

# SYNTHESIS, CHARACTERIZATION OF Fe<sub>3</sub>O<sub>4</sub>/CHITOSAN/GRAPHENE OXIDE NANOCOMPOSIT AND ITS APPLICATION FOR Cr(VI) REMOVAL

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## Abstract

Polluted Cr(III/VI) ions were generated from electroplating industry, mining industry, leather tanning, metal finishing, steel fabrication, textile industries... In which, Cr (III) is much less toxic than that Cr (VI). Health effects of exposure to Cr(VI) reported by various studies are eye, nose, and throat irritation, nasal septum ulcerations and perforations, gastritis, gastrointestinal ulcers, contact dermatitis, ulcers, lung cancer. Therefore, removal of Cr (VI) is necessary and urgent need. In this work, we propose the use of Fe<sub>3</sub>O<sub>4</sub>/chitosan/graphene oxide nanocomposit (FCGs) as an effective adsorbent for Cr(VI) removal. FCGs adsorbents can be recovered and regenerated after adsorption process, moreover, FCGs has adsorption capacity (200 mg/g) thanks to the role of graphene oxide (GO). The FCGs synthesis procedure, the use of FCGs for Cr(VI) ion removal and the regeneration results are also described and discussed in the paper.

*Keywords: Fe<sub>3</sub>O<sub>4</sub>/chitosan/graphene oxide (FCGs) nanocomposit, Cr(VI) ion, adsorption, regeneration, graphene oxide (GO)*

## 1. INTRODUCTION

The most common oxidation states of Cr in nature are Cr(III) and Cr(VI). Chromium(VI) is more hazardous than Cr(III) as it can diffuse as CrO<sub>4</sub><sup>2-</sup> or HCrO<sub>4</sub><sup>-</sup> through cell membranes and oxidize biological molecules. The adsorption processes are the most common method to remove Cr(VI) from aqueous solution because of its high efficiency and low cost, can adsorb effectively even in low concentration of heavy metal ions[1-5]. Compared to the traditional micron-sized adsorbent, the nano-sized adsorbents display better performance due to high specific surface area and the absence of internal diffusion resistance. However, the nano-adsorbents cannot be separated easily from aqueous solution by filtration or centrifugation, therefore, the application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years[3-5]. Graphene oxide (GO) is made of single layer of carbon atoms which are closely packed into honeycomb two dimensional (2D) lattices. Having the large surface area (~2630 m<sup>2</sup>/g), oxygen containing surface functionalities such as hydroxyl, carboxylic, carbonyl, and epoxide groups, and high water solubility makes GO become a material of great interest in adsorption-based technologies as well as in other fields[4,5]. Basing on above reasons, in the this work, we have presented the use of Fe<sub>3</sub>O<sub>4</sub>/chitosan/graphene oxide nanocomposite for Cr(VI) ions removal.

## 1. METHODS

### 2.1. Preparation of Fe<sub>3</sub>O<sub>4</sub>/chitosan/graphene oxide (FCGs)

Graphene oxide (GO) was synthesized from pencil's graphite and Fe<sub>3</sub>O<sub>4</sub>/chitosan/graphene oxide nanocomposite (FCGs) was synthesized following previous report [4,5] by co-precipitation method.

### 2.1. Cr(VI) removal procedure

0.04 g FCGs powder was added into a 10 ml of 200 mg.L<sup>-1</sup>Cr(VI) solution. The mixture was incubated for various contact times at different temperatures. To adjust pH in range of pH3, the

0.1M HCl solution was used. The residue concentration of Cr(VI) in solution after adsorption process has been obtained by measure UV-Vis spectra.

## 2.2 Batch adsorption and kinetic experiment

The amount of Cr(VI) uptake by FCGs ( $q_e$ ,  $\text{mg.g}^{-1}$ ) was calculated following equation:

$$q_e = \frac{C_0 - C_e}{m_a} \quad (\text{Eq.1})$$

The Langmuir equation (2) and Freundlich equation (3) isotherms can be linearized into the following forms:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_{\max}} + \frac{1}{q_{\max}} \cdot C_e \quad (\text{Eq.2})$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (\text{Eq.3})$$

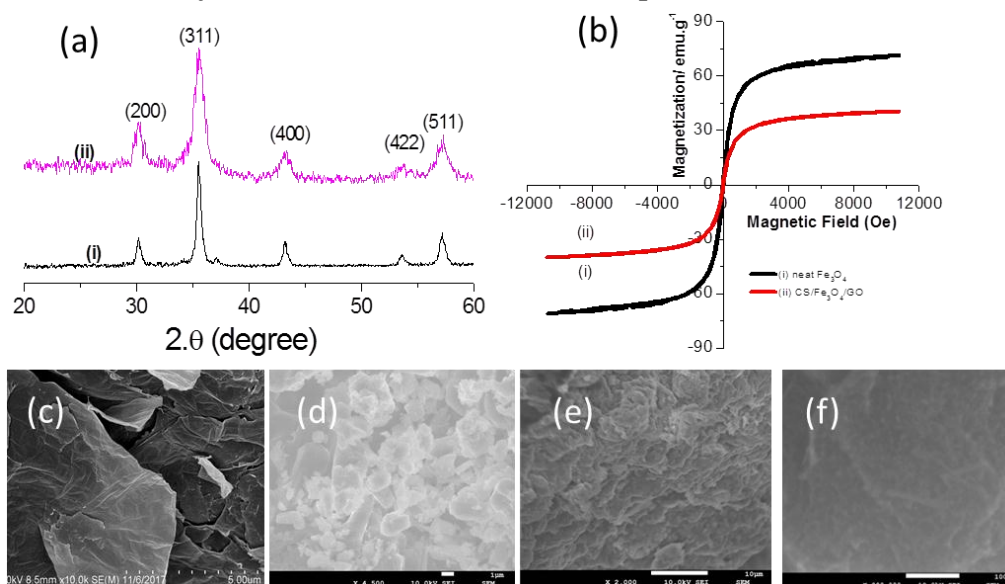
Where:  $C_0$  and  $C_e$  ( $\text{mg.L}^{-1}$ ) are the initial and equilibrium concentrations of Cr(VI) in solution, respectively;  $m_a$  is the concentration of FCGs ( $\text{g.L}^{-1}$ );  $q_e$ ,  $q_{\max}$  is the equilibrium Cr(VI) concentration on the adsorbent and the monolayer capacity of the adsorbent ( $\text{mg.g}^{-1}$ ), respectively.  $K_L$  is the Langmuir constant ( $\text{L.mg}^{-1}$ ) and related to the free energy of adsorption;  $K_F$  is the Freundlich constant ( $\text{L.g}^{-1}$ ) and  $n$  (dimensionless) is the heterogeneity factor.

## 2.3. Methods

Absorbance measurements (UV- Vis) spectra were measured using Agilent 8453 UV- Vis spectrophotometer system with the wavelength in a range of 200 – 1200 nm. X-ray Diffraction (XRD) patterns of FCGs samples were obtained at room temperature by D8 Advance, Bruker ASX, using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the range of  $2\theta = 10^\circ - 60^\circ$ . Morphology of GO and FCGs nanocomposite were analyzed by Field Emission Hitachi S-4500 Scanning Electron Microscope (FE-SEM). The magnetic behaviors of the samples were measured at room temperature using a vibrating sample magnetometer (VSM 880 DMS/ADE Technologies, USA) at fields ranging from  $-10$  to  $10$  kOe at  $25^\circ\text{C}$ , with accuracy of  $10^{-5}$  emu.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterizations of CS/ $\text{Fe}_3\text{O}_4$ /GO (FCGs) nanocomposite

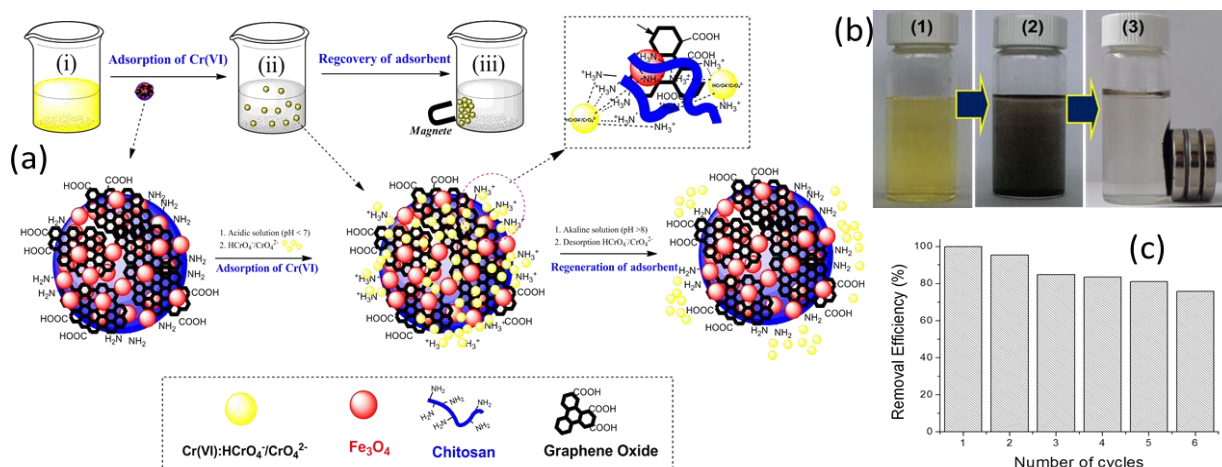


**Figure 1.** (a) XRD of (i) pure  $\text{Fe}_3\text{O}_4$ ; (ii)  $\text{CS}/\text{Fe}_3\text{O}_4/\text{GO}$ ; (b) VSM of (i)  $\text{Fe}_3\text{O}_4$  and (ii)  $\text{CS}/\text{Fe}_3\text{O}_4/\text{GO}$  and (c-f) FESEM of (c) GO; (d)  $\text{Fe}_3\text{O}_4/\text{CS}$  and (e-f)  $\text{CS}/\text{Fe}_3\text{O}_4/\text{GO}$

Figure 1a showed XRD patterns of pure  $\text{Fe}_3\text{O}_4$  (curve i) and  $\text{CS}/\text{Fe}_3\text{O}_4/\text{GO}$  (curve ii). Six characteristic peaks for  $\text{Fe}_3\text{O}_4$  corresponding to (220), (311), (400), (422), (511) and (440) were observed in  $\text{Fe}_3\text{O}_4$  as well as XRD spectrum of FCGs. To test whether the synthesized FCGs

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  $\text{Fe}_3\text{O}_4$  nanoparticles (Fig.1b, curve i) and FCGs (curve ii) and results indicate that the saturation magnetization values ( $M_s$ ) for pure  $\text{Fe}_3\text{O}_4$  and FCGs nanocomposite was 70.5 emu/g and 40.2 emu/g, respectively. Figure 1c shows FE-SEM images of the obtained GO flakes. The images of chitosan/ $\text{Fe}_3\text{O}_4$  composite (Fig. 1d) shown that the material has porous surface and much holes. FESEM of FCGs (Fig. 1e and Fig. 1f) showed that FCGs has surface more porous than that CS/ $\text{Fe}_3\text{O}_4$ . It can be seen that  $\text{Fe}_3\text{O}_4$  nanoparticles, which particles size around of 30-40 nm, were deposited onto GO sheets. It can be explained that the role of GO for creating the new 3D structures in FCGs and therefore, increasing the surface area of FCGs.

### 3.2. Cr(VI) removal by CS/ $\text{Fe}_3\text{O}_4$ /GO



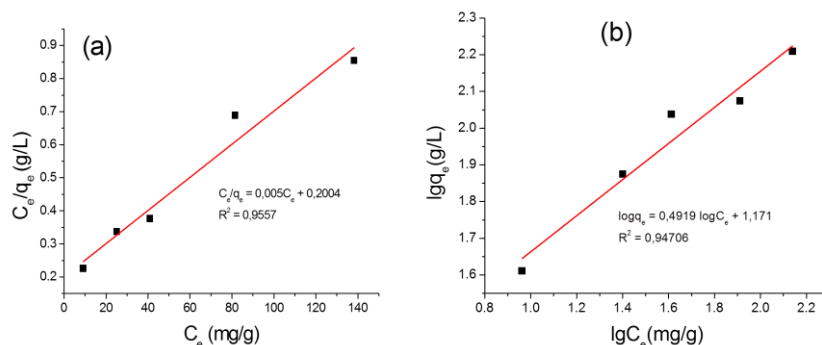
**Figure 2.** (a) Illustration scheme for adsorption of Cr(VI) onto FCGs surface; (b) digital photos of (1) initial Cr(VI) solution; (2) a mixture solution of Cr(VI) solution and FCGs adsorbent; and (3) removal of FCGs nanocomposite from solution by external magnet; (c) Effect of recycling number on Cr(VI) adsorption efficiency of FCGs nanocomposites.

The adsorption mechanism of Cr(VI) onto FCGs adsorbent is proposed in Figure 2. Here, amino ( $-\text{NH}_2$ ) groups of chitosan coating on FCGs surface in acidic solution (pH3) have been protonated as ( $-\text{NH}_3^+$ ), therefore, FCGs adsorbent becomes cations and they are easy to attract chromium anions (as  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$  as negative charge) on the surface by electrostatic attraction and thereby the results the adsorption efficiency increases. To confirm that Cr(VI) ions have been loaded on FCGs after adsorption, we have analyzed EDX of FCGs before and after Cr(VI) adsorption (data not shown). Results indicated that the original FCGs sample includes only C, O, Fe from their compositions (Fig. 6d), however, after adsorption Cr(VI), two new peaks have appeared at 0.5 keV and 5.5 keV which can be attributed to successfully adsorbed Cr(VI) on FCGs surface.

### 3.3. Adsorption isotherm

Adsorption isotherm of Cr(VI) on FCGs following Langmuir and Freundlich are shown in Figure 3. The data of the Cr(VI) adsorbed at equilibrium ( $q_e$ ,  $\text{mg}\cdot\text{g}^{-1}$ ) and the equilibrium Cr(VI) concentration ( $C_e$ ,  $\text{mg}\cdot\text{L}^{-1}$ ) were fitted to the linear form of Langmuir adsorption model. The obtained results are shown on Fig. 5 with the obtained correlation coefficients ( $R_{\text{Langmuir}}^2 = 0.9557$  and  $R_{\text{Freundlich}}^2 = 0.94706$ ) showed that dye adsorption equilibrium data were fitted well to the Langmuir isotherm (Fig. 3a) rather than Freundlich isotherm (Fig. 3b). The maximum monolayer capacity  $q_{\text{max}}$  was calculated from the Langmuir model as  $200 \text{ mg}\cdot\text{g}^{-1}$ , which is higher

than that comparing to the other adsorbent, magnetite/chitosan ( $55.8 \text{ mg.g}^{-1}$ ), acid activated carbon ( $71 \text{ mg.g}^{-1}$ ) or nano iron oxide impregnated in chitosan bead ( $69.8 \text{ mg.g}^{-1}$ ).



**Figure 3.** (a) Langmuir plot and (b) Freundlich plot for Cr(VI) adsorption onto FGC surface.

### 3.4. Regeneration of FCGs adsorbent

After Cr(VI) adsorption, FCGs can be recovered from working solution using an external magnet (Fig. 2b). Then, FCGs can be recycled using NaOH solution. To evaluate the recyclable of the FGC nanocomposite, we performed the desorption experiments. As can be seen in Fig. 2c, the sorption capacity of Cr(VI) ions decreases with the increasing cycle number. After 6 cycles, the adsorbed efficient is about 75% of the first cycle (after 6 cycles,  $q_{\max} \sim 150 \text{ mg.g}^{-1}$ ).

## 4. CONCLUSIONS

In this work, we demonstrated a high potential for application of a FCGs nanocomposite used for a magnetically separable adsorbent for highly efficient Cr(VI) ion removal. The adsorption isotherms studies revealed that the adsorption process of Cr(VI) was fitted well with the Langmuir isotherm model and adsorption capacity of FCGs was found of  $200 \text{ mg.g}^{-1}$ . After 6<sup>th</sup> regenerate cycle, the adsorbed efficient of FCGs was still 75%, it can be concluded that the FCGs nanocomposite has a long-term stability and can be used as an excellent adsorbent for removal of Cr(VI) ions.

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# TỔNG HỢP, ĐẶC TRƯNG VẬT LIỆU $\text{Fe}_3\text{O}_4/\text{CHITOSAN}/\text{GRAPHENE}$ OXIDE NANOCOMPOSIT VÀ ỨNG DỤNG ĐỂ HẤP PHỤ INON Cr(VI)

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## TÓM TẮT

Nước thải từ công nghiệp mạ điện, công nghiệp khai thác mỏ, nung đốt các nhiên liệu hóa thạch... là nguồn gốc gây ô nhiễm Cr(III/VI). Cr(III/VI) có thể có mặt trong nước mặt và nước ngầm; trong đó Cr(III) ít độc hơn nhiều so với Cr(VI). Khi xâm nhập vào cơ thể Cr(VI) có thể làm kết tủa protein, các axit nucleic và ức chế hệ thống enzyme cơ bản. Cr(VI) chủ yếu gây các bệnh ngoài da như loét da, viêm da tiếp xúc, loét thủng màng ngăn mũi, viêm gan, viêm thận, ung thư phổi....Do đó việc loại bỏ Cr(VI) là rất cần thiết. Trong công trình này, chúng tôi đề xuất sử dụng vật liệu  $\text{Fe}_3\text{O}_4/\text{chitosan}/\text{graphene}$  oxide nanocomposit (FCGs) làm chất hấp phụ hiệu quả Cr(VI). FCGs là vật liệu hấp phụ có khả năng thu hồi, tái sinh và có dung lượng hấp phụ cao (200mg/g) nhờ vai trò của graphen oxid (GO). Cách tổng hợp, sử dụng và tái sinh FCG để hấp phụ Cr(VI) cũng được mô tả và thảo luận trong bài báo.

*Từ khóa:*  $\text{Fe}_3\text{O}_4/\text{chitosan}/\text{graphene}$  oxide nanocomposit, Cr(VI), hấp phụ, tái sinh, graphen oxid (GO).