Adsorption performance of CuFe₂O₄/rGO nanocomposites towards organic dye

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Abstract

A facile and efficient approach was employed to synthesize CuFe₂O₄/rGO (reduced graphene oxide) nanocomposites. The morphology, crystal structure and properties of the prepared CuFe₂O₄/rGO nanocomposites were characterized by transmission electron microscopy, energy-dispersive X-ray spectroscopy, powder X-ray diffraction and thermo-gravimetric analysis. The CuFe₂O₄/rGO nanocomposites were applied as adsorbents to study their adsorption performance for Congo red. The adsorption capacity and recyclability, adsorption dynamics and adsorption models were investigated. The results show that the CuFe₂O₄/rGO nanocomposites are efficient and recyclable adsorbents.

KEY WORDS: CuFe₂O₄/rGO, magnetically recoverable, adsorption, recycling

1. Introduction

Polluted water caused by dyes has been of great concern because of their high color degree and toxicity. Since it is a global environmental issue, some technologies to treat waste water have been developed, such as chemical oxidation [1], biological method [2], ion-exchange [3], adsorption [4], and electrodialysis [5]. Of all these methods, adsorption is of special interest due to its

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high separation efficiency, low-cost and simple operation process. Adsorption method is primarily based on excellent adsorptive capacity of materials that have high specific surface area and surface energy. At present, many materials, including zeolites [6], kaolinite [7], activity carbon [8], chitosan [9], have been used to treat waste water.

Recently, graphene is drawing attention from researchers in many areas for its excellent characters. Graphene, a flat monolayer of sp^2 -bonded carbon atoms tightly packed into a two-dimensional honeycomb lattice, possesses huge surface area, chemical stability, unique electronic and mechanical properties and excellent adsorptivity [10-17]. So graphene holds great promise for potential applications in many fields. For example, Mülhaupt et al prepared Pd nanoparticles on chemically derived graphene as catalysts for catalyzing Suzuki–Miyaura coupling reaction and attained a high reaction yield [18]. MnO_2/rGO nanocomposites, as electrode materials, showed excellent electrochemical performance with a highest specific capacitance of about 330 F.g^{-1} [19].

Magnetic materials are becoming attractive to the researchers who engage in chemical reactions and environmental protection like water treatment, although they are usually interested to the researcher in the fields of anti-electromagnetic interference, electronic devices, biomedicine and so on [20-22]. Magnetic nanoparticles or their composites can be collected easily from the reaction system or waste water because of their excellent magnetic response to external magnetic fields.

In this paper, a facile one-step hydrothermal route was exploited to directly fabricate magnetic $CuFe_2O_4/rGO$ nanocomposites as adsorbent for Congo red removal. It was found that they exhibited excellent adsorptive properties and stability toward Congo red removal. Thus, the $CuFe_2O_4/rGO$ nanocomposites are potential recyclable adsorbents for water treatment.

2. Experimental

2.1 Materials

Graphite was provided by Qingdao Graphite Factory. Potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), concentrated sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2 , 30%), hydrochloric acid (HCl), cupric nitrate ($\text{Cu}(\text{NO}_3)_2$), ferric chloride (FeCl_3), ethylene glycol (EG), sodium acetate anhydrous (CH_3COONa), Congo red (CR) were all from Tianjin Chemical Reagent Co., Ltd. All the chemicals were used as received.

2.2 Preparation of $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites

In a typical experiment, GO (2 mL), which was prepared from purified natural graphite by a modified Hummers method [23], was dispersed into a solution composed of 9 mL EG and 9 mL distilled water. The mixture was ultrasonically treated for 10 minutes before 0.5 mL FeCl_3 (0.0762 g/mL), 0.5 mL $\text{Cu}(\text{NO}_3)_2$ (0.0341 g/mL) and 0.12 g CH_3COONa were introduced and stirred for 1 h at room temperature. After that, the mixture was transferred to a 25 mL Teflon-lined stainless autoclave and heated at 170 °C for 6 h under autogenous pressure. After the autoclave was cooled down to room temperature, the precipitate was filtered, washed with distilled water and ethanol for several times, and dried in a vacuum oven at 60 °C for 12 h to acquire the $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites.

2.3 characterizations

Fourier transform infrared (FT-IR) spectra of $\text{CuFe}_2\text{O}_4/\text{rGO}$ and GO were measured with a Perkin-Elmer Paragon-1000 FT-IR spectrometer. The X-ray diffraction (XRD) diagrams of the $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites were obtained using an X-ray diffractometer (BDX3300) with reference target: Cu K α radiation ($\lambda=1.54\text{\AA}$), voltage: 30 kV and current: 30 mA. The sample was scanned from 10 to 90° (2θ) with

steps of $4^{\circ} \text{ min}^{-1}$. Prior to thermo-gravimetric analysis (TGA), the samples were dried in a vacuum at 30° C for 2 days. The TGA diagrams were recorded with a Rigaku-TD-TDA analyzer with a heating rate of $10^{\circ} \text{ C min}^{-1}$. Composition of the $\text{CuFe}_2\text{O}_4/\text{rGO}$ was analyzed on an X-ray photoelectron spectrometer (XPS, PHI1600 ESCA System, PERKIN ELMER, US). The $\text{CuFe}_2\text{O}_4/\text{rGO}$ samples for transmission electron microscopy observation (TEM, Tecnai G2 F20) and energy dispersive X-ray spectroscopy (EDX) were prepared by depositing their aqueous suspensions onto carbon coated nickel grids, drying under ambient conditions and then placing into the chamber for observation.

2.4 Measurement of adsorption property

Adsorption was tested using a batch equilibrium technique by placing 5 mg of the $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites in glass bottles (20 mL) containing 10 mL of CR solutions at various concentrations. The adsorption was allowed to take place and the light adsorption intensities of the CR solutions were measured with a UV–Vis spectrophotometer (TU-1901). The concentrations of the CR solutions were determined by using linear regression equation obtained by plotting a calibration curve for CR over a range of concentrations. The amount of CR adsorbed by $\text{CuFe}_2\text{O}_4/\text{rGO}$ (q_t) was determined by the difference between the initial concentration of CR solution and concentration at time t according to the equation below:

$$q_t = (C_0 - C_t) V/m$$

where, C_0 and C_t are the concentrations of CR (mg/L) at initial and time t , m is the mass of $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites (g), and V is the volume of solutions (L). If the contact time is long enough, the q_t value will not change any more. This indicates that the adsorption reaches equilibrium. The q_t at equilibrium is called saturated adsorption (q_e) that represents adsorption capacity of an adsorbent.

After the adsorption, the $\text{CuFe}_2\text{O}_4/\text{rGO}$ was removed using an external magnet, washed with water and immersed in ethanol for desorption. Every 30 minutes, the ethanol was replaced until no color was observed. Finally, it was washed two times with deionized water and then a new round of adsorption is conducted.

3. Results and discussion

The $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposite was prepared by hydrothermal method and their shape, average diameter and crystal structure were observed by TEM. The TEM photo in Figure 1a shows that rGO sheets are smooth and near-transparent. CuFe_2O_4 nanoparticles with a shape of fusiform are homogeneously dispersed on the rGO sheets, and their average diameter is about 65.59 nm calculated from the data in Figure 1c. The HRTEM (High Resolution Transmission Electron Microscopy) image of the CuFe_2O_4 nanoparticles in Figure 1b shows that the lattice spacing is 0.297 nm which corresponds to the (220) plane of CuFe_2O_4 [24].

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Figure 1 TEM images (a, b) and size distribution (c) of the CuFe₂O₄/rGO nanocomposites

To further characterize CuFe₂O₄/rGO nanocomposites, XRD pattern of the CuFe₂O₄/rGO was determined as shown in Figure 2. There are diffraction peaks located at 2θ of 30.1° , 35.5° , 43.5° , 54.1° , 57.3° , 62.4° , 72.8° and 76.2° . These peaks respectively correspond to the (220), (311), (400), (312), (511), (440), (533) and (422) planes of crystalline CuFe₂O₄ [25-27]. In addition, FTIR spectra of GO and CuFe₂O₄/rGO (Figure S1) [29, 30] and XPS spectra of the CuFe₂O₄/rGO nanocomposite (Figure S2) [31-36] also demonstrated the formation of CuFe₂O₄/rGO nanocomposite.

Figure 2 XRD pattern of the CuFe₂O₄/rGO nanocomposite

The thermal stability of the CuFe₂O₄/rGO nanocomposite is evaluated by TG-DTA in air flow and the result is shown in Figure 3. There is a rapid mass loss in the range of 300-480 °C in the TGA curve. This is attributed to the combustion of rGO [4]. Since the rGO has been completely decomposed at 800 °C, final remaining mass equals to the CuFe₂O₄ percentage in the CuFe₂O₄/rGO. So the CuFe₂O₄/rGO contains about 36.2% CuFe₂O₄.

Figure 3 TGA curve of CuFe₂O₄/rGO in air atmosphere

Wastewater polluted by dyes is increasingly prominent with rapid development

of industry, and these dyes are often highly toxic and refractory. So adsorption is considered as an efficient method for wastewater treatment. Usually, pollutants can be efficiently removed by adsorbents because they have high specific surface area. Because of high specific surface area of graphene sheets, magnetic $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites are expected to have excellent adsorption performance towards chemicals. Here, CR is chosen as a model molecule to investigate the adsorption performance of $\text{CuFe}_2\text{O}_4/\text{rGO}$.

In order to study the effect of contact time on the adsorption of CR and find the time for reaching adsorption equilibrium, $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites were dispersed in CR aqueous solutions to start adsorption. The absorbance intensities of CR aqueous solutions were detected at different times, based on which corresponding amount of adsorption (q_t) and removal efficiency (R) were calculated and the results are shown in Figure 4. The adsorption capacity increased quickly in initial 20 min because of high initial concentration of CR and then it slowed down and finally leveled off in 90 min. At 100 min, q_t reached a nearly constant value of 9 mg/g (q_e) and R gained 90 %. So CR can be efficiently removed from aqueous solution when CR concentration is low.

Figure 4 Effect of contact time on the adsorption to CR

Conditions: CR=5 mg/L (10 mL), sorbent=5 mg

The effect of $\text{CuFe}_2\text{O}_4/\text{rGO}$ mass on the adsorption was also investigated. Different amount of $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites were dispersed in 10 mL dilute CR aqueous solutions (5 mg/L) to start adsorption. The absorbance values of CR in absorption equilibrium were detected and the corresponding adsorption capacity and removal efficiency were calculated subsequently. Relationships between $\text{CuFe}_2\text{O}_4/\text{rGO}$ mass, adsorption capacity and removal efficiency are shown in Figure 5. Obviously, along with increase of $\text{CuFe}_2\text{O}_4/\text{rGO}$ mass, adsorption capacity and removal efficiency change in the opposite direction. When concentration of CR solutions is constant, R increases as the adsorbent mass increases over the range 1.25~20 mg, but q_e decreases at same time. The increase of R can be attributed to an increase of adsorbent surface or adsorption sites, while the decrease of q_e is due to the insufficiency of CR relative to $\text{CuFe}_2\text{O}_4/\text{rGO}$.

Figure 5 Effect of sorbent mass on the adsorption to CR
Conditions: CR=5 mg/L (10 mL)

Effect of initial CR concentration on adsorption process is presented in Figure 6. The adsorption capacity of $\text{CuFe}_2\text{O}_4/\text{rGO}$ increased as initial dye concentration grew but removal efficiency lowered simultaneously. Increasing CR concentration brings the promoting of the driving force from the concentration gradient, which enforces diffusion rate of CR towards $\text{CuFe}_2\text{O}_4/\text{rGO}$, changes the equilibrium concentration of CR solution, and increases the amount of dye adsorbed by per unit of $\text{CuFe}_2\text{O}_4/\text{rGO}$. So it is beneficial for the adsorption for CR. The simultaneous decrease of R is owing to the change of adsorbent/CR ratio. Generally, decreasing this ratio leads to reduction of R.

Figure 6 Effect of initial CR concentration on adsorption
Conditions: sorbent=5 mg

Another effect factor that influences adsorption is pH value of CR solution. Figure 7 illustrates the q_e value of $\text{CuFe}_2\text{O}_4/\text{rGO}$ measured in CR solutions with different pH. When pH value is lower than 7, q_e value fall down as pH value decreases. However, as pH is over 7, q_e changes litter as pH value grow. CR is anodic dye and certainly it is less easily absorbed by negative sorbents. At high pH value, both rGO and CR are negative charged. The negative groups repel each other and reduce adsorptive ability. However, the hydrogen bonds are easily formed between $-\text{NH}_2$ groups on CR and $-\text{OH}$ groups on rGO, leading to the increase of adsorptive ability. The two actions may offset each other, so q_e is nearly unchanged. At low pH value, $-\text{NH}_2$ groups turn to $-\text{NH}_3^+$. This may reduce the possibility of hydrogen bond formation between CR and rGO, so q_e decreases.

Figure 7 Effect of pH on adsorption

Condition: CR=5 mg/L (10 mL), sorbent=5 mg

Adsorption equilibrium isotherm deals with the relationships of adsorbent and adsorbate molecules that distribute in the liquid or solid phases when the adsorption reaches equilibrium state. The adsorption isotherms of CR adsorbed by $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites at 298, 313 and 323 K are shown in Figure 8. The curves unravel that q_e increases simultaneously with equilibrium concentration of CR (C_e). If the equilibrium concentration of CR is high, more CR molecules surround $\text{CuFe}_2\text{O}_4/\text{rGO}$, resulting in the increase of adsorption.

Figure 8 Adsorption isotherms of CR onto CuFe₂O₄/rGO.
Conditions: CR=5 mg/L (10 mL), sorbent=5 mg, pH=7

The Langmuir [24] and Freundlich [25] isotherms are two usual models to describe adsorption. Here, they are used to describe the relationship between concentration of CR solution and amount of CR adsorbed by CuFe₂O₄/rGO. The Langmuir isotherm theory has following fundamental assumptions: (1) adsorbent surface is homogenous; (2) it is monomolecular layer adsorption; (3) there are no interactions between adsorbate molecules. Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (1)$$

$$\frac{1}{q_e} = \frac{1}{C_e q_m b} + \frac{1}{q_m} \quad (2)$$

Where C_e (mg/L) is the equilibrium concentration of CR, q_e (mg/g) is the ratio of adsorbed CR mass to adsorbent mass, q_m is the maximum adsorption capacity of the adsorbent (mg/g) and b (L/mg) is the Langmuir constants related to adsorption rate.

When $1/q_e$ is plotted against $1/C_e$, a straight line with a slope of $1/q_m b$ is obtained (Figure 9a), it indicates that the adsorption of CR by CuFe₂O₄/rGO nanocomposites follows the Langmuir isotherm. The Langmuir constants b can be calculated from the equation or straight line and their values are listed in Table 1. Furthermore, the separation factor R_L is calculated from the equation (3) [26]:

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

Where b still represents the Langmuir constant (L/mg) and C_0 (mg/L) is the initial CR concentration. R_L can be used to evaluate whether an adsorption is favorable or

unfavorable. If $R_L > 1$, $R_L = 1$, $0 < R_L < 1$, or $R_L = 0$, it indicates that the isotherm type is unfavorable, linear, favorable or irreversible, respectively. From the data in Table 1, it can be seen that all the R_L values at different temperatures are $0 < R_L < 1$, indicating that adsorption is favorable. The $q_{\max}$ values at 298, 313 and 323 K are 41, 64 and 81 mg/g respectively. The maximum adsorption capacity of the $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites is superior to those reported in references. Activated carbons of commercial grade or laboratory grade, activated carbon prepared from coir pith or *Myrtus communis*, silver nanoparticles loaded on activated exhibited maximum adsorption capacities of 0.635, 1.875, 6.720, 19.23 and 66.7 mg/g, respectively [37-40]. Magnetic cellulose/ Fe_3O_4 /activated carbon and Fe_3O_4 @graphene demonstrated maximum adsorption capacities of 66.09 and 33.66 mg/g to CR [41, 42].

Figure 9 Langmuir (a) and Freundlich (b) isotherms
Condition: CR=5 mg/L (10 mL), sorbent=5 mg, pH=7

Table 1 Isotherm parameters for CR adsorption by CuFe₂O₄/rGO composites

Isotherm	parameter	Temperature (K)		
		298	313	323
Langmuir	q_m (mg/g)	41	64	81
	b (L/mg)	0.47	0.35	0.33
	R_L	0.299	0.364	0.377
	R^2	0.998	0.989	0.982
	K_F [mg/g(L/mg) ^{1/n}]	13.17	15.65	18.71
Freundlich	$1/n$	0.546	0.796	0.983
	R^2	0.935	0.970	0.972

Freundlich isotherm theory is different from the ideal adsorption model of Langmuir isotherm in that it assumes adsorbent surface being non-homogenous. The Freundlich equation is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Where, K_F and n are Freundlich constants. Parameter K_F represents adsorption capacity. The slope $1/n$ is considered as a standard to evaluate how favorable the adsorption process is. Usually, when $1/n$ ranges between 0 and 1, it demonstrates the adsorption process being favorable [43]. The plots of $\ln (q_e)$ versus $\ln (C_e)$ are given

in Figure 9b. They are straight lines, from which Freundlich the constants (K_F and n) were obtained and listed in Table 1. It can be concluded that adsorption of CR by $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites also follows the Freundlich isotherm from linear parameter R^2 and the adsorption is favorable from n values listed in Table 1.

Chemical kinetic is related to parameters like solution concentration and temperature, contact time between adsorbent and adsorbate. Adsorption dynamics can be developed after studying adsorption capacity of $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites at different contact time and temperature or initial adsorbate concentration. Figure 10 shows change of adsorption capacity along with contact time at different temperature. The curves indicate that increasing temperature accompanies with growth of adsorption capacity. The reasons may be: (1) high temperature increase adsorbate molecules mobility, which meaning more probability of interaction between adsorbate molecules and adsorbent; (2) high temperature may reduce solution viscosity, so promotes diffusion of adsorbate molecules through reducing mobile resistance.

Figure 10 Adsorption capacities at different temperature and different contact time
CR=5 mg/L (10 mL), sorbent=5 mg, pH=7

Adsorption dynamics is often analyzed by different kinetic models based on

changes of adsorptive capacity with contact time. Pseudo first-order model and pseudo second-order model are two of the common adsorption kinetic models.

Pseudo first-order model assumes that adsorption process is controlled by diffusion step. Its linear equation is:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (5)$$

Where, q_e and q (mg/g) are adsorption capacities of CuFe₂O₄/rGO at equilibrium and at any time t , k_1 is rate constant (min⁻¹) of pseudo first-order kinetic adsorption. Plot of $\ln(q_e - q)$ versus t is usually fitted as a straight line and the values of q_e and k_1 can be obtained from the slope and intercept.

Pseudo second-order model assumes that adsorption is controlled by chemical adsorption involving valence forces through exchanging electrons between adsorbent and adsorbate. It is expressed by equation (6):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where, q_e and q (mg/g) are adsorption capacities of CuFe₂O₄/rGO at equilibrium and at any time. k_2 is rate constant (g·mg⁻¹·min⁻¹) of pseudo second-order kinetic adsorption. Plots of (t/q) versus t can be fitted as a straight line and the values of q_e and k_2 can be calculated from the slope and intercept.

Figure 11 shows the fitting curves according to pseudo first-order model and pseudo second-order model and table 2 lists the values of relevant parameters. The Correlation coefficients (R^2) for the pseudo first-order model are lower than those for the pseudo second-order model, and it seems that there are different $\ln(q_e - q)$ - t relationships before and after 40 min, which demonstrates that the adsorption behavior of CuFe₂O₄/rGO nanocomposites towards CR does not fit the pseudo first-order model. The reason is not clear. It may be owing to the reason that the

adsorption mechanism is depends on the adsorption time, or adsorption extent of the absorber. However, Correlation coefficients (R^2) of the pseudo second-order model are all beyond 0.99. The q_e (Cal) values obtained from the pseudo second-order model are more near q_e (Exp) values as compared with those from pseudo first-order model. It is apparently that the pseudo second-order kinetic model is more suitable to describe the adsorption behavior of $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites towards CR.

Figure 11 linear fitting curves of $\ln(q_e - q)$ versus t for Pseudo-first-order model (a) and (t/q) versus t for pseudo-second-order model (b)

Table 2 Parameters of pseudo first-order and second-order adsorption kinetic models

Models	parameters	Temperature (K)		
		298	313	323
Pseudo first-order model	q_e Cal. (mg/g)	8.178	8.866	8.622
	k_1 (min^{-1})	0.017	0.015	0.016
	R^2	0.914	0.920	0.877
Pseudo second-order model	q_e Cal. (mg/g)	9.432	9.591	9.923
	k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	0.004	0.004	0.005
	R^2	0.997	0.999	0.996
	q_e Exp. (mg/g)	9.573	9.708	9.961

Since $\text{CuFe}_2\text{O}_4/\text{rGO}$ is magnetic response, it is easy to remove it from solution with an external magnet, so it can be utilized again for adsorption. Figure 12 shows the remaining adsorption capacity percentage based on the first adsorption capacity in six successive adsorptions. The adsorption capacity really decreases but not so much. It still remains about 92 % after six rounds of adsorption, so $\text{CuFe}_2\text{O}_4/\text{rGO}$ is considered good recyclable adsorbents.

Figure 12 Remaining adsorption capacity in six successive adsorptions

4. Conclusion

The $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites were prepared by a hydrothermal method and their basic physical characters such as morphology and crystalline phase were analyzed by TEM, XRD, XPS, FTIR, and TGA. The adsorption performance of the

as-prepared $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites to CR was estimated through a batch adsorption experiment. When the adsorption process arrived equilibrium state, the adsorption capacity gained 45 mg/g and it increased simultaneously with temperature increasing. The adsorption process of CR by $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites follows Langmuir and Freundlich isothermal adsorption theory, and the maximum adsorption was estimated to be 81 mg/g. Compared with the pseudo first-order, the pseudo second-order kinetic model is more fit to the adsorption dynamics of CR by $\text{CuFe}_2\text{O}_4/\text{rGO}$. Moreover, $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanocomposites exhibit good magnetic recyclability. The above merits make $\text{CuFe}_2\text{O}_4/\text{rGO}$ be potential adsorbents for wastewater treatment.

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