

## SYNTHESES OF D-GLUCAMINE AND N-METHYL-D-GLUCAMINE MODIFIED CHITOSAN FOR BORON ADSORPTION

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Two types of biodegradable chitosan-base boron adsorbents were synthesized by introducing D-glucamine and N-methyl-D-glucamine functional groups. Structural analysis was carried out using <sup>1</sup>H-NMR. The maximum boron adsorption values were 3.5 mg g<sup>-1</sup> (equilibrium concentration, C<sub>e</sub> = 192 ppm) and 7.3 mg g<sup>-1</sup> (C<sub>e</sub> = 173 ppm) for D-glucamine and N-methyl-D-glucamine type chitosan adsorbents, respectively. The obtained boron adsorption capacity of N-methyl-D-glucamine modified chitosan was found to be 7.3 mg g<sup>-1</sup> (C<sub>e</sub> = 173 ppm) higher than that of the boron adsorbent Amberlite IRA743. Thus, the biodegradable N-methyl-D-glucamine-modified chitosan synthesized in this study is expected to be useful as a commercial product.

*Keywords:* Boron adsorption; chitosan; N-methyl-D-glucamine.

### 1. Introduction

Boron compounds such as boric acid are widely utilized various fields such as glass industry, ceramic industry, detergent, etc. and discharged from non-ferrous metal industries and coal-fired power plants. Since high concentration of boron are harmful to living organisms, effluent standards have been set for discharged into water bodies.<sup>1</sup> The polymers which contains ortho polyol functional groups have been synthesized to separate boron from aqueous solutions. The well-known polymer adsorbent for boron is Amberlite IRA 743, which contains N-methyl-D-glucamine functional group. The N-methyl-D-glucamine group is a kind of ortho polyol consisting of adjacent hydroxyl groups, which adsorbs boric acid to form esters.<sup>2</sup> Since Amberlite IRA 743 is a

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polystyrene-based adsorbent, it does not degrade naturally. However, considering environmental issues such as microplastics, it is desirable that the material has the property of being degraded in the natural environment. Therefore, biodegradable adsorbents will be an inexpensive and environmentally friendly product. Chitosan is an environment-friendly biodegradable natural polymer, and the amino groups present in it facilitate the introduction of functional groups. Our previous report showed the synthesis of glucosylated chitosan-based boron adsorbents by reaction with gluconolactone.<sup>3</sup> In this report, two types of modified chitosan adsorbents were synthesized by introducing D-glucamine and *N*-methyl-D-glucamine functional groups and their boron adsorption capacity was measured. Similar chitosan adsorbents with *N*-methyl-D-glucamine groups have been synthesized, but they required five synthetic steps.<sup>4</sup> In contrast, the synthesis method employed in the present study can be carried out in two steps.

## 2. Experiments

The scheme for synthesis method of D-glucamine and *N*-methyl-D-glucamine modified chitosan are shown in Fig. 1. The D-glucamine modified chitosan was synthesized applying the procedure introduced in the literature.<sup>5</sup> The chitosan (3.33 g) was dissolved in the mixed solution of 1%(v/v) acetic acid solution (100 mL) and methanol (100 mL). The D-glucose (10.8 g) and NaBH<sub>3</sub>CN (8.32 g) were dissolved in 166 mL water, and it was added dropwise to the chitosan solution with stirring. After stirring for 24 hours, yielded soft white solid was collected by vacuum filtration and washed with methanol three times. To remove boron content in the solid, the soft white solid dispersed in a little amount of 2-propanol was added to 100 mL of 3 mol L<sup>-1</sup> HCl solution while stirring vigorously. Then, the solid was dissolved in HCl solution, 200 mL of methanol was added to precipitate the solid. After the soft white solid was collected by vacuum filtration, it dissolved in HCl, and reprecipitation by methanol was repeated four times. Then collected by vacuum filtration and dried, 7.86 g of soft white solid was yielded as the D-glucamine modified chitosan.

The *N*-methyl-D-glucamine modified chitosan was synthesized applying the procedure introduced in the literature.<sup>6</sup> 16 mL of formic acid, 21 mL of formaldehyde, and 95 mL of water were added to 5.27 g of the D-glucamine modified chitosan. The mixture was heated at 70 °C for 118 hours. The resulted solution was concentrated under reduced pressure. The 1 mol L<sup>-1</sup> NaOH solution was added to the yielded solution to adjust at pH = 12. The resulting precipitate was collected by centrifuge and the precipitate was dissolved in 1 mol L<sup>-1</sup> HCl solution and adjusted to pH = 4. The solution was purified by dialysis, concentrated under reduced pressure, and freeze-dried to yield 1.50 g of *N*-methyl-D-glucamine modified chitosan.

For boron adsorption, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O was dissolved to prepare 50–400 ppm (concentration based on boron) solution. The D-glucamine modified chitosan and *N*-methyl-D-glucamine modified chitosan were put into 20 mL of the boric acid solutions with different concentrations (initial concentration named as C<sub>i</sub> [ppm as B]) separably and shake at 25 °C in an isothermal bath for 24 hours. The filtrate obtained by filtration

and the concentration of the filtrate was named as  $C_e$  [ppm as B], equilibrium concentration. The boron concentration of  $C_i$  and  $C_e$  were determined by the azomethine H absorptiometric method.<sup>7</sup> The adsorbed amount of boron, named as  $W$  [ $\text{mg g}^{-1}$ ], was calculated as  $W = (C_i - C_e) \times \text{Water volume [L]} / \text{Weight of adsorbent [g]}$ .

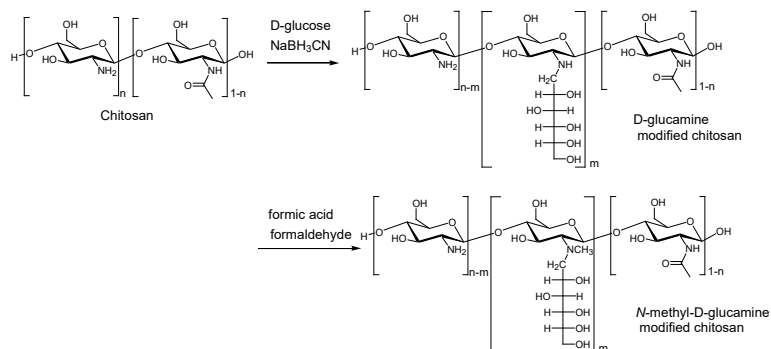


Fig. 1. Scheme for the synthesis of the D-glucamine and *N*-methyl-D-glucamine modified chitosan.

### 3. Results and Discussions

The <sup>1</sup>H-NMR spectra of the products are shown in Fig. 2. To obtain dissolved NMR sample, chitosan (Fig. 2a) and D-glucamine modified chitosan (Fig. 2b) were measured in D<sub>2</sub>O containing 2% CF<sub>3</sub>COOH and *N*-methyl-D-glucamine modified chitosan (Fig. 2c) in D<sub>2</sub>O containing 20% CF<sub>3</sub>COOH. Therefore, a large amount of H<sup>+</sup> present in the sample, and a strong solvent residue signal was detected at 4.79 ppm. In Fig. 2a, peaks were due to chitosan alone, but in Fig. 2b, peaks due to the D-glucamine group were added, and in Fig. 2c, peaks caused by the introduction of the *N*-methyl group were complicatedly added. Peaks in Fig. 2c shifts to a high magnetic field due to its high H<sup>+</sup> concentration. Peaks at 1.81 ppm (Fig. 2a), 1.82 ppm (Fig. 2b), and 0.93 ppm (Fig. 2c) are assigned to CH<sub>3</sub> of the acetyl group.<sup>8</sup> Peaks at 2.92 ppm (Fig. 2a), 2.94 and 3.10 ppm (Fig. 2b), 1.8–2.1 ppm (Fig. 2c) are assigned to the H of C connected to the amino group.

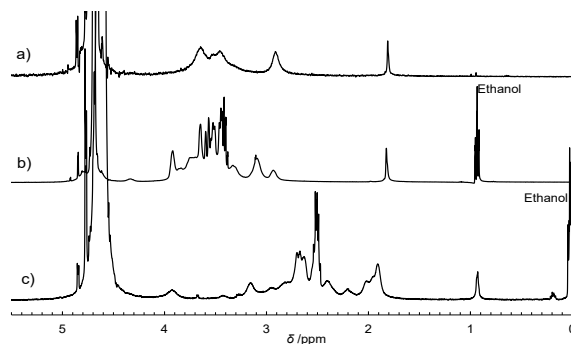


Fig. 2. <sup>1</sup>H-NMR spectra (400 MHz) of chitosan (a), D-glucamine modified chitosan (b), *N*-methyl-D-glucamine modified chitosan (c).

Fig. 3 shows the plot of equilibrium concentration ( $C_e$ ) versus the adsorbed amount of boron ( $W$ ). In Amberlite IRA 743 (Fig. 3a and 3b,  $\times$  and solid line),  $W$  values followed well the Langmuir adsorption isotherm, and the maximum adsorption amount was  $5.6 \text{ mg g}^{-1}$ . In D-glucamine modified chitosan (Fig. 3a,  $\blacktriangle$ ),  $W$  values were lower than Amberlite IRA743, with a maximum value of  $3.5 \text{ mg g}^{-1}$  ( $C_e = 192 \text{ ppm}$ ). In Fig. 3b, the different marks ( $\blacksquare$ ,  $\square$ ,  $\diamond$ ) represent the results of *N*-methyl-D-glucamine-modified chitosan obtained in different synthetic batches. The  $W$  values varied even in the same  $C_e$  and did not show a constant value. Although it was difficult to reproducibly synthesize *N*-methyl-D-glucamine-modified chitosan, some of the products obtained exceeded the adsorption amount of Amberlite IRA743 (Maximum value:  $7.3 \text{ mg g}^{-1}$ ,  $C_e = 173 \text{ ppm}$ ).

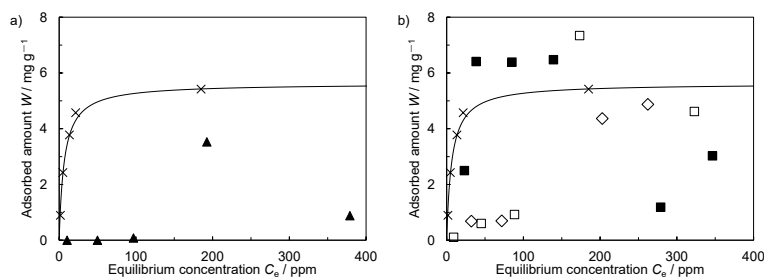


Fig. 3. Adsorption of boron using Amberlite IRA 743 ( $\times$ , solid line), D-glucamine modified chitosan ( $\blacktriangle$ ), and *N*-methyl-D-glucamine modified chitosan ( $\blacksquare$ ,  $\square$ ,  $\diamond$ ).

#### 4. Conclusions

D-glucamine and *N*-methyl-D-glucamine modified chitosan were synthesized in two steps and characterized using <sup>1</sup>H-NMR. The maximum values of boron adsorption for obtained *N*-methyl-D-glucamine modified chitosan was  $7.3 \text{ mg g}^{-1}$  ( $C_e = 173 \text{ ppm}$ ) which is higher than well-known boron absorbent Amberlite IRA743. This indicates that biodegradable *N*-methyl-D-glucamine-modified chitosan has a high boron adsorption potential and may have even higher performance than commercially available products. Nevertheless, the improvement of synthetic reproducibility was essential.

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