Magnetic Sulfonated Chitosan composite beads for Mercury removal from Aqueous solutions

Lelifajri¹, Rahmi¹ and A S W Ayu¹

¹Chemistry Department, Faculty of Mathematics and Natural Sciences, Universitas Syiah Kuala, Banda Aceh, Indonesia.

E-mail: rahmi@fmipa.unsyiah.ac.id

Abstract. Magnetic sulfonated chitosan composite beads had been prepared and applied for mercury removal from aqueous solutions. Preparation of magnetic sulfonated chitosan composite beads was initially performed by the sulfonation of chitosan and continued with the addition of iron oxide particles prepared from local iron sand to form composite beads. The magnetic sulfonated chitosan beads were characterized by FTIR and XRD analysis. FTIR spectra confirmed the formation of magnetic sulfonated chitosan beads. The patterns of XRD exhibited the decrease of chitosan crystallinity after modification. The result of adsorption experiments showed that the addition of sulfonation and iron oxide particles can improve the adsorption capacity of chitosan.

1. Introduction

Water contamination by heavy metals is a serious environmental problem because heavy metals are toxic to most organisms. By far the most toxic heavy metal is mercury. Sources of mercury in the environment typically come from human activities such as gold mining and chemical industries, but it can also be obtained from the natural process of volcanic eruptions [1]. In order to remove mercury ions from water several methods have been applied; one of them being adsorption by using chitosan [2-6].

Chitosan is the second most abundant biopolymer in nature, and it can be readily obtained from shrimp, crab and lobster shells. As an adsorbent, chitosan has several advantages such as it being biodegradable, easily found, easily modified and environmentally friendly and it also has a large adsorption capacity. However, the use of chitosan alone as an adsorbent has some disadvantages such as it being easily dissolvable in acidic solutions and it is difficult to be separated after the adsorption process. In order to overcome the disadvantages of chitosan and to improve the performance of chitosan on mercury removal from water, we have modified chitosan by a sulfonation process of chitosan and the addition of iron oxide extracted from iron sand. The purpose of the sulfonation process was to increase the active sites of chitosan. The addition of iron oxide was to provide magnetic properties to the chitosan where magnetic chitosan could be separated easily from a solution.

The sulfonation process of chitosan was performed using a sulfonation agent that was prepared from NaNO₂ and NaHSO₃. The obtained sulfonated chitosan was combined with iron oxide particles prepared from local iron sand with several different compositions which resulted in magnetic sulfonated chitosan composite beads. The magnetic sulfonated chitosan composite beads were characterized by FTIR and XRD analysis. The adsorption performance of the adsorbents was examined for mercury removal from the water.
2. Methods

2.1 Separation of iron oxide from iron sand
The iron oxide was separated from local iron sand by using a magnet bar. The obtained iron oxide was then processed with ball milling for 20 hours.

2.2 Preparation of the sulfonating agent
NaNO$_2$ solution was poured into NaHSO$_3$ solution with a ratio of 1: 4.25 while being stirred in a water bath for 90 minutes using a magnetic stirrer at 90 °C. The obtained solution was characterized by FTIR analysis.

2.3 Preparation of magnetic sulfonated chitosan composite beads
Chitosan was soaked in a sulfonating agent solution for 24 hours at pH 5. Then washed with distilled water and dried in an oven at 40°C for 7 hours. Chitosan that had been sulfonated with a composition variation of 0.35; 0.40; 0.45; 0.50; 0.55; 0.60; 0.65 and 0.7 g were dissolved with 20 mL 2% acetic acid and stirred using a magnetic stirrer for 2 hours. Then 0.5 grams of iron oxide were added and stirred for 1 hour. Then the mixture was put into a syringe and dropped it into a 3 M NaOH solution. The beads formed were then washed, filtered and dried in an oven at 40°C.

2.4 Mercury adsorption process
A total of 0.1 gram of the adsorbent was added to 10 mL of a 300-ppm mercury solution. After the adsorption process, the adsorbent was separated from the solution by using a permanent magnet and the mercury concentration of the solution was examined by using AAS

3. Results and Discussion

3.1. Sulfonation agent
In order to confirm the formation of the sulfonating agent (N(NaSO$_3$)$_3$), the obtained solution from reaction of NaNO$_2$ and NaHSO$_3$ was characterized by FTIR analysis and the result was shown in Figure 1.

![Figure 1. FTIR spectrum of the sulfonating agent N(NaSO$_3$)$_3$.](image)

The wave number 1090 cm$^{-1}$ shows the vibration of the O=S=O bond from the sulfonate groups; which is in accordance with research conducted by Kabiri, 2009 [7]. The wave number 1241 cm$^{-1}$ shows
the vibration of the –SO₃ functional group [8]. The wave number 1031 cm⁻¹ indicates the presence of S=O functional groups. These prove that the sulfonation agent has been successfully obtained and can be used as sulfonation agent

3.2. Magnetic sulfonated chitosan composite beads
This work was initially performed by the preparation of a sulfonating agent, by sulfonating chitosan. The obtained sulfonated chitosan was then combined with iron oxide at various compositions to form magnetic sulfonated chitosan composite beads. The sulfonated chitosan was dissolved in acetic acid (2%) and then the iron oxide prepared from iron sand was added to the solution. The mixture was then dropped into NaOH solution to form magnetic sulfonated chitosan composite beads. The obtained magnetic sulfonated chitosan composite beads are shown in Figure 2b. Chitosan beads without modification show a transparent beige color (Figure 2a) and the magnetic sulfonated chitosan composite beads show a black color. The black color of magnetic sulfonated chitosan composite beads is due to the addition of iron oxide.

![Figure 2](image.png)

Figure 2. Chitosan beads (a) and magnetic sulfonated chitosan composite beads (b).

![Figure 3](image.png)

Figure 3. Adsorption capacity of a magnetic sulfonated chitosan composite beads prepared from different sulfonated chitosan compositions.

Based on Figure 3, the adsorption capacity of magnetic sulfonated chitosan composite beads increases by increasing the sulfonated chitosan content. The highest adsorption capacity was obtained at a composition of sulfonated chitosan of 56.5% (0.65 g). The increase of adsorption capacity was due
to the increasing of active sites of the adsorbent where chitosan contains hydroxyl and amine groups [9-11] Sulfonated chitosan contains an additional active site namely the sulfonate functional groups. These functional groups will improve the ability of the adsorbent to adsorb mercury from water. These results confirm that the sulfonation process with the addition of iron oxide can improve the performance of chitosan for the removal of mercury from water.

In order to study the crystallinity of magnetic sulfonated chitosan composite beads, the XRD analysis was performed and the results were shown in Figure 4.

![Figure 4. XRD patterns of chitosan (a) and magnetic sulfonated chitosan composite beads (b).](image)

Figure 3a shows the peak at $2\theta = 20^\circ$ which is typical of chitosan [12]. The peak has a high intensity and is broad, which indicates that chitosan contains both crystalline and amorphous phases. After modification by the sulfonation process and the addition of iron oxide to the chitosan to form magnetic sulfonated chitosan composite beads, the crystalline phase of the chitosan decreased and the chitosan became an amorphous material (Figure 5b). Amorphous material is favourable for an adsorption process because the accessibility of adsorbate to reach active sites is high.

FTIR analysis was also conducted to magnetic sulfonated chitosan composite beads and the result was compared with FTIR spectrum of chitosan (Figure 5). The FTIR spectrum of chitosan (Figure 4a) shows the absorption band at wave number 3446.79 cm$^{-1}$ which correlates with -OH stretching vibration overlapping with -NH$_2$ stretching vibration. This absorption band then shifted to a lower wave number 3427.51 cm$^{-1}$ in the FTIR spectrum of magnetic sulfonated chitosan composite beads. An absorption band at wave number 1654.92 cm$^{-1}$ in chitosan FTIR spectrum is in accordance with the vibration of amide I and also shifts to a lower wave number 1633.71 cm$^{-1}$ in magnetic sulfonated chitosan composite beads FTIR spectrum. These shifts are due to the presence of sulfonate group bonds within the chitosan amine group and the electrostatic interactions between the functional groups of chitosan and iron oxide. The absorption band of C-O-S vibration of C-O-SO$_3$ groups in magnetic sulfonated chitosan composite is shown at wave number 896.90 cm$^{-1}$ [13, 14]. Magnetic sulfonated chitosan composite beads FTIR spectrum shows a new absorption band at wave number 578.64 cm$^{-1}$ which correlates with the Fe-O vibration of the iron oxide.
4. Conclusions
Magnetic sulfonated chitosan composite beads had been prepared and applied as an adsorbent of mercury ions. The sulfonation process of chitosan improves its adsorption capacity. The highest adsorption capacity was obtained at 56.5% of sulfonated chitosan. FTIR spectra confirmed the formation of magnetic sulfonated chitosan composite beads.

References
[1] Liu J, Liu J, Chen X and Guo W 2012 Volcanic Natural Resources and Volcanic Landscape Protection: An Overview IntechOpen DOI: 10.5772/54586
[2] Jeon C and Park K H 2005 Adsorption and desorption characteristics of mercury(II) ions using aminated chitosan bead Water Research 39 16 3938-3944
[3] Li N, Bai R and Liu C 2005 Enhanced and Selective Adsorption of Mercury Ions on Chitosan Beads Grafted with Polyacrylamide via Surface-Initiated Atom Transfer Radical Polymerization Langmuir 21 25 11780–11787
[4] Caner N, Sari A and Tüzen M 2015 Adsorption Characteristics of Mercury(II) Ions from Aqueous Solution onto Chitosan-Coated Diatomite Ind. Eng. Chem. Res. 54 30 7524–7533
[5] Bessa A, Gonçalves G, Henriques B, Domingues E M, Pereira E and Marques P A A P 2020 Green Graphene–Chitosan Sorbent Materials for Mercury Water Remediation Nanomaterials 10 8 1474
[6] Jeon C and Höll W H 2003 Chemical modification of chitosan and equilibrium study for mercury ion removal Water Research 37 19 4770–4780

[7] Kabiri K, Zohuriaan-Mehr M J, Mirzadeh H and Kheirabadi M 2009 Solvent-, ion- and pH-specific swelling of poly(2-acrylamido-2-methylpropane sulfonic acid) superabsorbing gels Journal of Polymer Research 17 2 203–212

[8] Basha S, Murthy Z V P and Jha B 2009 Sorption of Hg (II) onto Carica Papaya: Experimental Studies and Design of Batch Sorber Chemical Engineering Journal 147 226–34

[9] Kumar M N V R 2000 A review of chitin and chitosan applications Reactive and Functional Polymers 46 1–27

[10] Dutta, Pradip K, Dutta J and Tripath V S 2014 Chitin and Chitosan: Chemistry, Properties and Applications. Journal of Scientific & Industrial Research 63 19–31

[11] Rinaudo M Chitin and chitosan: Properties and applications Progress in Polymer Science 31 7 603–632

[12] Karimi M H, Mahdavinia G R, Massoumi B, Baghban A and Saraei M 2018 Ionically crosslinked magnetic chitosan/κ-carrageenan bioadsorbents for removal of anionic eriochrome black-T International Journal of Biological Macromolecules 113 361–75

[13] Priyadarshana G, Kottegoda N, Senaratne A, Alwis A D and Karunaratne V 2015 Synthesis of magnetite nanoparticles by top-down approach from a high purity ore Journal of Nanomaterials 2015 317312 https://doi.org/10.1155/2015/317312

[14] Wang T, Zhou Y, Xie W, Chen L, Zheng H and Fan L 2012 Preparation and Anticoagulant Activity of N-Succinyl Chitosan Sulfates International Journal of Biological Macromolecules 51 5 808–14