Synthesis of magnetite macro-bead for water remediation: process optimization via manipulation of bead size and surface morphology

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Abstract. Particulate-based adsorbents have been actively researched for water remediation. Despite being successful, this approach raises technical concern toward the end of its’ implementation whereby the adsorbents are to be separated from the treated water. Separating the adsorbents via common filtration or centrifugation can be energy-intensive. Noting this, the present study prepared magnetite macro-beads (MMB) which can be easily isolated using a magnetic collector. Here, magnetite nanoparticles were impregnated into calcium alginate bead via facile drop-wise addition. The formed MMB was found effective in dye removal and the efficiency can be optimized by manipulate the bead’s size and surface morphology. In specific, MMB of size 2.0 mm outperformed the bigger counterparts. In terms of surface morphology, large quantity of magnetite nanoparticles loading (≥ 10 g/L) blocked major pores of the alginate surface and reduced its efficiency. More importantly, the MMB can be rapidly separated (in < 5 seconds) using a NdFeB magnet owing to cooperative magnetophoresis effect.

Keywords Macro-bead; Adsorption; Alginate; Magnetite; Surface Morphology

1. Introduction

Adsorption has been an extensively used technique for purification of groundwater and industrial effluents. The wide employment of adsorption as compared to other purification techniques such as biological treatment, advanced oxidation, membrane filtration can be ascribed to its simplicity in implementation, effectiveness and low starting cost. Accordingly, numerous particulate-based adsorbents, such as activated carbon, nanoparticles, alginate bead, fly ash, particle of plants were synthesized for this purpose. Magnetic nanoparticle is one of the emerged materials which is efficient in adsorption owing to their high specific surface area and magnetic separable characteristics. Experimental works have shown that the separation of magnetic nanoparticles is achievable even at low gradient magnetic field (< 100 T/m) [1]. This gave a great advantage as energy intensive filtration or centrifugation method can be omitted in the subsequent downstream treatment. Unfortunately, recollection of nanoparticles (include magnetic nanoparticles) from a large volume of treated water can be rather challenging [2]. The uncollected nanoparticles will retain in the environment and serve as a threat to nanotoxicity. Hence, recent researches have focused on impregnating these nanoparticles into polymeric bead to reduce the risk of nanotoxicity [3, 4].

In this study, magnetic nanoparticles were impregnated into alginate bead to form a magnetically-responsive macro-bead. Up to now, there is little known about how the bead’s size and surface morphology can affect its adsorption performance. Size and surface morphology of the bead can be manipulated by changing the synthesis condition such as the loading quantity of magnetic nanoparticles.
It is hypothesized that a high nanoparticles loading might limit the adsorption capacity due to potential blockage of the surface pore. Hence, this paper was structured in such a way to produce magnetic macro-bead (MMB) of various sizes and loading amount of nanoparticles, as well as to correlate the surface properties of these MMBs to their performance in dye removal.

2. Methodology and Experimental Setup

2.1 Preparation of Adsorbent

2.1.1 Preparation of macro-bead (MB). A solution of 1% sodium alginate (Chemiz) was stirred under heating at 75 °C for 30 mins. The solution was then dropwise added into 2% CaCl₂ (Chemiz) bath to form solidified beads. The beads were kept in the CaCl₂ solution for 1 day to ensure the gelation reaction fully conducted in the whole volume of bead. Later on, the beads were washed 3 times with distilled water to remove unbound calcium ions. Note that the size of the macro-beads is depending on the size of pipette tips used to drop the sodium alginate solution into CaCl₂ bath.

2.1.2 Preparation of magnetite macro-bead (MMB). MMB was prepared using the same method as the one used to prepare MB except that a known quantity of magnetite nanoparticles (Nanoamor Inc.) was pre-added to the 1% sodium alginate solution. The mixture was sonicated before added to CaCl₂ bath.

2.2 Characterization

Surface morphology, functional group, and magnetic property of the beads were determined using scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FTIR), and vibrating-sample magnetometer (VSM) analysers.

2.3 Application of MB and MMB for dye removal

All the dye adsorption experiments were performed in batch mode using fixed amount (i.e., 0.3 g) of MB or MMB, 20 mL of dye solution, and 2 h stirring at 300 rpm. A pre-screening study was conducted to evaluate the effect of bead size on dye adsorption efficiency. Next, MMBs loaded with different amounts of magnetite nanoparticles (i.e., 0.1-50 g/L) were used for dye adsorption. In all the adsorption studies, the dye concentration both before and after adsorption was identified using spectrophotometer at wavelength 664 nm for methylene blue (a cationic dye). The removal percentage, \( R(\%) \) was then calculated via equation \( R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \), where \( C_0 \) (mg/L) and \( C_e \) (mg/L) are respectively the initial and equilibrium concentration of adsorbate.

3. Results and Discussion

3.1. Effect of bead size on dye removal efficiency

The MB and MMB were prepared in three different sizes and applied for methylene blue removal. The obtained beads and their corresponding bead sizes are shown in Fig. 1. As shown in Fig. 1, the bead sizes were 2.0 mm, 2.5 mm and 3.0 mm for MB and 2.0 mm, 2.6 mm and 3.2 mm for MMB, respectively. The polydispersity index of the beads falls below 0.01, indicates that all the beads were monodispersed.

![Fig. 1 Photo showing MMB and MB prepared at different sizes using three different pipette tips.](image-url)
Fig. 2 shows the methylene blue removal efficiency achieved by using the three different sizes of MB and MMB. As shown in Fig. 2, the dye removal efficiency decreased with the increase in bead size. This observation applied to both MB and MMB. In particular, the 72.04±2% removal efficiency achieved by small-sized MB reduced to 62.6±5% with large-sized MB. Meanwhile, small-sized MMB induced 71.6±3% removal efficiency; this value decreased to 57.6±4% when big-sized MMB was used. Such observation can be ascribed to surface area effect whereby a smaller-sized bead exhibits higher exposed surface area-to-volume ratio. This shall provide more active sites for dye adsorption. Note that for all bead sizes, the MB slightly outperformed MMB in dye removal. One possible reason for this observation is that the adsorption of methylene blue (a cationic dye) was mainly governed by its electrostatic attraction toward the anionic bead surface; while a portion of the bead surface has been spent to accommodate magnetite nanoparticles, the available sites in MMB for dye adsorption has reduced [5]. This led to slightly poorer performance in dye removal. Considering the small-sized MMB has better efficiency in dye removal than other sizes, all the MMB used in the subsequent studies were prepared in this size range (i.e. 2.0 mm).

![Fig. 2 Effect of bead size on methylene blue removal (m=0.300g, Co=50mg/L, pH=8 and t=2h).](image)

### 3.2. Effect of magnetite loading amount on dye removal efficiency

Next, MMB loaded with different amounts of magnetite nanoparticles (0.1 g/L – 50 g/L) were prepared and tested for methylene blue removal. The experimental results are delineated in Fig. 3. As shown in Fig. 3, the dye removal efficiency slightly increased from 72.0 ± 1.6 % to 75.2 ± 0.2 % when the magnetite nanoparticles loading was increased from none to 1g/L. The mild loading of magnetite nanoparticles provided extra available nano-adsorption site for methylene blue [6]. Nevertheless, the removal efficiency dropped when the magnetite loading being increased to ≥ 10g/L, indicates that blockage of the bead’s pore might begin at this loading amount. To correlate the result shown Fig. 3 to the surface morphology of the MMB, SEM analysis was conducted on the blank bead and on the MMBs loaded with different amounts of magnetite nanoparticles. The SEM images are presented as Fig. 4.

![Fig. 3 Effect of the magnetite nanoparticles loading in MMB on methylene blue removal (m=0.300g, Co=50mg/L, pH=8 and t=2h).](image)
Overall View                         External Surface                         Internal Surface

As viewed from Fig. 4, all the beads appear as shrank sphere due to vacuum drying that applied onto the beads during SEM sample preparation. There were significant changes in surface morphology along with the increase of magnetite loading amount. In terms of external surface, the blank MB appears to be clear, fibrous, and smooth (Fig. 4a). On the other hand, the external surface of MMB loaded with 1 g/L magnetite is slightly rougher (Fig. 4b); while the MMB loaded with 10 g/L magnetite nanoparticles exhibited the roughest surface whereby agglomerates of nanoparticles can be seen deposited on the fibrous structure (Fig. 4c). In terms of internal surface, large open structures of interconnected pores were clearly seen on the MMB loaded with 1 g/L magnetite. These pores were shielded by large quantity of agglomerated nanoparticles when the amount of nanoparticles being increased to 10 g/L. The agglomerated magnetite nanoparticles have covered major portion of the alginate surface and thus lead to lesser active sites for dye adsorption. This explains the poorer dye removal efficiency using MMB loaded with 10 g/L magnetite nanoparticles as compared to the 1 g/L-loaded counterpart.

3.3 Functional group determination with FTIR analysis

Fig. 5 shows the FTIR spectra of all the prepared samples. For MB, a broad peak around 3310 cm\(^{-1}\) was corresponded to –OH stretching vibration; while the bands appear at 1620 cm\(^{-1}\) and 1430 cm\(^{-1}\) were assigned to asymmetric and symmetric vibrations of -COO group of MB, respectively [7]. The weak band at 1090 cm\(^{-1}\) may be assigned to C–O and C–C stretching vibrations of pyranose; while the small band at 1030 cm\(^{-1}\) can be assigned to C–O stretching vibrations [8]. The spectra for MMB delineated no difference from MB’s spectra despite it has been impregnated with magnetite. The typical Fe-O bands in the fingerprint region (<1000 cm\(^{-1}\)) was not observed here possibly due to the domination of another broad peak started at 896 cm\(^{-1}\). Upon spend for dye adsorption, the transmittance % at both 1430 cm\(^{-1}\) and 1090 cm\(^{-1}\) bands was found to reduce. Also, peak originally located at 1620 cm\(^{-1}\) and 1030 cm\(^{-1}\) have slightly shifted to 1650 cm\(^{-1}\) and 1040 cm\(^{-1}\), respectively. The shortening and shifting of these peaks indicate that the dye molecules were adsorbed onto the -COO of the bead.
3.4 Adsorption isotherms and kinetic modelling

The mechanism governing dye adsorption onto the MMB was studied using isotherm and kinetic models’ fittings. As shown in Fig. 6a-c, the adsorption process best fitted to Freundlich model \((R^2=0.9959)\), indicating the adsorption is of multilayer. Based on analysis, the \(1/n\) value for the Freundlich model is 1.152, which is slightly higher than 1, suggested that the dye molecules are competed with water molecules for adsorption sites at low concentration [9]. Meanwhile, based on Fig. 6e-f, our experimental data fitted well with the pseudo second order kinetic with very high correlation. Such result indicated that chemisorption is the rate-limiting step in this adsorption process.

![Fig. 5 FTIR spectra of the bead samples.](image)

**Fig. 5** FTIR spectra of the bead samples.

3.5 Saturation magnetization (Ms) and magnetophoresis of MMB under low gradient magnetic field

Fig. 7a shows the magnetophoresis of the MMBs under low gradient magnetic field. As expected, the higher the loading amount of magnetite nanoparticles, the rapier the MMB being separated. In fact, almost instant separation was achieved for MMB loaded with 1 g/L and 10 g/L magnetite nanoparticles. Note that the magnetite nanoparticles were impregnated into the bead in the form of agglomerates (as verified from SEM image, Fig. 4c); agglomerates of magnetite nanoparticles offer cooperative magnetophoresis which is faster than magnetophoresis of individual nanoparticles [10]. In line with the magnetophoresis profile shown in Fig 7a, VSM analysis also showed that the \(Ms\) value of MMB loaded with 0.1 g/L, 1 g/L, and 10 g/L magnetite were 0.0349, 0.290, and 1.042 emu/g, respectively (Fig. 7b).
4. Conclusion.
MMB with dye adsorption and magnetic separable bi-functionalities was successfully synthesized. The dye removal efficiency can be further optimized by modifying the MMB’s size and surface morphology. Here, MMB of the smallest size (i.e. 2.0 mm) performed better than MMB of size 2.5 mm and 3.0 mm. In terms of surface morphology, large quantity of magnetite loading covered major part of the alginate surface, leading to reduction of active sites for dye adsorption. Outcomes from this study can serve as a guideline for future real application of MMB in water treatment whereby the treatment efficiency can be optimized via manipulation of bead’s size and surface morphology. Also, a magnetic collector (of low magnetic field gradient) can be installed at the treatment outlet for separation of the spent MMBs.

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