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REMOVAL OF Cr(III) FROM AQUEOUS SOLUTION BY LOW-COST Fe_3O_4 /TALC NANOCOMPOSITE

Abstract. The Fe_3O_4 /Talc nanocomposite was synthesized by using the chemical co-precipitation method. The reaction was carried out under a nonoxidizing oxygen-free environment. The Cr^{3+} adsorption by Fe_3O_4 /Talc nanocomposite was carried out in batch conditions. The kinetic data of the adsorption reactions were described by pseudo-first-order and pseudo-second-order equations and intraparticle diffusion models. Results showed that the pseudo-order was fitted to the kinetic data. The isotherms of adsorption were also studied using Langmuir and Freundlich equations in linear forms. It found that the Langmuir equation showed better linear correlation with the experimental data than the Freundlich. The maximum monolayer coverage, q_{max} at 297 K were found to be 54.35 mg/g.

Keywords: nanocomposite, Langmuir and Freundlich equations, cleaning of drains.

1. Introduction

Heavy metal ions pollutants exist in the aqueous has increased over the last some decades due to industrial. In which, Cr is widely used in industry as plating, alloying, tanning of animal hides, inhibition of water corrosion, textile dyes and mordants, pigments, ceramic glazes, refractory bricks, ... [1]. Due to this wide anthropogenic use of Cr, the consequential environmental contamination increased and has become an increasing concern in the last years [2]. The toxic ions enter the food chain and then the human body [3]. Water pollution by heavy metals is one of the most serious threat to public health and the environment. Because heavy metals are non-biodegradable and are more difficult to remediate [4]. Some in place treatment technologies are mainly based on physico-chemical, electrochemical or advanced oxidation processes. Physicochemical processes include membrane filtration, chemical precipitation, ion-exchange, and adsorption. Electrocoagulation, electroflotation, and electrodeposition are categorized under the name of electrochemical methods [5]. Recently, nanotechnology is a practical approach in treating wastewaters, too. Among all these possible methods, those with cost-effective, environment-friendly and no further pollutants features are the favorites [6].

In recent years, the use of natural compounds [7], agricultural waste material [8], industry [9], it is inexpensive to make adsorbent materials to remove heavy metals of interest. Such as, Talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$], is a natural compound widely used in the form of a fine powder in several industrial products. The structure of talc is the well-known 2:1 (T–O–T) layer configuration consisting of an octahedral magnesium (Mg) coordinated sheet (O) sandwiched between two tetrahedral silicon (Si) coordinated sheets (T) [10]. Talcum powder (30–50 μm) for preparing the nanocomposite was supplied by Talcum powder Phu Tho – Viet Nam. Talc-based materials have been synthesized and applied as adsorbent materials for removing toxic agents such as heavy metals [11], wastewater containing organic dyes [12].

In this work, the adsorption isotherm, kinetic of Cr^{3+} ion onto Fe_3O_4 /Talc nanocomposite produced from Talc (Phu Tho – Viet Nam) were studied.

2. Experiments

2.1. Fe_3O_4 /Talc nanocomposite

The material is synthesized by the co-precipitation method on the talc layers in an inert atmosphere, with the 1:2 ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$. The synthesis process is carried out as document [13] with talc

powder of Vietnam (particle size $\leq 50 \mu\text{m}$; density 2.4 g/cm^3 ; main components include: SiO_2 : 56.8%; MgO : 31.5%; Fe_2O_3 : 3.5%).

The materials structure was determined by Field Emission Scanning Electron Microscope method (FESEM, Jeol 6610LA, Japan). Nitrogen adsorption-desorption isotherms were performed at 77 K in Tristar 3000-Micromeritics equipment, USA, using 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 and magnetic properties by measuring with a vibrating-sample magnetometer.

2.2. Studying the adsorption of Cr^{3+} ion by $\text{Fe}_3\text{O}_4/\text{Talc}$ nanocomposite

The process of adsorption of Cr^{3+} ion in aqueous solution is carried out in interrupted conditions at a temperature of 297 K. Stirring speed of 200 v/min, the initial concentration of Cr^{3+} is varied within 10–200 ppm. The solution's pH was surveyed from 4–7, the volume of Cr^{3+} solution was 50 ml, the amount of adsorbent used was 0.1 g. The concentration of before and after Cr^{3+} adsorption is calculated by oxidizing the sample to determine the total Cr concentration and subtracting Cr (VI) concentration, in which Cr (VI) is determined by colorimetric method. when chelating with 1.5-Diphenylcarbazide, the total Cr was determined by FAAS method on the ContrAA 700 device

of Analytikjena at a wavelength of 359.34888 nm; Acetylene/air stream; 50 mm lamp height.

Adsorption capacity of $\text{Fe}_3\text{O}_4/\text{Talc}$ nanocomposite is calculated by the formula [14]:

$$q = \frac{(C_o - C_t) \cdot V}{m} \quad (1)$$

Where, V is the volume of solution (l); m is the mass of adsorbent (g); C_o , C_t are Cr^{3+} concentrations in the initial solution and at time t respectively (mg/l);

kinetics of the adsorption process is studied by basing on the pseudo-first-order adsorption kinetics equation (B_1) in linear form: $\ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t$ (2), where: k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption kinetics process; q_e , q_t are the adsorption capacities at the equilibrium time and time t . The pseudo-second-order adsorption kinetics equation in linear form: $\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 \cdot q_e^2}$ (3), Where: k_2

(mg/g.min) is the rate constant of the adsorption kinetics process [15; 16]. Diffusion kinetics equation: $\ln(q_t) = \ln(k_d) + 0.5 \cdot \ln(t)$ (4), where: k_d (mg/g. ($\text{min}^{0.5}$)) is the diffusion coefficient [17]. Elovich equation: $q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$ (5) where: α and β are constants of Elovich – type equation [18].

3. RESULTS AND DISCUSSION

3.1. Properties of $\text{Fe}_3\text{O}_4/\text{Talc}$ nanocomposite

The surface properties, porosity or pore size is one of the factors to evaluate the adsorption capacity of the material. Figure 1 is the FESEM image of $\text{Fe}_3\text{O}_4/\text{Talc}$ nanocomposite.

Figure 1. Scanning electron microscopy image of Talc (a) and the synthesized $\text{Fe}_3\text{O}_4/\text{Talc}$ (b, c)

From the results of (Figure 1), it is shown that Talc surface material has particle sizes in the range of 30–50 nm, cubic particles are less uniform and have smooth surface. Nanocomposite materials at different magnifications (Fig. 1.b, 1.c), had distribution of

Fe_3O_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 2. Nitrogen adsorption – desorption isotherms and Barrett-Joyner-Halenda (BJH) pore-size distribution for Talc, Fe_3O_4 /Talc nanocomposite at 77K

From the results in (Figure 2), it is shown that the talc surface material has adsorption-desorption isotherm of the intermediate form between III and IV with the appearance of H_3 hysteresis loop, Fe_3O_4 /Talc nanocomposite samples give adsorption-desorption isotherm of type IV and H_3 hysteresis loop, rod-shaped and letter-shaped according to IUPAC classification [19]. This allows the prediction that synthetic nanocomposite materials contain both large pores and medium pore, in which the medium pores are more numerous. The specific surface area of talc surface material is $3.45 \text{ m}^2/\text{g}$ which is much smaller than that of the nanocomposite material, which reaches $78.95 \text{ m}^2/\text{g}$. In particular, large pore area of the nanocomposite $S_{\text{macro}} = S_{\text{BET}} - S_{\text{BJH, ads}} - S_{\text{micro}} = 8.27 \text{ m}^2/\text{g}$; the pore diameter averages 11.8 nm.

The magnetic properties of materials are assessed by the method of vibrating-sample magnetometry. The results for a material sample with near zero magnetic coercivity, with a saturation magnetization of

32.4 emu/g, this indicates that the survey sample is superparamagnetic, iron oxide particles is 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 [20].

3.2. Adsorption process of Cr^{3+} on Fe_3O_4 /Talc nanocomposite

Effects of pH: The temperature is 24°C for 60 minutes. Filter and determine the concentration of Cr^{3+} in the solution after adsorption.

The results in (Figure 3) show that when pH gradually increases, the adsorption capacity of lead increases, so the ability to treat lead contamination in water depends on the environmental pH. However, the survey process was carried out from $\text{pH} = 4$ to $\text{pH} = 7$ because, at points of pH less than 4, the dissolution of Fe_3O_4 nanoparticles occurs, in addition, at lower pH, the adsorbate solution will be positively charged thus making H^+ ions compete effectively

with Cr³⁺ cations, which may reduce lead adsorption [21], with pH greater than 7, the hydrolysis of chromium occurs. Therefore, subsequent surveys will be chosen with a pH value = 6.5.

Figure 3. Effect of pH on adsorption of Cr³⁺ onto Fe₃O₄/Talc (50 ml of Cr³⁺ 98.6 mg/l, 0.1 g sorbent)

Determining the time to reach adsorption equilibrium:

The Cr³⁺ survey solution has a concentration of C = 106.5 mg/l, adjusting solution's pH to pH = 6.5. Proceed on a magnetic stirrer at a speed of 140 rev/min, a temperature of 24 °C during the time periods in turn: 5 to 120 minutes. Then, filter and collect the filtrate for survey.

Figure 4. Effect of contact time on adsorption Cr³⁺ onto Fe₃O₄/Talc (50 ml of Cr³⁺ 106.5 mg/l, 0.1 g sorbent)

Survey results show that, in the range of 5–60 minutes, the adsorption capacity of materials increases with adsorption time. After 60 minutes, the adsorption capacity is almost unchanged, so the time to reach adsorption equilibrium 60 minutes.

Isothermal adsorption kinetics:

The isothermal adsorption kinetics of the material is studied with two models of Langmuir and Freundlich Fe₃O₄/Talc. The survey solution contains Cr³⁺ and 0.1 g of material to be stirred at a speed of 140 rev/min, a temperature of 24 °C for a period of 60 minutes. The isothermal adsorption model is given in (Figure 5).

Figure 5. Cr³⁺ adsorption isotherm on Fe₃O₄/Talc fitted to Langmuir and Freundlich

Table 2. – Langmuir and Freundlich isotherm constants for the adsorption of Cr^{3+} ion by $\text{Fe}_3\text{O}_4/\text{Talc}$

Freundlich isotherm				Langmuir isotherm		
$1/n$	n	$K_f \text{ mg/g}$	R^2	$Q \text{ mg/g}$	$K_L \text{ L/mg}$	R^2
0.511	1.9566	8.4720	0.9918	54.3478	$K=0.1658$	0.9919

From the survey results fitted to Langmuir and Freundlich adsorption models, it is shown that the adsorption process of Cr^{3+} by $\text{Fe}_3\text{O}_4/\text{Talc}$ nanocomposite is more suitable with Langmuir model, however, with the absorption process also complies with the Freundlich isothermal equation. This shows that the synthetic material has adsorption centers with nearly the same surface energy. This shows that the lead adsorption process of $\text{Fe}_3\text{O}_4/\text{Talc}$ nanocomposite conforms to the Langmuir model in theory, but the empirical data also obeys the Freundlich model, which is due to the range of studied concentrations lies within the linear distribution range according to Freundlich model.

3.3. Survey of adsorption kinetics

The linear regression equations of $\ln(q_e - q_t)$ on t for first-order kinetic model, $\frac{t}{q_t}$ on t for second-

order kinetic model and $\ln(q_e)$ on $\ln(t)$ for diffusion kinetics model, q_t on $\ln t$ for Elovich model are shown in (Figure 5). From the value of the slopes and the intercepts of the straight line equations, it is possible to calculate the respective kinetic equation constants given in (table 3), (figure 6).

From the results in (Table 3), it is shown that the quadratic equation of type 2 has a correlation coefficient of approximately 1, 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^{3+} ion.

Figure 6. The kinetic models of adsorption of Cr^{3+} ion on the $\text{Fe}_3\text{O}_4/\text{Talc}$

Table 3. – Kinetic parameters for the removal of Cr³⁺ onto Fe₃O₄/Talc

Co (ppm)	Pseudo 1 st order		Pseudo 2 st order		Intraparticle diffusion		Elovich model		
	R ²	k ₁	R ²	k ₂	R ²	K _d	R ²	α	β
98.80	0.9816	0.0533	0.990	0.00128	0.9948	5.7208	0.9875	–0.0149	–0.1667
149.91	0.9848	0.0581	0.9928	0.001364	0.9315	7.6126	0.9776	–0.0193	–0.1758
201.14	0.9744	0.0484	0.9904	0.000973	0.9367	7.8618	0.9806	–0.0013	–0.1131

3. Conclusion

The Fe₃O₄/Talc nanocomposite was synthesized with the Talcum powder Phu Tho – Viet Nam by the chemical co-precipitation method. The reaction was carried out under a nonoxidizing oxygen-free. The surface area of the nanoparticles was determined to be 78.95 m²/g with an average diameter of 11.8 nm and the saturation magnetization of 32.4 emu/g.

The experimental results indicate that the Fe₃O₄/Talc nanocomposite is an effective adsorbent of Cr³⁺

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 53.35 mg/g occurred at pH 6.5 and 298 K. These results permit us to conclude that Fe₃O₄/Talc nanocomposite is a promising low-cost adsorbent for Cr³⁺ removal from wastewater and can be applied in a magnetically-assisted water treatment technology.

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