Effect of magnetite on alginate-based hydrogel beads composite bio-sorbent for copper removal

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Abstract. A composite magnetite alginate-based bio-sorbent in hydrogel beads form as adsorbent for copper ion removal was prepared through this work. Two types of composite bio-sorbents which are cellulose-magnetite-alginate (CeMA) and chitosan-magnetite-alginate (CMA) hydrogel beads were synthesized by the physical cross-linking method. Ratios of magnetite iron oxide 0, 0.1, and 1.0 were used during the synthesis of bio-sorbents to observe the effect of magnetite ratios on copper ion removals. Based on the performance of bio-sorbents on copper removals, 24.6\% of the highest percentage copper removal was achieved by CMA with a magnetite ratio of 0.1 at an adsorption equilibrium time of 24 hours and initial concentration of 100 mg/L. In addition, through this work, magnetite embedded bio-sorbent with the simple synthesized method was done by utilizing the capability of alginate to instantaneously form hydrogel beads upon addition into calcium chloride (Ca\textsuperscript{2+}). Therefore, this work proves the potential of magnetite embedded in alginate-based composite bio-sorbent hydrogel beads for heavy metal industrial wastewater.

1. Introduction

Contamination of water sources resulting from industrial activities had recently been in the spotlight due to multiple health risks to humans and the environment [1]. Industrial wastewater contained common heavy metals such as copper, lead and chromium are usually associated with the manufacturing industry, such as the electroplating industry. Heavy metals are known as toxic and harmful to humans and living beings even if ingested or exposed at low levels which can initiate disorders and even diseases due to accumulation in living tissues [2, 3]. Ingestion of heavy metal copper over the permissible amount in the human body leads to kidney, liver, stomach, and intestines damage and failure. Therefore, the National Water Quality Standards of Malaysia (NWQS) outlined the permissible limit for copper discharge into the watercourse at 0.02 mg/L. Presently, synthetic polymers are being commercialized for heavy metals removal, such as polyacrylamide (PAAM) as it is efficient in heavy metal removal through a coagulation-flocculation process [3]. However, the incorporation of PAAM in wastewater treatment creates another issue, which is environmental
pollution due to its disposal [4]. Hence, the application of renewable resources in industries and daily lives was seen as a way towards environmentally friendly industrialization [5]. In recent years, researchers had commonly used processes such as membrane filtration, adsorption, coagulation/flocculation, ion exchange, and catalytic oxidation for heavy metal removals [6]. However, out of all processes, adsorption process has gained massive interest due to its simplicity and efficiency using the force of attractions between bodies during the removal of a certain substance from wastewater [2].

Currently, the development of natural polysaccharides such as cellulose, chitosan, and alginate as adsorbents had been in the centre of focus among researchers [1, 3, 4, 6–9]. Cellulose is a naturally occurred polysaccharides consist of building units of β-1,4-linked anhydro-D-glucose that can be found from the cell wall of plants [4]. Aside from that, cellulose has multiple beneficial properties such as high tensile strength, flexibility, thermal stability and high surface area that is admirable for researchers to develop an environmentally friendly composite sorbent [10]. Whereas chitosan is a linear polysaccharide consist of poly[β-(1-4)-linked-2-amino-2-deoxy-D-glucose] in which is high in functional groups amine (NH₂) and hydroxyl (OH). These functional groups were proven to have a high affinity towards heavy metals cation due to different particle charges that are attracted towards one another [1]. Other than that, alginate consists of α-L-guluronic acid and 1-4 linked β-D-mannuronic acid which is abundant in carboxyl functional groups (COOH) which also proven to be attracted towards heavy metal cation [1]. Besides, alginate also possessed a great ability to bind with divalent ions such as calcium (Ca²⁺) instantaneously in an aqueous medium through the cross-linking process [11]. Recently, the addition of magnetite in adsorbents had been sought after by researchers to produce adsorbents with an easier separation process from an aqueous medium. Conventional separation techniques such as centrifugation and filtration had been the limitation in the development of adsorbents [6]. Hence, the addition of magnetite will solve this limitation.

Previously, a study made by Yi et al. 2018 had focused on the removal of heavy metals copper and uranium by composite alginate chitosan hydrogel beads. However, up to our knowledge, very limited research was found on studying the effect of magnetite ratios in hydrogel bead adsorbents. Therefore, through this work, a composite alginate-based bio-sorbent in hydrogel beads form was synthesized and the effect of magnetite ratios (0, 0.1, and 1.0) in the bio-sorbents on copper removal performance was studied. The addition of magnetite in the hydrogel bead was proposed for easier separation of adsorbents from an aqueous medium. Besides, an easy sol-gel and cross-linking process using alginate to form adsorbent in hydrogel beads form are found to be desirable due to its temperature-independent formation process. Cross-linking of alginate with other natural polysaccharides, which is cellulose, and chitosan was also made to overcome the limitations of individual components, which are their thermal and mechanical properties. Two types of composite bio-sorbents, which are cellulose-magnetite-alginate (CeMA) and chitosan-magnetite-alginate (CMA) was synthesized and compared throughout this work. The effect of pH and contact time on copper removal were investigated for all composite bio-sorbent hydrogel beads synthesized in this work. Other than that, SEM analysis was also done in this work to characterize the morphological surface of synthesized bio-sorbents in this work.

2. Experimental section

2.1. Materials

Microcrystalline cellulose (MCC) C.P, copper (II) sulphate anhydrous and sodium alginate C.P was purchased from R&M Chemicals. Chitosan (De-acetylation degree > 90%) is purchased from Bio Basic. Magnetite iron (II, III) oxide powder with a particle size of 50 µm was purchased from Sigma Aldrich. Calcium chloride anhydrous powder is purchased from Merck. All chemical reagents purchased are of analytical grade and acquired from commercial sources in Malaysia.
2.2. Synthesis of CeMA hydrogel beads
Sodium alginate solution was prepared by mixing 4 g sodium alginate into 200 mL ultrapure water. The solution then was stirred for 1 hour. Then, 2 g microcrystalline cellulose powder and magnetite iron oxide with different ratios, CeMA x: y was added into the solution to study the effect of magnetite ratios on copper removal performance. In which, x = 1 representing mass of microcrystalline cellulose powder, whereas y = 0, 0.1, and 1.0 representing mass ratios of magnetite iron oxide to cellulose added into the formulation. Then, for the formation of hydrogel beads, the well-mixed solution was dropped into 100 mL of 0.2 M calcium chloride solution using a burette at a constant speed with approximately 10 cm distance from the solution after 3 hours of mixing. The hydrogel beads formed was left to cure in the calcium chloride solution for 24 hours at room temperature. The collected hydrogel beads undergo multiple rinsing using deionized water and stored for further study.

2.3. Synthesis of CMA hydrogel beads
Sodium alginate solution was prepared by mixing 4 g sodium alginate into 200 mL ultrapure water. The solution then was stirred for 1 hour. Then, 2 g chitosan powder and magnetite iron oxide with different ratios, CMA x: y was added into the solution to study the effect of magnetite ratios on copper removal performance. In which, x = 1 representing mass of chitosan powder, whereas y = 0, 0.1, and 1.0 representing mass ratios of magnetite iron oxide to chitosan added into the formulation. Then, for the formation of hydrogel beads, the well-mixed solution was dropped into 100 mL of 0.2 M calcium chloride solution using a burette at a constant speed with approximately 10 cm distance from the solution after 3 hours of mixing. The hydrogel beads formed was left to cure in the calcium chloride solution for 24 hours at room temperature. The collected hydrogel beads undergo multiple rinsing using deionized water and stored for further study.

2.4. Characterization of hydrogel beads bio-sorbent
Morphological surfaces of hydrogel beads bio-sorbent were analyzed through scanning electron microscopy (SEM, Quanta FEG 650). All samples were dried before the analysis.

2.5. Copper removal performance
The performance of each hydrogel bead on copper removal was performed in a 250 mL conical flask containing 100 mL copper solution with a concentration of 100 mg/L. 0.4 g of hydrogel beads were poured into each flask and undergoes constant shaking at 150 rpm in a thermoshaker incubator. An adequate amount of samples were taken and filtered through a 0.45 micron filter every 10 min, 20 min, 30 min, 60 min, 120 min, 240 min, 24 hours, and 48 hours before subjected to AAS analysis to observe the effect of contact time on copper removal. The effect of pH on the performance of copper removal was investigated in pH 3 and 5 with 0.4 g hydrogel beads weight at room temperature for 48 hours. All flasks were sealed to reduce the evaporation of the solution. All data were taken in triplicate. A blank solution containing copper solution without any hydrogel beads were also prepared to ensure no adsorption of heavy metal ion to flask wall occurred.

3. Results and discussion

3.1. Characterization of hydrogel beads bio-sorbent

3.1.1. SEM analysis. The morphological surface of CeMA and CMA was observed by SEM. Figure 1(a), (b), (c), and (d) shows SEM images of CeMA and CMA of magnetite ratios 0.1 and 1.0 to compare the effect of magnetite on the morphological surface of bio-sorbents. Based on figures 1(a), (b), (c), and (d), the morphological surface of the bio-sorbents was observed to be rough and uneven. This could be contributed by the particle aggregation that occurred between magnetite iron oxide with cellulose (in figure 1(a) and 1(b)) and chitosan (in figure 1(c) and 1(d)) [9]. Besides that, agglomeration of magnetite iron oxide particles on the surface of bio-sorbents occurred due to the
existence of strong inter-particle Van Der Waals force and magnetic attraction [12]. Other than that, porous structures could be seen in figures 1(a), (b), (c), and (d). However, based on figures 1(b) and (d), porosity structures on surface of CeMA 1.0 and CMA 1.0 are less compared to CeMA 0.1 and CMA 0.1. This might be due to magnetite particles filling in the pores on the surface of the adsorbent as the magnetite ratio increase [6]. As reported by previous studies, high porosity structure in adsorbent will assist in high adsorption or removal of heavy metals [9, 13]. Hence, the porosity structures possess by the hydrogel beads bio-sorbent in this work proves that there are potentials as an efficient adsorbent for heavy metal removal.

![SEM images of (a) CeMA 0.1, (b) CeMA 1.0, (c) CMA 0.1, (d) CMA 1.0.](image)

3.2. Copper removal performance

3.2.1. Effect of pH. pH is one of the important parameters that affect metal adsorption by adsorbents due to the influence of ions that exist in the metal solution and functional groups on the surface of adsorbents. The removal of copper ions from copper solution as a function of pH is portrayed in figure 2. The removal of copper increases with the increase in pH. The low copper removal percentage at pH 3 is possibly due to the existence of hydronium ion, H⁺ that is competing with copper ion Cu²⁺ for active sites on the surface of adsorbents [1]. This is causing less interaction between copper ions and
The adsorption mechanism by heavy metal ion and adsorbent is ion exchange and/or electrostatic interaction due to different charges that exist [14]. Therefore, the negatively charged functional groups -COOH in alginate, -NH₂ in chitosan, and -OH in both cellulose and chitosan that exist on the surface of the bio-sorbent hydrogel beads were possibly responsible for the adsorption of the positively charged copper ions, Cu²⁺. This is also supported by the findings from Yu et al. 2013, Wang et al. 2019, and Hu et al. 2017, in which the metal ion forms complex with the functional groups on the surface of the composite chitosan and composite cellulose adsorbents [3, 14–15]. Figure 3 shows a schematic diagram of the possible adsorption mechanism through electrostatic interaction between copper ions with CeMA and CMA.

**Figure 2.** Effect of pH on copper removal at the initial concentration of copper solution at 100 mg/L and contact time at 48 hours.
3.2.2. Effect of contact time. The removal of copper ions against time is presented in figure 4. It can be seen from figure 4 that the removal of copper increased until they reached equilibrium at 24 hours. The same trends can be observed in both CeMA and CMA hydrogel beads. Therefore, it can be concluded that the bio-sorbent hydrogel beads synthesized in this work reach their equilibrium in 24 hours. This is due to vacant active sites on the surface of adsorbent during the initial stage in the adsorption process, causing rapid adsorption of copper ions. However, as time increases, vacant active sites on the surface of the adsorbent gradually filled with copper ions until no more vacant active sites left [3]. This leads to slower and constant percentage removal of copper ions as all vacant active sites in adsorbent are filled, thus indicating that concentration equilibrium between adsorbate solution and adsorbent has been reached. Moreover, the smooth curve increasing up to the equilibrium point suggesting that the adsorption of copper ions onto adsorbent is by surface monolayer adsorption [16].
3.2.3. Effect of magnetite ratios on copper removal. To investigate the effect of magnetite ratios on the performance of hydrogel beads in copper removal, different magnetite ratios of 0, 0.1, and 1.0 were formulated during the synthesis of CeMA and CMA composite hydrogel beads bio-sorbent. Based on figure 5 and figure 6, the magnetite ratio of 0.1 shows the best copper removal in CeMA and CMA compared to magnetite ratios 0 and 1.0. This implied that the addition of magnetite in the composite hydrogel bead improves the percentage of copper removal. Besides, it is also proven that magnetite plays an important role in enhancing the removal of copper from the solution. However, at a magnetite ratio of 1.0, the removal of copper ions is slightly reduced. The same trends can be seen in findings by Zhang et al. 2017 which may be explained by magnetite filling the active sites on the adsorbent, hence reducing the interactions between adsorbent and copper ion [6].

Furthermore, the percentage of copper removal was also seen to be higher in CMA compared to CeMA. This could be contributed by the 3D porous network composite in CMA that is high in multiple active functional groups hydroxyl and amine with high affinity towards metal ions on the surface of bio-sorbent [1, 13]. Therefore, through this work, it can be concluded that the presence of magnetite in CMA exhibited the highest percentage of copper removal compared to CeMA.
4. Conclusions
Cellulose-magnetite-alginate (CeMA) and chitosan-magnetite-alginate (CMA) composite bio-sorbent in hydrogel beads form were successfully synthesized using the sol-gel method in this work. The addition of magnetite in the composite bio-sorbent hydrogel beads was also proven to enhance the removal of copper from copper solution. Besides, through this work, the different magnetite ratios in composite bio-sorbent hydrogel beads were proven to be affecting the percentage of copper removal from the solution. The highest percentage of copper removal was achieved at 24.60% by CMA at a
magnetite ratio of 0.1 in 24 hours. Therefore, it can be concluded that the magnetite composite biosorbent in hydrogel beads form synthesized through the sol-gel method in this work have the potential to be further studied for the development of efficient heavy metal bio-sorbents.

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