Preparation of magnetic chitosan microspheres using iron sand particles prepared by ball milling method

Rahmi*, Lelifajri1, and ASW Ayu1
1Chemistry Department, Faculty of Mathematics and Natural Sciences, Universitas Syiah Kuala, Banda Aceh, Indonesia

*email: rahmi@fmipa.unsyiah.ac.id

Abstract. Iron sand particles prepared by ball milling method have been used in the magnetic chitosan microspheres preparation. FTIR, XRD and SEM analyses were performed to characterize the magnetic chitosan microspheres. SEM images and FTIR spectra confirmed the formation of magnetic chitosan microspheres. The patterns of XRD showed the presence of iron sand particles reduced the crystallinity of chitosan. The adsorption experiments were conducted for mercury removal from aqueous solutions. AAS was performed to determine the mercury concentrations in the solutions after the adsorption process. The results showed the adsorption capacity (Q) of the magnetic chitosan microspheres was not significantly different from magnetic chitosan microspheres prepared using iron oxide.

1. Introduction
Chitosan is the second abundant polymer in nature after cellulose. Chitosan is one of the attractive polymers in the adsorption process due to its high adsorption capacity. It contains amine and hydroxyl groups on the chain backbone that can form complex with heavy metal ions. However, the use of chitosan in the powder form in the adsorption process will be difficult to be separated from the solution after the adsorption process.

Some studies have been conducted to modify chitosan such as magnetic chitosan microspheres preparation by using iron oxide. The magnetic chitosan microspheres can be removed easily from the solution using a magnet after the adsorption process, without centrifugation or filtration [1]. Most studies reported the iron oxide used in the magnetic chitosan microspheres preparation was commercial iron oxide that will produce high-cost adsorbent [2-5]. While it is known that iron sand contains a high content of iron oxide. Iron sand is easily found and abundant in the environment especially in Aceh, Indonesia [6]. Therefore, in order to get low-cost adsorbent, iron sand can be used as an iron oxide source for magnetic chitosan microspheres preparation. In our previous work, iron oxide nanoparticles have been prepared from iron sand [7-10]. The iron oxide nanoparticles were used in the magnetic chitosan microspheres preparation. However, in order to obtain the iron oxide nanoparticles, some chemicals were used that produce chemical wastes. Therefore, in this study, we used iron sand nanoparticles obtained by the ball milling method which is a green method without using any chemicals.

In this work, magnetic chitosan microspheres preparation was conducted using iron sand particles obtained by ball milling method. The magnetic chitosan microspheres were characterized by FTIR, XRD and SEM analysis. The adsorption capacity of magnetic chitosan microspheres was evaluated for mercury ions and the result was compared with the magnetic chitosan microspheres prepared using iron oxide.
2. Methods

2.1. Preparation of iron sand particles
Iron sand was collected using a magnet, washed with hot distilled water several times and dried at 70°C overnight. And then, the iron sand was powdered using a ball mill for 20 hours.

2.2. Preparation of magnetic chitosan microspheres
Chitosan was placed in an Erlenmeyer flask containing acetic acid (2%, 20 mL) and stirred for 2 hours to form a chitosan solution. Iron sand particles were dispersed in the chitosan solution and stirred for an hour. The mixture was inserted into the syringe and dripped gradually into the solution of NaOH (3 M). The obtained magnetic chitosan microspheres were filtered and washed with distilled water until neutral pH was reached. Finally, it was dried at 40°C for 7 hours.

2.3. Adsorption
Magnetic chitosan microspheres (0.1 g) were added in a beaker containing mercury solution (300 ppm, 10 mL). The mixture was shaken (135 rpm) at room temperature for 80 minutes. The magnetic chitosan microspheres were separated from the solution by a magnet after the adsorption process. AAS analysis was performed to determine the mercury concentration after adsorption. The adsorption capacity (Q) was calculated using the equation:

\[ Q = \frac{(C_i - C_e)V}{w} \]  

(1)

where Ce is the mercury concentration at equilibrium and Ci is the initial concentration of mercury. V is the volume of the mercury solution and W is the mass of the adsorbent.

2.4. Instrumentations
The concentration of mercury metal ions was determined by Atomic Absorption Spectrometer (Shimadzu AA-6300). FTIR spectra were analyzed by Shimadzu FTIR-Prestige 21 Series Fourier Transform Infrared Spectrometer; wave number from 4500-400 cm\(^{-1}\). The XRD patterns were analyzed by Shimadzu XRD-7000 Series X-Ray Diffractometer which operated at 40 kV and 30 mA produced Cu\(\text{K}\)α with \(\lambda = 0.154 \text{ nm} \) at a distance of \(20 = 10°-80° \) using the step size of 0.02°/minute. JSM-6510A/JSM-6510LA (Analytical/Analytical low vacuum SEM) was performed to obtain the micrographs at 100× and 30,000× magnifications.

3. Results and Discussion

3.1. FTIR
In order to ensure the interaction between components of the microspheres and to observe the functional groups of the materials, the FTIR spectroscopic analysis was performed. The results of FTIR analysis of iron sand, chitosan and magnetic chitosan microspheres were shown in Figure 1.

Figure 1a shows the FTIR spectrum of iron sand, where the existence of the Fe-O vibration is observed at wave number 582.50 cm\(^{-1}\). The FTIR spectrum of chitosan is shown in Figure 1b, where it shows the absorption band of OH stretching vibrations at wave number 3446.79 cm\(^{-1}\), aliphatic -CH vibration at wave number 2922.16 cm\(^{-1}\) and -CH\(_2\) bending vibrations at wave number 2879.72 cm\(^{-1}\). The absorption band of amide vibration is observed at wave number 1654.92 cm\(^{-1}\). Figure 1c shows the spectrum of magnetic chitosan, where the absorption band of OH vibration appears at a lower wavenumber (3427.51 cm\(^{-1}\)) than the absorption band of OH vibration of chitosan. The absorption band of amide vibration also shifted to lower wavenumber (1633.71 cm\(^{-1}\)). It was due to the interactions between chitosan and iron sand such as hydrogen bonding and electrostatic force. The absorption band of Fe-O vibration of magnetic chitosan appears at a lower wavenumber (576.72 cm\(^{-1}\)) than iron sand. It confirmed the interaction between a component in the magnetic chitosan and the formation of magnetic chitosan.
Figure 1. FTIR spectra of iron sand particles (a), chitosan (b) and chitosan magnetic microsphere (c)

Figure 2. XRD patterns of iron sand particles (a), chitosan (b) and magnetic chitosan microsphere (c)
3.2. XRD
The structural features of materials were studied by XRD analysis. The XRD pattern of iron sand particles prepared by the ball mill method is shown in Figure 2a. It exhibits typical peaks of Fe$_3$O$_4$ at $2\theta = 35.43^\circ$ and $62.56^\circ$ because Fe$_3$O$_4$ is the main component of iron sand. Figure 2b is the XRD pattern of chitosan that shows semicrystalline materials. It exhibits a typical peak of chitosan at $2\theta = 20.79^\circ$ [11]. Figure 2c shows the XRD pattern of magnetic chitosan microspheres, where chitosan loses its crystallinity. This is because the structure of chitosan is more amorphous due to less organized. During the adsorption process, mercury has high accessibility to bind to the active side of an amorphous polymer.

Typical peaks of Fe$_3$O$_4$ are also found in the magnetic chitosan diffractogram at $2\theta = 35.64^\circ$ and $62.48^\circ$. It confirmed that the iron sand main composition was not changed during modification and the iron sand particles distributed on the surface of chitosan polymer.

3.3. SEM
The SEM images of iron sand particles prepared by the ball mill method and the magnetic chitosan microspheres are shown in Figure 3. Figure 3a is an SEM image of iron sand at magnification 30,000×. It shows irregular shapes of particles with various particle sizes from micro to nanosized particles.

Figure 3b is an SEM image of magnetic chitosan microspheres at magnification 100×. It shows a microsphere shape of chitosan magnetic, where iron sand particles were covered by chitosan polymer. The formation of a microsphere was performed at an alkaline solution because chitosan is a pH-responsive polymer where chitosan dissolves at low pH (acid solution) and shrinks at high pH (alkaline solution). Based on the SEM images, the formation of magnetic chitosan microspheres was successfully performed.

![SEM analysis of iron sand particles prepared by ball mill method at magnification 30,000×](image1)

![SEM analysis of magnetic chitosan microspheres at magnification 100×](image2)

Figure 3. SEM analysis of iron sand particles prepared by ball mill method at magnification 30,000× (a) and magnetic chitosan microspheres at magnification 100×

3.4. Adsorption Study
Adsorption experiments were performed to investigate the adsorption capacity of magnetic chitosan microspheres for mercury ions and the results are shown in Figure 4. It shows that the magnetic chitosan microspheres prepared using iron sand particles have lower adsorption capacity than the magnetic chitosan microspheres prepared using iron oxide. It was due to the iron sand particles prepared by the ball mill method still contained impurities and the particle size was relatively larger than iron oxide. However, the difference in their adsorption capacities was not significantly. The adsorption capacity of the magnetic chitosan microspheres prepared using iron oxide particles and
magnetic chitosan microspheres prepared using iron sand particles was 29.94 mg/g and 28.62 mg/g, respectively, where the difference was only 4.52%.

These results indicate that the preparation of magnetic chitosan microspheres using iron sand particles obtained by the ball mill method was a relatively green method and low cost because the preparation of iron sand particles without chemicals and the adsorption capacity was not significantly different with magnetic chitosan microspheres prepared using iron oxide.

![Figure 4. The adsorption capacity of magnetic chitosan microspheres prepared using iron sand particles (A) and magnetic chitosan microspheres prepared using iron oxide (B)](image)

### 4. Conclusions
Iron sand particles prepared through the mechanical milling process were used in magnetic chitosan microspheres preparation. The characterizations confirmed the formation of magnetic chitosan microspheres. The adsorption capacity of magnetic chitosan microspheres prepared using iron sand particles was not significant with the adsorption capacity of magnetic chitosan microspheres prepared using iron oxide particles. This study recommends the low-cost and green adsorbent for mercury.

### References
[1] El-Reash Y G A 2016 *Journal of Environmental Chemical Engineering* **4** 3835-3847
[2] Alizadeh B, Delvanaz M, Shakeri A 2018 *Carbohydrate Polymers* **182** 675-683
[3] Zhao W, Huang X, Wang Y, Sun S, Zhao C 2016 *Carbohydrate Polymers* **150** 201-208
[4] Xu B, Zheng H, Zhou H, Wang Y, Luo K, Zhao C, Peng Y and Zheng X 2018 *Journal of Molecular Liquids* **256** 424-432
[5] Ma H, Pu S, You Y, Zhu R, Zinhenko A and Chu W 2018 *Chemical Engineering Journal* **345** 556-565
[6] Jalil Z, Sari E N, and Handoko E 2014 *Journal of Applied Physics* **4(1)** 110–14
[7] Rahmi, Fathurrahmi, Lelifajri, and PurnamaWati F 2019 *Heliyon* **5** e01731.
[8] Rahmi, Ishmaturrahmi, Mustafa I 2019 *Microchemical Journal* **144** 397-402.
[9] Rahmi, Fathurrahmi, Lelifajri, Purnamawati F, Sembiring R 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **276** 012004.
[10] Ishmaturrahmi I, Rahmi R, Mustafa I 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **523** 012020
[11] Mahdavinia G R, Soleymani M, Etemadi H, Sabri M 2018 *Journal of Biological Macromolecules* **107** 719-729