

# Adsorption of Metal Cations by Water-Soluble N-Alkylated Disaccharide Chitosan Derivatives

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**ABSTRACT:** In the present study, the metal-adsorption ability of various water-soluble chitosan derivatives prepared by N-alkylation of chitosan with maltose, cellobiose, or lactose and with various degrees of substitution (DS) was first determined and compared with the native chitosan. The effects of the pH and reaction time on the metal-adsorption ability and the selective metal adsorption of the disaccharide chitosan derivatives with a DS of 30–40% were further examined. Results revealed that the metal-adsorption ability of chitosan was enhanced after N-alkylation with the disaccharides tested and with certain DS values. All the N-alkylated disaccharide derivatives and the native chitosan exhibited the highest adsorption for Pb<sup>2+</sup> and the lowest adsorption ability for Mg<sup>2+</sup> among all the metal ions that were tested. The DS with disaccharide affects the metal-adsorption ability of the tested chitosan derivatives. In general, the

adsorption ability of these chitosan derivatives for Cu<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>2+</sup>, and Mg<sup>2+</sup> decreased whereas the adsorption ability for Ca<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Cd<sup>2+</sup> increased upon increasing the DS. Further study with disaccharide chitosan derivatives with 30–40% DS also revealed that the adsorption of Zn<sup>2+</sup> and Pb<sup>2+</sup> by these chitosan derivatives was a fairly rapid process. The Zn<sup>2+</sup> and Pb<sup>2+</sup> adsorption ability of these derivatives generally increased as the pH increased. These disaccharide chitosan derivatives also displayed the best selective adsorption for Pb<sup>2+</sup> in mixed solutions with Zn<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup>. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 564–570, 2005

**Key words:** chitosan; metal-adsorption ability; N-alkylated disaccharide chitosan derivatives; water soluble

## INTRODUCTION

Chitosan, a deacetylated derivative of chitin, is composed of  $\beta(1-4)$  glucosidic linkage. Because of its unique polycationic nature, chitosan and its derivatives have been proposed for various applications in the fields of agriculture, food, biomedicine, biotechnology, and pharmaceuticals. Its uses include as a coagulant or flocculent in waste treatment, as a biodegradable polymer for packaging materials, as a beverage-clarifying agent, as an antimicrobial preservative, and so forth.<sup>1,2</sup> However, these applications are often limited by the insolubility of chitosan at neutral or high pH values.<sup>3</sup> To overcome this solubility limitation, chemical modification of chitosan has been conducted by numerous researchers to prepare functional derivatives with enhanced solubility in water.<sup>3–6</sup>

Through the reductive N-alkylation of chitosan with various mono- and disaccharides as described

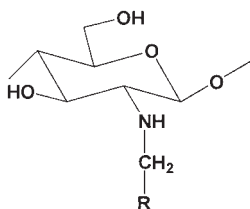
by Sashiwa and Shigemasa,<sup>7</sup> we previously prepared mono- and disaccharide chitosan derivatives.<sup>8</sup> We observed that the solubility of the N-alkylated chitosan derivatives with lactose, maltose, or cellobiose was markedly increased. Furthermore, these disaccharide chitosan derivatives were also demonstrated to possess antioxidative activity<sup>9</sup> and exhibit a higher antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* than did the native chitosan at pH 7.0, suggesting that it is a potentially useful antimicrobial agent.<sup>2</sup> Along with these property changes, it is also reasonable to speculate that the metal-binding nature of chitosan, one of the most attractive functions of chitosan, may also be altered after N-alkylation with maltose, lactose, or cellobiose. Because the metal-adsorption properties different from those of native chitosan have been observed in various chemically modified chitosan derivatives such as ascorbic chitosan derivatives,<sup>10</sup> chitosan phosphate,<sup>11</sup> phosphorylated chitosan,<sup>12</sup> glutaraldehyde chitosan,<sup>13</sup> N-carboxymethyl chitosan,<sup>14</sup> and so forth. Therefore, in the present study, we further investigated the metal-binding properties of the various water-soluble N-alkylated disaccharide chitosan derivatives.

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## EXPERIMENTAL

Chitosan from shrimp shells with 99% N-deacetylation as determined by colloid titration<sup>15</sup> was obtained from China League Biotechnology Associates Ltd. Lytone Enterprise, Inc. (Taipei, Taiwan).

The chitosan derivatives were prepared and characterized according to the procedures described by Yang et al.<sup>2</sup> Briefly, chitosan dissolved in a 1 : 1 mixture (pH 5.5) of methanol and 1% aqueous acetic acid was mixed with various amounts of disaccharides. After being kept at room temperature for 1 h, NaCNBH<sub>3</sub> was added and it was kept at room temperature for a period of 2–48 h, generally until a white solidified mass was formed. The solidified mass was then collected and washed with methanol, washed with diethyl ether, air-dried, and finally dried under a vacuum. If no solidified mass formed, the mixture was dialyzed against distilled water and then freeze-dried. The residue was dissolved in distilled water, and centrifuged (8000 rpm, 15 min). The supernatant and precipitate were separated by decanting, and the supernatant was freeze-dried again. The methods of Sannan et al.<sup>16</sup> and Tōei and Kohara<sup>15</sup> with minor modifications as described by Yang et al.<sup>2</sup> were followed to determine the degree of substitution (DS) of the prepared chitosan disaccharide derivatives. According to Sashiwa and Shigemasa,<sup>7</sup> the reaction products of chitosan derivatives have the following structure:



where R is lactose, cellobiose, or maltose.

### Comparison of adsorption ability of chitosan derivatives and native chitosan

In this study, solutions of chitosan and solutions containing N-alkylated chitosan derivatives (DS = 20–30, 30–40, and 40–50%) at a concentration of 200 mg/100 mL were first prepared by dissolving an appropriate amount of either chitosan or chitosan derivatives in deionized water. The solution was then mixed with equal volumes of 4 mM metal-ion solution prepared by dissolving an appropriate amount of Pb(ClO<sub>4</sub>)<sub>2</sub> · 3H<sub>2</sub>O (Aldrich Chemical Co., Milwaukee, WI), ZnCl<sub>2</sub> (Sigma Chemical Co., St. Louis, MO), NiCl<sub>2</sub> · 6H<sub>2</sub>O (Sigma) or CdCl<sub>2</sub> (Sigma) in deionized water. The metal-ion concentration in the supernatant fraction obtained by centrifugation (8000 × g, 15 min) was determined at 0 and after 6 h of holding at 25°C with shaking (100 rpm).

### Studies on pH effects, reaction time effects, and selective metal-ion adsorption

In these studies, solutions of chitosan derivatives with 30–40% DS were mixed with equal volumes of deionized water containing either a single metal ion (for pH and adsorption rate studies) or various metal ions simultaneously, as listed in previously (for the selective adsorption study). They were kept at 25°C with shaking at 100 rpm for a period of 6 h for the pH effect and selective adsorption studies or 24 h for the adsorption rate study. During the experimental period, the metal-ion concentration in the supernatant of the adsorbent metal-ion solution at a predetermined time was determined.

When the pH effect was ascertained, the adsorbent metal-ion solution was adjusted to a pH of 5.0–8.0 with either 1N HCl or 5N NaOH solution.

### Determination of metal ions

To determine the metal-ion concentration, samples were first centrifuged at 8000 × g for 15 min. The metal ions in the supernatant fractions were then analyzed with an atomic adsorption spectrometer (Z-6100 AA, Hitachi Instruments, Inc.), according to standard methods.

The adsorption ability (mg/g) is defined as  $V(C_b - C_a)/M$ , where  $V$  is the sample volume;  $C_b$  and  $C_a$  are the metal-ion concentrations (mg/L) before and after adsorption, respectively; and  $M$  is the weight (g) of chitosan or chitosan derivatives.

### Statistical analysis

The mean values and standard deviations were calculated from the data obtained with triplicate trials. These data were then compared by the Duncan multiple range method.<sup>17</sup>

## RESULTS AND DISCUSSION

### Metal-adsorption ability of various disaccharide chitosan derivatives

Onsøyen and Skaurud<sup>18</sup> indicated that making chemical derivatives is one way to alter the metal-interacting characteristics of chitosan. Table I shows the metal-ion adsorption ability of unmodified chitosan and the N-alkylated disaccharide chitosan derivatives with different DS. It was found that all the disaccharide chitosan derivatives and the native chitosan showed the highest adsorption ability for Pb<sup>2+</sup>, whereas their adsorption ability for Mg<sup>2+</sup> was the lowest among all the metal ions tested.

The N-alkylation of chitosan with disaccharides, regardless of the DS and the kinds of disaccharides, resulted in a notably higher adsorption ability for

TABLE I  
Effect of Degree of Substitution (DS) on Adsorption of Metal Ions by Chitosan and N-Alkylated Chitosan Derivatives in Deionized Water

Chitosan and N-alkylated chitosan derivatives <sup>b</sup>	Adsorption capacity <sup>a</sup> (mg/g)								
	Cu <sup>2+</sup> +c	Pb <sup>2+</sup>	Fe <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	
Chitosan	23.77 ± 0.32A <sup>d</sup>	40.22 ± 0.76D	23.8 ± 0.72A	0.37 ± 0.06F	18.13 ± 5.14CDE	24.13 ± 0.31AB	27.33 ± 1.15E	32.50 ± 0.00c	
Lactose									
DS 20–30%	15.33 ± 1.34BC	59.89 ± 5.69AB	12.93 ± 0.12CD	1.63 ± 0.12A	5.07 ± 1.60F	15.60 ± 0.60F	8.00 ± 0.001	27.50 ± 0.00D	
DS 30–40%	9.62 ± 1.42E	53.39B ± 7.49CD	11.47 ± 0.31E	1.43 ± 0.06BC	15.23 ± 1.72e	17.00 ± 0.69E	10.67 ± 1.15H	40.00 ± 0.00B	
DS 40–50%	9.72 ± 2.14E	46.89 ± 4.01CD	0.47 ± 0.12I	0.83 ± 0.12E	23.27 ± 1.81AB	21.73 ± 0.76D	18.67 ± 1.15F	57.50 ± 2.50A	
Maltose									
DS 20–30%	23.21 ± 1.96A	67.06 ± 5.00A	16.93 ± 0.42B	1.47 ± 0.06B	5.93 ± 1.84F	22.27 ± 1.10CD	12.00 ± 0.00G	10.83 ± 1.44I	
DS 30–40%	17.28 ± 1.00B	66.06 ± 4.27A	12.60 ± 0.35D	1.37 ± 0.06BCD	19.90 ± 2.07BCD	24.67 ± 0.23A	50.00 ± 0.00B	12.50 ± 0.00IH	
DS 40–50%	17.02 ± 0.84B	55.22 ± 1.76BC	3.80 ± 0.20H	1.27 ± 0.06D	21.30 ± 1.28ABC	24.87 ± 0.42A	72.00 ± 0.00A	22.50 ± 0.00E	
Cellobiose									
DS 20–30%	15.36 ± 1.34BC	50.39 ± 2.47CD	13.47 ± 0.42C	1.63 ± 0.12A	16.90 ± 1.10DE	23.07 ± 0.76BC	12.00 ± 0.00G	14.17 ± 1.44GH	
DS 30–40%	13.41 ± 2.07CD	48.56 ± 6.56CD	7.00 ± 0.40F	1.30 ± 0.00CD	23.77 ± 2.02AB	24.63 ± 0.95A	36.00 ± 0.00d	15.00 ± 0.00G	
DS 40–50%	11.14 ± 1.14DE	45.56 ± 6.56D	5.47 ± 0.42G	1.23 ± 0.12D	25.43 ± 1.33A	24.93 ± 0.70A	48.00 ± 0.00C	19.17 ± 1.44F	

<sup>a</sup> Determination was made after 6-h contact at 25°C.

<sup>b</sup> Solution containing 100 mg/100 mL of chitosan or N-alkylated chitosan derivative, which was dissolved in deionized water.

<sup>c</sup> Solution contained 2 mM metal ion.

<sup>d</sup> Values within the same metal ion with different letters are significantly different ( $p < 0.05$ ) in the Duncan multiple range test.

$\text{Pb}^{2+}$  and  $\text{Mg}^{2+}$  than the unmodified chitosan. We also observed that disaccharide chitosan derivatives with 20–30% DS showed the highest adsorption ability of 50.39–67.06 and 1.47–1.63 mg/g for  $\text{Pb}^{2+}$  and  $\text{Mg}^{2+}$ , respectively, and they decreased as the DS increased.

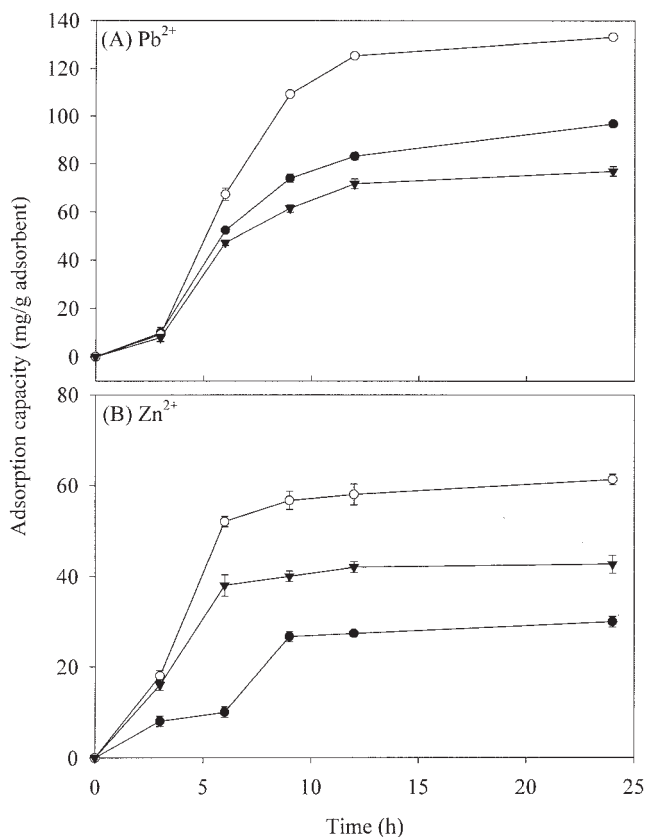
Contrary to the observations for  $\text{Pb}^{2+}$  and  $\text{Mg}^{2+}$ , all the tested N-alkylated disaccharide chitosans displayed less adsorption ability for  $\text{Fe}^{2+}$  compared to the unmodified chitosan.

Cellobiose chitosan derivatives with 40–50% DS displayed the highest adsorption ability of 25.43 mg/g for  $\text{Ca}^{2+}$  among all the disaccharide chitosan derivatives that were tested. This chitosan derivative along with the cellobiose chitosan derivative with 30–40% DS and the lactose chitosan derivative with 40–50% DS all exhibited a significantly higher ( $p < 0.05$ )  $\text{Ca}^{2+}$  adsorption ability than did the native chitosan. We also found that N-alkylation of chitosan with lactose, regardless of the DS, resulted in significantly less adsorption ability for  $\text{Ni}^{2+}$ . Similar results were also noted with maltose derivatives with 20–30% DS. In contrast, the  $\text{Ni}^{2+}$  adsorption capacity of other disaccharide chitosan derivatives showed no significant difference ( $p > 0.05$ ) from that of the unmodified chitosan.

Changes in the adsorption ability for  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  were also noted with the N-alkylated disaccharide chitosan derivatives. Among them, maltose and cellobiose derivatives with 30–40 and 40–50% DS exhibited a significantly ( $p < 0.05$ ) higher  $\text{Zn}^{2+}$  adsorption ability than did the native chitosan. The  $\text{Cd}^{2+}$  adsorption capacity of lactose derivatives with 30–40 and 40–50% DS was found to be significantly higher than that of the native chitosan.

The data shown in Table I demonstrate that the adsorption ability of chitosan for all the tested metals, except  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$ , can be improved after N-alkylation with disaccharide and with certain DS values. Similar differences in the metal-adsorption ability of these disaccharide chitosan derivatives were also reported by Delben et al.,<sup>19</sup> who studied the  $\text{Cu}^{2+}$  binding capacity of *N*-carboxybutyl chitosan and *N*-carboxymethyl chitosan.

It is interesting to note from Table I that the DS with disaccharide affects the metal-adsorption ability of the chitosan derivatives. In general, as the DS increases, the adsorption ability of the chitosan derivatives for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Mg}^{2+}$  decreases whereas the adsorption ability for  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  increases. The increased DS with disaccharide resulted in a reduced number of amino groups and a relatively increased number of hydroxyl groups on the surface of chitosan derivative molecules. Therefore, in addition to the different chemical structures in the disaccharide, the number of amino groups and hydroxyl groups, which vary with the DS, available on the molecules of disaccharide chitosan derivatives may



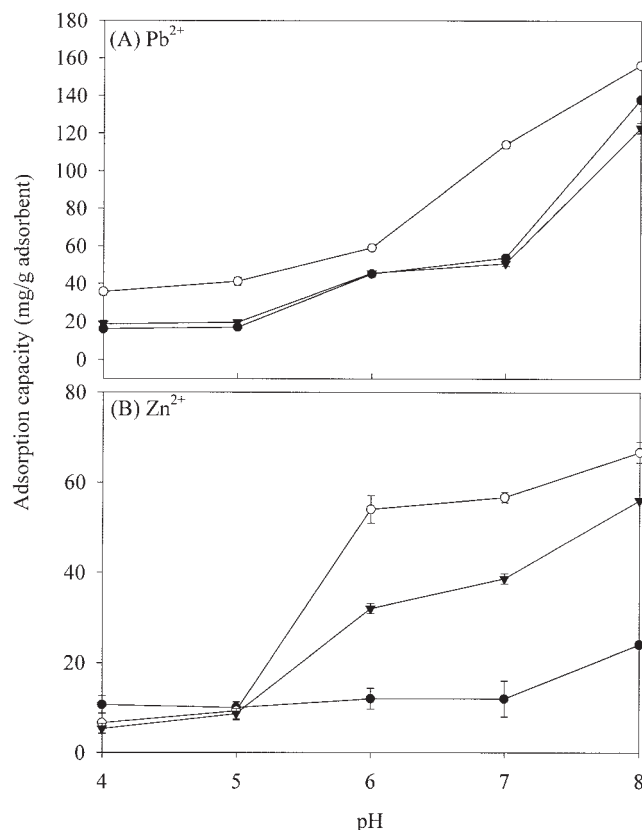
**Figure 1** The rate of adsorption of (A)  $\text{Pb}^{2+}$  and (B)  $\text{Zn}^{2+}$  on N-alkylated chitosan derivatives (30–40% DS, 100 mg/100 mL); (●) lactose with 30–40% DS, (○) maltose with 30–40% DS, and (▼) cellobiose with 30–40% DS.

play an important role that leads to the different metal-adsorption abilities observed with the various disaccharide chitosan derivatives. Changes in the metal-adsorption capacity of phosphorylated chitosan when varying the number of amino groups on the chitosan derivative molecules was also observed by Nishi et al.<sup>20</sup>

### Adsorption rate

As shown in Table I, the disaccharide chitosan derivatives (30–40% DS) exhibited a very strong adsorption ability for  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ . Therefore, the adsorption rate of these chitosan derivatives was further examined and the results are shown in Figure 1.

It was noted that the metal-adsorption rate varies with the chitosan derivatives and metal ions under testing. The adsorption of  $\text{Pb}^{2+}$  by all the chitosan derivatives was very rapid at the beginning and reached its adsorption equilibrium after approximately 12 h of exposure [Fig. 1(A)]. In contrast, the adsorption equilibrium for  $\text{Zn}^{2+}$  of these chitosan derivatives was found after a shorter period of exposure (ca. 6–9 h). Further extending the exposure time be-



**Figure 2** The effect of the pH on the adsorption of (A) Pb<sup>2+</sup> and (B) Zn<sup>2+</sup> by N-alkylated chitosan derivatives (30–40% DS, 100 mg/100 mL); (●) lactose with 30–40% DS, (○) maltose with 30–40% DS, and (▼) cellobiose with 30–40% DS.

yond the equilibrium point did not further increase the metal-ion adsorption by the disaccharides chitosan derivatives. The observed phenomenon was also reported by various investigators of chitosan and its derivatives.<sup>11,21,22</sup> Among the various disaccharide chitosan derivatives that were tested, the maltose chitosan derivative exhibited the highest adsorption rate for Pb<sup>2+</sup> and Zn<sup>2+</sup>. In contrast, the lowest adsorption rate for Pb<sup>2+</sup> and Zn<sup>2+</sup> was found with cellobiose and lactose chitosan derivatives, respectively. Furthermore, the data in Figure 1 also demonstrate that the adsorption of Zn<sup>2+</sup> and Pb<sup>2+</sup> by these N-alkylated disaccharide chitosan derivatives was a fairly rapid process.

### Effect of pH

The effect of the pH on the adsorption of Pb<sup>2+</sup> and Zn<sup>2+</sup> by lactose, cellobiose, and maltose chitosan derivatives was studied over the pH range of 4–8; the results are shown in Figure 2. The binding of metal ions by chitosan was previously reported to be influenced by pH.<sup>23,24</sup> Bassi et al.<sup>24</sup> found that the adsorption of metal ions by chitosan was highest at pH 6.0

and was reduced as the pH increased. Sakaguchi and Nakajima<sup>11</sup> reported that uranium adsorbed by both chitin phosphate and chitosan phosphate had a maximum at pH 5.0, whereas above and below pH 5.0 there was a rapid decrease in uranium adsorption. Contrary to these observations, the adsorption of Pb<sup>2+</sup> and Zn<sup>2+</sup> by the N-alkylated disaccharide chitosan derivatives generally increased as the pH increased (Fig. 2). Among the various pH levels tested, these disaccharide chitosan derivatives showed the highest adsorption ability for Zn<sup>2+</sup> and Pb<sup>2+</sup> at pH 8.0.

As shown in Figure 2, all the disaccharide chitosan derivatives showed an increase in Pb<sup>2+</sup> adsorption when the pH was above 5.0. In contrast, a marked increase in the adsorption of Zn<sup>2+</sup> by maltose and cellobiose chitosan derivatives was noted as the pH increased from 5.0 to 7.0 and there was a slight adsorption increase as the pH increased to 8.0. In contrast, increases in the Zn<sup>2+</sup> adsorption by lactose chitosan was noted only when the pH increased from 7.0 to 8.0.

At higher pH there are fewer hydrogen ions, which would compete with metal ions for the absorption site of the chitosan derivatives<sup>10</sup> and thus lead to a higher adsorption of Zn<sup>2+</sup> and Pb<sup>2+</sup> by the disaccharides chitosan derivatives at higher pH, as observed in the present study. Similar phenomena were also observed on dithiocarbamate chitosan, glutamate glucan, and aminogluconate glucan.<sup>25</sup> In contrast, we cannot rule out the possible formation of metal hydroxide precipitation that possibly also contributed to the higher adsorption of Zn<sup>2+</sup> and Pb<sup>2+</sup> that was observed.

The nature of high metal-binding capacity at high pH indicates the merits of further research on N-alkylated disaccharide chitosan derivatives as potentially more efficient metal-removal agents than chitosan, especially with high pH. This is particularly true because the solubility and metal-absorption capacity of chitosan both decrease when the pH is higher than 6.0.

### Selective adsorption of metal ions

Because of their metal-chelating ability, chitosan and its related materials have been proposed for use in the removal of toxic metals from industrial and contaminated drinking water. The water sources to be treated usually contain various metals simultaneously and, depending on the kinds of adsorbents, these chitosan and chitosan derivatives simultaneously exerted different degrees of selective adsorption for metals in a system containing different metals. For example, Tokura et al.<sup>26</sup> observed that the carboxymethyl-chitin bound calcium ions work especially well among alkali-earth metals, even in the presence of monovalent cations such as sodium or potassium. They also reported that in a mixed solution containing Ca<sup>2+</sup> and

TABLE II  
Selective Adsorption of Metal Ions by *N*-Alkylated Chitosan Derivatives

<i>N</i> -Alkylated chitosan derivatives <sup>c</sup>	Adsorption capacity (mg/g) <sup>a</sup>				Distribution coefficient <sup>b</sup>			Affinity orders
	Pb <sup>+2d</sup>	Zn <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Pb <sup>+2</sup> /Zn <sup>+2</sup>	Pb <sup>+2</sup> /Ni <sup>+2</sup>	Pb <sup>+2</sup> /Cd <sup>+2</sup>	
Lactose DS 30–40%	45.83 ± 0.50	4.00 ± 1.15	7.07 ± 0.40	28.33 ± 1.44	11.46	6.48	1.62	Pb <sup>2+</sup> > Cd <sup>2+</sup> > Ni <sup>2+</sup> > Zn <sup>2+</sup>
Maltose DS 30–40%	53.33 ± 2.65	31.33 ± 3.06	9.20 ± 0.23	5.00 ± 1.44	1.70	5.80	10.67	Pb <sup>2+</sup> > Zn <sup>2+</sup> > Ni <sup>2+</sup> > Cd <sup>2+</sup>
Cellobiose DS 30–40%	41.00 ± 1.15	19.33 ± 1.15	8.87 ± 0.50	8.33 ± 1.44	2.12	4.62	4.92	Pb <sup>2+</sup> > Zn <sup>2+</sup> > Ni <sup>2+</sup> > Cd <sup>2+</sup>

<sup>a</sup> Determination was made after 6-h contact at 25°C.

<sup>b</sup> Adsorption capacity of Pb<sup>2+</sup>/adsorption capacity of Zn<sup>2+</sup>, Ni<sup>2+</sup>, or Cd<sup>2+</sup>.

<sup>c</sup> Solution containing 100 mg/100 mL of *N*-alkylated chitosan derivative.

<sup>d</sup> Solution contained 2 mM Pb, 2 mM Zn, 2 mM Ni, and 2 mM Cd.

Mg<sup>2+</sup>, the carboxymethyl-chitin showed a high selectivity toward calcium ions. Sakaguchi and Nakajima<sup>11</sup> studied the selective adsorption of metal ions and indicated that the relative order of magnitude of metal ions adsorption was UO<sub>2</sub> > Cu<sup>2+</sup> > Cd<sup>2+</sup> > Mn<sup>2+</sup> > Zn<sup>2+</sup> > Mg<sup>2+</sup> > Co<sup>2+</sup> > Ni<sup>2+</sup> > Ca<sup>2+</sup> for chitin phosphate and UO<sub>2</sub> > Cu<sup>2+</sup> > Cd<sup>2+</sup> > Zn<sup>2+</sup> > Co<sup>2+</sup> > Ni<sup>2+</sup> > Mg<sup>2+</sup> > Ca<sup>2+</sup> for chitosan phosphate. By contrast, Muzzarelli and Zattoni<sup>25</sup> investigated the competitive collection of metal ions on glutamate glucan and aminogluconate glucan, both obtained from chitosan. They revealed that the chelating ability of glutamate glucan for Cr<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> simultaneously in solution was in the order of Cu<sup>2+</sup> > Cr<sup>2+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup>. For aminogluconate glucan, the order of affinity is Cu<sup>2+</sup> > Cr<sup>2+</sup> > Zn<sup>2+</sup> > Co<sup>2+</sup> > Ni<sup>2+</sup>. To ensure its successful practical application as a metal-removing agent, the nature of the selective metal-binding ability of the chitosan and its related material thus becomes critical. Therefore, experiments were conducted to examine the selective adsorption of several metal ions by these disaccharide chitosan derivatives from the mixed solution containing an equivalent concentration (2 mM) of Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup>; the results are shown in Table II. In agreement with the highest Pb<sup>2+</sup> binding capacity observed in a solution containing only one kind of metal ion (Table I), the adsorption of Pb<sup>2+</sup> by these disaccharide chitosan derivatives was found to be much greater than those of other metal ions in the mixed solution containing Zn<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup>, in addition to Pb<sup>2+</sup>. After 6 h of mixing in the mixed solution containing various kinds of metals, the disaccharide chitosan derivatives still exhibited a Pb<sup>2+</sup> adsorption capacity of 41.00–45.83 mg/g adsorbent, which is slightly less than that observed in the solution containing only Pb<sup>2+</sup> (Table II). Furthermore, Table II

shows that the relative order of magnitude of metal ions adsorption was Pb<sup>2+</sup> > Cd<sup>2+</sup> > Ni<sup>2+</sup> > Zn<sup>2+</sup> for lactose chitosan derivatives, whereas the selective adsorption ability for maltose and cellobiose chitosan derivatives was in the order Pb<sup>2+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Cd<sup>2+</sup>.

## CONCLUSION

Based on data obtained from the present study, we concluded that the metal-adsorption ability of chitosan may be enhanced through the *N*-alkylation of chitosan with maltose, cellobiose, or lactose. Adsorption of Zn<sup>2+</sup> and Pb<sup>2+</sup> by the *N*-alkylated disaccharide chitosan derivatives with 30–40% DS was a fairly rapid process. In addition, these derivatives exhibited a higher adsorption ability at high pH and possessed the best selective adsorption for Pb<sup>2+</sup>. Therefore, they are potentially more efficient metal-binding agents than chitosan, especially under a condition with high pH.

## References

- Shahidi, F.; Arachchi, J. K. V.; Jeon, Y.-J. *Trends Food Technol* 1999, 10, 37.
- Yang, T. C.; Chou, C. C.; Li, C. F. *Int J Food Microbiol* 2005, 22, 29.
- Sugimoto, M.; Morimoto, M.; Sashiwa, H.; Saimoto, H.; Shigemasa, Y. *Carbohydr Polym* 1998, 36, 49.
- Holme, K. R.; Perlin, A. S. *Carbohydr Res* 1997, 302, 7.
- Lillo, L. E.; Matsuhira, B. *Carbohydr Polym* 1997, 34, 397.
- Yalpani, M.; Hall, L. D. *Macromolecules* 1984, 17, 272.
- Sashiwa, H.; Shigemasa, Y. *Carbohydr Polym* 1999, 39, 127.
- Yang, T. C.; Chou, C. C.; Li, C. F. *Food Res Int* 2002, 35, 707.
- Lin, H. Y. M.S. Thesis, National Taiwan University, Taipei, Taiwan, 2002.
- Saucedo, I.; Guibal, E.; Roulph, C. H.; LeCloirec, P. *Environ Technol* 1992, 13, 1101.

11. Sakaguchi, T.; Nakajima, A. In Proceedings of the Second International Conference on Chitin and Chitosan; Hirano, S.; Tokura, S., Eds.; Japanese Society of Chitin and Chitosan: Tokyo, 1982; p 187.
12. Nishi, N.; Ebina, A.; Nishimura, S.; Tsutsumi, A.; Hasegawa, O.; Tokura, S. *Int J Biol Micromol* 1986, 8, 311.
13. Koyama, Y.; Taniguchi, A. *J Appl Polym Sci* 1986, 31, 1951.
14. Muzzarelli, R. A. A.; Weckx, M.; Filippini, O. *Carbohydr Polym* 1989, 11, 293.
15. Töei, K.; Kohara, T. *Anal Chim Acta* 1976, 83, 59.
16. Sannan, T.; Kurita, K.; Iwakura, Y. *Makromol Chem* 1976, 177, 3589.
17. Sashiwa, N. C.; Shigemasa, Y., Eds. *SAS User's Guide: Statistics, Version 6*; SAS Institute: Cary, NC, 1998.
18. Onsøyen, E.; Skaurud, Ø. *J Chem Technol Biotechnol* 1990, 49, 395.
19. Delben, F.; Stefancich, S.; Muzzarelli, R. A. A. *Carbohydr Polym* 1992, 19, 17.
20. Nishi, N.; Maekita, Y.; Nishimura, S.; Hasegawa, O.; Tokura, S. *Int J Biol Macromol* 1987, 9, 109.
21. Ramachandran Nair, R. K.; Madhavan, P. In Proceedings of the Second International Conference on Chitin and Chitosan; Hirano, S.; Tokura, S., Eds.; Japanese Society of Chitin and Chitosan: Tokyo, 1982; p 187.
22. Peniche-Covas, C.; Alvarez, L. W.; Arguelles-Monal, W. *J Appl Polym Sci* 1992, 46, 1147.
23. Robert, G. A. F. *Chitin Chemistry*; Macmillian Press Ltd.: London, 1992; p 350.
24. Bassi, R.; Prasher, S. O.; Simpson, B. K. *Environ Technol* 1999, 20, 1177.
25. Muzzarelli, R. A. A.; Zattoni, A. *Int J Biol Macromol* 1986, 8, 137.
26. Tokura, S.; Nishimura, S.; Nishi, N. *Polym J* 1983, 15, 597.