OPTIMAL CONDITIONS FOR SYNTHESIS OF POLYOL-FUNCTIONALIZED CHITOSAN PARTICLES

Ho Hong Quyen*, Vu Chi Mai Tran

The University of Danang - University of Science and Technology, Vietnam

*Corresponding author: hhquyen@dut.udn.vn

(Received: August 07, 2024; Revised: September 26, 2024; Accepted: October 15, 2024)

DOI: 10.31130/ud-jst.2024.562E

Abstract - Adsorbents functionalized with polyol are considered to be effective for the removal of boron from aqueous solutions. In this work, polyol-functionalized chitosan particles were successfully synthesized. Batch experiments were conducted for the determination of the optimal conditions for the highest degree of gluconated groups being grafted to chitosan substrate. The results suggested that acetic acid is the most appropriate solvent for the dissolution of chitosan powder. Furthermore, an efficient mole ratio of 1:3 between chitosan and D-(+) - glucono - 1,5 lactone (DGL) was determined. The maximum level of gluconated groups grafted to chitosan was attained at a reaction temperature of 110°C and a reaction time of 24h. These optimized parameters exhibit potential for practical implementations in the boron removal from aqueous solutions.

Key words - Boron removal; synthesis; polyol; optimal conditions; chitosan

1. Introduction

Even though boron is considered a crucial micronutrient for crop growth, the range between its insufficiency and toxicity levels is relatively small, and it becomes poisonous for both crops and human beings with boron excessiveness. Symptoms observed in crops affected by boron toxicity include altered metabolic processes, reduced development rates in both shoots and rhizomes, decreased enzyme reaction rate, disorders in leaves (such as yellowing, spotting, and leaf dryness), premature fruit decay, and plant mortality in the presence of high boron concentrations [1-3]. Furthermore, excessive boron consumption can adversely affect the immune, central nervous, cardiovascular, reproductive, and renal functions and bone metabolism [2, 4]. An investigation conducted on rats demonstrated that the lowest observed adverse effect level (LOAEL) for boron was established at 13.3 mg/kg body weight per day while the no observable adverse effect level (NOAEL) was found at 9.6 mg/kg body weight per day [1]. The World Health Organization (WHO) has provided a guideline boron concentration value of 2.4 mg/L in drinking water; however, many countries strictly set a boron level in drinking water of 1 mg/L for the control of boron in water sources.

Boron contamination predominantly originates from anthropogenic sources as it is found in various industries such as manufacturers of ceramics, glass, electronics, semiconductors, pharmaceuticals, nuclear reactors, fertilizer, and wastewater from coal-fired power plants [5-6]. A series of methods, such as adsorption [7], constructed wetland [8], chemical precipitation [9], coagulation [10], electrocoagulation [11], electrodialysis [12], and reverse osmosis [13] have been developed for boron elimination from wastewater. The adsorption method stands out for its effectiveness in boron removal and is capable of practical application. This method has employed a variety of adsorbents, such as activated carbon [14], natural materials [15], red mud [16], fly ash [17], nanoparticles [7], layered double hydroxides [18], selective resins [19], biopolymer-based adsorbents [20], and synthetic polymer-based adsorbents [21]. The structure of biopolymer-based adsorbents consists of functional groups grafted to a backbone derived from biopolymers such as chitosan, cellulose, sugar, and alginate [22]. In terms of practicality, biopolymer-based adsorbents are more cost-effective than other traditional ion exchange resins. In addition, these adsorbents display environmentally friendly characteristics and produce limited secondary pollutants generation after the boron removal process due to their biodegradable property.

Chitosan is a natural polymer that exhibits a diverse area of applications owing to its distinctive characteristics including biocompatibility, biodegradability, ecological safety, non-toxicity, reactivity and low cost [23]. Chitosan is recognized as an ideal material for adsorption applications owing to the existence of amine ($-NH_2$) and hydroxyl (-OH) functional groups, which facilitate the adsorption of dyes, heavy metals, and pharmaceutical compounds. Chitosan is modified by grafting functional groups to active amine ($-NH_2$) and hydroxyl (-OH) groups. The introduction of new functional groups into chitosan structure through the application of grafting techniques potentially enhances the adsorption capacity of pollutants [24]. Chitosan exhibits solubility in acidic environments, with its dissolution mechanism primarily attributed to the protonation of the amine ($-NH_2$) group in acidic conditions. The dissolution of chitosan in acidic media yields a viscous chitosan solution. As a result, different shapes of chitosan are formed such as particles, beads, films or membranes [25-27].

In our previous work, DGL was functionalized to chitosan flake to offer polyol for boron removal [28]. In this research, chitosan powder was selected as the substrate to enhance the level of grafting functional groups. A series of parameters in the synthesis process including the kinds of acid for dissolving chitosan, the mole ratio of chitosan and DGL, synthesis temperature, and synthesis time was investigated to determine the optimal conditions for the highest grafting functional groups.

2. Experiment

2.1. Reagents

Chitosan powder was purchased from Glentham Life Sciences, UK. DGL was provided from Tokyo Chemical Industry, Japan. Acetic acid (purity > 99.7%), lactic acid (purity > 85.0%), oxalic acid (purity > 99.5%), hydrochloric acid (purity 35.0% - 37.0%), and sodium hydroxide (purity > 97.0%) were provided from Kanto, Japan. Toluidine blue indicator solution ($C_{15}H_{16}ClN_3S$) and N/400 potassium polyvinyl sulfate solution were obtained from Wako Company, Japan. All reagents were used as received without further purification.

2.2. Preparation of adsorbent

Modified chitosan particles were synthesized based on previous work with some adjustments [28]. During the procedure, 5 g of chitosan powder was added to 400 mL of acid (1% *v/v*) under stirring at room temperature for 8h. Then, DGL was dissolved in chitosan solution at a certain temperature. The reaction mixture was gradually cooled to room temperature; afterwards, 1 M NaOH solution was introduced to induce particle formation. These particles were separated from the supernatant through centrifugation, followed by immersion in acetone and recovery through filtration. The particles underwent a dialysis process in ultrapure water using a dialysis membrane (14,000 molecular weight cutoff) to eliminate residual unreacted DGL. The modified chitosan particles were rinsed with ultrapure water, dried further in a freeze-dryer, and finely ground to ensure homogeneity before further experiment.

2.3. Degree of grafting functional groups

The degree of glucosamine groups (*DG*%) in chitosan powder and modified chitosan samples was conducted through colloidal titration. In detail, 0.1 g of chitosan or modified chitosan and 8.6 mL of acetic acid were subjected to a 200 mL volumetric flask. Following this, ultrapure water was added to the volumetric flask until the solution obtained the marked line. The mixture was magnetically strired for the sample dissolving completely then underwent titration using N/400 PVSK with toluidine blue as an indicator. The titration process was considered complete upon the color change of the solution from blue to light pink (Figure 1). This titration investigation was repeated 6 times.

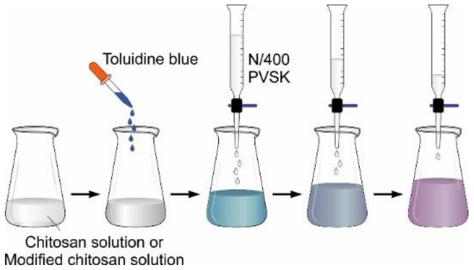

Figure 1. *The experiment of colloidal titration*

The degree of glucosamine groups of chitosan powder (*DG₁*%) was given as follows:

$$DG_1(\%) = \frac{g_1}{\frac{M_1 - M_G g_1}{M_N} + g_1} 100 \qquad (1)$$

Where g_1 is the mole of glucosamine groups (mol), M_1 is the dry mass of chitosan (g), and M_G and M_N are the molar weight of glucosamine groups (161 g/mol) and *N*-acetylglucosamine groups (204 g/mol), respectively.

The degree of glucosamine groups of modified chitosan sample (DG_2%) was represented as follows:

$$DG_2(\%) = \frac{g_2}{\frac{M_2 - M_N n - M_G g_1}{M_F} + n + g_2} 100 \qquad (2)$$

Where g_2 is the mole of glucosamine groups (mol), *n* is the mole of *N*-acetylglucosamine groups (mol), M_F is the molar weight of functional unit grafting to chitosan (340 g/mol), and M_2 is the dry mass of modified chitosan (g).

The degree of functional groups (*DF*%) is calculated as follows:

$$DF(\%) = DG_1(\%) - DG_2(\%) \qquad (3)$$

The level of functional groups grafting to chitosan (*LF*%) is described as follows:

$$LF(\%) = \frac{DF}{DG_1} 100 \qquad (4)$$

3. Results and discussion

3.1. Synthesis of modified chitosan particles

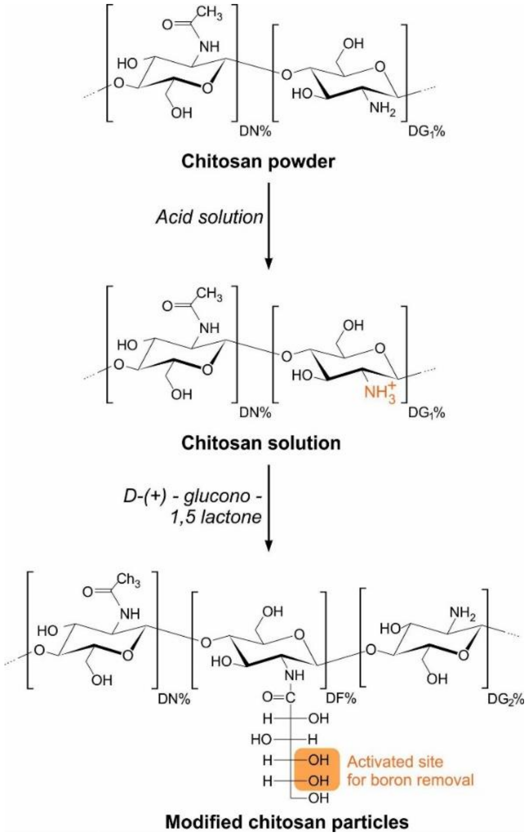

Figure 2. *The preparation of modified chitosan particles (DN% is N-acetylglucosamine groups)*

The reaction between chitosan powder and DGL was conducted in an aqueous environment. In the acidic solution, the acceleration of the reaction involving the gluconated groups was directly grafted in the amine (-NH_2) group of chitosan [28]. The synthesis of gluconated groups grafted to chitosan resulted in solid particles, and the determination of the degree of grafting funtional groups relied mainly on the conditions of the synthesis process. The formation of modified chitosan particles is presented in Figure 2.

3.2. Effect of various acids

According to the colloidal titration, *DG*$_1$% in chitosan powder was determined, and this value accounted for 85.60%. After the reaction of chitosan and DGL, *DF*% and *LF*% were mathematically calculated. Even though chitosan exhibits many advantages, the low porosity and low surface area in the form of powder and flakes can limit their application. To address this problem, physical modification was developed by transferring chitosan powder to particles, beads or membranes. In this work, the conversion of chitosan powder to particles was conducted by dissolving chitosan powder in acid, and the particles were formed by dipping in an alkaline environment (1 M NaOH solution).

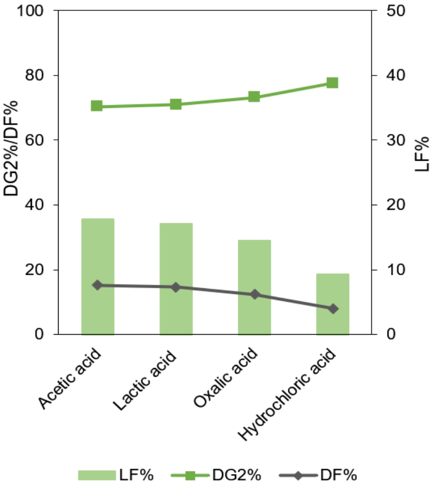

Figure 3. *The effect of various acids on the degree of DG*$_2$*%, DF% and LF%*

Different acids were used to dissolve chitosan powder, including acetic acid, lactic acid, oxalic acid, and hydrochloric acid. The mole ratio of chitosan and DGL was 1:5, and the reaction was conducted at 110°C for 24h. The *DG*2%, *DF*%, and *LF*% in modified chitosan samples with various kinds of acids are presented in Figure 3. It has been reported that chitosan shows the polycationic property. Owing to the pKa value of the amine group ($-NH_2$) in glucosamine units being approximately 6.3, chitosan becomes positively charged in acidic media [29]. Consequently, the acidic treatment at low pH levels protonates the amine groups, resulting in the generation of NH_3^+. This protonation enhances the electrostatic interaction between NH_3^+ and functional groups from DGL. Based on the data of Figure 3, *DG*$_2$% of modified chitosan samples increased sequentially when using acids in order of acetic acid, lactic acid, oxalic acid, and hydrochloric acid. It is attributed that amine groups in glucosamine units are grafted by functional groups, leading to a decrease in *DG*$_2$%. The more functional groups are grafted to chitosan, the less amine groups exist in chitosan. Notably, the highest *DF*% with acetic acid was obtained at 15.26%, with the maximum *LF*% at 17.83%. This finding strongly suggests that acetic acid is the most suitable acid for protonation of chitosan. In addition, similar results reported by previous works indicated that the preferred solvent for chitosan dissolution widely utilized is acetic acid. Lactic acid, oxalic acid, and hydrochloric acid have the potential to be used as solvents for chitosan. Therefore, acetic acid was chosen for the next experiments.

3.3. Effect of mole ratio of chitosan and DGL

The mole ratio of chitosan and DGL was tested at 1:1, 1:2, 1:3, 1:4, and 1:5. The experimental procedure involved the reaction at a temperature of 110°C for a duration of 24h, in which acetic acid used as the solvent for dissolving the chitosan powder. The results obtained from the analysis of modified chitosan particle samples with different mole ratios of chitosan and DGL are depicted in Figure 4, illustrating *DG*$_2$%, *DF*%, and *LF*%. An observable trend was noted, showing that *DF*% increased proportionally with the rise in DGL mole. Particularly, *DF*% remained constant at 15.24% for the mole ratios of 1:3 and 1:4, then exhibited a slight increase to 15.26% at the mole ratio of 1:5. *LF*% was calculated at 17.80% for the mole ratios of 1:3 and 1:4 while it reached 17.83% for the mole ratio of 1:5. Based on the variations observed and considering the economic efficiency in terms of reagent usage, the mole ratio of 1:3 for chitosan and DGL was chosen as the optimal condition for subsequent investigations.

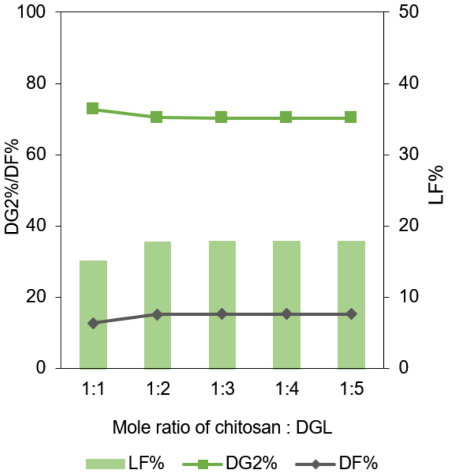

Figure 4. *The effect of the mole ratio of chitosan and DGL on DG*$_2$*%, DF%, and LF%*

3.4. Effect of reaction temperature

The reaction temperature is a crucial parameter for accelerating the rate of reaction. In this experimental setup, acetic acid was employed to dissolve the chitosan powder. The ratio of mole between chitosan and DGL was 1:3. The reaction process took place within the range of 70°C to 120°C for 24h. The effect of reaction temperature is detailed in Figure 5. The results indicated a significant correlation between the reaction temperature and *DF*%. It was observed that *DF*% showed a rapid escalation as the temperature increased from 70°C to 110°C, reaching its peak at 15.24% at 110°C. Nevertheless, as the reaction temperature rose to 120°C, *DF*% dropped to 15.09%. Upon observation, it was noted that the color of the reaction solution transformed from yellow to dark orange within the temperature range of 70°C to 110°C, eventually turning brown at 120°C. This alteration signifies the decomposition of DGL at elevated temperatures, a phenomenon explained by the Maillard reaction [30]. *DF*% declined as the temperature surpassed 110°C. Therefore, the reaction temperature of 110°C was chosen for the next experiment.

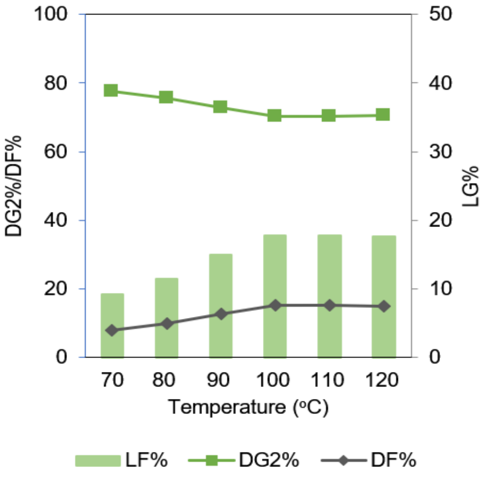

Figure 5. *The effect of the reaction temperature on DG_2%, DF%, and LF%*

3.5. Effect of reaction time

In this investigation, optimal parameters of previous experiments were applied. In detail, acetic acid was selected for dissolving chitosan powder. The mole ratio between chitosan and DGL was established at 1:3. The reaction solution was heated to 110 °C, and the reaction time was investigated from 6h to 24h. The effect of reaction time can be observed in Figure 6. The finding exhibited that *DF*% increased sharply from 6h to 18h, then enhanced slightly until the time reached to 24h. The maximum *DF*% and the *LF*% were recorded at 15.24% and 17.80 % after 24h, respectively. Hence, the reaction time of 24h was chosen for the optimal grafting gluconated groups.

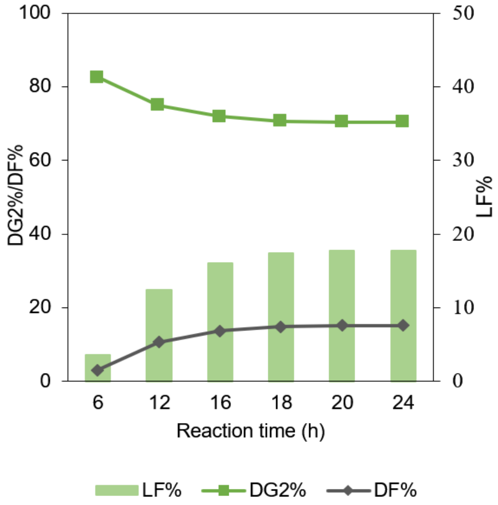

Figure 6. *The effect of the reaction time on DG_2%, DF%, and LF%*

4. Conclusion

Modified chitosan functionalized with gluconated groups for boron removal was successfully prepared. A series of parameters were examined to find out the optimal conditions for grafting gluconated groups. Acetic acid is the most suitable acid for chitosan powder dissolution. The most effective mole ratio between chitosan and DGL was found to be 1:3. The highest *LF*% was achieved at the reaction temperature of 110 °C and the reaction time of 24h. These optimal parameters could be applied for further practical applications in boron removal from aqueous solution.

Acknowledgments: This work was financially supported by the Ministry of Education and Training of Vietnam (Project No: B2023.DNA.09).

REFERENCES

[1] I. Uluisik, H. C. Karakaya, and A. Koc, “The importance of boron in biological systems”, *Journal of Trace Elements in Medicine and Biology*, vol. 45, pp. 156-162, 2018.

[2] F. Al-Badaii, K. M. Jansar, N. A. A. Jalil, and A. A. Halim, “Sustainable boron removal from aqueous solutions using pomegranate peel adsorbents: A comprehensive study on isotherms, kinetics, and thermodynamics”, *Desalination and Water Treatment*, vol. 317, pp. 100045, 2024.

[3] K. Yıldırım, “Transcriptomic and hormonal control of boron uptake, accumulation and toxicity tolerance in poplar”, *Environmental and Experimental Botany*, vol. 141, pp. 60-73, 2017.

[4] X. Wang, H. Shao, Z. Chen, X. Yin, Y. Chen, Y. Liu, and W. Yang, “PEI grafted defective MOF-808 for enhanced boron removal”, *Separation and Purification Technology*, vol. 336, pp.126293, 2024.

[5] J. Lin and Y. Huang, “Enhanced boron removal via seed-induced crystal growth of barium perborate in sequential fluidized-bed crystallization”, *Chemosphere*, vol. 361, pp. 142569, 2024.

[6] Y. Li, Y. Liu, C.Yen, and C. Hu, “Boron removal from high sulfate-containing coal-fired power plant wastewater by an ultrasound/bipolar electrocoagulation process with aluminum electrodes”, *Journal of Environmental Chemical Engineering*, vol. 11, 5, pp. 110473, 2023.

[7] T. Chen, Q. Wang, J. Lyu, P. Bai, and X. Guo, “Boron removal and reclamation by magnetic magnetite (Fe_3O_4) nanoparticle: An adsorption and isotopic separation study”, *Separation and Purification Technology*, vol. 231, pp. 115930, 2020.

[8] K. Yildirim and G. Ç. Kasim, “Phytoremediation potential of poplar and willow species in small scale constructed wetland for boron removal”, *Chemosphere*, vol. 194, pp. 722-736, 2018.

[9] A. Siciliano, C. Limonti, G. M. Curcio, and F. Marchio, “Boron removal from oilfield produced water through a precipitation process with bottom ash leachate and $Ca(OH)_2$”, *Journal of Water Process Engineering*, vol. 50, pp. 103310, 2022.

[10] J. Lin, N. N.N. Mahasti, and Y. Huang, “Recent advances in adsorption and coagulation for boron removal from wastewater: A comprehensive review”, *Journal of Hazardous Materials*, vol. 407, pp. 124401, 2021.

[11] G. Yao, F. Zeng, Z. An, H. Li, T. Zhu, and J. Fang, “Enhancement mechanism for boron removal at high anodic polarization potential during electrocoagulation using iron-based materials”, *Journal of Environmental Chemical Engineering*, vol. 10, 2, pp. 107279, 2022.

[12] W. Hung, R. Horng, and C. Tsai, “Effects of process conditions on simultaneous removal and recovery of boron from boron-laden wastewater using improved bipolar membrane electrodialysis (BMED)”, *Journal of Water Process Engineering*, vol. 47, pp. 102650, 2022.

[13] Q. Lyu and L, Lin, “Rational design of reverse osmosis membranes for boron removal: A counter-intuitive relationship between boron rejection and pore size”, *Separation and Purification Technology*, vol. 331, pp. 125699, 2024.

[14] J. Kluczka, W. Pudło, and K. Krukiewicz, “Boron adsorption removal by commercial and modified activated carbons”, *Chemical Engineering Research and Design*, vol. 147, pp. 30-42, 2019.

[15] V. Masindi, M. Gitari, H. Tutu, and M. Debeer, “Removal of boron from aqueous solution using magnesite and bentonite clay composite”, *Desalination and Water Treatment*, vol. 57, 19, pp. 8754-8764, 2016.

[16] Y. Cengeloglu, A.Tor, G. Arslan, M. Ersoz, and S. Gezgin, “Removal of boron from aqueous solution by using neutralized red mud”, *Journal of Hazardous Materials*, vol. 142, 1–2, pp. 412-417, 2007.

[17] I. Polowczyk, J. Ulatowska, T. Koźlecki, A. Bastrzyk, and W. Sawiński, “Studies on removal of boron from aqueous solution by fly ash agglomerates”, *Desalination*, vol. 310, pp. 93-101, 2013.

[18] T. Kameda, J. Oba, and T. Yoshioka, “Removal of boron and fluoride in wastewater using Mg-Al layered double hydroxide and Mg-Al oxide”, *Journal of Environmental Management*, vol. 188, pp. 58-63, 2017.

[19] İ. İpek, N. Kabay, and M. Yüksel, “Modeling of fixed bed column studies for removal of boron from geothermal water by selective chelating ion exchange resins”, *Desalination*, vol. 310, pp. 151-157, 2013.

[20] A. A. Oladipo and M. Gazi, “Hydroxyl-enhanced magnetic chitosan microbeads for boron adsorption: Parameter optimization and selectivity in saline water”, *Reactive and Functional Polymers*, vol. 109, pp. 23-32, 2016.

[21] B.F. Senkal and N. Bicak, “Polymer supported iminodipropylene glycol functions for removal of boron”, *Reactive and Functional Polymers*, vol. 55, pp. 27-33, 2003.

[22] M. M. Nasef, M. Nallappan, and Z. Ujang, “Polymer-based chelating adsorbents for the selective removal of boron from water and wastewater: A review”, *Reactive and Functional Polymers*, vol. 85, pp. 54-68, 2014.

[23] E. Salehi, P. Daraei, and A. A. Shamsabadi, “A review on chitosan-based adsorptive membranes”, *Carbohydrate Polymers*, vol. 152, 5, pp. 419-432, 2016.

[24] F. Kaya and A. Özer, “Selective sulfate sorption from boric acid factory process liquor: Chitosan-bentonite biocomposite film synthesis as sorbent”, *Minerals Engineering*, vol. 187, pp. 107777, 2022.

[25] S. Shenvi, A. F. Ismail, and A. M. Isloor, “Preparation and characterization study of PPEES/chitosan composite membrane crosslinked with tripolyphosphate”, *Desalination*, vol. 344, pp. 90-96, 2014.

[26] A. Homez-Jara, L. D. Daza, D. M. Aguirre, J. A. Muñoz, J. F. Solanilla, and H. A. Váquiro, “Characterization of chitosan edible films obtained with various polymer concentrations and drying temperatures”, *International Journal of Biological Macromolecules*, vol. 113, pp. 1233-1240, 2018.

[27] Z. A. Sutirman, M. M. Sanagi, K. J. Abd Karim, W. A. W. Ibrahim, and B. H. Jume, “Equilibrium, kinetic and mechanism studies of Cu(II) and Cd(II) ions adsorption by modified chitosan beads”, *International Journal of Biological Macromolecules*, vol. 116, pp. 255-263, 2018.

[28] H.Q. Ho, “*Synthesis of eco-friendly adsorbents for the removal of contaminants in wastewater*”, Doctoral dissertation, Tokushima University, 2019.

[29] B. S. Farias, T. R. Sant'Anna, C. Junior, and L. A. A. Pinto, “Chitosan-functionalized nanofibers: A comprehensive review on challenges and prospects for food applications”, *International Journal of Biological Macromolecules*, vol. 123, pp. 210-220, 2019.

[30] H. B. Cardoso, P. A. Wierenga, H. Gruppen, and H. A. Schols, “Maillard induced aggregation of individual milk proteins and interactions involved”, *Food Chemistry*, vol. 276, pp. 652-661, 2019.