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Technical paper

Synthesis and Characterization of Alginate Encapsulated Zirconium-Based Ferromagnetic Sorbent for Adsorptive Removal of Dyes

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Abstract

This paper provides insight on the removal of dyes from water using magnetic separation technique. A new alginate encapsulated zirconium-based encapsulated ferromagnetic sorbent has been synthesized by co-precipitation and electrostatic extrusion techniques. The ferromagnetic sorbent has the alginate as outer polymeric shell and zirconium-based iron oxides as inner ferromagnetic cores. The sorbent has the multi-functional properties as it is can be easily separated using external magnetic force, and effective in adsorptive removal of congo red, methyl violet, and methylene blue dyes. The sorbent was characterized by particle size analyser, Scanning Electron Microscope (SEM), Thermal Gravimetric-Differential Thermal Analyzer (TG-DTA), and Fourier Transform Infrared Spectroscopy (FT-IR). Adsorption assays were performed in batch using methyl violet, methylene blue, and congo red dyes as contaminants. The alginate encapsulated zirconium-based ferromagnetic sorbent was a potential candidate for removal of dyes under a magnetic field as separating agent. The present investigation demonstrates the ferromagnetic sorbent exhibiting good performance to remove the methyl violet, congo red, and methylene blue dyes from aqueous solutions. The adsorption experiments reveal that the adsorption performance is higher for the cationic dye than the anionic dye. The SEM and FT-IR studies show that the interaction characteristics between the dyes and the ferromagnetic sorbent where the surface of the ferromagnetic sorbent became smoother and less porous when the metal-O group (Zr-O and Fe-O) of the ferromagnetic sorbent attaches to the dye.

Keywords: *Adsorption; Congo red; Dyes; Magnetic separation; Methyl blue; Methyl violet.*

1. Introduction

Dyes which are widely used in painting, textiles, printing, cosmetic, laundry, synthesis, tannery, pulp mill, leather, and food industries are one of the common organic contaminants in wastewater. Congo red dye has anionic property whereas methylene blue and methyl violet dyes are both cationic charges in nature [1]. These dyes are considered as hazardous contaminants due to their toxicity to living organisms. Therefore, these dyes in effluents of wastewater streams have to be sufficiently treated before they are discharged into water bodies. Based on previous findings from other researchers, adsorption process is one of the most efficient methods used for decontaminant of the dyes [2].

Magnetic adsorbents which have high catalytic activity and are easily separated from water system have advantageous over the traditional sorbent materials in practical application as sorbent. More specifically, the excellent ferromagnetic property has enabled easy recovery of the materials by magnetic separation technique after decontamination of contaminants, which overcomes the difficulty of separation in common adsorbents [3].

In the same way, the magnetic iron oxide particles exhibit amphoteric surface activity, easy dispersion ability, and their very small size and dimensions, a high surface-to-volume ratio, resulting in a high adsorption capacity [4]. Furthermore, the magnetite, Fe_3O_4 is known to have low toxicity and good biocompatibility, which is beneficial for water treatment in practice. Other elements such as Mn, Ce, Zr, and Al have been incorporated and integrated with iron oxides to prepare bimetal oxide composites to enhance the performance of adsorption process [5]. In this study, zirconium based ferromagnetic particles were encapsulated by calcium alginate through electrostatic extrusion to produce an innovative ferromagnetic sorbent. As this ferromagnetic sorbent has both zirconium-based ferromagnetic particles (which consist of Zr, Fe, and O elements) and calcium alginate, it demonstrates multi-functional adsorption properties for both anionic and cationic contaminants for dyes removal.

2. Materials and Method

2.1. Materials

All chemicals used in this study were of analytical reagent grade. The materials that were used for sorbent synthesization were iron (II) chloride tetrahydrated ($FeCl_2 \cdot 4H_2O$) of 99% purity (Sigma-Aldrich, France), iron (III) chloride ($FeCl_3$) (greater than 97%, Sigma-Aldrich, France), distilled water, sodium hydroxide solution (NaOH) (50% solution in water, Sigma-Aldrich, France), sodium alginate ($C_5H_7O_4COONa$) (99.999%, Aldrich, U.S.A), zirconium (IV) sulfate ($Zr(SO_4)_2$)(35 weight % solution in water, 99.9%, Aldrich, U.S.A) and calcium chloride dihydrated ($CaCl_2 \cdot 2H_2O$)(99.9%, Merck, Germany). The stock solution dyes were prepared by dissolving methyl violet (99.999%, Fluka, India), methylene blue hydrate (99.999%, Fluka, India), and congo red

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(99.999%, Fluka, India) in appropriate amounts of ultrapure water. All experimental solutions were freshly prepared by diluting the stock solutions to the desired concentrations.

2.2. Preparation of Sorbent

The zirconium-based ferromagnetic particles were prepared using the co-precipitation method. 4.5 g of $FeCl_2.4H_2O$ and 8.9 g of $FeCl_3$ together with and 8 mL of $Zr(SO_4)_2$ were dissolved into 80 mL of ultrapure water with continuous stirring at 750 rpm for 30 minutes with a temperature of 70°C in a Memmert water bath (Model WNE 14). 15 M of NaOH was then added drop wisely into the mixture until the mixture reaches pH approximately 8. After that, the solution was stirred under constant stirring speed and temperature for another 1h. The formed precipitate was then washed using ultrapure water until the supernatant pH reached approximately 7. The precipitate was separated using magnetic decantation technique and dried in an oven at 65°C for 24 h.

Then, the alginate encapsulated ferromagnetic sorbent was prepared using the electrostatic extrusion method. 1.2 g of the sodium alginate and 5 g of the precipitated zirconium based ferromagnetic particles were dissolved into 50 mL of ultrapure water using an ultrasonicator. The $CaCl_2$ solution was also prepared by dissolving 5.5 g of the $CaCl_2$ into 100 mL of ultrapure water. After that, the sodium alginate solution with the zirconium based ferromagnetic particles was flowed through a needle that is attached to a high voltage power generator into the $CaCl_2$ solution with the aid of a peristaltic pump. The electrostatic extrusion were operated at 6 kV of voltage, 2 rpm of pumping rate, 0.8 mm of diameter of needle, 0.6 cm of diameter of hose, 2 cm of height between needle and surface of $CaCl_2$ solution, and 13 cm of height between needle and bottom of $CaCl_2$ solution. The resulting encapsulated beads were collected, washed until pH reached approximately 7, and then dried using a freeze dryer.

2.3. Characterization of Sorbent

The mean diameter of the zirconium based ferromagnetic particles was measured using a Cilas 1090 Particle Size Analyzer (France) which is operated by a laser diffraction based dynamic light scattering. The mean diameter of the alginate encapsulated zirconium-based ferromagnetic sorbent was measured by microscope with camera (B-350, Optika, Italian). The surface morphology of the ferromagnetic sorbents were analysed using a Scanning Electron Microscope (SEM; JEOL, JSM-6390LA, Japan). To quantify the chemical compositions of the sorbent, an energy dispersive X-ray with a Scanning Electron Microscope (SEM-EDS) was used. Thermal Gravimetric-Differential Thermal Analyzer (TG-DTA) (DTG-60H, Shimadzu, Japan) was utilized to identify water content in samples and their thermal resistances. The ferromagnetic sorbent and dyes-loaded ferromagnetic sorbents were analyzed by the Fourier Transform Infrared (FT-IR) Spectroscopic analysis. Each sample was characterized with infrared transmission spectra using Iraffinity-1 (Shimadzu, Japan) spectrometer. The spectra were collected within the range of 400 cm^{-1} and 4000 cm^{-1}. All the recorded spectra were plotted in a same scale on the transmittance axis.

Acid–base titration was used to identify acid and base nature of the sample. 0.1 g of the alginate encapsulated zirconium-based ferromagnetic sorbent was shaken for 24 h with 100 mL of 0.001 M sodium nitrate at different initial pH values. The pH values were adjusted by adding small amount of 0.1M NaOH or 0.1M HNO_3. The initial and final values of the pH were recorded. The difference between the initial and final concentration of H^+ and OH^- indicates the amount of H^+ and OH^- being adsorbed by the particles.

2.4. Adsorption Experiments

All the batch adsorption experiments were carried out in single species of the congo red, methyl violet, and methylene blue dyes. In each experiment, 0.5 g of the dye in 1 L of ultrapure water was first prepared and then, 0.5 g/L of the ferromagnetic sorbent was subsequently added into the prepared dye solution. The solutions were agitated on a shaker for 48 hours with 200 rpm stirring speed at constant 30 °C temperatures. The concentrations of the dyes were analysed by a UV-VIS spectrophotometer (V-630, JASCO, Japan). All the experiments were performed at a controlled temperature of 293 K.

3. Results and Discussion

3.1. Properties of the Sorbent

The zirconium-based ferromagnetic particles were prepared by co-precipitation method. The $FeCl_2.4H_2O$, $FeCl_3$ and $Zr(SO_4)_2$ are the reactants for the co-precipitation process. The NaOH which was added drop wisely into the mixture of the reactants during the process is to generate an alkaline condition. Equation [1] shows the equation of reaction for the synthesis of the zirconium-based ferromagnetic particles.

$$1.6FeCl_2 \cdot 4H_2O + 3.2FeCl_3 + Zr(SO_4)_2 + 16.8NaOH \rightarrow ZrO(OH)_2 \cdot 1.6Fe_2O_4 \cdot 2.5H_2O + 12.8NaCl + 2Na_2SO_4 + 9H_2O \quad [1]$$

The zirconium-based ferromagnetic particles produced were encapsulated using the electrostatic extrusion technique to produce the alginate encapsulated zirconium-based ferromagnetic adsorbent. As this adsorbent has both zirconium based iron oxide and alginate elements, it demonstrates multi-functional adsorption properties for both anionic and cationic contaminants. Both the zirconium-based ferromagnetic particles and alginate encapsulated zirconium-based ferromagnetic sorbent display a good ferromagnetic property as shown in Figure 1. Both of the particles were instantly attracted to a permanent magnet. Once magnetized, the particles interact magnetically like small permanent magnets by forming aggregates [9].

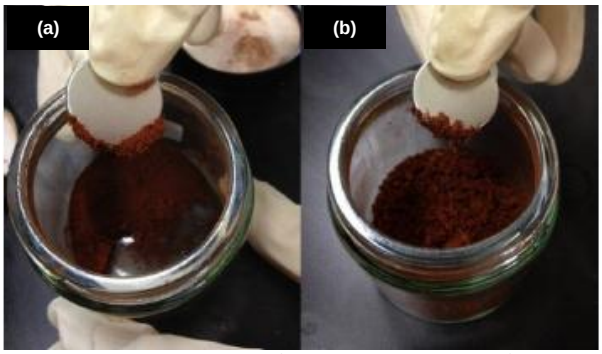


Fig. 1: Ferromagnetic responses of the: (a) zirconium-based ferromagnetic particles and (b) alginate encapsulated zirconium-based ferromagnetic sorbent in dry condition.

The mean diameter of the zirconium-based ferromagnetic particles is 34.98 μm. The mass ratio of alginate to zirconium-based ferromagnetic particles is approximately 1: 5. The alginate encapsulated zirconium-based ferromagnetic sorbent produced has a mean diameter of 1158.4 μm. Figure 2 shows the separation of the ferromagnetic sorbent from the aqueous solution which enables the separation of dispersions with the application of an external permanent magnetic field after sorption process. Thus, the technique

of ferromagnetic separation has appeared to be a promising method in the case of aqueous environmental samples [10].

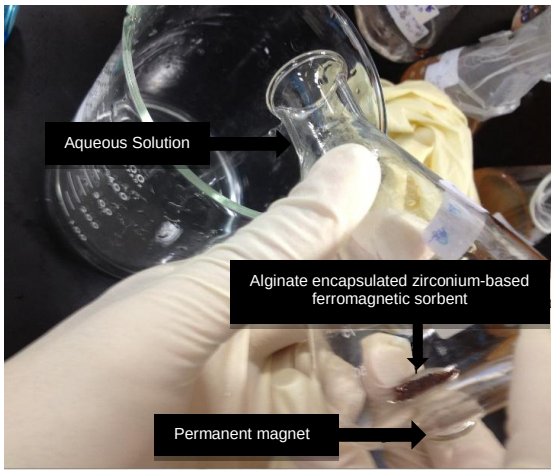


Fig. 2: Ferromagnetic responses of the alginate encapsulated zirconium-based ferromagnetic sorbent in wet condition.

On the other hand, the elemental analysis or chemical characterization of the alginate encapsulated zirconium-based ferromagnetic sorbent was characterized by SEM together with an EDS. Based on Figure 3, the qualitative EDS spectrum analyses revealed the energy spectrum of the X-ray character emitted from the element of iron (Fe), zirconium (Zr), carbon (C), and oxygen (O). No impurities were detected in all the samples that would be attributable to no contamination of chemical precursors.

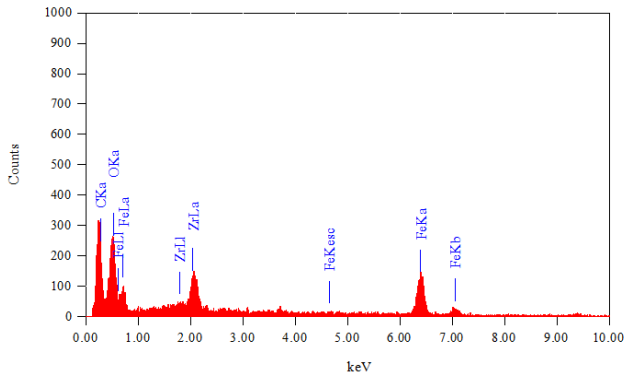


Fig. 3: EDS spectrum of the alginate encapsulated zirconium-based ferromagnetic sorbent

Acid-base titration for the alginate encapsulated zirconium-based ferromagnetic sorbent was performed to elucidate the acid-base nature of the sorbent and its equivalence point. Equivalence point indicates the pH_{zpc} value where the amount of $[H^+]$ and $[OH^-]$ are equivalent. Figure 4 shows the equivalence point is around 7 and buffering zone is around pH 4 to 10. This buffering zone indicates an amphoteric behavior where the sorbent could resist pH changes when acid or alkaline is added [10].

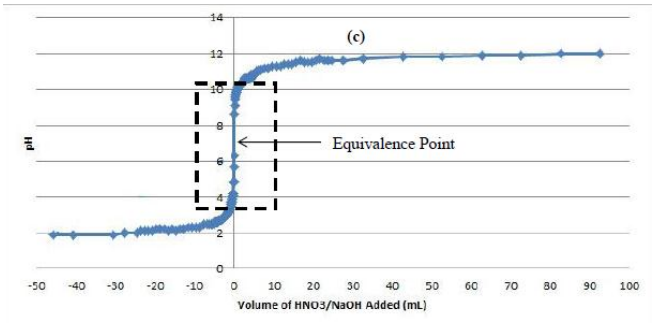


Fig. 4: Acid-base titration of alginate encapsulated zirconium-based ferromagnetic sorbent

Figure 5 shows the thermal stability of the alginate encapsulated zirconium-based ferromagnetic sorbent which is about 72% of its original weight at 800 °C. The weight loss of the ferromagnetic sorbent can be divided into three successive phases of weight loss. In region 1 at temperature between 26 °C and 100°C, the weight loss is approximately 16%. This may be due to the evaporation process of adsorbed water in the ferromagnetic sorbent [11]. In second region for temperature between 100°C and 220°C, the weight loss is approximately 2%. This might be due to the loss of chemically adsorbed lattice water. For the third region at temperature greater than 220°C, the total weight loss is approximately 10%. This might be due to the extraction of remaining water in the ferromagnetic sorbent and conversion of $ZrO(OH)_2$ into ZrO_2 and calcium alginate into calcium carbonate, calcium oxide and calcium hydroxide [11-13].

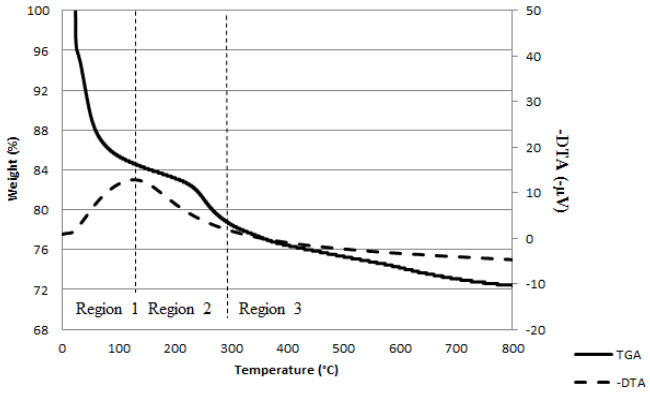


Fig. 5: TGA-DTA curves of the alginate encapsulated zirconium-based ferromagnetic sorbent

3.2. Adsorption Behaviour

Validation of the adsorption behavior of the ferromagnetic sorbent was performed with three different organic dyes (methyl violet, methylene blue, and congo red) in aqueous environment. This was to validate the adsorptive removal of the dyes by the prepared ferromagnetic sorbent. The experimental result in Figure 6 shows the ferromagnetic sorbent has good adsorption performance where it could remove about 58 to 95 % of the dyes (anionic or cationic dyes) in aqueous solution. The results indicate that the adsorption performance is higher for cationic dyes (methylene blue and methyl violet dyes) than anionic dye (congo red dye). Similar phenomena have been obtained for methylene blue and methyl violet adsorption on carbon nanotubes [14]. The SEM analysis found that the surface of the ferromagnetic sorbents became smoother and less porous (Figure 7). This observation is similar for all the surfaces of adsorbed dyes. This indicates that a coating of the adsorbed layer of dyes might be formed over the ferromagnetic sorbent surface and some of the pores were covered with the adsorbed dyes [15].

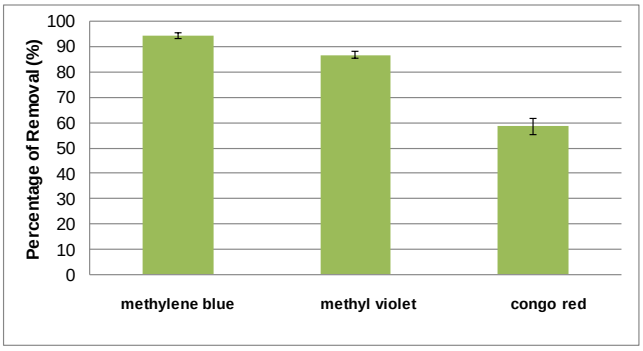


Fig. 6: Adsorptive removal percentages of the methyl violet, methylene blue, and congo red dyes using the alginate encapsulated zirconium-based ferromagnetic sorbent

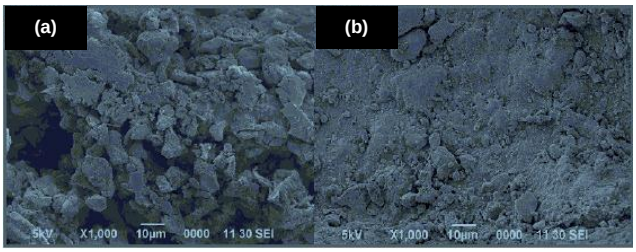


Fig. 7: SEM microscopic image of: (a) alginate encapsulated zirconium-based ferromagnetic sorbent and (b) methyl violet dye-loaded alginate encapsulated zirconium-based ferromagnetic sorbent.

To elucidate the changes in surface functional groups of the ferromagnetic sorbent, a FT-IR analysis was carried out with the data shown in Figure 8. The surface functional group of the alginate encapsulated zirconium-based ferromagnetic sorbent is shown in Figure 7(a). The peak at 3620.39 cm-1 indicates stretching vibration of OH group (3700–3200cm^{-1}). The bonds at 1691.57 and 1527.62 cm^{-1} are assigned to the appearance of C=O (1820–1600cm^{-1}) and C–C (1600–1450cm^{-1}). Metal oxides which are zirconium oxide and iron oxide are fall at the spectra from 600 to 400 cm^{-1}. The ferromagnetic sorbent loaded with methyl violet, methylene blue, and congo red were characterized and shown in Figure 8(b)-(d), respectively. The FT-IR spectra showed that stretching vibration of –OH group (3700–3200 cm^{-1}) was shifted. Besides, there were peaks appearances at about 2800cm^{-1} which indicate the uptake of the dyes where the function group from the dyes was bonded to the –OH group to form hydrogen bonding [16]. Another noticeable feature was the shapes of the spectra between 400 and 600 cm^{-1} of the ferromagnetic sorbent loaded with the dyes were different from the ferromagnetic sorbent. This change might be due to complexion of the dyes with metal-O surface functional group which were Zr-O and Fe-O [17].

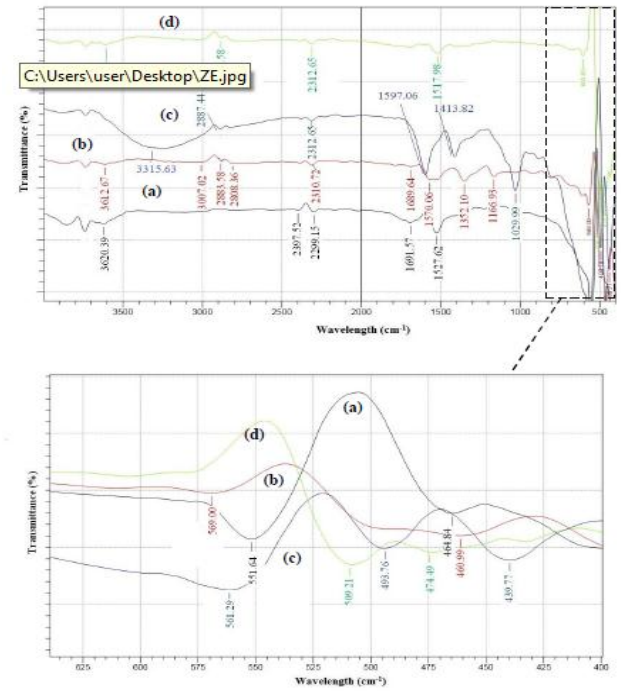


Fig. 8: FT-IR spectra of the: (a) alginate encapsulated zirconium-based ferromagnetic sorbent, (b) methyl violet dye-loaded alginate encapsulated zirconium-based ferromagnetic sorbent (c) congo red dye-loaded alginate encapsulated zirconium-based ferromagnetic sorbent, and (d) methylene blue dye-loaded alginate encapsulated ferrozirconium-based magnetic sorbent.

4. Conclusion

The present investigation confirms that the alginate encapsulated zirconium-based ferromagnetic sorbent with multi-functional properties can be easily separated using an external magnetic force and exhibiting good performance to remove the methyl violet, methylene blue, and congo red dyes from aqueous solutions. The adsorption experiments reveal that the adsorption performance is higher for the cationic dye than the anionic dye. The SEM and FT-IR studies show that the interaction characteristics between the dyes and the ferromagnetic sorbent where the surface of the ferromagnetic sorbent became smoother and less porous when the metal-O group (Zr-O and Fe-O) of the ferromagnetic sorbent attaches to the dye.

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