Influence of EDTA on thermal properties of magnetic chitosan as an adsorbent of methylene blue

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Abstract. Magnetic chitosan has been functionalized with EDTA in order to improve its adsorption capacity for the removal of methylene blue from water. The adsorbent was prepared using chitosan, PEGDE as a crosslinking agent, iron oxide prepared from local iron sand, and EDTA. The addition of EDTA on the adsorbent preparation was performed with different contents of EDTA. Adsorption experiments showed the EDTA addition improved the adsorption capacity of the adsorbent. The optimal content of EDTA in the adsorbent was 0.005 g. DSC and TGA analysis showed that the decomposition temperature of the adsorbent increased by increasing the EDTA content in the adsorbent.

1. Introduction

Water is a natural resource that is very important for living things, especially humans, for whom the most important need is drinking water. In order for water to be safely consumed, it must meet several criteria, one of which is that it must be free from contaminants. Many of these contaminant substances are produced from industries. The more rapid the development in the industrial sector, the more waste is generated. The resulting waste greatly affects environmental pollution, in both the air and water. Industrial waste, especially liquid waste, can contribute to water pollution [1]. Textile dye is a common cause of wastewater, a result of the global textile industry. In this industry, one of the main raw materials is textile dye and about 10-15% of the dyes that have been used are disposed of into water such as rivers. Textile dyes are generally made from compounds containing benzene groups such as methylene blue, rhodamine B, methanol yellow, tartrazine, malachite green, indigo carmine [2], basic yellow 28, and acid brown 75 [3].

Methylene blue is one of the most common dyes in liquid waste in the textile industry in Indonesia. Methylene blue is a dangerous dye which, if ingested, can cause respiratory tract irritation, and if it is touched can cause skin irritation [4-6]. The presence of methylene blue in a body of water, even at a concentration of only 1 ppm, can affect the photosynthetic process of plants in water because it inhibits the intake of sunlight [7]. Various attempts have been made to overcome the problem of dye pollution, including chemical treatment [8], biological methods, chemical physics methods [9], electrochemical processes, [10] and adsorption [11]. Adsorption is a separation method based on the adsorption or withdrawal of gas or liquid molecules from the adsorbent surface. Based on its performance, this method requires an adsorbent, which is a substance that acts as an adsorbent for molecules, whether liquid or gas. One of the natural polymers that can be used as dye adsorbent is chitosan [12].
Chitosan is a polysaccharide that can be easily obtained from natural resources such as shrimp, crab, shellfish and other animal waste. This compound is an alternative source that can be developed continuously due to its large number of renewable properties. Chitosan with its unique structure has a high affinity for dyes. Chitosan has been used to remove several dyes, such as Crystal violet [13], Congo Red & Direct Blue 1 and Remazol Brilliant Blue RN & Basic Blue 36 [14]. The choice of chitosan as an adsorbent is due to its non-toxic, biodegradable, and abundant availability. However, chitosan in pure form has disadvantages, such as high solubility at low pH and limited mechanical properties. Another thing that needs to be considered is the use of chitosan as an adsorbent, usually in the form of a powder. This fine size of chitosan makes it very difficult to separate chitosan from the solution after the adsorption process is complete. Therefore, it is necessary to modify chitosan.

Several attempts to modify chitosan to improve the mechanical properties and stability of chitosan in acidic conditions have been carried out in previous studies. One of them is the addition of crosslinking agents such as glutaraldehyde (GLA), epichlorohydrin, and polyethylene glycol diglycidyl ether (PEDGE). Modification of chitosan can also be done by adding iron sand. Iron sand aims to facilitate the separation of the adsorbent after application. Another compound that can be used to modify chitosan is ethylenediaminetetraacetic acid (EDTA). EDTA is a multidentate ligand capable of chelating with metal ions. Based on the research of Repo, 2013 [15], EDTA-modified chitosan was able to increase the adsorption capacity of chitosan.

Iron sand, which is magnetic, can convert chitosan-EDTA into magnetic chitosan-EDTA. The separation of adsorbent after adsorption process is easier, using a magnet separates out the magnetic chitosan-EDTA and leaves behind the solution. Previous studies used synthetic iron oxide particles in the preparation of magnetic-chitosan [16]. Meanwhile, we know that the availability of iron sand in Indonesia is quite abundant because Indonesia is an archipelago consisting of thousands of islands surrounded by beautiful beaches with abundant sand. The sand along this coastline contains valuable minerals such as iron, titanium, silica, and other elements. This iron sand containing iron oxide can later be used as a magnetic source in magnetic chitosan-EDTA preparation.

In this work, we focus on the discussion of the effects of EDTA addition on the methylene blue adsorption capacity of chitosan and the thermal properties of magnetic chitosan. Magnetic chitosan-EDTA adsorbents were prepared using iron oxide, PEDGE, and EDTA with different content. The adsorbent obtained was examined its adsorption capacity of methylene blue and characterized with DSC and TGA analysis.

2. Materials and methods
2.1. Preparation of iron oxide from iron sand
The iron sand was separated using a bar magnet which has paper around it, so that the iron sand containing Fe$_3$O$_4$ will stick to the bottom of the paper. This method was repeated many times until more iron sand containing Fe$_3$O$_4$ was obtained. The iron sand was washed with hot distilled water and then dried and repeated again the previous work steps. Iron sand containing 30 grams of Fe$_3$O$_4$ was mashed by ball milling for 30 hours.

2.2. Preparation of magnetic chitosan-EDTA
Chitosan (0.35 g) was dissolved with 20 mL 2% acetic acid and stirred for 2 hours with a magnetic stirrer. Then EDTA (0.005, 0.01 and 0.025 g) was added to chitosan solution and stirred for 2 hours. Next, PEDGE was added to the chitosan-EDTA solution and stirred for 2 hours. Then 0.5 grams of iron oxide was added and stirred again for 1 hour. After that, it was transferred using a dropper into a 3 N NaOH solution with a pH of 8 to form beads. The resulting beads were filtered and washed with distilled water until a neutral pH and then dried and stored [17]. The resulting adsorbent was then characterized using DSC and TGA.
2.3. Adsorption
The resulting magnetic chitosan-EDTA adsorbent was tested for its performance for methylene blue removal from water. Initially, the adsorbent weighed 0.1 grams and added to an Erlenmeyer flask, each of which was filled with 25 mL of 25 ppm methylene blue solution. The solution was stirred using a shaker at a constant speed of 150 rpm. Then the adsorbent was separated by pulling it with a magnet and the absorbance of the remaining solution was determined using a UV-Vis spectrophotometer.

3. Results and discussion
3.1. Magnetic chitosan-EDTA
The preparation of magnetic chitosan-EDTA was begun with dissolving chitosan using acetic acid and EDTA was added. After this, iron sand was added, creating a mixture of chitosan-EDTA and iron sand. Finally, this mixture was dropped into an NaOH solution to form magnetic chitosan-EDTA adsorbent. Magnetic chitosan-EDTA adsorbents that have been prepared in the form of beads were then used in the methylene blue adsorption process to determine the optimum composition of EDTA in order to achieve the best adsorption. The methylene blue adsorption process was performed for 25 minutes at a constant pH and methylene blue concentration. The adsorbed methylene blue was then separated from the magnetic chitosan-EDTA adsorbent using a permanent magnet and tested for its adsorption using a UV-Vis spectrophotometer. Furthermore, the adsorption capacity of each methylene blue that had been adsorbed using magnetic chitosan-EDTA was calculated with variations in the composition of EDTA and the resulting adsorption capacity was compared (Figure 1).

The results of the adsorption process show that the addition of EDTA can increase the adsorption capacity of the adsorbent. In the EDTA content of 0.005 grams, the adsorption capacity was greater than that of other EDTA content, namely 2.08 mg/g. Based on Repo, 2013, the increase in adsorption capacity was due to the increase in functional groups in chitosan [21]. EDTA reacts with chitosan through the bonds formed between NH$_2$ in chitosan and C = O from the carboxylate groups present in EDTA. However, when the EDTA content was increased, there was a decrease in the adsorption capacity. This was because EDTA reacts to the NH$_2$ groups in chitosan, which causes a decrease in the active side of chitosan, thus causing a decrease in adsorption capacity.

![Figure 1. Adsorption capacity (Q) of magnetic chitosan-EDTA adsorbent at different content of EDTA (0.005, 0.01 and 0.025 g).](image-url)
In order to study the thermal properties of the adsorbent, DSC and TGA analyses were performed. DSC is an instrument that measures the energy absorbed and the energy released by the sample when the sample is heated or cooled. Figure 2 is the result of the analysis of chitosan and magnetic chitosan-EDTA adsorbent with different content of EDTA in the adsorbent. The thermogram of chitosan obtained from DSC analysis in this study showed a wide endothermic peak at 170.28°C and an exothermic peak at 320.02°C. The endothermic peak that appears at 170.28°C is not the glass transition temperature (Tg) of chitosan, it is due to the presence of the sample moisture factor or the presence of residual solvent (acetic acid). This is supported by the TGA thermogram of chitosan (Figure 3) which shows the mass loss at a temperature of 170.28°C. The Tg value of chitosan is difficult to determine because of the semicrystalline nature of chitosan. However, based on research conducted by Sakurai (2000), the Tg value of chitosan was successfully obtained after several repetitions of the DSC thermal analysis test where the Tg value of chitosan obtained was 203°C. The exothermic peak at 320.02°C is an indication that the sample has begun to decompose.

DSC thermograms of magnetic chitosan-EDTA at different weight content of EDTA also had endothermic peaks. Similar to the pure chitosan thermogram, endothermic peak the magnetic chitosan-EDTA is due to the moisture and the presence of residual acetic acid or water in the sample. The exothermic peaks of magnetic chitosan-EDTA adsorbents with various content of EDTA appear at different temperatures. Based on the DSC thermograms, magnetic chitosan-EDTA adsorbents showed higher decomposition temperatures than chitosan. The higher the EDTA content in the adsorbent, the higher the decomposition temperature, which indicates an increase in thermal properties. Based on Figure 2, the lowest decomposition temperature is chitosan with a decomposition temperature of 320.02°C, followed by magnetic chitosan-EDTA containing 0.005 g EDTA with a decomposition temperature of 325.02°C, then magnetic chitosan-EDTA containing 0.01 g EDTA with a decomposition temperature of 327.85°C, and finally, magnetic chitosan-EDTA containing 0.025 g EDTA with a decomposition temperature of 329.34°C.

**Figure 2.** DSC analysis of magnetic chitosan-EDTA adsorbent at different content of EDTA (0.005, 0.01, and 0.025 g).
Figure 3. TGA analysis of magnetic chitosan-EDTA adsorbent at different content of EDTA (0.005, 0.01, and 0.025 g).

In this study, thermal analysis was also performed using TGA analysis. TGA is an instrument used to measure the change in weight of a sample when heated or cooled (temperature change). Figure 3 shows the curves of the four samples, namely chitosan, magnetic chitosan-EDTA adsorbents with different contents of EDTA (0.005, 0.01, 0.025 g). It can be seen that the four samples exhibited a decrease in weight at the beginning of the curve. The difference occurs at the time when the decomposition temperature is reached. In accordance with the results of the analysis by DSC, the mass reduction of chitosan occurred at a lower temperature compared to magnetic chitosan-EDTA adsorbents. The factors that influence the curve of the TGA analysis are the weight of the sample, the size of the particles, and the compactness of the sample. The decomposition temperatures of magnetic chitosan-EDTA adsorbents were higher than chitosan due to the presence of iron oxide which has higher decomposition temperature than chitosan. Moreover, the composite formation of chitosan, iron oxide, PEDGE, and EDTA will improve the stability of chitosan thereby increasing its decomposition temperature. Increasing in EDTA content in the adsorbent improved the decomposition temperature of the adsorbent. It was probably due to the reaction between EDTA and chitosan, which produced a more stable and compact compound. The compactness of the sample is directly proportional to decomposition temperature of the sample. Magnetic chitosan-EDTA adsorbents have less mass loss and chitosan has the most mass loss.

4. Conclusion
Magnetic chitosan-EDTA can be used as an adsorbent of methylene blue. The results of this adsorption study showed that the addition of EDTA could increase the adsorption capacity of chitosan for methylene blue adsorption and the optimal content of EDTA was 0.005 g. The thermal properties of magnetic chitosan-EDTA adsorbents are better than pure chitosan. The best thermal properties were obtained in magnetic chitosan-EDTA adsorbent containing 0.025 g EDTA.

5. References
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