SYNTHESIS AND APPLICATION OF CHITOSAN/GRAPHENE OXIDE/MAGNETITE NANOSTRUCTURED COMPOSITE FOR Fe(III) REMOVAL FROM AQUEOUS SOLUTION

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Abstract. In this work, we have proposed a method for synthesis of chitosan/Fe_3O_4/graphene oxide (CS/Fe_3O_4/GO) nanocomposite and its application for efficient removal of Fe(III) ions from aqueous solutions. For this purpose, first, graphene oxide (GO) was prepared from graphite by Hummer's method, then, after CS/Fe_3O_4/GO was synthesized via chemical co-precipitation method from a mixture solution of GO, Fe^{3+}, Fe^{2+} and chitosan. The synthesized GO and CS/Fe_3O_4/GO were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), vibrating sample magnetometer (VSM), dynamic light scattering (DLS) and measuring zeta potential techniques. Optimized adsorption conditions for Fe^{3+} removal such as pH and contact time were investigated. Fe(III) adsorption equilibrium data were fitted well to the Langmuir isotherm and the maximum monolayer capacity (q_{max}), was calculated as of 6.5 mg.g^{-1}. In addition, the recoverable and recyclable of CS/Fe_3O_4/GO nanocomposite has been investigated. Data showed that after 6 adsorption-regeneration cycles, the Fe^{3+} removal efficiency of CS/Fe_3O_4/GO was still higher than 60 %. The results indicated CS/Fe_3O_4/GO nanocomposite can be used as a cheap and efficient adsorbent for removal of heavy metal ions from aqueous solutions.

Keywords: graphene oxide (GO), Fe_3O_4 nanoparticles, heavy metal ions, Fe(III), chitosan, nanocomposite; magnetic adsorbent.

Classification numbers: 2.4; 3.3; 3.7.

1. INTRODUCTION

Iron and its compounds are contaminants and commonly found in wastewater produced by several industries, including plating, minerals, and cements. Fe^{3+} is toxic and can pose risks to human health such as gastrointestinal disease [1]. It is dreadful even of people just take in a low

amount of Fe^{3+} at 60 mg kg^{-1} of body weight [2]. There are many chemical and physical processes that have been developed for the removal of Fe^{3+} ions contaminant from wastewater such as supercritical fluid extraction, bioremediation, oxidation with oxidizing agent, coagulation/ flocculation, membrane filtration and biological treatment [3-5]. These techniques were found not effective due to either extremely expensive or too inefficient to reduce such high levels of ions from the large volumes of water. Therefore, the effective process must be low cost-effective technique and simple to operate. It found that the adsorption process using natural adsorbents realize these prerequisites. Additionally, adsorbents generally have large specific surface areas and high removal of heavy metal ions. Therefore, the adsorption to remove Fe^{3+} from wastewater displays a number of advantages, such as rapid action and strong adaptability. Traditional adsorbents, such as kaolinite, montmorillonite [3], activated carbon [6], zeolites [7], plant wastes [8] and other porous materials have been investigated widely. In addition, the magnetic field assisted separation technologies have a potential to provide new opportunities. Magnetic separation based on the Ni@C [2], Fe_3O_4 [2, 10] have received high attention and has been widely used in wastewater treatment due to its convenience, economy and efficiency.

In this paper, we report a simple process for preparation of new adsorbent based on chitosan/graphene oxide/Fe_3O_4 (CS/Fe_3O_4/GO) nanocomposite for removal of Fe^{3+} from aqueous solution. The advantages of this adsorbent are fast adsorption of Fe^{3+}, high adsorption capacity, recoverable and recyclable adsorbent. Moreover, this material not only can be applied for Fe^{3+} removal but also can be extended to other heavy metal ions and organic compounds.

2. MATERIALS AND METHODS

2.1. Preparation of chitosan/Fe3O4/graphene oxide nanocomposite (CS/Fe$_3$O$_4$/GO)

Graphene oxide was synthesized from pencil's graphite using Hummer's method. Then after, the chitosan/Fe_3O_4/graphene oxide nanocomposite (CS/Fe_3O_4/GO) was synthesized following previous report [10] using co-precipitation method from three solutions of precursors materials: (i) a solution of Fe^{2+} and Fe^{3+} ions was prepared by dissolving of $FeSO_4.4H_2O$ and $FeCl_3.6H_2O$ appropriate molar ratio of Fe^{2+}: Fe^{3+} of 2: 1 into distilled water; (ii) GO solution was prepared by dispersion on graphene oxide into distilled water under sonication condition. (iii) a chitosan solution (2.5 wt.%) was prepared by adding of 7.08 g chitosan into an acid acetic 1 v/v.% solution.

2.2. Characterization methods

The X-ray Diffraction (XRD) patterns were obtained at room temperature by D8 Advance, Bruker ASX, using CuKα radiation (λ = 1.5406 Å) in the range of 2θ = 10°–60°, and a scanning rate of 0.02 s^{-1}. Morphology of composites was analyzed by Field Emission Hitachi S-4500 Scanning Electron Microscope (FE-SEM). The magnetic properties were measured with vibrating sample magnetometer (VSM) and evaluated in terms of saturation magnetization and coercivity. Size distribution of GO was characterized by DLS method and zeta potential of GO was measured on Horiba SZ-100 system.

2.3. CS/Fe$_3$O$_4$/GO nanocomposite for Fe^{3+} removal

To study adsorption of Fe^{3+} on CS/GO/Fe_3O_4 nanocomposite, 20 mg of CS/GO/Fe_3O_4 nanocomposite was added into 20 mL of 30 mg.L^{-1} of Fe^{3+} solution, which was prepared from

$FeCl_3.6H_2O$ salt. After Fe^{3+} adsorption, the $CS/Fe_3O_4/GO$ adsorbent was quickly separated from solution using a magnet. The residual Fe^{3+} concentration in the solution was determined by spectrophotometric using NH_4SCH as complexed reagent at wavelength of 472 nm (specific absorbance peak of the $[Fe(SCN)]^{2+}$ complex). The amount of Fe^{3+} uptake by the $CS/Fe_3O_4/GO$, q_e (mg.g^{-1}), was obtained as follows:

$$q_e = \frac{C_0 - C_e}{m_a} \qquad (1)$$

The Langmuir equation (3) and Freundlich equation (4) isotherms can be linearized into the following forms:

$$\frac{C_e}{q_e} = \frac{1}{K_L.q_{max}} + \frac{1}{q_{max}}.C_e \qquad (2)$$

$$logq_e = logK_F + \frac{1}{n}logC_e \qquad (3)$$

where: C_0 and C_e (mg.L^{-1}) are the initial and equilibrium concentrations of Fe^{3+} in solution, respectively; m_a is the concentration of $CS/Fe_3O_4/GO$ (g.L^{-1}); q_e, q_{max} are the equilibrium Fe^{3+} concentration on the adsorbent and the monolayer capacity of the adsorbent (mg.g^{-1}), respectively. K_L the Langmuir constant (L.mg^{-1}) and related to the free energy of adsorption; K_F the Freundlich constant (L.g^{-1}) and n (dimensionless) is the heterogeneity factor.

3. RESULTS AND DISCUSSION

3.1. Characterizations of CS/Fe$_3$O$_4$/GO

Figure 1a and Fig. 1d show digital photograph of GO and $CS/Fe_3O_4/GO$, respectively. It can be seen that the obtained GO as dark-brown flakes and $CS/Fe_3O_4/GO$ as black powder. DLS analysis result of GO (Fig.1b) indicated the size of obtained GO around 3-8 µm with mean size about 5.7 µm. Zeta result (Fig.1c) indicated GO in water solution has negative charged with potential around -50 mV. Figure 1e showed XRD patterns of pure chitosan (CS) (curve i); pure Fe_3O_4 (curve ii) CS/Fe_3O_4 (curve iii) and $CS/Fe_3O_4/GO$ with different GO content (curve iv and v). Six characteristic peaks for Fe_3O_4 corresponding to (220), (311), (400), (422), (511) and (440) were observed in Fe_3O_4; CS/Fe_3O_4 and $CS/Fe_3O_4/GO$ samples. To test whether the synthesized $CS/Fe_3O_4/GO$ nanocomposite could be used as a magnetic adsorbent in the magnetic separation processes, magnetic measurements were performed on VSM. The magnetization hysteresis loops of the pure Fe_3O_4 nanoparticles (Fig. 1b, curve i) and $CS/Fe_3O_4/GO$ (Fig. 1b, curve ii) nanocomposite with mass ratio of m_{CS}: m_{Fe3O4}: m_{GO} was 0.36:0.54:0.10, were measured at room temperature. Our experimental results indicate that the saturation magnetization values (M_s) for pure Fe_3O_4 and $CS/Fe_3O_4/GO$ nanocomposite was 70.5 emu/g and 40.2 emu/g, respectively.

Figure 1g shows FE-SEM image of the obtained GO flakes. The GO material consisted of randomly aggregated, thin, crumpled sheets closely associated with each other to form a disordered solid. The images of chitosan/Fe_3O_4 composite are showed in the Fig. 1h. It can be seen that the material has porous surface and much holes. Fig. 1e is showed that $CS/Fe_3O_4/GO$ has the surface more porous than CS/Fe_3O_4 material. In Fig. 1i, it can be seen that Fe_3O_4 nanoparticles, which particles size around of 30-40 nm, were deposited onto GO sheets. It can be explained that the role of GO in $CS/Fe_3O_4/GO$ creating the new 3D structures, make increasing the surface area with high porosity. It is very promissory in applications $CS/Fe_3O_4/GO$ for adsorbing Fe^{3+} ions.
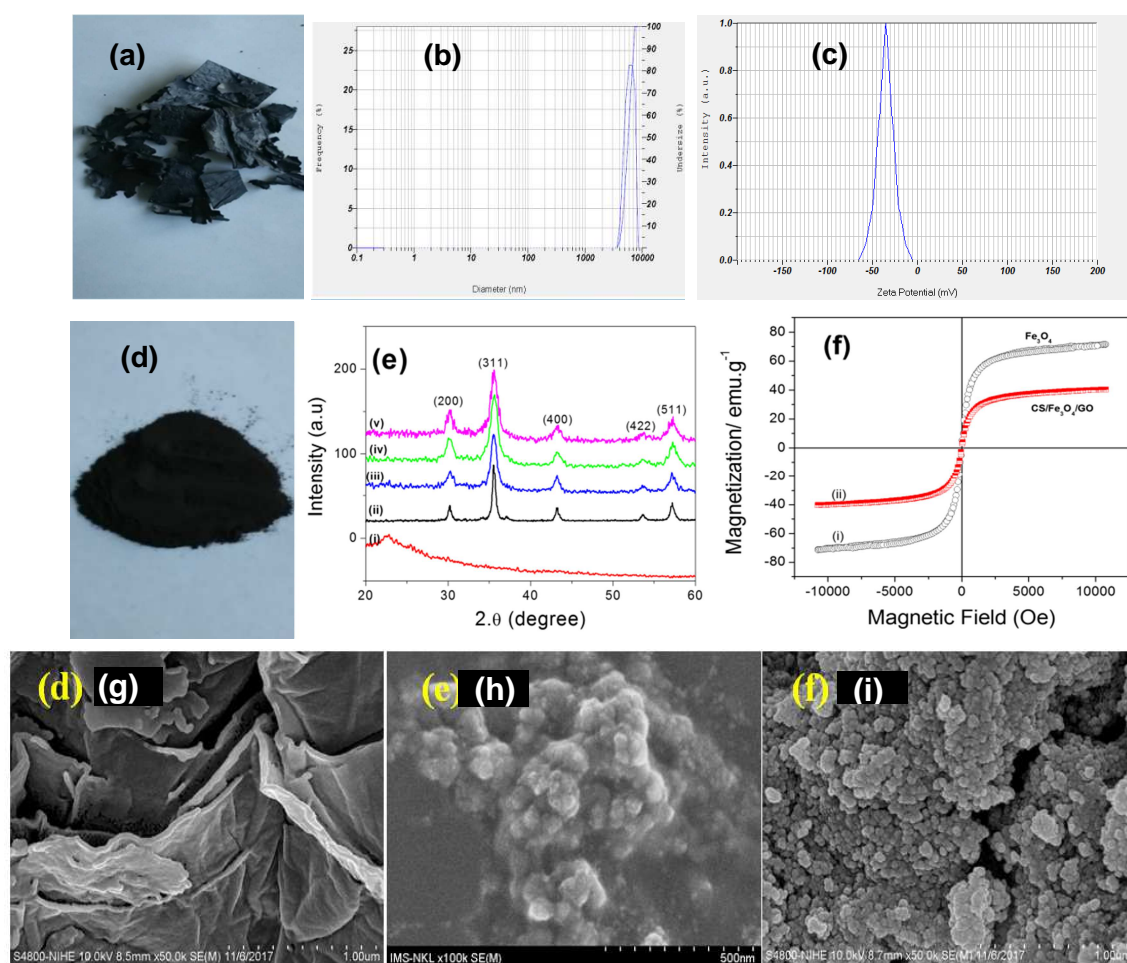
Figure 1. (a) Digital photograph of GO; (b) size distribution of GO by DLS; (c) Zeta potential of GO; (d) Digital photograph of CS/Fe$_3$O$_4$/GO; (e) XRD patterns of (i) CS; (ii) pureFe$_3$O$_4$; (iii) CS/Fe$_3$O$_4$ and (iv, v) CS/Fe$_3$O$_4$/GO; (f) Ms vs H of (i)Fe$_3$O$_4$ and (ii) CS/Fe$_3$O$_4$/GO, and (c-e) SEM images of (g) GO; (h) Fe$_3$O$_4$/CS and (i) CS/Fe$_3$O$_4$/GO.

3.2. Removal of Fe(III) by CS/Fe$_3$O$_4$/GO

3.2.1. Optimization conditions for Fe(III) removal

The UV-vis spectrum of [Fe(SCN)$_2$]$^+$ complexes are shown in Fig. 2a and the calibration curve for determining of Fe(III) concentration in solution was generated Fig. 2a (insert). To enhance the adsorption capacity Fe^{3+} of CS/Fe$_3$O$_4$/GO, some adsorption effected factors have been optimized such as contact time (Fig. 2b); liquid/solid ratio (Fig. 2b); pH (Fig. 2c) and Fe^{3+} initial concentration (Fig. 2d). Therefore, the optimized conditions have been obtained: pH 2.5; contact time was 40 min and liquid/solid ratio was 20 ml/10 mg.
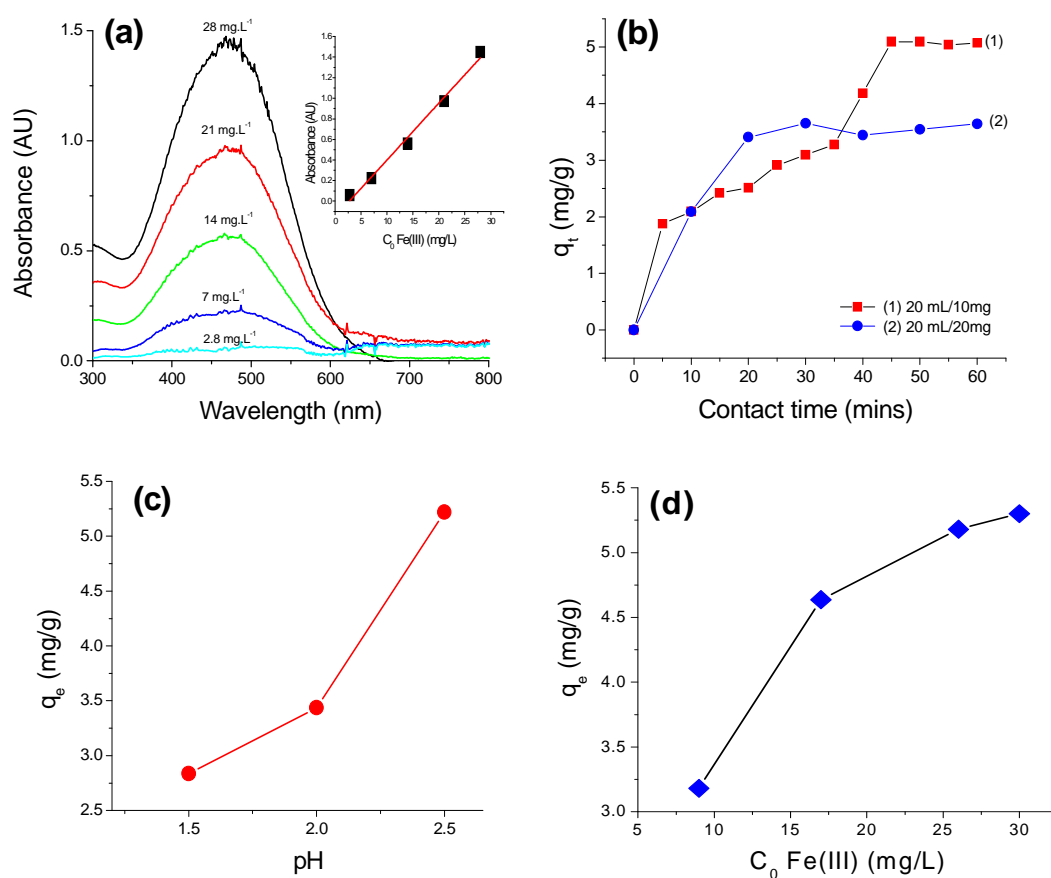
Figure 2. (a) UV-vis spectrum of standard solutions with different concentration of Fe^{3+} after complexed with SCN^- (insert: the calibration curve for measuring of Fe^{3+}); (b) Effect of solid/liquid ratio with (1) S/L = 10/10 and (2) 10/20 mg/mL; (c) Effect of pH and (d) Effect of initial concentration of Fe^{3+}.

3.2.2. Adsorption isotherms

In order to optimize the use of $CS/Fe_3O_4/GO$ for Fe^{3+} removal, it is important to establish the most appropriate adsorption isotherm. The amounts of Fe^{3+} in the solution were determined after equilibration and its concentration in solution was to be extracted form calibration curve. The result is shown in Fig. 2d. The data of the Fe^{3+} adsorbed at equilibrium (q_e, mg.g^{-1}) and the equilibrium Fe^{3+} concentration (C_e, mg.L^{-1}) were fitted to the linear form of Langmuir adsorption model. The obtained results are shown on Fig. 3 with the obtained correlation coefficients ($R^2_{Langmuir}$ = 0.9958 and $R^2_{Freundlich}$ = 0.9737) indicating that dye adsorption equilibrium data were fitted well to the Langmuir isotherm (Fig. 3a) rather than Freundlich isotherm (Fig. 3b). The maximum monolayer capacity q_{max} and K_L the Langmuir constant (L.mg^{-1}) were calculated from the Langmuir model as 6.5 mg g^{-1} and 0.175 L.mg^{-1}, respectively. It is also evident from these data that the surface of the $CS/Fe_3O_4/GO$ is made up of homogenous adsorption patches than heterogeneous adsorption patches.
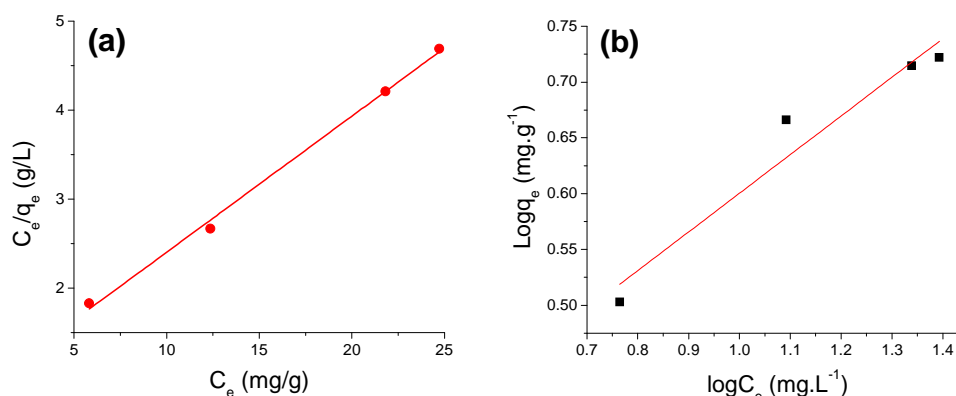
Figure 3. (a) Langmuir plot and (b) Freundlich plot for removal of Fe^{3+} using $CS/Fe_3O_4/GO$ adsorbent.

Notably, in the literature, there are not many reports on removal of Fe^{3+} due to hard conditions of process: low pH level, low adsorption capacity and very difficult to regenerate the adsorbent. Compared to other adsorbents, the adsorption capacity of $CS/Fe_3O_4/GO$ is higher than ZrO-kaolinite [3], natural quartz, natural bentonite [4] or natural apatite [5]; and lower than $Fe_3O_4@mSiO_2$ core-shell [1], Ni@C composite [2] and ZrO-montmorillonite [3].
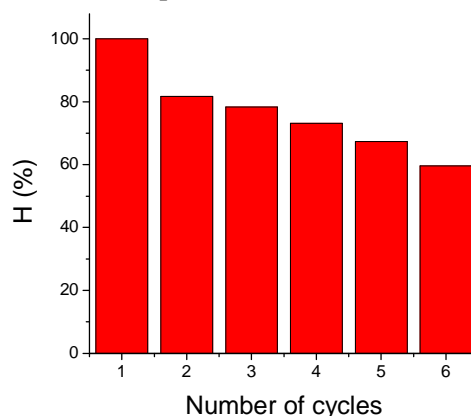

Figure 4. Removal efficiency for Fe^{3+} on original and regenerated $CS/Fe_3O_4/GO$ with evolution of adsorption-regeneration cycles.

After recovery by an external-magnet, $CS/Fe_3O_4/GO$ was regenerated by 0.1M EDTA solution for de-adsorption of Fe^{3+}. Then the adsorption was dried for reuse. The Fe^{3+} removal efficient of regeneration materials was compared to original materials (as synthesized) and the results are shown in Fig. 4. It can be seen that after 6 adsorption-regeneration cycles the Fe^{3+} removal efficient of $CS/Fe_3O_4/GO$ was still higher than 60 %, which is better than $Fe_3O_4@mSiO_2$ core-shell (~70 % after 4 cycles) [1].

4. CONCLUSIONS

In the present work, graphene oxide (GO) was successfully synthesized by Hummers method and it was used to prepared chitosan/magnetite/graphene oxide ($CS/Fe_3O_4/GO$) - a novel magnetically separable adsorbent - by a simple co-precipitation route. The Fe_3O_4 nanoparticles

with average sizes 30– 40 nm were formed and stably anchored on the surface of GO sheets by chitosan. We demonstrated a high potential for application of a $CS/Fe_3O_4/GO$ nanocomposite used for a magnetically separable adsorbent for highly efficient Fe^{3+} ion removal from water. The adsorption isotherms was studies revealed that the adsorption process of Fe^{3+} on $CS/Fe_3O_4/GO$ was fitted well with the Langmuir isotherm model and adsorption capacity of $CS/Fe_3O_4/GO$ was found of 6.5 mg.g^{-1}. The proposed materials can be recovery and reused at least 6 cycles with removal efficiency was still higher than 60 %. Based on the obtained results, we do believe that the $CS/Fe_3O_4/GO$ nanocomposite can also be applied for removal of other heavy metal ions and/or organic compounds in aqueous solution.

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