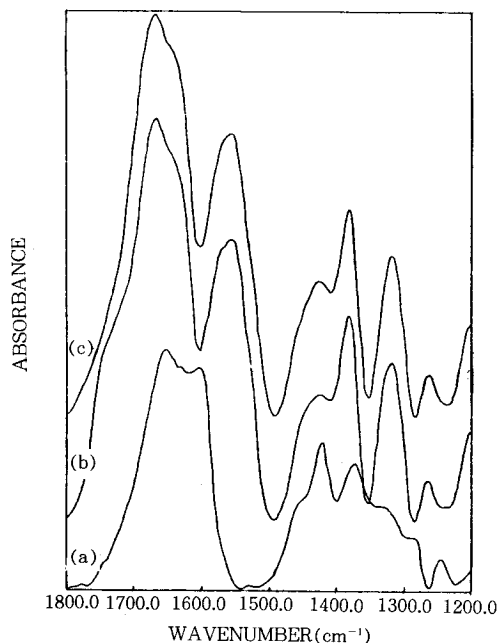
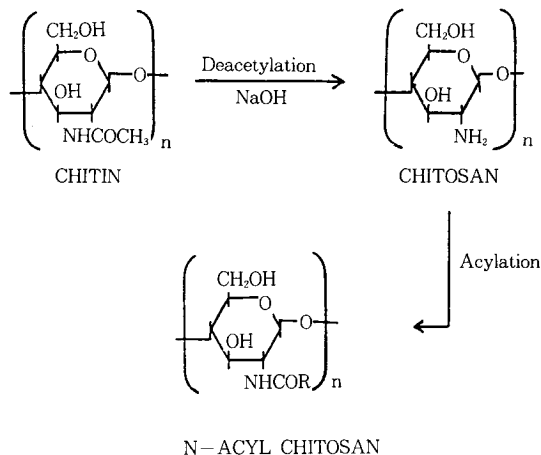


Fig. 3. Infrared spectra in the $1800\sim 1200\text{cm}^{-1}$ region. (a) chitosan, (b) acylchitosan bead, (c) *N*-acyl chitosan bead treated with KOH solution.

results, the presence of both *N*- and *O*-Acyl groups in acylchitosan was confirmed in agreement with results of Hirano et. al[33]. The *O*-acylation must be occurred in C-6 of chitosan because the hydroxyl group of C-6 is more reactive than that of C-3 of chitosan.

To investigate the adsorptivity of *N*-acylchitosan beads, they were dipped overnight in 0.5mol alcoholic KOH solution at room temperature to remove any *O*-acyl groups formed. *N*-Acyl chitosan treated with KOH solution as in Fig. 3(c) showed strong IR absorptions for *N*-acyl groups at 1660cm^{-1} (C=O) and 1550cm^{-1} (N-H), but no absorptions for *O*-acyl groups at 1750cm^{-1} (C=O) and 1240cm^{-1} (C=O) were observed. Accordingly, the product obtained was exclusively *N*-acylated derivative of chitosan.



Scheme

3. 3. Structure determination of *N*-acylchitosans.

N-Acylchitosans were prepared with above mentioned reaction conditions (Scheme). Table 1 shows the carboxylic anhydrides used as the acylating agents and *N*-acylchitosans (*N*-acetyl, *N*-propionyl, *N*-butyryl, *N*-hexanoyl, *N*-decanoyl and *N*-maleated chitosan).

The degree of substitution (D.S.) for *N*-acyl groups was in the range of 0.65~0.96 per hexosaminide residue. The degree of substitution of acyl groups larger than *N*-propionyl decreased. These decreases are supposed to be due to the steric hindrance of bulky substituent groups. The degree of substitution has a profound effect on the adsorptivity. But the effect of the degree of substitution for acyl group on the adsorptivity of Cu^{2+} ion has already been reported. The adsorptivity abruptly increases with the D.S. until about 0.2, and then a decline in the adsorptivity is observed. Then in the D.S. higher than 0.4, the adsorptivity is almost constant. Accordingly, the range of D.S. in *N*-acylchitosans shown in Table 1 is supposed not to affect on the adsorptivity.

In the IR spectra (Fig. 4) of chitin, chitosan and *N*-acetyl chitosan, The amide I band of

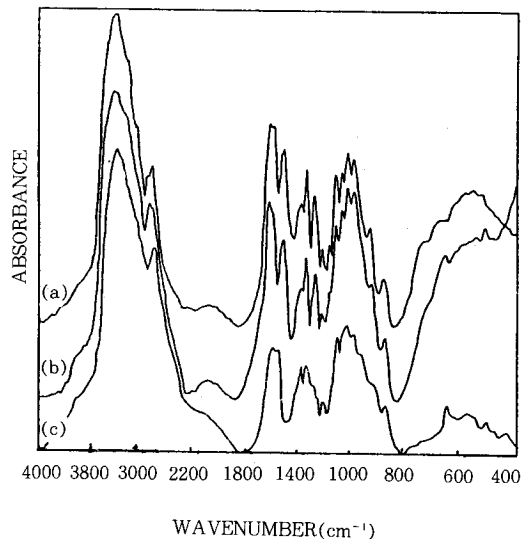


Fig. 4. Infrared spectra of (a) chitin, (b) *N*-acetylchitosan, (c) chitosan.

chitosan at 1660cm^{-1} ($\text{C}=\text{O}$) became larger for *N*-acetylchitosan, the amide II band at 1595cm^{-1} due to the primary amino group of chitosan shifted to 1550cm^{-1} , but even weak shoulders at 1750cm^{-1} ($\text{C}=\text{O}$) and 1240cm^{-1} ($\text{C}-\text{O}$) for *O*-acyl group did not appear. In addition, the broad bands at $3500\sim 3100\text{cm}^{-1}$ ($\text{O}-\text{H}$ and NH) and the $\text{C}-\text{H}$ stretching bands at 2900cm^{-1} were observed. The IR spectrum of *N*-acetylchitosan was identical with that of chitin.

The IR spectra of *N*-propionyl, *N*-butyryl, *N*-hexanoyl, *N*-decanoyl, and *N*-maleated chitosan are shown in Fig. 5 and Fig. 6. The amide I, II bands appeared at 1660cm^{-1} and 1550cm^{-1} , respectively, as those of *N*-acetylchitosan. And the IR spectra showed a progressive increase of the $\text{C}-\text{H}$ stretching band at 2900cm^{-1} , due to the methylene groups with increasing aliphatic chain length in *N*-acyl groups. For *N*-maleated chitosan, the strong IR absorption for the carboxyl group appeared at 1715cm^{-1} ($\text{C}=\text{O}$).

Fig. 7 shows X-ray diffraction curves of the

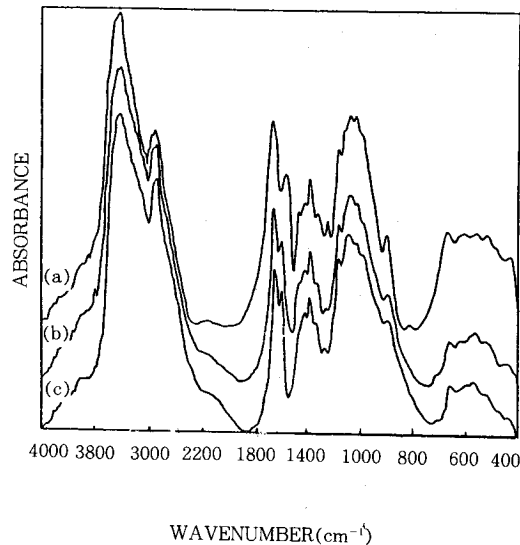


Fig. 5. Infrared spectra of (a) *N*-propionylchitosan, (b) *N*-butyryl chitosan, (c) *N*-hexanoylchitosan.

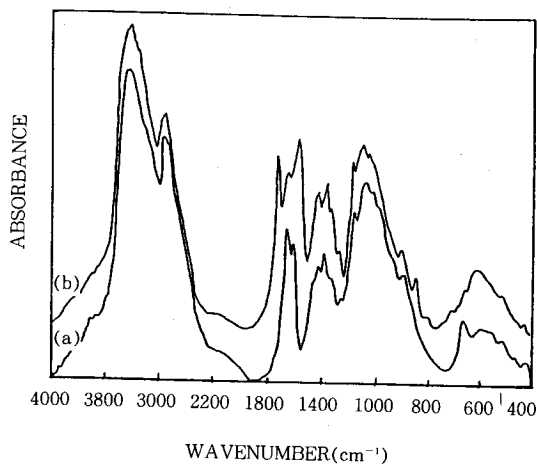


Fig. 6. Infrared spectra of (a) *N*-decanoylchitosan, (b) *N*-maleated chitosan.

chitin and *N*-acylchitosans. Peaks appeared at around 10° (2θ) are assigned to $\text{be}(001)$ and (100) , and those at around 20° are known to be a mixture of (01) and (002) . The peak intensity of *N*-acetylchitosan was weaker than

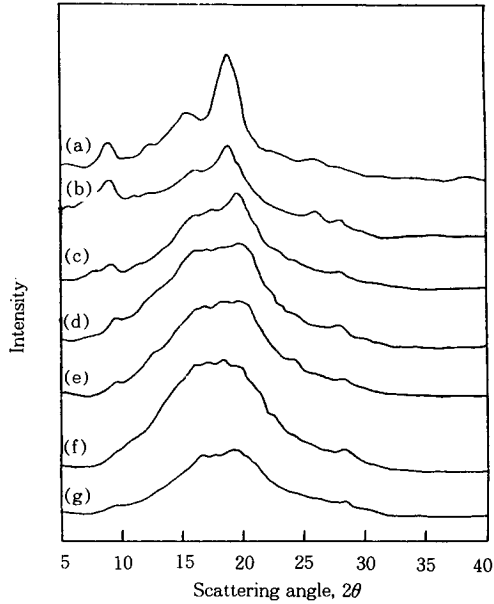
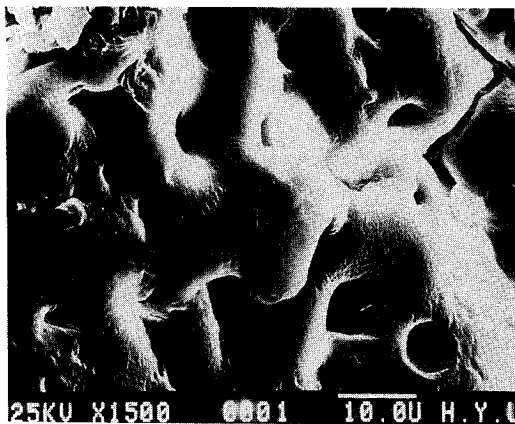
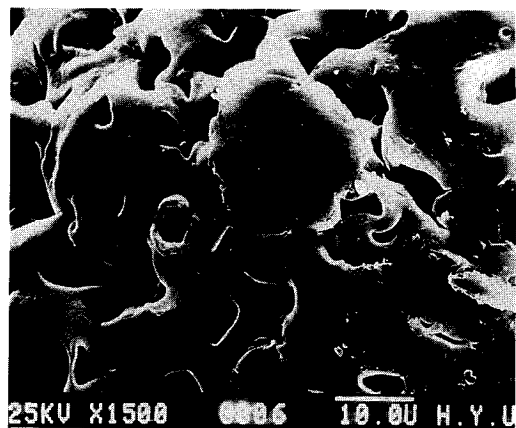


Fig. 7. X-ray diffraction curves of (a) chitin, (b) *N*-acetylchitosan, (c) *N*-propionylchitosan, (d) *N*-butyrylchitosan, (e) *N*-hexanoylchitosan, (f) *N*-decanoylchitosan, (g) *N*-maleated chitosan.

that of chitin, and the larger *N*-acyl group was substituted, the weaker peak intensities were observed.



(a)



(b)

3. 4. Porosity and adsorptivity

The porosity of *N*-acetylchitosan bead mainly depends upon the amount of the surfactant. Their morphology was observed with SEM (Fig. 8). The most porous bead were obtained at 0.1 mole surfactant per 1 mole of toluene of porosity-regulating agent. It also showed the best adsorptivity (Fig. 9) because the adsorptivity is affected by the surface area of substrates. The adsorptivity of beads having more than 0.2 mole of surfactant increased again due to the shrinkage of bead surface, but adsorptivity was less than that of the bead containing 0.1 mol of the surfactant.

The surface of freeze-dried and vacuum dried *N*-acylchitosan beads were compared (Fig. 10). Freeze-dried beads were more porous than the vacuum dried sample. The bead was not so rigid.

Fig. 11 shows the surface of acylchitosan and *N*-acylchitosan bead treated with KOH solution. In the *N*-acylchitosan bead, micro pores were created due to the elimination of any *O*-acyl group.

In the Fig. 12 the adsorptivities of Cu^{2+} ion of acetylated chitosan beads are shown. The

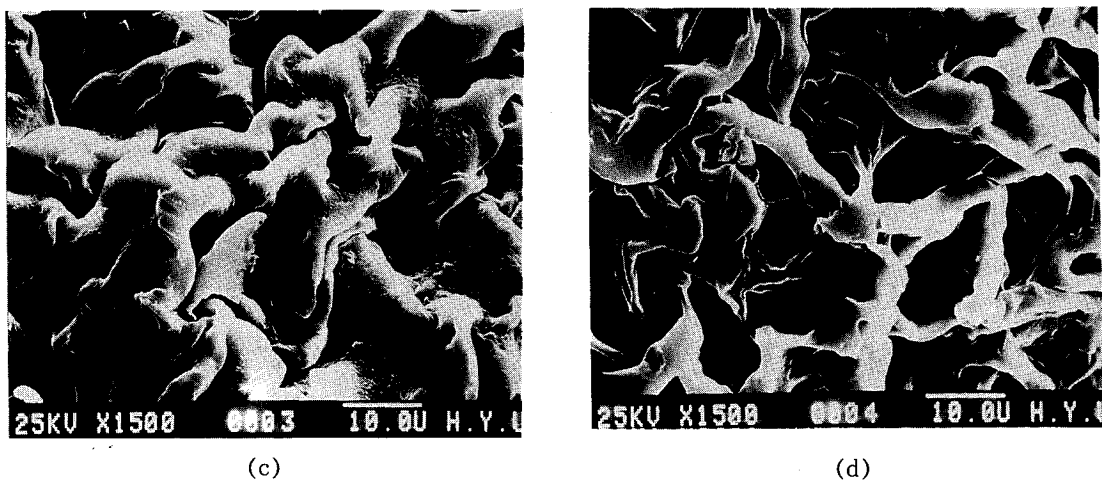


Fig. 8. SEM. Effect of surfactant mole ratio in the porosity of *N*-acylchitosan bead. (a) 0.05M, (b) 0.1M, (c) 0.2M, (d) 1M.

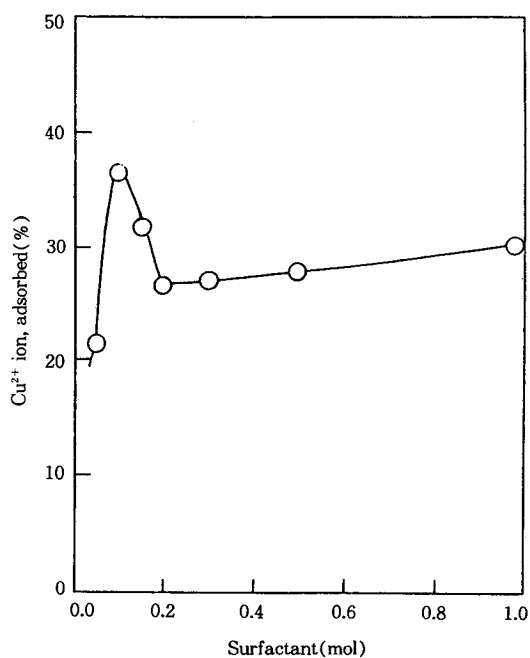
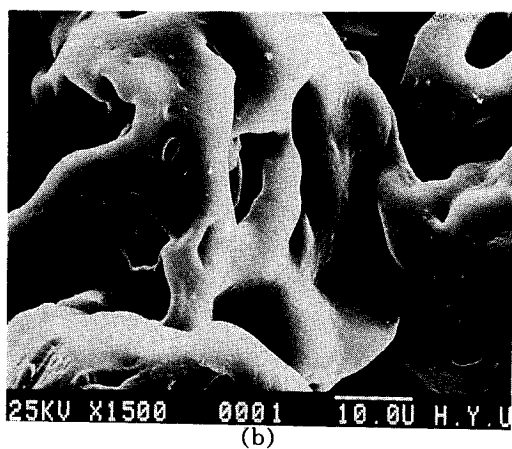
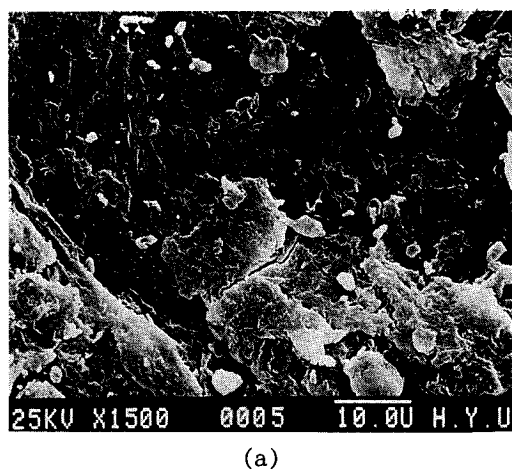
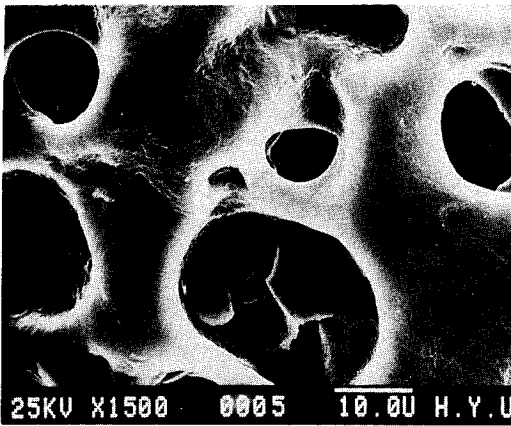
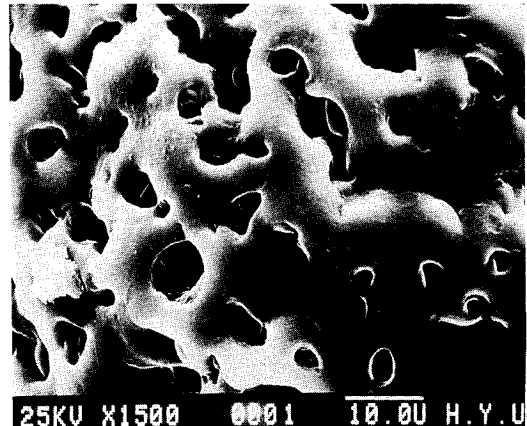


Fig. 9. Adsorptivities of Cu^{2+} ions by *N*-acetylchitosan beads in the reaction with the variation of surfactant mole ratio. Concentration of Cu^{2+} ions in the adsorption solution was 100ppm, and contact time was 24hrs, at pH 6.





(c)

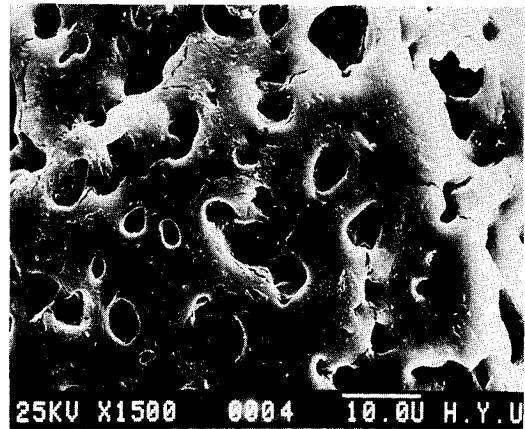


(a)

Fig. 10. SEM of chitin and N-acylchitosan beads surface. (a) chitin, (b) N-acylchitosan bead dried in vacuum oven, (c) N-acylchitosan bead freeze dried.

beads were vacuum dried or freeze-dried, and treated with KOH solution or not. The adsorptivity of freeze-dried bead increased about 5% in comparison with that of vacuum dried. *N*-acetylchitosan bead treated with KOH solution showed the better adsorptivity than the acetylchitosan bead. The reason why the adsorptivity of the freeze-dried bead is superior to that of vacuum dried is considered to be caused by the difference of the porosity (Fig. 10).

The superiority of the adsorptivity of *N*-acetylchitosan treated in KOH solution than that of acetylchitosan is due not only to the increase of surface area by the creation of micro pore, but also the remaining acids interrupt the formation of chelate between metal ions and primary, secondary amino groups in acetylchitosan. That is to say, the primary and secondary amino groups are protonated by the acid to be $-NH_3^+$ ($-NH_3^+O-COR$) and $-NH_2^+$ COR , respectively. As the chelate forming abil-



(b)

Fig. 11. SEM of beads surface. (a) acylchitosan bead, (b) N-acylchitosan bead treated with KOH solution.

ity of these ligands decreases, the adsorptivity of metal ions decrease. But they were deprotonated by treatment with the alkaline solution to be $-NH_2$ and $-NHCOR$, and then the chelate forming ability increased. Accordingly, if any *O*-acyl group is removed, the adsorptivity also increases.

In the dry method, while adsorptivity of the freeze-dried bead was better than that of ther-

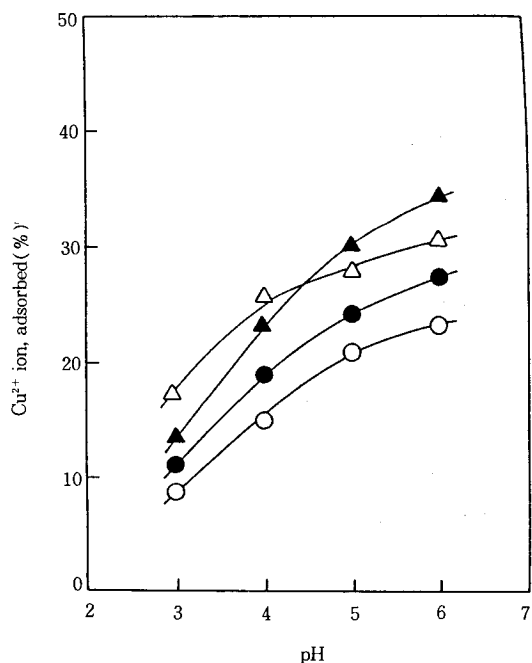


Fig. 12. Adsorptivity of Cu^{2+} ions by acylchitosan beads. Concentration of Cu^{2+} ions in the adsorption solution was 100ppm and contact time was 24hrs, at pH3-6. (○) acetylchitosan dried in vacuum oven, (●) acetylchitosan freeze dried, (△) *N*-acetylchitosan dried in vacuum oven, (▲) *N*-acetylchitosan freeze dried.

mally dried bead in vacuum oven, the strength of freeze-dried bead was weaker, the density was lower and it was difficult to reuse the bead for adsorption. Accordingly, vacuum drying was more profitable than freeze-drying for possible practical applications.

3. 5. Adsorption of metal ions

In the adsorption of metal ions, such as Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , and Ag^+ , Fig. 13 shows the adsorptivity of the metal ions onto *N*-acetylchitosan in a batch containing individual

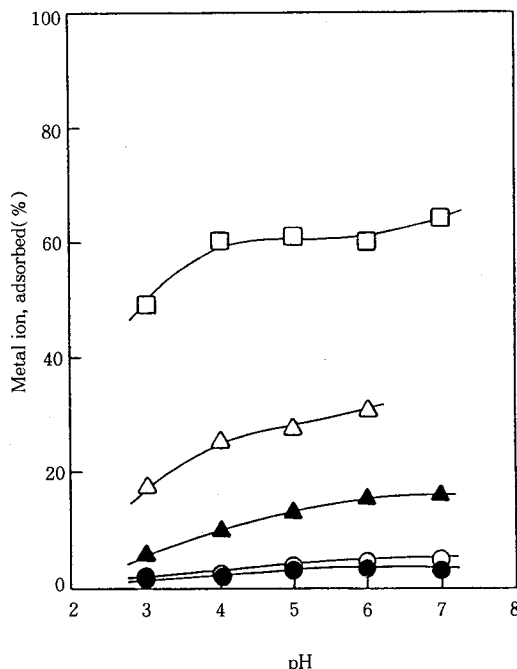


Fig. 13. Effect of pH on the adsorption of metal ions by *N*-acetylchitosan beads. Concentration of metal ions in the adsorption solution was 100ppm and contact time, 24hrs. (△) Cu^{2+} , (▲) Ni^{2+} , (○) Co^{2+} , (●) Mn^{2+} , (□) Ag^+ .

100ppm-initial solutions. 60% of Ag^+ ion was adsorbed in the range of pH 4~6, 30% of Cu^{2+} ion, 15% of Ni^{2+} ion and about 5% of Co^{2+} and Mn^{2+} ion were adsorbed.

As the chain length of acyl group increased for propionyl to butyryl, the adsorption capacity was enhanced(Fig. 14 and 15). However, the adsorptivity of hexanoyl and decanoic chitosan were similar to that of *N*-butyryl chitosan(Fig. 16 and 17).

However, the adsorptivity of *N*-maleated chitosan showed different to other *N*-acylchitosans and *N*-maleated chitosan adsorbed 90~98% of all metal ions(Fig. 18). These results are supposed to be due to the carboxyl group which is a better ligand for

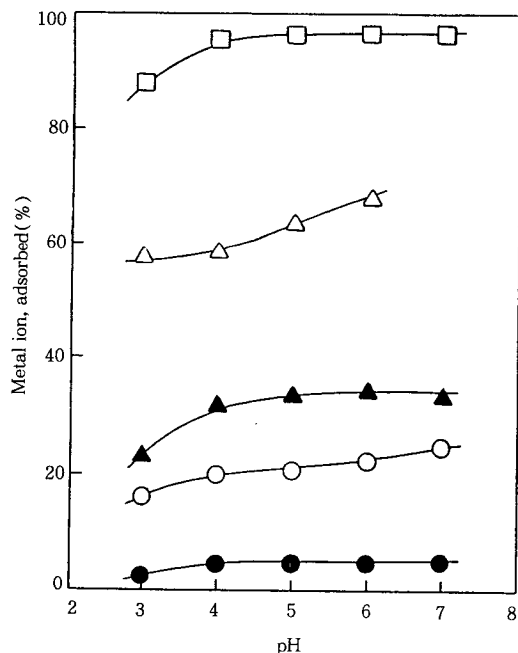


Fig. 14. Effect of pH on the adsorption of metal ions by *N*-propionyl chitosan beads. Concentration of metal ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)Cu²⁺, (\blacktriangle)Ni²⁺, (\circ)Co²⁺, (\bullet)Mn²⁺, (\square)Ag⁺.

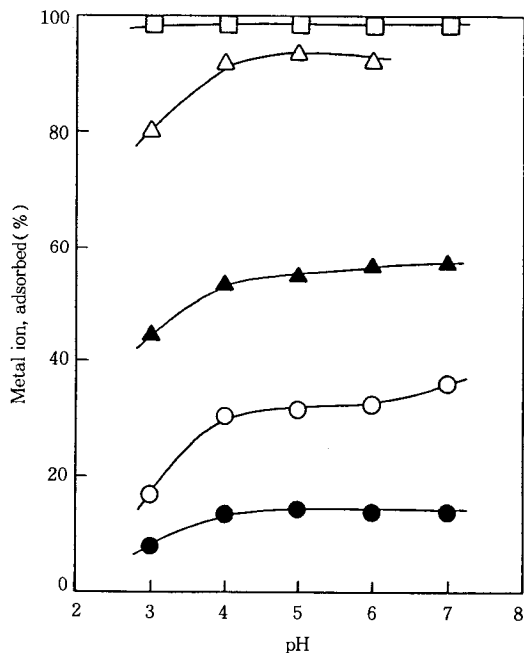


Fig. 15. Effect of pH on the adsorption of metal ions by *N*-butyryl chitosan beads. Concentration of metal ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)Cu²⁺, (\blacktriangle)Ni²⁺, (\circ)Co²⁺, (\bullet)Mn²⁺, (\square)Ag⁺.

chelation with many metal ions. That is, amino group and carboxyl group reinforce the metal ion adsorptivity.

3. 6. Comparison between adsorptivity of chitin and *N*-acylchitosans

The adsorptivity of each metal ions to *N*-acylchitosans was compared with that of chitin. Fig. 19 shows the adsorptivity of Cu²⁺ ion. Chitin adsorbed 20% of Cu²⁺ ion, but *N*-acetylchitosan, which is similar to chitin in chemical structure, adsorbed 30% and this 10% increase is attributed to the increase of amorphous region and the increase of the surface area as the crystallinity decreases. The adsorptivity of *N*-propionylchitosan was about 60% and those of *N*-butyryl, *N*-hexanoyl and

N-decanolchitosan increased to about 90%. As the larger acyl groups are introduced, hydrogen bonds are gradually disrupted and chitosan chains become more separated apart. *N*-Decanoylchitosan, however, adsorbed less Cu²⁺ ion than *N*-butyryl and *N*-hexanoylchitosan, due to steric hindrance of the bulky *N*-decanoyl group and *N*-maleated chitosan adsorbed 95% of Cu²⁺ ion because of above mentioned effect of carboxyl group.

The adsorptivities of Ni²⁺ and Co²⁺ ion were lower than that of Cu²⁺ ion, but the tendency of adsorption to *N*-acylchitosan was similar as shown in Fig. 20 and 21, respectively.

Fig. 22 shows that the adsorptivity of Mn²⁺ ion to *N*-maleated chitosan was more than 90%, while those of chitin and the other *N*-acylchit-

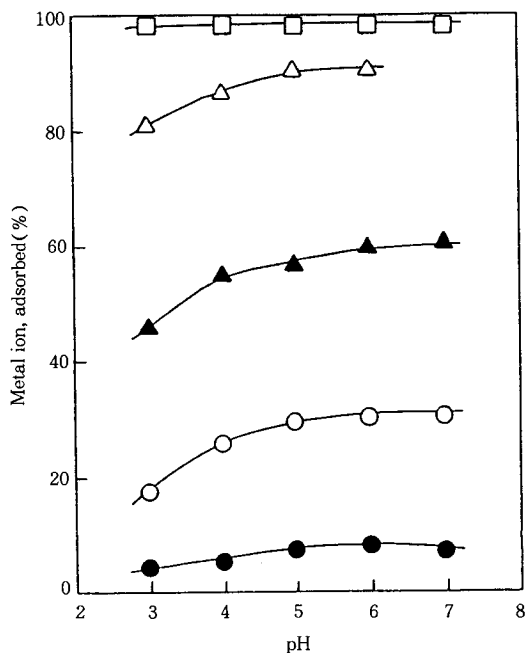


Fig. 16. Effect of pH on the adsorption of metal ions by *N*-hexanoyl chitosan beads. Concentration of metal ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)Cu²⁺, (\blacktriangle)Ni²⁺, (\circ)Co²⁺, (\bullet)Mn²⁺, (\square)Ag⁺.

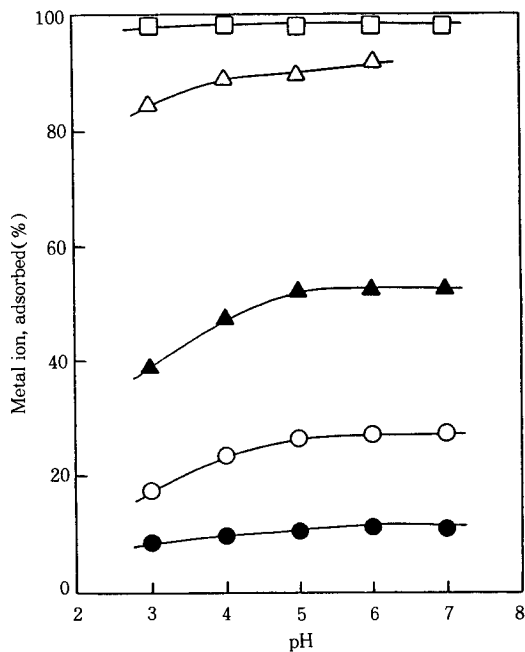


Fig. 17. Effect of pH on the adsorption of metal ions by *N*-decanoyl chitosan beads. Concentration of metal ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)Cu²⁺, (\blacktriangle)Ni²⁺, (\circ)Co²⁺, (\bullet)Mn²⁺, (\square)Ag⁺.

osan was less than 20%. It is considered also due to the carboxyl group. In general, the adsorptivity of Mn²⁺ ion to the derivatives of chitosan has known as low. However, it is characteristic that *N*-maleated chitosan shows good adsorptivity of Mn²⁺ ion.

The adsorptivity of Ag⁺ ion is shown in Fig. 23. *N*-Acylchitosans except *N*-acetylchitosan adsorbed about 95% of Ag⁺ ion.

3. 7. Selective in metal ion adsorption

The selective adsorptivity of *N*-acylchitosans and chitin is compared in Table 2 using 100ppm solution of mixed metal ions.

Chitin adsorbed Cu²⁺ and Ag⁺ ion selectively, but their adsorptivities were low. *N*-Acetylchitosan appeared better adsorptivity

than chitin. As the larger acyl group is introduced, the adsorptivity of Cu²⁺ and Ag⁺ ion increased remarkably, and that of Ni²⁺ ion increased slightly. Those of Co²⁺ and Mn²⁺ ion, however, did not increase. These enhanced selectivity of *N*-acylchitosans was observed in metal ion adsorption. Accordingly, it is concluded that *N*-acylchitosans porous beads are good chelate resins.

4. CONCLUSION

Throughout the present study, chitosan which was the deacetylated product of chitin was acylated to afford *N*-acylchitosan porous beads, their adsorption characteristics of metal ions in various porosity and pH were measured. The following conclusions were obtained.

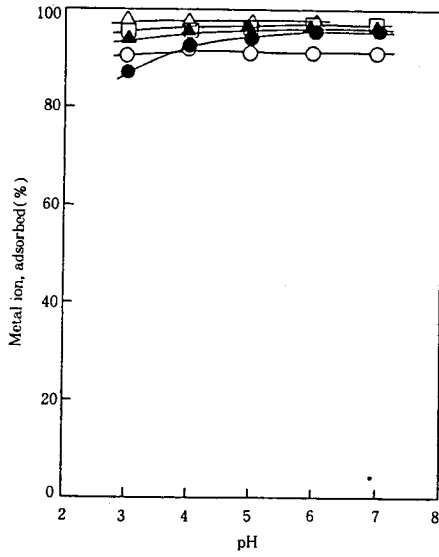


Fig. 18. Effect of pH on the adsorption of metal ions by N-maleated chitosan beads. Concentration of metal ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)Cu²⁺, (\blacktriangle)Ni²⁺, (\circ)Co²⁺, (\bullet)Mn²⁺, (\square)Ag⁺

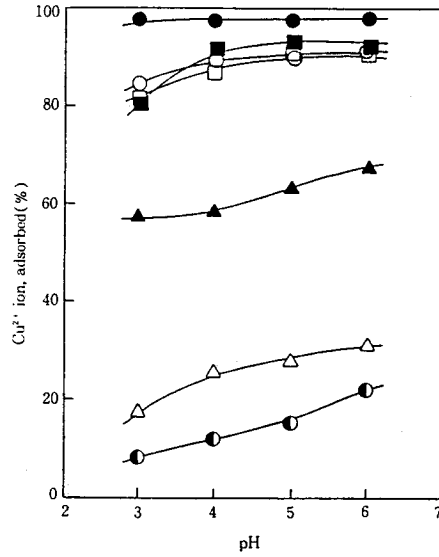


Fig. 20. Effect of pH on the adsorption of Ni²⁺ ions by chitin and N-acylchitosan beads. Concentration of Ni²⁺ ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)N-acetylchitosan, (\blacktriangle)N-propionylchitosan, (\square)N-butrylchitosan, (\blacksquare)N-hexanoylchitosan, (\circ) N-decanoylchitosan, (\bullet)N-maleated chitosan, (\ominus)chitin.

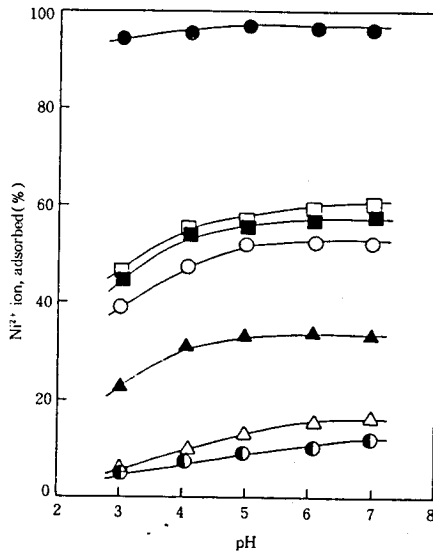


Fig. 19. Effect of pH on the adsorption of Cu²⁺ ions by chitin and N-acylchitosan beads. Concentration of Cu²⁺ ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)N-acetylchitosan, (\blacktriangle)N-propionylchitosan, (\square)N-butrylchitosan, (\blacksquare)N-hexanoylchitosan, (\circ) N-decanoyl chitosan, (\bullet)N-maleated chitosan, (\ominus)chitin.

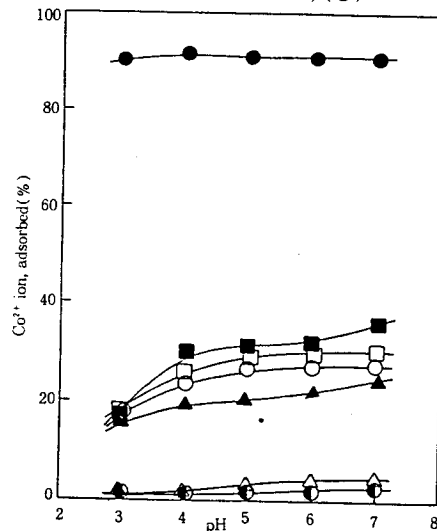


Fig. 21. Effect of pH on the adsorption of Co²⁺ ions by chitin and N-acylchitosan beads. Concentration of Co²⁺ ions in the adsorption solution was 100ppm and contact time, 24hrs. (\blacktriangle)N-propionylchitosan, (\square)N-butrylchitosan, (\blacksquare)N-hexanoylchitosan, (\circ) N-decanoyl chitosan, (\bullet) N-maleated chitosan, (\ominus)chitin.

Table 2. Adsorptivities of Mixed Metal Ions* by *N*-Acylchitosan Beads

	unit : %				
	Cu ²⁺	Ni ²⁺	Co ²⁺	Mn ²⁺	Ag ⁺
Chitin	12	0	5	0	16
<i>N</i> -acetyl chitosan	24	0	3	0	45
<i>N</i> -propionyl chitosan	78	14	0	0	97
<i>N</i> -butyryl chitosan	98	47	0	2	100
<i>N</i> -hexanoyl chitosan	98	52	2	5	100
<i>N</i> -decanoyl chitosan	98	50	2	8	100
<i>N</i> -maleated chitosan	99	88	15	13	100

* Concentration of metal ions in the adsorption solution were 100ppm and contact time was 24hrs, at pH 6.

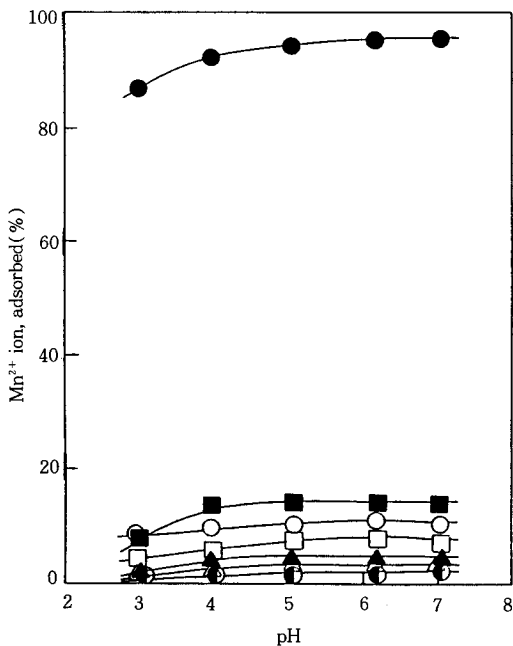


Fig. 22. Effect of pH on the adsorption of Mn²⁺ ions by chitin and *N*-acylchitosan beads. Concentration of Mn²⁺ ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)*N*-acetylchitosan, (▲)*N*-propionylchitosan, (□)*N*-butyrylchitosan, (■)*N*-hexanoylchitosan, (○) *N*-decanoyl chitosan, (●)*N*-maleated chitosan, (●)chitin.

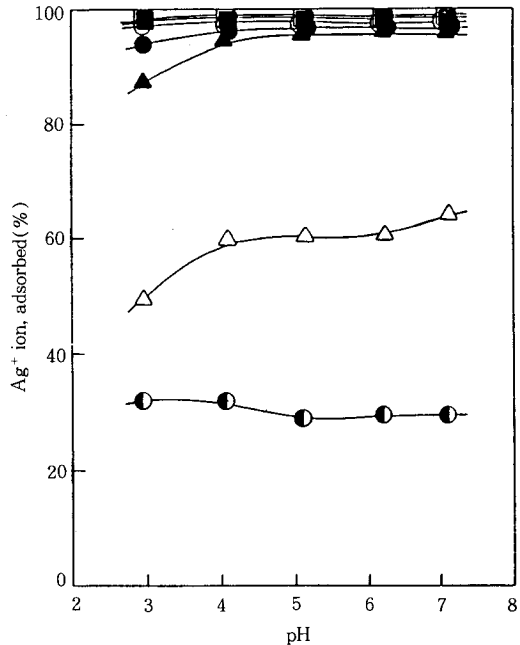


Fig. 23. Effect of pH on the adsorption of Ag⁺ ions by chitin and *N*-acylchitosan beads. Concentration of Ag⁺ ions in the adsorption solution was 100ppm and contact time, 24hrs. (Δ)*N*-acetylchitosan, (▲)*N*-propionylchitosan, (□)*N*-butyrylchitosan, (■)*N*-hexanoylchitosan, (○) *N*-decanoyl chitosan, (●)*N*-maleated chitosan, (●)chitin.

As porosity of *N*-acylchitosan bead increased, adsorptivity of metal ions increased. Adsorptivity of *N*-acylchitosan, treated with KOH solution, was superior to that of raw acylchitosan because of the effect of porosity and deprotonation. Even adsorptivity of freeze-dried bead was superior to that of bead dried in vacuum oven, but dry in vacuum oven was more adequate for practical use.

As the larger acyl group was introduced, original crystallinity of chitin decreased gradually and adsorptivity of metal ions increased. Adsorptivity of *N*-decanoylchitosan somewhat decreased due to steric hindrance of the bulky

N-decanoyl group. *N*-Maleated chitosan containing carboxyl group in its *N*-acyl group showed good adsorptivity(90~98%) for used metal ions. And *N*-acylchitosans showed the better selectivity in metal ion adsorption than chitin as a chelate resin.

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