Synthesis Fe₃O₄/Talc nanocomposite by coprecipitation-ultrasonication method and advances in hexavalent chromium removal from aqueous solution

Nguyen Thi Huong, Nguyen Ngoc Son and Vo Hoang Phuong
Institute of Chemistry and Materials, Hanoi, Vietnam

Cong Tien Dung
Department of Chemistry, Faculty of Basic Science, Hanoi University of Mining and Geology, Hanoi, Vietnam

Pham Thi Mai Huong
Faculty of Chemical Technology, Hanoi University of Industry, Hanoi, Vietnam

Le Thanh Son
Faculty of Chemistry, VNU University of Science, Hanoi, Vietnam

Abstract
The Fe₃O₄/Talc nanocomposite was synthesized by the coprecipitation-ultrasonication method. The reaction was carried out under a inert gas environment. The nanoparticles were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), fourier-transform infrared spectroscopy (FT-IR) and vibrating sample magnetometry techniques (VSM), the surface area of the nanoparticles was determined to be 77.92 m²/g by Brunauer-Emmett-Teller method (BET). The

Corresponding author:
Nguyen Thi Huong, Institute of Chemistry and Materials, 17 Hoang Sam, Cau Giay, Ha Noi, Viet Nam.
Email: nguyenhuong0916@gmail.com

Creative Commons CC BY: This article is distributed under the terms of the Creative Commons Attribution 4.0 License (https://creativecommons.org/licenses/by/4.0/) which permits any use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (https://us.sagepub.com/en-us/nam/open-access-at-sage).
kinetic data showed that the adsorption process fitted with the pseudo-second order model. Batch experiments were carried out to determine the adsorption kinetics and mechanisms of Cr(VI) by Fe₃O₄/Talc nanocomposite. The adsorption process was found to be highly pH-dependent, which made the material selectively adsorb these metals from aqueous solution. The isotherms of adsorption were also studied using Langmuir and Freundlich equations in linear forms. It is found that the Langmuir equation showed better linear correlation with the experimental data than the Freundlich. The thermodynamics of Cr(VI) adsorption onto the Fe₃O₄/Talc nanocomposite indicated that the adsorption was exothermic. The reusability study has proven that Fe₃O₄/Talc nanocomposite can be employed as a low-cost and easy to separate.

Keywords
Fe₃O₄/Talc nanocomposite, hexavalent chromium, kinetics, thermodynamics

Introduction

Chromium used for many applications in different industries, including alloy fabrication, corrosion protection of metals, paint, textile, tanning, electroplating (Sueker, 1964). Chromium discharged from these industries has caused serious pollution in the water environment. Chromium has five oxidation states (from +2 to +6) but three of them (Cr(0), Cr (III), Cr(VI)) are used commercially and present in the environment. The oxidation state of chromium affects its toxicity and mobility in aquatic media. In the aquatic environment, Chromium is found in predominantly two forms, trivalent chromium (Chromium (III) or Cr³⁺) which is nontoxic, less mobile and has a tendency to absorb to clays, sediments, organic matter, and hexavalent chromium, which is toxic, more mobile (Wilbur et al., 2000). According to WHO guidelines, the concentration of chromium in drinking water should not exceed 0.05 mg/l. IARC has classified chromium (VI) as carcinogenic (Group 1) and chromium (III) as noncarcinogen (Group 3) (WHO, 2003). There are many methods that used generally to remove chromium and other heavy metal from water (Mahmoodi et al., 2019; Mostafavi et al., 2019), such as adsorption (Chávez-Guajardo et al., 2015; Deveci and Kar, 2013), filtration (Gherasim et al., 2011; Jayalakshmi et al., 2012), precipitation [(Golbaz et al., 2014), ion exchang (Alvarado et al., 2013; Kalantari et al., 2014), electrochemical treatment (Malkoc et al., 2006). In recent years, nanotechnology is a practical approach in treating wastewaters, too. Among all these possible methods, those with cost-effective, environment-friendly and no further pollutant features are the favorites (Lofrano et al., 2017). The solid wastes could be used the development of new adsorbents, low – cost from biogenic sources (Badruddoza et al., 2013); waste materials from industry (Bhatnagar et al., 2011); locally available agricultural waste (Ligate and Mdoe, 2015). This adsorbent materials are capable of capturing heavy metal ions form aqueous solution. Such as nano Talc doped Fe₃O₄ materials, are many methods to produce the nano Fe₃O₄ materials such as coprecipitation (Jahanbakhsh et al., 2017; Wei et al., 2012), solvothermal reduction (Sun and Zeng, 2002; Vuong et al., 2015), polyol (Laurent et al., 2008), copolymer gels (Qi et al., 2011), electrochemical (Jouyandeh et al., 2019a; Jouyandeh et al., 2019b)), ... Maryam Jouyandeh (Jouyandeh et al., 2019c) et al. have electrochemically synthesized...
Zn$_3$Fe$_{3-x}$O$_4$ magnetic nanoparticles to apply in curing epoxy. Now, to stabilize liquid particles, increase the dispersity and increase the specific surface area, scientists use Talc [Mg$_3$Si$_4$O$_{10}$(OH)$_2$] coatings on the surface of Fe$_3$O$_4$ particles. Talc has a platy structure that consists of three layers, including a magnesium hydroxide layer sandwiched between two silicate layers. Adjacent layers are connected by weak van der Waals forces. The surface of talc powder has a large number of Mg-O, OH, Si-O-Si and O-Si-O bonds that will cooperate or complex with heavy metal ions in water or soil to immobilize them on the surface of talc powder (Wang et al., 2018). Talc has been studied as an adsorbent for heavy metals in both forms: unmodified and modified talc. M.E. Ossman et al. used talc powder as an adsorbent for removing Cr(VI) from water. The results showed that the adsorption fitted well with the Freundlich model, optimization conditions include pH = 4, a contact time of 70 minutes to reach equilibrium (Ossman et al., 2014). Recently, some studies have been done on Fe$_3$O$_4$/Talc nanomaterial. Kamyar Shameli et al. (Kalantari et al., 2013) prepared Fe$_3$O$_4$ nanoparticles in talc as substrate using an environmentally friendly process. Fe$_3$O$_4$ MNPs have a mean size of 1.95–2.59 nm on the talc layers. K. Kalantari et al. (Kalantari et al., 2014) prepared Fe$_3$O$_4$/talc nanocomposites and used them as adsorbents for removing Cu(II), Ni(II), Pb(II) ions in the aqueous system. In optimal conditions, removal time of 120 s, removal efficiency for Cu(II), Ni(II), Pb(II) are 72.15%, 50.23%, 91.35%, respectively. The adsorption kinetics comply with the pseudo-second order kinetic equation and the Langmuir isotherm fitted well with data of the adsorption process. Shalini Rajput et al. (Rajput et al., 2016) synthesized Fe$_3$O$_4$ nanoparticles and used them for aqueous Cr(VI) and Pb(II) removal. Sorption data abided by pseudo-second order kinetics. The adsorptions of Cr(VI) and Pb(II) are in good agreement with the Sips and Langmuir models, respectively. The maximum adsorption capacities were 34.87 mg/g for Cr(VI) ions and 53.11 mg/g for Pb$^{2+}$ ions at 45°C.

In Ultrasonic-assisted synthetic (Sonochemical synthesis) method, chemical reactions are facility due to the application of powerful ultrasound radiation (20 kHz–10 MHz). Sonochemistry generates small, hot bubbles that can achieve high temperature (5000–25,000 K), pressure of more than 1000 atmospheres and rate of cooling/heating that can exceed $10^{-11}$ K/s. These can break chemical bonds or produce chemical and physical effects that can be used for the production or modification of nanostructured materials (Qiao et al., 2011). Ultrasonic-assisted reaction produced the smaller size, purer and more dispersible nanomaterials (Jiang et al., 2012).

In this work, The Fe$_3$O$_4$/Talc nanocomposites were synthesized on the surface of talc layers in aqueous solution using Ferric chloride hexahydrate (FeCl$_3$.6H$_2$O), ferrous chloride tetrahydrate (FeCl$_2$.4H$_2$O), NH$_4$OH as the iron precursor and reduction agent and Talcum powder substrate (Mg$_3$Si$_4$O$_{10}$(OH)$_2$). Talcum powder (30–50 μm) for preparing the nanocomposite was supplied by Talcum powder Phu Tho-Viet Nam. The adsorption isotherm, kinetic of Cr(VI) ion onto Fe$_3$O$_4$/Talc nanocomposite produced from Talc (Phu Tho – Viet Nam) were studied.

**Materials and methods**

**Materials**

Ferric chloride hexahydrate (FeCl$_3$.6H$_2$O), ferrous chloride tetrahydrate (FeCl$_2$.4H$_2$O) and potassium dichromate (K$_2$Cr$_2$O$_7$) was purchased from Merck. The Talc – VietNam (particle
size ≤50 μm; density 2.4 g/cm³; main components include: SiO₂: 56.8%; MgO: 31.5%; Fe₂O₃: 3.5%). NH₄OH were obtained from Macklin-China, India. A stock solution of 1000 mg l⁻¹ Cr(VI) ions was made by dissolving 2.8289 g of K₂Cr₂O₇ in distilled water. The working solutions of desired concentrations were made by suitable dilution of the stock solution with distilled water. Deionized water was used for the preparation of all aqueous solutions.

**Synthesis of Fe₃O₄/Talc nanocomposite**

The material is synthesized by the coprecipitation-ultrasonication method on the talc layers in an inert atmosphere, with the 1:2 ratio of Fe²⁺/Fe³⁺. The Fe₃O₄/Talc nanocomposite was prepared by mixing FeCl₃.6H₂O and FeCl₂.4H₂O with a ratio of 2:1 into 100 ml of distilled water. Adding Talc to the solution and vigorously stirring by a magnetic stirrer for 120 minutes. The sonication of the reaction mixture was then performed by an ultrasonic probe (Sonics & materials – VCX500; 500 w, 20 kHz), 20 ml of 25–28% NH₃ solution was dropped gradually.

These procedures resulted in the formation of black precipitates of Fe₃O₄/Talc nanoparticles that was washed with distilled water several times until it reached the neutral pH, followed by washing twice with ethanol before dried in an oven at a temperature of 343 K. Figure 1 describes preparation process of the nanocomposite.

The structure of materials was characterized by X-ray diffraction patterns of the solid powders on a P'Pret Pro – PANalytical X-ray diffractometer at 1.8kW (40 mA/45 KV) using Cu Kα (λ = 1.5406 Å) radiation. FTIR spectra of the solid samples were recorded by KBr pellet method using a Bruker FTIR spectrometer. FESEM measurements were carried out using a Hitachi S-4800, EMAX operating at 20 keV. The minimal amount of solid sample was dispersed in ethanol and small drops were placed on an aluminium grid. The grid was dried from 1–2 h in a vacuum over at 40°C prior to the FESEM studies. Magnetic measurements of the solid samples were performed at room temperature (25°C) using a Magnet B-10 Vibrating sample magnetometer (VSM).

Nitrogen adsorption-desorption isotherms were performed at 77 K in Tristar 3000-Micromeritics equipment, USA, using the static adsorption procedure. Samples were degassed at 80°C and 10⁻⁶ Torr for minimum 12 h prior to analysis. BET surface areas were calculated from the linear part of BET plot according to IUPAC recommendation, pore size distributions of the samples were calculated via the conventional BJD model.

**Figure 1.** The procedure for preparation of Fe₃O₄/Talc nanocomposite.
**Batch adsorption procedure**

Hexavalent chromium (Cr(VI)) adsorption was evaluated by the batch method, which permits to determinate of influence of parameters on the adsorption process easily. The batch adsorption experiments were carried out to investigate the influence of major affecting parameters like adsorbent dosage, pH, contact time, initial hexavalent chromium concentration and temperature on the amount of adsorption capacity. In the batch method, a fixed quantity of Fe₃O₄/Talc nanocomposite is mixed continuously with a specific volume of Cr (VI) solution and constantly shakened at 303 ± 1 K, until the equilibrium was reached. The contents in the flask were shaken in incubator Orbital shaker (OXYOS) at 120 r.min⁻¹. After shaking, the solutions were filtered through a Whatman No. 42 filter paper. The filtrate was collected in polyethylene tubes and diluted before analysis. During the study, the adsorbent dosage varied from 0.5 to 6.0 g.l⁻¹, pH from 4.0 to 9.0, the initial Cr(VI) concentration from 10 to 30 mg.l⁻¹, the temperature from 293 to 313 K and the contact time from 0 to 120 min. The pH of Cr(VI) solution was adjusted using either 0.1 N HCl or 0.1 N NaOH solutions to the required value.

For adsorption isotherms, a series of 100-ml flask glass were filled with 50 mL Cr(VI) solution of varying concentrations (10–30 mg.l⁻¹), maintained at the desired temperature and pH. After the amount of Fe₃O₄/Talc nanocomposite used for Cr(VI) solutions was 2.0 g.l⁻¹. The optimum uptake time 60 min the concentrations of chromium ion was calculated by taking the difference in their initial and final concentrations. In each experiment constant shaking of the solution was performed by using a shaker. All the experiments were repeated three times and average values were reported. The standard deviation was found to be ±2.0%.

Thermodynamic studies of Cr(VI) adsorption onto the Fe₃O₄/Talc nanocomposite were also carried out at three temperatures (297, 303 and 313 K). Kinetic studies of adsorption by Fe₃O₄/Talc nanocomposite were also carried out at four initial chromium concentrations from 10 to 25 mg.l⁻¹ at 303 K where in the extent of adsorption was analyzed at regular time intervals.

**Analysis of Cr(VI) ions**

The concentration of Cr(VI) ions in the sample was determined by UV visible spectrophotometer with GENESYS 10S UV-Vis using 1,5-Diphenylcarbazide in acidic solution (H₃PO₄). The absorbance of the purple colored complex was measured at 540 nm wavelength (Clesceri et al., 1998).

Adsorption capacity of Fe₃O₄/Talc nanocomposite was calculated by the formula (Ngah and Fatinathan, 2010):

\[
q = \frac{(C_0 - C_t) \cdot V}{m}
\]  

(1)

Where, q is the amount of Cr(VI) ion adsorbed per unit mass of adsorbent (mg.g⁻¹), V is the volume of solution (l); m is the mass of adsorbent (g); C₀, C₄ are Cr(VI) concentrations in the initial solution and at time t respectively (mg.l⁻¹).

The Cr(VI) ion removed by adsorbent was calculated by the formula:
\[
\% R = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]  

(2)

R is the percentage of Cr(VI) adsorbed by Fe₃O₄/Talc nanocomposite and Cₑ is Cr(VI) equilibrium concentrations (mg.l⁻¹).

**Results and discussion**

**Characterization of Fe₃O₄/Talc nanocomposite**

The resulted brown-black precipitate can be attracted by a permanent magnet (Figure 1) that proved the formation of Fe₃O₄ crystals onto Talc. Characterization of the material reveals X-ray, FESEM-EDX, BET, FT-IR and VSM measurements. The X-ray patterns (a) and FT-IR (b) of synthesized material are shown in Figure 2.

Figure 2(a) depicts the powder X-ray diffraction (XRD) patterns of the Talc substrates and Fe₃O₄/Talc nanocomposite samples. The position and relative intensity of all diffraction peaks in both XRD patterns are fully matched. The peaks related to talc are observed at \(2\theta = 34.41°\), 36.10°, 40.53°, 42.69°, 48.61°, 54.52°, 60.46°, 66.48°, 70.04° and 72.39°.

The Fe₃O₄/Talc nanocomposite samples, all diffraction peaks were in agreement with the standard card of Fe₃O₄ (00–072-2303). It is worth noting that the main peak (311) of Fe₃O₄/Talc nanocomposite samples is clearly the characteristic peak of magnetite (Daou et al., 2006). However, all the peak positions at 18.2 (111), 35.4 (311), 57.2 (511) and 62.6 (440) are consistent with the standard X-ray data for the magnetite phase of the Fe₃O₄/Talc nanocomposite. The change in the d spacing of Talc after interaction with Fe₃O₄ nanoparticles is negligible and these signify that the nanoparticles are on the external surface of the Talc (Kalantari et al., 2013). Figure 2 showed that, the original d-spacing (ds) of Talc at \(2\theta = 9.35\) degrees was 0.95 nm, which gradually decreased to 0.91 nm at \(2\theta = 9.50\) degrees by the formation of Fe₃O₄ nanoparticles on the surface of Talc layers.

Figure 2(b) shows the FT-IR spectra of Talc substrate and Fe₃O₄/Talc nanocomposite samples. There are three obvious peaks at 3633, 3429–34,271,630 cm⁻¹ and 450–669 cm⁻¹ in

![Figure 2](image-url)

**Figure 2.** X-ray patterns (a) and FT-IR (b) of Talc and Fe₃O₄/Talc nanocomposite.
the spectrum of Talc and the synthesized nanoparticles. The peaks basically represent the vibrations of Mg-OH, O-H stretching, H-O-H bending and Mg-O, Si-O-Mg, Si-O, respectively (Kalantari et al., 2013; Li et al., 2015). However, the peak areas of Mg-O bonds (451 cm\(^{-1}\)), Si-O-Mg bonds (529 cm\(^{-1}\)) and Si-O (669 cm\(^{-1}\)) were all decreased in the spectrum of Fe\(_3\)O\(_4\)/Talc nanocomposite. It is because the ordering and bonding effects were influenced in the layer structure, since some of the Mg-O bonds were broken with radiant energy from the microwave synthesis system, making the binding force weaken in the interlayer. Finally, the Mg\(^{+}\) and Si-O\(^{-}\) were exhibited [Li S-F et al., 2015]. The peak at 580 cm\(^{-1}\) in the spectrum of Fe\(_3\)O\(_4\)/Talc nanocomposite was attributed to Fe-O stretch vibrations of nano Fe\(_3\)O\(_4\) (Willis et al., 2005), confirming the nature of the iron oxide nanoparticles. These FT-IR and X-ray results imply that the nanoparticles were synthesis successful.

The surface properties, porosity or pore size is one of the factors to evaluate the adsorption capacity of the material. Figure 3 is the FESEM image, BET and VMS of Fe\(_3\)O\(_4\)/Talc nanocomposite.

Figure 3(a) showed the Talc surface material has particle sizes in the range of 30–50 \(\mu\)m, cubic particles are less uniform and have smooth surface. Nanocomposite materials at different magnifications, had distribution of Fe\(_3\)O\(_4\) nanoparticles with dimensions less than 30 nm. Then, the synthetic nanocomposite material will give a larger surface area than the base material, which will be shown through the measurement of specific surface area by BET.

Figure 3(b) showed the Fe\(_3\)O\(_4\)/Talc nanocomposite samples which give adsorption-desorption isotherm of the intermediate form between III and IV with the appearance of H3 hysteresis loop, rod-shaped and letter-shaped according to IUPAC classification (Thommes et al., 2015). This allows the prediction that synthetic nanocomposite materials contain both macropores and mesopores, in which mesopores are more numerous. The pore size distribution obtained from the BJH analysis, the BJH curve shows narrow and intensity peaks in the pore size distribution curve. The hole size distribution curve shows that appear

![Figure 3](image-url)
in a range 1 to 150 nm. The specific surface area of talc surface material is 3.45 m².g⁻¹ which is much smaller than that of the nanocomposite material, which reaches 77.92 m².g⁻¹. In particular, macropore area of the nanocomposite \( S_{\text{macro}} = S_{\text{BET}} - S_{\text{BJH,ads}} - S_{\text{micro}} = 8.27 \text{ m}^2. \text{g}^{-1} \); the pore diameter averages 11.8 nm. A similar types of Fe₃O₄ nanocomposite were also reported by some other workers (Chávez-Guajardo et al., 2015; Cui et al., 2015).

The magnetic properties of materials are assessed by the method of vibrating-sample magnetometry. The results of saturation magnetization of Fe₃O₄/Talc nanocomposite was 38.06 emu.g⁻¹, this indicates that the survey sample is superparamagnetic, the iron oxide particles are distributed with nano size on the soluble surface. Therefore, the material is convenient to separate from the aqueous solution after adsorption with the help of external magnetic fields (Lv et al., 2014).

### Adsorption studies

**Effect of pH:** One of the most influential factors on Cr(VI) removal is the pH of the solution, which influences on the properties of the adsorption process. In this experiment, the initial of Cr(VI) was 10 and 20 mg.l⁻¹; the initial pH values of the adsorption solution were adjusted in the range of 4 to 9; the contact time was 60 min. The amount of Cr(VI) adsorbed depends on the distribution of \( \text{Cr}_2\text{O}_7^{2-}, \text{HCrO}_4^- \), and \( \text{CrO}_4^{2-} \) which are controlled by pH of the solution. In acidic medium, Cr(VI) exists in the form of oxyanions such as \( \text{HCrO}_4^- \) (pKₐ 0.8), \( \text{Cr}_2\text{O}_7^{2-} \) (pKₐ 1.52), \( \text{CrO}_4^{2-} \) (pKₐ 6.5). The lowering of pH causes the surface of the adsorbent to be protonated to a higher extent, a strong attraction exists between these oxyanions of Cr(VI) and the positively charged surface of the adsorbent (Dubey and Gopal, 2007; Gupta et al., 2010). Hence, the uptake increases with increasing pH from 4.0 to 6.0 of the solution. At high pH, there will be abundance of negatively charged hydroxyl ions in aqueous solution, causing hindrance between negatively charged ions \( \text{Cr}_2\text{O}_7^{2-}, \text{CrO}_4^{2-}, \ldots \) and negatively charged adsorbent, resulting in a decrease of adsorption (Dubey and Gopal, 2007; Gupta et al., 2010). However, the survey process was carried out from pH = 4 to pH = 9 because, at points of pH less than 4, the dissolution of Fe₃O₄ nanoparticles occurs (Iram et al., 2010). Figure 4 describes the effect of pH on the adsorption of Cr(VI) on the Fe₃O₄/Talc nanocomposite at 303 K. Figure 4 showed equilibrium chromium sorption which was suitable by acidic of 4.0–5.5.

![Figure 4. Effect of pH (adsorbent dosage = 0.1 g/100 ml; [Cr(VI)] = 10 and 20 mg/l; t = 60 min; agitation 120 rpm).](image-url)
Effect of contact time: Figure 5 shows the comparative data of the effect of contact time on the extent of adsorption of Cr(VI) on the Fe₃O₄/Talc nanocomposite at 10, 15, 20 and 25 mg.l⁻¹ initial chromium concentration at pH 5.0 and temperature 303 K. It has been observed that the metal adsorption rate is high at the beginning and then increases slowly till saturation levels were completely reached at the equilibration point of 60 minutes. In the

**Figure 5.** Effect of contact time (adsorbent dosage = 0.1 g/10 ml; pH = 5.0; agitation 120 rpm).

**Figure 6.** Effect of adsorbent dosage ([Cr(VI)] = 10 mg/l; t = 60 min; agitation 120 rpm, pH = 5.0, T = 303 K).
study, the data were further used to successfully evaluate the kinetics of the adsorption process.

Effect of sorbent dosage: In this study, to determine the effect of adsorbent dosage, different amounts from 0.05 to 5 g.l\(^{-1}\) of adsorbent were suspended in 50 ml chromium solution and at pH 5.0, 303 K. The effects of adsorbent dosage on the amount of Cr(VI) adsorbed and extent of removal Cr(VI) for the adsorbent are shown in Figure 6. Figure 6 showed that, the extent of Cr(VI) removal was 24% for 0.5 g.l\(^{-1}\) of adsorbent and 68% for 2 g.l\(^{-1}\) of adsorbent. However, it has been observed that there was only a slow change in the extent of Cr(VI) adsorption for Fe\(_3\)O\(_4\)/Talc nanocomposite, when the adsorbent dose was over 2 g.l\(^{-1}\). At a low dose, all types of sites are entirely exposed and the adsorption on the surface is saturated faster, showing a higher capacity adsorption value. At a higher adsorbent dose, the availability of higher energy sites decreases with a larger fraction of lower energy sites occupied, resulting in a lower capacity adsorption value. Thus, all the experiment was selected 2 g.l\(^{-1}\) as sorbent dosage.

Effect of Cr(VI) concentration: In this study, to determine the effect of Cr(VI) concentration, different initial of Cr(VI) from 10 to 30 g.l\(^{-1}\) of solution adsorption at pH 5.0 and temperature 303 K. The effects of Cr(VI) concentration on the amount of Cr(VI) adsorbed and extent of removal Cr(VI) for the adsorbent are shown in Figure 7.

Figure 7 showed that, the \(q_e\) increases from 4.45 to 7.17 mg.g\(^{-1}\) and removal efficiency decreases from 89.13 to 47.86%, respectively Cr(VI) initial concentration increases from 10 to 30 mg.l\(^{-1}\). When, higher initial concentrations, the active sites of prepared adsorbent would be surrounded with more Cr(VI) ions in the solution, the equilibrium adsorption capacity of Fe\(_3\)O\(_4\)/Talc nanocomposite increases with the increase of the Cr(VI) ion concentration which enhances the adsorption process. In addition, the removal percentage decreases by the increase in metal initial concentration. At low initial concentrations, the ratio of initial number of chromium ions to the accessible active sites of adsorbent is low; therefore, the removal efficiency of Cr(VI) is higher and at higher
concentrations, further residual Cr(VI) ions remain in the aqueous solution (Radnia et al., 2012; Aydin et al., 2008).

**Adsorption isotherm modeling**

To understand the adsorption mechanism and surface characteristics of the Fe₃O₄/Talc nanocomposite, the mathematical models developed by Langmuir and Freundlich have been applied to the data. The linear equations of Langmuir and Freundlich isotherm models can be described as equation (3) (Ossman et al., 2014).

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}}
\]

where \(C_e\) is the concentration of Cr (VI) ion (mg/L) at equilibrium, \(q_{\text{max}}\) is the monolayer capacity of the adsorbent (mg/g) and \(K_L\) is the Langmuir sorption constant (L/mg). The plot of \(C_e/q_e\) versus \(C_e\) was given as a straight line (Figure 8) and the values of \(q_{\text{max}}\) and \(K_L\) can be calculated from the slope and intercept of the plot.

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Where \(C_e\) is the equilibrium concentration (mg/L), \(K_F\) is a roughly indicator of the adsorption capacity and \(n\) is an empirical parameter. The plot of the \(\log q_e\) versus \(\log C_e\) gives a straight line (Figure 8) and \(K_F\) and \(n\) values are calculated from the intercept and slope of this straight line.

The related values of parameters and constants for these isotherms are presented in Table 1. The values of regression coefficient obtained from these models were used as the fitting criteria to find out these isotherms.

Table 1 showed both plots depicted the linearized form of the isotherms at all temperatures and extremely high correlation coefficients (\(R^2 = 0.97\) to 0.99), thus indicating both monolayer and heterogeneous surface conditions. Also, from the Langmuir adsorption constant \(q_e\), the adsorption capacity of Cr(VI) on Fe₃O₄/Talc nanocomposite was observed.

![Figure 8](image-url)  

Figure 8. Langmuir isotherm and Freundlich isotherm (adsorbent dosage = 0.1 g/100 ml; pH 5.0; \(t = 60\) min; agitation 120 rpm).
as 7.17, 7.47 to 35.84 mg.g$^{-1}$ with the rise in temperature from 293, 303 to 313 K, respectively. This result also showed that the value of $R_L$, and the separation factor fell in the range of 0 to 1 which clearly showed that the adsorption process is favorable. Freundlich constant also varied from 1 to 10 which again proved that the adsorption is favorable. At pH = 5, the existence of Cr(VI) in solution was HCrO$_4$ (Dubey and Gopal, 2007; Gupta et al., 2010). So, the formation and mechanism for the adsorption of Cr(VI) onto Fe$_3$O$_4$/Talc nanocomposite was described at Figure 9.

Table 2 compares maximum adsorption capacities and rate of removal obtained in this study with some other values reported in the article The adsorption capacity for Cr(VI) using Fe$_3$O$_4$/Talc nanocomposite, a low-cost adsorbent from the fertilizer industry. The adsorption capacity for Cr(VI) of Fe$_3$O$_4$/Talc nanocomposite is of the same order of magnitude has been found using similar adsorbents.

Table 1. Langmuir and Freundlich isotherm constants for the adsorption of Cr(VI) on Fe$_3$O$_4$/Talc nanocomposite at different temperatures and pH 5.0.

| Temperature (K) | Langmuir isotherm | Freundlich isotherm |
|----------------|-------------------|---------------------|
|                | $R^2$ | $K_L$ | $q_{max}$ | $R_L$ | $R^2$ | $K_F$ | $n$ |
| 293 K          | 0.9958 | 0.81 | 7.17 | 0.10–0.25 | 0.9933 | 1.99 | 6.05 |
| 303 K          | 0.9907 | 0.30 | 7.47 | 0.04–0.11 | 0.9782 | 4.39 | 5.93 |
| 313 K          | 0.9740 | 0.05 | 35.84 | 0.33–0.67 | 0.9902 | 3.77 | 1.28 |

Figure 9. Illustration of the prepared Fe$_3$O$_4$/Talc nanocomposite and mechanism for the adsorption of Cr(VI) onto Fe$_3$O$_4$/Talc nanocomposite.
Adsorption kinetics

Kinetics of the adsorption process is studied based on the pseudo-first-order adsorption kinetics equation (B1) in linear form:

\[ \ln (q_e - q_t) = \ln (q_e) - k_1 \cdot t \]

(5)

where: \( k_1 \) (min\(^{-1}\)) is the rate constant of the pseudo-first-order adsorption kinetics process; \( q_e, q_t \) (mg/g) are the adsorption capacities at the equilibrium time and time \( t \). The pseudo-second-order adsorption kinetics equation in linear form:

\[ \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 \cdot q_e^2} \]

(6)
Where: $k_2$ (mg/g.min) is the rate constant of the adsorption kinetics process (Ho, 1995; Yuh-Shan, 2004). Intraparticle diffusion kinetic equation:

$$\ln(q_t) = \ln(k_D) + 0.5 \ln(t)$$

(7)
where: \( k_D \) (mg/g.(min)\(^{0.5}\)) is the diffusion coefficient (Ge and Li, 2011). Elovich equation:

\[
q_t = \frac{1}{b} \ln(a) + \frac{1}{b} \ln(t)
\]

(8)

where: \( a \) and \( b \) are constants of Elovich – type equation (Thajeel, 2013). The adsorption rate constant \( k_1, k_2, k_D, \alpha, \beta \) for Cr(VI) was calculated from the slope of the linear plot of \( \ln(q_e - q_t) \) versus time, plot between \( t/q_t \) against \( t \), and plot of \( \ln(q_t) \) versus \( \ln(t) \), plot between \( q_t \) against \( \ln(t) \) as shown in Figure 10. The kinetic rate constants obtained form pseudo-first- and -second-order, diffusion kinetic, elovich equations are given in Table 3.

Table 3 showed the values of correlation coefficient \( R^2 \) for the Pseudo-second-order adsorption model which is relatively high (\( R^2 > 0.999 \)), furthermore, the values of the \( k \) constant are almost unchanged, which indicates that the speed constant does not depend on concentration. This proves that the adsorption process depends on the number of adsorption centers on the surface and the adsorbate is the Cr(VI) ion.
**Thermodynamic study**

In this study, the thermodynamics of adsorption of Cr(VI) onto Fe₃O₄/Talc nanocomposite, thermodynamic constants such as: enthalpy change $\Delta H^o$, free energy change $\Delta G^o$ and entropy change $\Delta S^o$ can be related to the Langmuir isotherm constant by the following equations (Gupta et al., 2004).

$$\Delta G^o = -RT \ln(K_L)$$  \hspace{1cm} (9)

$$\ln(K_L) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R.T}$$  \hspace{1cm} (10)

Thus, a plot of $\ln(K_L)$ versus $1/T$ should be a straight line. $\Delta H^o$ and $\Delta S^o$ values could be obtained from the slope and intercept of this plot. The values of these parameters are given in Table 4. Figure 11 show thermodynamic data of adsorption of Cr(VI) onto Fe₃O₄/Talc nanocomposite.

Table 4 showed that the values of $\Delta H^o$ $(-105.804 \text{ kJ/mol})$ is negative. And it also indicate that the adsorption is the process of chemical adsorption and the process is exothermic. The negative values of $\Delta S^o$ $(-0.362 \text{ kJ/mol})$ indicate that there is a decrease in the degree of freedom of the adsorbed. The positive $\Delta G^o$ value corresponds, showed that the instability activation complex of the adsorption reaction is increased with increasing temperature (Zhang et al., 2012).

**Conclusion**

The Fe₃O₄/Talc nanocomposite was synthesized with the Talcum powder Phu Tho – Viet Nam by the coprecipitation-ultrasonication method. X-ray, FTIR, FESEM, BET and VSM analyses were performed for characterizing the synthesized nanocomposite. The surface area of the nanoparticles was determined to be $77.92 \text{m}^2\text{g}^{-1}$ with an average diameter of 11.8 nm and the saturation magnetization of 38.06 emu.g$^{-1}$. The peak positions at 18.2 (111), 35.4 (311), 57.2 (511) and 62.6 (440) are consistent with the standard X-ray data for the magnetite phase of the Fe₃O₄/Talc nanocomposite. The original d-spacing (ds) of talc at 2$\theta$ 9.35 degrees was 0.95 nm, and 0.91 nm at 2$\theta$ 9.50 degrees by the formation of Fe₃O₄ nanoparticles on the surface of Talc layers. The peak at 580 cm$^{-1}$ in the spectrum of Fe₃O₄/Talc nanocomposite was attributed to Fe-O stretch vibrations, confirming the nature of the iron oxide nanoparticles. These FT-IR and X-ray results imply that the nanoparticles were synthesis successful.

The batch studies experimental results indicate that the Fe₃O₄/Talc nanocomposite is an effective adsorbent of Cr(VI) ion from the aqueous solution. The adsorption equilibrium data fitted very well to the Langmuir and Freundlich adsorption isotherm models. The kinetic data showed that the adsorption process followed the pseudo-second order kinetic model. The maximum adsorption capacities of 35.84 mg/g occurred at pH 5.0 and 313 K, with adsorption dosage is 2 g.l$^{-1}$. The adsorption is the process of chemical and exothermic. These results permit us to conclude that Fe₃O₄/Talc nanocomposite is a promising low-cost adsorbent for Cr(VI) removal from wastewater and can be applied in a magnetically-assisted water treatment technology.
Declaration of Conflicting Interests
The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding
The author(s) received no financial support for the research, authorship, and/or publication of this article.

ORCID iDs
Nguyen Thi Huong https://orcid.org/0000-0003-2716-936X
Nguyen Ngoc Son https://orcid.org/0000-0001-7772-059X
Cong Tien Dung https://orcid.org/0000-0002-7703-3092

References
Alvarado L, Torres IR and Chen A (2013) Integration of ion exchange and electrodeionization as a new approach for the continuous treatment of hexavalent chromium wastewater. *Separation and Purification Technology* 105: 55–62.
Aydin H, Bulut Y and Yerlikaya Ç (2008) Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *Journal of Environmental Management* 87(1): 37–45.
Bhatnagar A, Vilar VJ, Botelho CM, et al. (2011) A review of the use of red mud as adsorbent for the removal of toxic pollutants from water and wastewater. *Environmental Technology* 32(3–4): 231–249.
Chávez-Guajardo AE, Medina-Llamas JC, Maqueira L, et al. (2015) Efficient removal of Cr (VI) and Cu (II) ions from aqueous media by use of polypyrrole/maghemite and polyaniline/maghemite magnetic nanocomposites. *Chemical Engineering Journal* 281: 826–836.
Clesceri LC, Greenberg AE and Eaton AD (1998) *Standard Methods for the Examination of Water and Wastewater*. 20th ed. Washington: American Public Health Association.
Cui L, Guo X, Wei Q, et al. (2015) Removal of mercury and methylene blue from aqueous solution by xanthate functionalized magnetic graphene oxide: Sorption kinetic and uptake mechanism. *Journal of Colloid and Interface Science* 439: 112–120.
Daou T, Pourroy G, Bégin-Colin S, et al. (2006) Hydrothermal synthesis of monodisperse magnetite nanoparticles. *Chemistry of Materials* 18(18): 4399–4404.
Deveci H and Kar Y (2013) Adsorption of hexavalent chromium from aqueous solutions by bio-chars obtained during biomass pyrolysis. *Journal of Industrial and Engineering Chemistry* 19(1): 190–196.
Dubey SP and Gopal K (2007) Adsorption of chromium (VI) on low cost adsorbents derived from agricultural waste material: A comparative study. *Journal of Hazardous Materials* 145(3): 465–470.
Ge P and Li F (2011) Kinetics and thermodynamics of heavy metal Cu (II) adsorption on mesoporous silicates. *Polish Journal of Environmental Studies* 20: 339–344.
Gherasim C-V, Bourceanu G, Olariu R-I, et al. (2011) A novel polymer inclusion membrane applied in chromium (VI) separation from aqueous solutions. *Journal of Hazardous Materials* 197: 244–253.
Golbaz S, Jafari AJ, Rafiee M, et al. (2014) Separate and simultaneous removal of phenol, chromium, and cyanide from aqueous solution by coagulation/precipitation: Mechanisms and theory. *Chemical Engineering Journal* 253: 251–257.
Gupta V, Mittal A, Krishnan L, et al. (2004) Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Separation and Purification Technology* 40(1): 87–96.
Gupta VK, Rastogi A and Nayak A (2010) Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *Journal of Colloid and Interface Science* 342(1): 135–141.

Ho Y-S (1995) *Absorption of Heavy Metals From Waste Streams by Peat.* Birmingham: University of Birmingham.

Iram M, Guo C, Guan Y, et al. (2010) Adsorption and magnetic removal of neutral red dye from aqueous solution using Fe3O4 hollow nanospheres. *Journal of Hazardous Materials* 181(1–3): 1039–1050.

Jahanbakhsh A, Pirsa S and Bahram M (2017) Synthesis and characterization of magnetic nanocomposites based on hydrogel-Fe3O4 and application to remove of organic dye from waste water. *Main Group Chemistry* 16(2): 85–94.

Jayalakshmi A, Rajesh S, Senthilkumar S, et al. (2012) Epoxy functionalized poly(ether-sulfone) incorporated cellulose acetate ultrafiltration membrane for the removal of chromium ions. *Separation and Purification Technology* 90: 120–132.

Jiang H-M, Yan Z-P, Zhao Y, et al. (2012) Zincon-immobilized silica-coated magnetic Fe3O4 nanoparticles for solid-phase extraction and determination of trace lead in natural and drinking waters by graphite furnace atomic absorption spectrometry. *Talanta* 94: 251–256.

Jouyandeh M, Ali JA, Aghazadeh M, et al. (2019a) Curing epoxy with electrochemically synthesized ZnxFe3-xO4 magnetic nanoparticles. *Progress in Organic Coatings* 136: 105246.

Jouyandeh M, Ganjali MR, Ali JA, et al. (2019b) Curing epoxy with electrochemically synthesized MnxFe3-xO4 magnetic nanoparticles. *Progress in Organic Coatings* 136: 105199.

Jouyandeh M, Ganjali MR, Ali JA, et al. (2019c) Curing epoxy with polyethylene glycol (PEG) surface-functionalized GdxFe3-xO4 magnetic nanoparticles. *Progress in Organic Coatings* 137: 105283.

Kalantari K, Ahmad M, Masoumi H, et al. (2014) Rapid adsorption of heavy metals by Fe3O4/talc nanocomposite and optimization study using response surface methodology. *International Journal of Molecular Sciences* 15(7): 12913–12927.

Kalantari K, Ahmad MB, Shameli K, et al. (2013) Synthesis of talc/Fe3O4 magnetic nanocomposites using chemical co-precipitation method. *International Journal of Nanomedicine* 8: 1817–1823.

Laurent S, Forge D, Port M, et al. (2008) Magnetic iron oxide nanoparticles: Synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. *Chemical Reviews* 108(6): 2064–2110.

Li S-F, Yang S-C, Zhao S-L, et al. (2015) Microwave and acid-modified talc for the adsorption of methylene blue in aqueous solution. *Journal of the Serbian Chemical Society* 80(4): 563–574.

Ligate FJ and Mdoe JE (2015) Removal of heavy metal ions from aqueous solution using rice husks-based adsorbents. *Tanzania Journal of Science* 41: 90–102.

Lozano G, Libralato G and Brown J (2017) *Nanotechnologies for Environmental Remediation.* Berlin: Springer.

Lv X, Xue X, Jiang G, et al. (2014) Nanoscale zero-valent iron (nZVI) assembled on magnetic Fe3O4/graphene for chromium (VI) removal from aqueous solution. *Journal of Colloid and Interface Science* 417: 51–59.

Mahmoodi NM, Roudaki MSMA, Didehban K, et al. (2019) Ethylenediamine/glutaraldehyde-modified starch: a bioplatform for removal of anionic dyes from wastewater. *Korean Journal of Chemical Engineering* 36(9): 1421–1431.

Malkoc E, Nuhoglu Y and Dundar M (2006) Adsorption of chromium (VI) on pomace – An olive oil industry waste: Batch and column studies. *Journal of Hazardous Materials* 138(1): 142–151.

Mostafavi S, Rezaevidinejad V and Pirsa S (2019) Design and fabrication of nanocomposite-based polyurethane filter for improving municipal waste water quality and removing organic pollutants. *Adsorption Science & Technology* 37(1–2): 95–112.
Ngah WSW and Fatinathan S (2010) Adsorption characterization of Pb (II) and Cu (II) ions onto chitosan-tripolyphosphate beads: Kinetic, equilibrium and thermodynamic studies. *Journal of Environmental Management* 91(4): 958–969.

Ossman M, Mansour M and Fattah M (2014) Peanut shells and talc powder for removal of hexavalent chromium from aqueous solutions. *Bulgarian Chemical Communications* 3: 629–639.

Qi H, Yan B, Lu W, et al. (2011) A non-alkoxide sol-gel method for the preparation of magnetite (Fe₃O₄) nanoparticles. *Current Nanoscience* 7(3): 381–388.

Qiao SZ, Liu J and Qing Lu G (2011) Chapter 21 – Synthetic chemistry of nanomaterials. In: Xu R, Pang W and Huo Q (eds) *Modern Inorganic Synthetic Chemistry*. Amsterdam: Elsevier, pp.479–506.

Radnia H, Ghoreyshi AA, Younesi H, et al. (2012) Adsorption of Fe (II) ions from aqueous phase by chitosan adsorbent: Equilibrium, kinetic, and thermodynamic studies. *Desalination and Water Treatment* 50(1–3): 348–359.

Rajput S, Pittman CU and Mohan D (2016) Magnetic magnetite (Fe₃O₄) nanoparticle synthesis and applications for lead (Pb²⁺) and chromium (Cr⁶⁺) removal from water. *Journal of Colloid and Interface Science* 468: 334–346.

Sani HA, Ahmad MB and Saleh T (2016) Synthesis of zinc oxide/talc nanocomposite for enhanced lead adsorption from aqueous solutions. RSC Advance, 6: 108819–108827.

Sueker JK (2005) Chromium. *Environmental Forensics* 5: 81–95.

Sun S and Zeng H (2002) Size-controlled synthesis of magnetite nanoparticles. *Journal of the American Chemical Society* 124(28): 8204–8205.

Thaheel AS (2013) Isotherm, kinetic and thermodynamic of adsorption of heavy metal ions onto local activated carbon. *Aquatic Science and Technology* 1: 53–77.

Thommes M, Kaneko K, Neimark AV, et al. (2015) Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). *Pure and Applied Chemistry* 87(9–10): 1051–1069.

Vuong TKO, Le TL, Pham DV, et al. (2015) Synthesis of high-magnetization and monodisperse Fe₃O₄ nanoparticles via thermal decomposition. *Materials Chemistry and Physics* 163: 537–544.

Wang Y, Lin H, Lin Z, et al. (2018) Application and prospect of talc as heavy metal passivation agent. *IOP Conference Series: Materials Science and Engineering* 392: 032029.

Wei Y, Han B, Hu X, et al. (2012) Synthesis of Fe₃O₄ nanoparticles and their magnetic properties. *Procedia Engineering* 27: 632–637.

WHO (2003) Chromium in drinking-water: Background document for development of WHO guidelines for drinking-water quality. Available at: WHO/SDE/WSH/03.04/04

Wilbur S, Ingerman L, Citra M, et al. (2000) Toxiological Profile for Chromium. USA: US Department of Health and Human Services, *Public Health Service, Agency for Toxic Substances Disease Registry*, pp.1–419.

Willis AL, Turro NJ and O’Brien S (2005) Spectroscopic characterization of the surface of iron oxide nanocrystals. *Chemistry of Materials* 17(24): 5970–5975.

Yuh-Shan H (2004) Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* 59(1): 171–177.

Zhang D, Ma Y, Feng H, et al. (2012) Adsorption of Cr (VI) from aqueous solution using carbon-microsilica composite adsorbent. *Journal of the Chilean Chemical Society* 57(1): 964–968.