

Synthesis of *N*-methyl-D-glucamine Modified Chitosan Nanofibers for Boron Adsorption

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Abstract. The *N*-methyl-D-glucamine modified chitosan nanofiber was synthesized using chitosan nanofiber. It was synthesized by reacting chitosan nanofiber with D-glucose and NaBH₃CN to obtain D-glucamine-modified chitosan nanofiber, followed by the reaction with formic acid and formaldehyde. After swelling with water, the contained boron was removed by condensing with NaHCO₃. The maximum value of boron adsorption was 12.8 mg g⁻¹ (equilibrium concentration, C_e = 179 ppm) and the value was higher than non-nanofiber *N*-methyl-D-glucamine modified chitosan obtained in previous study.

Keywords: Boron adsorption, Chitosan, Nanofiber, *N*-methyl-D-glucamine.

1 Introduction

Boron compounds, such as boric acid, are widely used in glass, ceramic, detergent, and other industries. Since the high boron concentration is toxic to living organisms, effluent standards are set when boron is discharged into water bodies [1]. The amount of boron in drinking water according to WHO guidelines is 2.4 mg L⁻¹ [2]. Amberlite IRA 743, which contains an *N*-methyl-D-glucamine functional group, is a well-known polymeric adsorbent for boron. This group is a type of ortho polyol, which consists of adjacent hydroxyl groups that adsorb boric acid and form an ester [3]. The problem is that the adsorbents cannot be naturally decomposed because they are mainly synthetic polymers. Therefore, it is necessary to develop a new adsorbent that is economical and environmentally friendly. Chitosan is a kind of natural polymer, easy to be chemically modified, environment-friendly, and biodegradable. Our previous reports showed the syntheses of glycosylated [4] and *N*-methyl-D-glucamine modified [5] chitosan-based boron adsorbents and their boron adsorption capacity. The maximum boron adsorption per weight of adsorbent was 5.8 mg g⁻¹ for the former and 7.3 mg g⁻¹ for the latter. The adsorption isotherms of the former followed the Langmuir model well, while the latter lacked reproducibility in the amount of adsorption. Additionally, chitosan nanofiber has been manufactured as a dispersed solution, and its specific surface area is 100 times

higher than that of general chitosan flake. In this study, we synthesized *N*-methyl-D-glucamine modified chitosan from chitosan nanofibers to increase the amount of boron adsorption and measured its boron adsorption capacity.

2 Experiments

The synthesis of D-glucamine and *N*-methyl-D-glucamine modified chitosan nanofiber is depicted in Fig. 1. To synthesize the D-glucamine modified chitosan nanofiber, the procedure outlined in the literature [5, 6] was followed. Initially, 192 g of chitosan nanofiber (2 wt% from Sugino Machine Ltd.), 1.2 g of acetic acid, and 120 mL of methanol were mixed and stirred until the chitosan nanofiber was dissolved. Then, a mixture of D-glucose (12.9 g) and NaBH₃CN (10.2 g) in 86 mL of water was slowly added to the chitosan nanofiber solution while stirring. The resulting soft white solid was separated via vacuum filtration after being stirred for 24 hours and washed with methanol to yield the D-glucamine-modified chitosan nanofiber.

The *N*-methyl-D-glucamine modified chitosan nanofiber was synthesized in accordance with the procedure outlined in the literature [5, 7]. An amount of 14.6 g of D-glucamine modified chitosan nanofiber was mixed with 26.3 mL of formic acid, 35.6 mL of formaldehyde, and 158 mL of water. The mixture was heated to 70°C and kept at that temperature for 118 hours. The resulting solution was evaporated to reduce the water content and then dropped into a 3 mol L⁻¹ NaOH solution. The *N*-methyl-D-glucamine-modified chitosan nanofibers were obtained in the form of beads.

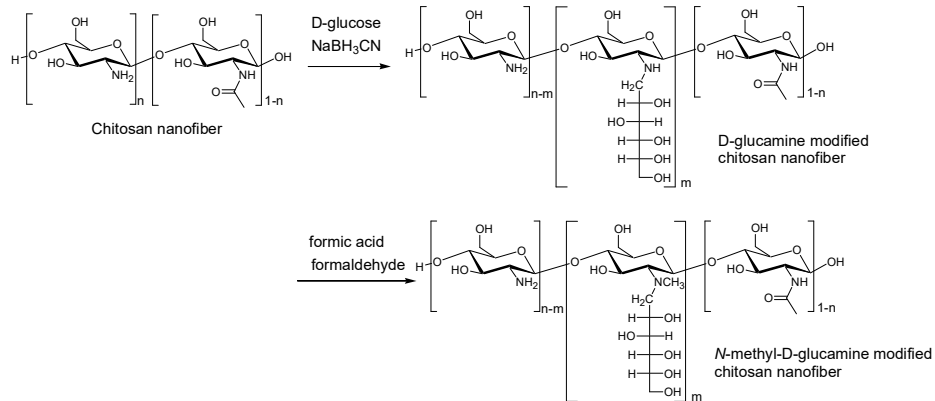


Fig. 1. Synthesis scheme of the D-glucamine and *N*-methyl-D-glucamine modified chitosan nanofiber.

To test the effectiveness of boron adsorption, solutions of Na₂B₄O₇·10H₂O were prepared at concentrations of 200 ppm and 400 ppm (boron concentration). These boron solutions contained NaHCO₃ equivalent to 0.5 mol L⁻¹. *N*-methyl-D-glucamine modified chitosan nanofibers were then added to 20 mL of the solutions with varying concentrations of boric acid, with the initial concentration denoted as C_i [ppm as B]. The

mixture was agitated in an isothermal bath at 25°C for 24 hours. The equilibrium concentration of the filtrate was noted as C_e [ppm as B], and both C_i and C_e were determined using the azomethine H absorptiometric method [8]. The amount of boron adsorbed was denoted as W [mg g⁻¹] and calculated as $W = (C_i - C_e) \times \text{volume of water [L]} / \text{weight of adsorbent [g]}$.

3 Results and Discussions

The yielded *N*-methyl-D-glucamine modified chitosan nanofiber contained boron because NaBH₃CN was used in the reaction to modify the chitosan nanofiber with D-glucamine. The boron concentration increased when the *N*-methyl-D-glucamine modified chitosan nanofiber was used as is for boron adsorption experiments because boron was released without being adsorbed. The Boron desorption in acidic aqueous solutions was impossible because this material is readily soluble in acids. There is literature [9] on the insolubilization of acid-soluble chitosan by cross-linking with EGDE (ethylene glycol diglycidyl ether), but this material did not react with EGDE. This material could not even be washed with water because it swells in water and becomes a fragile gel. Fig. 2(a) shows the loss of liquid phase as the material swells as a gel. Since this material precipitates in basicity, the boron was removed by condensing it once swollen with water and then adding NaHCO₃ to bring the solution to 0.5 mol L⁻¹. Fig. 2(b) shows the material precipitating as an irregularly shaped gel. This process of precipitation with NaHCO₃ after swelling with water was repeated six times until no boron was detected in the filtrate.

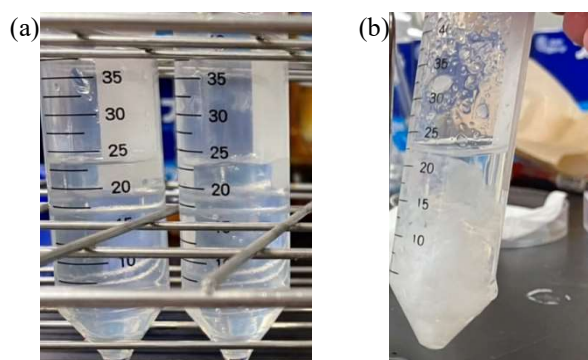


Fig. 2. The *N*-methyl-D-glucamine modified chitosan nanofiber swollen with water (a) and precipitated with NaHCO₃ (b).

Fig. 3 shows C_e , equilibrium concentration, vs. W , the adsorbed amount of boron. The amount of boron adsorbed by the *N*-methyl-D-glucamine modified chitosan was $W = 8.6$ and 12.8 mg g⁻¹ for $C_e = 56.7$ and 179 ppm, respectively. While the conditions for boron solutions were not the same, these values were greater than the boron adsorption of Amberlite IRA 743 and non-nanofiber *N*-methyl-D-glucamine modified chitosan

obtained in previous study [5]. This result was caused by the large surface area of the nanofibred chitosan, which resulted in a large amount of modification to the *N*-methyl-D-glucamine group, and efficient contact with the aqueous solution during boron adsorption.

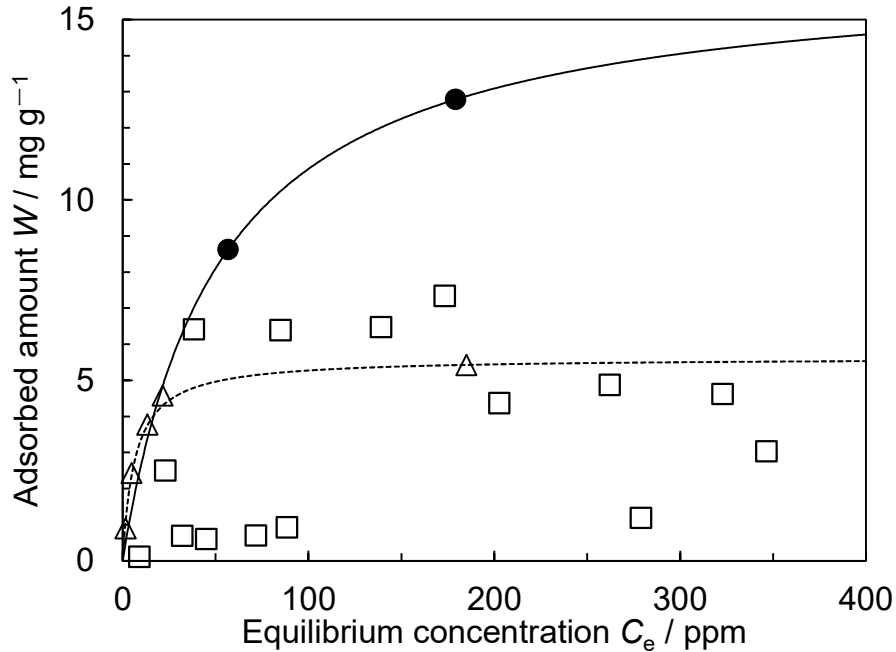


Fig. 3. Adsorption of boron using *N*-methyl-D-glucamine modified chitosan nanofiber (filled circle). Solid line follows Langmuir model. Triangles and squares indicate the amount of boron adsorbed by Amberlite IRA 743 (dotted line follows Langmuir model) and *N*-methyl-D-glucamine modified chitosan from previous study [5], respectively.

4 Conclusions

The *N*-methyl-D-glucamine modified chitosan nanofiber was synthesized using chitosan nanofibers. The maximum value of boron adsorption was 12.8 mg g^{-1} ($C_e = 179 \text{ ppm}$) and the value was higher than non-nanofiber *N*-methyl-D-glucamine modified chitosan obtained in previous study [5]. Using nanofibred chitosan as a base material can yield more highly functional adsorbent.

References

1. Wang, B., Guo, X., P. Bai, P.: Removal technology of boron dissolved in aqueous solutions – A review. *Colloids Surf. A* 444, 338-344 (2014).

2. World Health Organization: Boron in drinking-water: background document for development of WHO guidelines for drinking-water quality. World Health Organization, Geneva (2009).
3. Wada, Y., Matsukami, T., Mori, S.: Ultra-efficient boron removal technology from water (Japanese). *Plant and Process*. 54, 53-58 (2012).
4. Ho Hong, Q.: Synthesis of Eco-Friendly Adsorbents for the Removal of Contaminants in Wastewater. Doctoral thesis, Tokushima University (2019), <https://repo.lib.tokushima-u.ac.jp/113385>, last accessed 2022/11/30.
5. Kurashina, M., Li, H., Shiba, K., Morishita, Y., Shibata, K., Yasuzawa, M., Ho Hong, Q.: Syntheses of D-glucamine and *N*-methyl-D-glucamine modified chitosan for boron adsorption. *Mod. Phys. Lett. B* 36(16), 2242001 (2022).
6. M. Yalpani, M., Hall, L. D.: Some chemical and analytical aspects of polysaccharide modifications. 3. Formation of branched-chain, soluble chitosan derivatives. *Macromolecules* 17, 272-281 (1984).
7. Verheul, R. J., Amidi, M., van der Wal, S., van Riet, E., Jiskoot, W., Hennink, W. E.: Synthesis, characterization and in vitro biological properties of *O*-methyl free *N,N,N*-trimethylated chitosan. *Biomaterials* 29(27), 3642-3649 (2008).
8. Ogawa, T.: Spectrophotometric determination of boron in glass with 1-(salicylideneamino)-8-hydroxynaphthalene-3,6-disulfonic acid. *Bunseki Kagaku* 35(8), 709-712 (1986).
9. Wan Ngah, W. S., Ab Ghani, S., Kamari, A.: Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads. *Bioresour. Technol.* 96(4), 443-450 (2005).