CuFe₂O₄/activated carbon composite: A novel magnetic adsorbent for the removal of acid orange II and catalytic regeneration

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Abstract

CuFe₂O₄/activated carbon magnetic adsorbents, which combined the adsorption features of activated carbon with the magnetic and the excellent catalytic properties of powdered CuFe₂O₄, were developed using a simple chemical coprecipitation procedure. The prepared magnetic composites can be used to adsorb acid orange II (AO7) in water and subsequently, easily be separated from the medium by a magnetic technique. CuFe₂O₄/activated carbon magnetic adsorbents with mass ratio of 1:1, 1:1.5 and 1:2 were prepared. Magnetization measurements, BET surface area measurements, powder XRD and SEM were used to characterize the prepared adsorbents. The results indicate that the magnetic phase present is spinel copper ferrite and the presence of CuFe₂O₄ did not significantly affect the surface area and pore structure of the activated carbon. The adsorption kinetics and adsorption isotherm of acid orange II (AO7) onto the composites at pH 5.2 also showed that the presence of CuFe₂O₄ did not affect the adsorption capacity of the activated carbon. The thermal decomposition of AO7 adsorbed on the activated carbon and the composite was investigated by in situ FTIR, respectively. The results suggest that the composite has much higher catalytic activity than that of activated carbon, attributed to the presence of CuFe₂O₄. The variation of the adsorption capacity of the composites after several adsorption–regeneration cycles has also been studied.

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1. Introduction

Due to its high surface area, porous structure and special surface reactivity, activated carbon is well used in a variety of areas (Gadkaree, 1998) such as adsorbents in air and water pollution control, catalysts in the chemical and petrochemical industries, and purifiers in the food and pharmaceutical industries. In the water treatment field, activated carbon is often used as an adsorbent for the removal of various organic compounds. This sorbent is highly inert and thermally stable, and it can be used over a broad pH range. Furthermore, powdered activated carbon is low cost and

can quickly adsorb organic and inorganic contaminants from water. When the activated carbon becomes exhausted or the effluent reaches the maximum allowable discharge level, the carbon needs to be separated from the aquatic system and regenerated. However, filtration, the traditional method for separating powdered activated carbon, could cause the blockage of filters or the loss of carbon. Therefore, powdered activated carbon has been traditionally discarded with the process sludge after use in water and wastewater treatment (Clifford et al., 1983), resulting in the secondary pollution. Thus, the difficulties encountered in separating spent activated carbon and regeneration limit its applications in many fields.

Compared with filtration, magnetic separation is considered as a rapid and effective technique for separating

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magnetic particles. Magnetic separation, which represents a group of techniques based on the use of magnetic or magnetizable adsorbents, carriers and cells, has been used for many applications in biochemistry, microbiology, cell biology, analytical chemistry, mining ores, and environmental technologies (Setchell, 1985; Velsen and Vos, 1991; Šafařík et al., 1995). Recently, considerable attention has been focused on the application of magnetic separation technology to solve environmental problems. Examples of this technology are the use of polymer-coated magnetic particles for oil spill remediation (Orbell et al., 1977; Machado et al., 2006), magnetite particles to accelerate the coagulation of sewage (Booker et al., 1991), magnetic CuFe_2O_4 powder to adsorb azo-dye Acid Red B (Wu et al., 2004), and magnetic powder $\text{MnO-Fe}_2\text{O}_3$ composite for the adsorption of organic dyes (Wu et al., 2005). However, most of these materials have the drawbacks of small adsorption capacity and narrow application range. For example, CuFe_2O_4 powder and $\text{MnO-Fe}_2\text{O}_3$ composite could only be used to adsorb ionic organic pollutants. In addition, the applicable pH range of these materials was relatively narrow (Wu et al., 2004, 2005).

To overcome the disadvantages of powdered activated carbon and magnetic particles, several methods such as impregnation (Wang et al., 1994), ball milling (Rudge et al., 2000), and chemical coprecipitation (Šafařík et al., 1997; Oliveira et al., 2002) have been developed to combine them together to produce magnetic composites, which could be used as adsorbents to remove a wide range of organic pollutants over a broad pH range and be separated by magnetic separation technology conveniently. Among these methods, chemical coprecipitation is the most promising because it is simple and no special chemicals and procedures are demanded. Some researchers (Šafařík et al., 1997; Oliveira et al., 2002) have prepared activated carbon/iron oxide magnetic composites in this way. However, previous studies mainly focused on how to make activated carbon magnetic and no regeneration of the spent magnetic composites was involved. Besides, to our best knowledge, no information is available about the combination of CuFe_2O_4 powder with activated carbon to produce magnetic adsorbents.

Regeneration, especially catalytic regeneration, is a necessary process for preventing secondary pollution and re-establishing the sorptive capacity of the magnetic composites. Therefore, making activated carbon magnetic along with catalytic regeneration of exhausted magnetic composite is the focus of this study. High adsorption capacity and excellent catalytic activity CuFe_2O_4 /activated carbon magnetic composites were prepared by a chemical coprecipitation method. Copper ferrite was chosen as the magnetic particle because it can easily be obtained by chemical coprecipitation and has high catalytic activity (Wu et al., 2004), which will facilitate catalytic regeneration of activated carbon saturated with organic contaminants.

The main objectives of this study were (1) to prepare CuFe_2O_4 /activated carbon magnetic composites without

decreasing the carbon's adsorption capacity; (2) to evaluate acid orange II (AO7) adsorption capacities by examining the adsorption edge and isotherm; (3) to compare the thermal decomposition process of AO7 adsorbed on the activated carbon and the composite under inert atmosphere; and finally (4) to investigate the variation of the adsorption capacity of the composites after several adsorption–regeneration cycles.

2. Experimental

2.1. Materials

Coconut powdered activated carbon (200 mesh) was produced by Northern Suburb Activated Carbon Plant of Beijing (Beijing, China). Copper (II) chloride dihydrate, ferric chloride and Acid Orange II (AO7) were obtained from Beijing Chemical Co. (Beijing, China). Copper (II) chloride dihydrate and ferric chloride were both analytic grade and Acid Orange II was used without further purification to prepare solutions with distilled water ($100\text{--}1200\text{ mg l}^{-1}$). The chemical structure of the Acid Orange II is as follows:

2.2. Preparation of CuFe_2O_4 /activated carbon magnetic composites

CuFe_2O_4 /activated carbon magnetic composites were prepared using a coprecipitation method. The activated carbon was added into a 400 ml solution containing copper (II) chloride (0.02 mol) and ferric chloride (0.04 mol) at room temperature. The amount of activated carbon was adjusted to obtain CuFe_2O_4 /activated carbon mass ratios of 1:1, 1:1.5 and 1:2. Under vigorous magnetic-stirring, NaOH solution (5 mol l^{-1}) was added dropwise to raise the suspension pH to around 10 and stirring was continued for 1 h. Afterward, the suspension was heated to $98\text{--}100\text{ }^\circ\text{C}$ for 2 h. After cooling, the prepared magnetic composite was repeatedly washed with distilled water. By a simple magnetic procedure, the obtained materials was separated from water and dried in an oven at $105\text{ }^\circ\text{C}$.

2.3. Characterization of the composites

Specific saturation magnetization (σ_s), which is a measure of a particle's magnetism was determined by a VSM model 155 magnetic meter. The crystalline structure of CuFe_2O_4 in the composite was determined via the X-ray powder diffraction method using a D/Max-3A diffractometer (Rigaku Co., Japan) with Cu $\text{K}\alpha$ radiation. Scanning electron microscopy was carried out by means of a Hitachi

S-3500N Scanning Electron Microscope (Hitachi Co., Japan). BET surface area, pore diameter, and pore volume were determined by a surface analyzer (NOVA 4000, Quantachrome Co., USA) with N_2 as the adsorbate.

2.4. Adsorption of AO7

Adsorption studies were performed in glass vessels with agitation provided by a shaker. The temperature was controlled at $25 \pm 1^\circ\text{C}$ by air bath. The pH was adjusted by addition of 0.1 M HCl or NaOH solution. The suspensions containing 0.100 g composite varying amount of AO7 were shaken on an orbital shaker at 130 rpm. Samples were taken at different time intervals when the kinetic study was carried out. The concentration of AO7 was determined by a TOC analyzer (multi N/C 3000, Analyticjena Co. Germany) after $0.45\ \mu\text{m}$ membrane filtration. For the adsorption kinetics and the effect of pH on adsorption experiments, 50 ml AO7 solution (initial concentrations for CuFe_2O_4 and the 1:1.5 composite are $200\ \text{mg l}^{-1}$ and $500\ \text{mg l}^{-1}$, respectively) was used. Adsorption isotherms were obtained in batch equilibrium experiments with 0.100 g of the composites in 50 ml solutions of AO7 (concentrations up to $1200\ \text{mg l}^{-1}$ at $\text{pH } 5.2 \pm 0.1$).

2.5. In situ FTIR spectra of AO7 degradation

Thermal degradation tests were carried out using the following processes: After adsorption and magnetic separation, the collected composites containing AO7 were dried at 100°C , and then placed into a ceramic reactor. N_2 was let in at a flow of $30\ \text{ml min}^{-1}$, and the ceramic reactor temperature was raised at $30^\circ\text{C min}^{-1}$ and kept for 20 min at each specified temperature. Diffuse reflectance (DRIFT) spectra of azo-dye AO7 adsorbed on activated carbon and CuFe_2O_4 /activated carbon composite were determined by a Nicolet 5700 FTIR spectrophotometer (Nicolet Co., USA) equipped with a controlled-temperature and environment diffuse reflectance in situ chamber and a liquid nitrogen-cooled HgCdTe detector.

2.6. Regeneration

For regeneration, the spent composites were dried at 100°C , and then placed into a quartz reactor. N_2 was supplied at a flow of $60\ \text{ml min}^{-1}$, and the quartz reactor temperature was increased to 500°C at $30^\circ\text{C min}^{-1}$ and maintained for 1 h.

3. Results and discussion

3.1. Characterization of the composites

The composites were prepared by the precipitation of CuFe_2O_4 onto an activated carbon surface. The magnetism test with a permanent magnet (2300 G) showed that the

material was magnetic and completely attracted to the magnet.

The XRD analysis of pure CuFe_2O_4 (Fig. 1) indicated that the metal oxides mainly occurred in the form of spinel structure of CuFe_2O_4 ($d = 2.52, 2.98, 1.49, 1.61\ \text{\AA}$). Diffraction peak was also observed at $d = 2.42\ \text{\AA}$, suggesting the presence of small amounts of copper (II) oxide (CuO). For the 1:1 composite, these peaks appear weaker and two new diffraction peaks ($d = 2.46, 2.13\ \text{\AA}$) were observed, suggesting the presence of cuprite (Cu_2O), which likely resulted from the reduction of copper (II) oxide by reducing functional groups on the surface of the activated carbon or carbon itself during the preparation process. In addition, the sharp diffraction peaks ($d = 3.35\ \text{\AA}$) observed both in the composite and the original activated carbon may be related to the presence of some impurities in the original activated carbon.

The magnetization measurement, CuFe_2O_4 content, BET surface area and microporous volumes of the prepared composites are listed in Table 1. It can be observed from Table 1 that the specific saturation magnetization decreased for a low CuFe_2O_4 content in the composite. However, this decrease is very sharp, instead of being proportional to the decrease in CuFe_2O_4 content. This indicates that the content of non-magnetic oxides, such as copper (II) oxide, cuprite and amorphous iron oxide increases greatly for the composites with higher activated carbon content. Under the preparation conditions employed, three metal oxides can be formed, i.e., spinel copper ferrite (CuFe_2O_4), copper (II) oxide (CuO) and cuprite (Cu_2O). Only the first is magnetic. High carbon content in the composite favors the formation of cuprite, since more reducing reagents are available to reduce CuO . This may be the main reason for the sharp decrease of magnetization of the composite with higher carbon content.

The data shown in Table 1 suggest that the BET surface area and microporosity are not significantly affected by the

Fig. 1. Powder XRD for the prepared copper ferrite and the 1:1 CuFe_2O_4 /activated carbon composite.

Table 1

Magnetization, BET surface area and microporosity measurements for the CuFe_2O_4 /activated carbon composites

Composite	CuFe_2O_4 (wt%)	Specific saturation magnetization (emu g^{-1})	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Micro-pore volume ($\text{cm}^3 \text{g}^{-1}$)
Pure activated carbon	0	0	799	0.229
Composite 1:2	33	0.97	558 (794 ^a)	0.153 (0.223 ^a)
Composite 1:1.5	40	2.30	549 (857 ^a)	0.144 (0.231 ^a)
Composite 1:1	50	5.93	488 (889 ^a)	0.118 (0.223 ^a)
CuFe_2O_4	~100	22.5	87	0.013

^a Expressed on activated carbon mass basis.

presence of CuFe_2O_4 on the activated carbon. For example, for the 1:1.5 composite, reductions of the surface area from $799 \text{ m}^2 \text{g}^{-1}$ (for pure activated carbon) to $549 \text{ m}^2 \text{g}^{-1}$ and of the microporous volume from 0.229 to $0.144 \text{ cm}^3 \text{g}^{-1}$ are observed. In both cases, the reductions were expected due to the presence of CuFe_2O_4 in the 1:1.5 composite (40% CuFe_2O_4 and 60% activated carbon). Since CuFe_2O_4 has a relatively small surface area and microporous volume ($87 \text{ m}^2 \text{g}^{-1}$ and $0.144 \text{ cm}^3 \text{g}^{-1}$, respectively), its presence in the composites should cause a decrease in the surface area compared to pure activated carbon. However, the reductions of 31% and 37%, respectively, are lower than the expected value (40%). The surface area and microporous volume values expressed on a carbon mass basis are for the 1:1.5 composite, $857 \text{ m}^2 \text{g}^{-1}$ carbon ($549 \text{ m}^2 \text{g}^{-1}$ composite) and $0.231 \text{ cm}^3 \text{g}^{-1}$ carbon ($0.144 \text{ cm}^3 \text{g}^{-1}$ composite), respectively. These results show that the pores of the activated carbon are not blocked by the presence of magnetic CuFe_2O_4 ; the composites retain a large surface area and a high microporous volume.

The morphologies of activated carbon, the prepared pure copper ferrite and the 1:1.5 composite, were studied by SEM. Fig. 2a–c show the views of the pure activated carbon, copper ferrite aggregate and CuFe_2O_4 /activated carbon composite, respectively. It can be observed that small aggregates of copper ferrite which appear brighter are supported on the darker surface of the activated carbon. The fine particles of CuFe_2O_4 tended to cover specific parts of the activated carbon, instead of dispersing evenly on the whole surface. This may be a reason for maintaining the high surface area of activated carbon in the presence of copper ferrite powder.

3.2. Adsorption of AO7 onto composites

3.2.1. Adsorption kinetics

The adsorption kinetics of AO7 on activated carbon and 1:1.5 composite are illustrated in Fig. 3. The adsorption kinetics of AO7 on the composite were very similar to that of activated carbon. The adsorption process could be divided into two steps, a quick step and a slow one. In the first step, the adsorption rate was fast, and 83% of the equilibrium adsorption capacity was achieved within 30 min. In the subsequent step, the adsorption was slow and reached equilibrium at about 24 h. The quick adsorption may be due to the smaller particle size (200 mesh) of

Fig. 2. SEM micrographs of (a) pure activated carbon, (b) pure copper ferrite and (c) the 1:1.5 CuFe_2O_4 /activated carbon composite.

Fig. 3. Adsorption kinetics of AO7 on activated carbon and 1:1.5 composite (50 ml AO7 solution, initial concentration 500 mg l^{-1} , pH 5.2 ± 0.1 ; 0.100 g adsorbent; *1:1.5 composite containing 0.100 g carbon).

activated carbon and the composite, which was favorable for the diffusion of dye molecules onto the active sites of the adsorbent. As a result, higher adsorption efficiency was realized in a shorter adsorbing time. The enlarged curves of the quick adsorption step are shown in the graph on the right-lower part of Fig. 3. It can be seen from the small graph that the adsorption rate of AO7 onto the composite was a little faster than that of activated carbon in the first step when the added composite contains 0.100 g activated carbon. This result indicates that the adsorption capacity of activated carbon is not affected by the presence of CuFe_2O_4 .

3.2.2. Effect of pH on AO7 removal

Fig. 4 shows the effect of pH on the removal of AO7 by the CuFe_2O_4 powder and the 1:1.5 composite. The initial concentrations of AO7 for CuFe_2O_4 and the 1:1.5 composite are 200 mg l^{-1} and 500 mg l^{-1} , respectively. The adsorption of AO7 onto the CuFe_2O_4 powder was strongly pH dependent, compared with the composite. Adsorption decreased drastically when the pH value was above 5.5 and the adsorption reduced to negligible levels at pH 10. This result is similar to previous reports (Bandara et al., 1999; Wu et al., 2004). However, for the composite, the increase of pH value does not significantly decrease the removal of AO7 when the pH value is below 7.0. Though the reduction of AO7 removal is relatively marked when the pH value is above 7.0, the AO7 removal rate is still over 60% at equilibrium pH around 10. This indicates that the activated carbon in the composite is mainly responsible for the AO7 removal. Therefore, the prepared composite can be used over a broad pH range. The reduction of AO7 removal in higher pH solution may be ascribed to increase of repulsive force between the functional groups on the surface of activated carbon and AO7, which exists mainly as anion form at higher pH conditions, and thus

Fig. 4. Effect of solution pH on the adsorption of AO7 on CuFe_2O_4 and the 1:1.5 composite (50 ml AO7 solution, initial concentrations for CuFe_2O_4 and the 1:1.5 composite are 200 mg l^{-1} and 500 mg l^{-1} , respectively; 0.100 g adsorbent).

reduces the adsorption of AO7 onto the surface of the activated carbon. The adsorptive behavior of AO7 is similar to that of humic acid reported in the literature because the sulfonic and hydroxyl groups in the AO7 molecule are similar to carboxylic and phenolic groups contained in humic acid.

3.2.3. Adsorption isotherm

Adsorption capacity and adsorption behavior of azo-dye AO7 on activated carbon and the composite can be illustrated by adsorption isotherm. The adsorption isotherms are shown in Fig. 5a and b. Data from the adsorption isotherms were modeled using the Langmuir and Freundlich isotherm models with the resulting isotherm constants presented in Table 2.

Langmuir isotherm theory is based on the assumption of adsorption on a homogeneous surface. The Langmuir equation can be written in the following form:

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

where q_e is the solid phase equilibrium concentration (mg g^{-1}); C_e is the liquid equilibrium concentration of dye in solution (mg l^{-1}); k is the equilibrium adsorption constant related to the affinity of binding sites (l mg^{-1}); and q_m is the maximum amount of the dye per unit weight of adsorbent for complete monolayer coverage.

The Freundlich isotherm describes adsorption where the adsorbent has a heterogeneous surface with adsorption sites that have different energies of adsorption. The energy of adsorption varies as a function of the surface coverage (q_e) and is represented by the Freundlich constant K_F (l g^{-1}) in Eq. (2).

$$q_e = K_F C_e^m, \quad (2)$$

Fig. 5. Adsorption isotherm for AO7 on (a) original activated carbon and (b) the 1:1.5 composite. (50 ml AO7 solution, initial concentrations up to 1200 mg l⁻¹, pH 5.2 ± 0.1; 25 ± 1 °C; 0.100 g adsorbent).

where K_F is roughly an indicator of the adsorption capacity and n is the heterogeneity factor which has a lower value for more heterogeneous surfaces.

As seen in Fig. 5a, AO7 adsorption onto the activated carbon was well described by the Langmuir model with correlation coefficients of $R^2 = 0.992$. The calculated maximum adsorption capacity q_m is 404 mg g⁻¹. Results from the Freundlich analysis shown in Table 2 indicate that the correlation coefficient is significantly less than the Langmuir analysis in describing the adsorption of AO7 on the activated carbon. The fact that the Langmuir isotherm fits the experimental data very well may be due to

homogenous distribution of active sites on the activated carbon surface.

Fig. 5b illustrates the fits of the Langmuir and Freundlich isotherms to the experimental data for the adsorption of AO7 on the 1:1.5 composite. Results from the Langmuir and Freundlich analysis of the adsorption of AO7 on the 1:1.5 composite are also reported in Table 2. The fitting curves and correlation coefficient values both indicate that the Freundlich model describes better the adsorption onto the 1:1.5 composite. Because of the presence of copper ferrite small particles, the surface of the activated carbon is more heterogeneous. Thus, the adsorption behavior of AO7 on the composite is fit better by the Freundlich model.

It is interesting to note that the adsorption capacity of the 1:1.5 composite was close to that of activated carbon at low equilibrium dye concentrations (C_{eq} less than 300 mg l⁻¹) and even higher than that of the activated carbon at high equilibrium dye concentrations. The adsorption capacity expressed on a carbon mass basis for the 1:1.5 composite is 654 mg g⁻¹ carbon (392 mg g⁻¹ composite), which is significantly higher than that of the original activated carbon (404 mg g⁻¹). This indicates that the presence of copper ferrite increases, instead of decreases the adsorption capacity of the activated carbon in the composite. This phenomenon can be explained as follows. After modification with CuFe₂O₄ powder, the surface areas of the carbons were reduced and the surface was hence more heterogeneous. This may lead to change of the adsorption behavior of AO7 from monolayer adsorption to multilayer adsorption and consequently, the increase in adsorption capacity, especially at high equilibrium AO7 concentrations. As a result, the adsorption capacity of the composite did not change significantly with the decrease in surface area.

3.3. FTIR spectra for AO7 on the composite and its catalytic degradation

The FTIR spectra of AO7, activated carbon, the 1:1.5 composite, adsorbed AO7 on activated carbon and adsorbed AO7 on the 1:1.5 composite are shown in Fig. 6a. As for the spectra of AO7, the vibrations at 1600–1450 cm⁻¹ are characteristic of aromatic C=C stretching. The vibration at 1622 cm⁻¹ is due to a combination of phenyl ring vibrations with stretching of the C=N group. The intense adsorption at 1508 cm⁻¹ is attributed to N–H bending vibration. The vibration at 1453 cm⁻¹ is related to N=N stretching. The bands at 1255 and

Table 2
Langmuir and Freundlich isotherm constants for AO7 adsorption

Adsorbent	Langmuir model			Freundlich model		
	q_m (mg g ⁻¹)	b (l mg ⁻¹)	R^2	K_F (l g ⁻¹)	n	R^2
Activated carbon	404	0.056	0.992	104	0.224	0.828
1:1.5 Composite	392	0.081	0.842	156	0.150	0.981

1205 cm^{-1} are assigned to $\nu(\text{C}-\text{N})$ and $\nu(\text{N}-\text{N})$ stretching vibrations, and the peaks at 1123 and 1037 cm^{-1} are due to the coupling between the benzene mode and $\nu(\text{SO}_3)$ (Bandara et al., 1999; Styliadi et al., 2003, 2004; Zhang et al., 2005).

Fig. 6. FTIR spectra for (1) 1:1.5 composite, (2) AO7, (3) activated carbon, (4) AO7 adsorbed on activated carbon, and (5) AO7 adsorbed on 1:1.5 composite (a) and AO7 degradation processes on the original activated carbon (b) and 1:1.5 composite (c).

In the activated carbon sample, the peaks at 1599 cm^{-1} and 1455 cm^{-1} are assigned to the skeletal $\text{C}=\text{C}$ vibrations in the aromatic rings. For carbonaceous materials, in fact, $\text{C}=\text{C}$ stretching absorption frequently occurs at about 1600 cm^{-1} (Akhter et al., 1985; Gómez-Serrano et al., 1996). For the composite, the peak at 1455 cm^{-1} disappeared owing to the presence of CuFe_2O_4 . It should be noted that the phenyl ring vibrations of the AO7 adsorbed on activated carbon and the composite could not be distinguished from those resulting from aromatic rings occurring on the surface of activated carbon. However, the vibrations at 1504 cm^{-1} , 1452 cm^{-1} , 1120 cm^{-1} and 1033 cm^{-1} in the spectra of AO7 adsorbed on activated carbon are obvious and the shift of these absorptions toward lower wavenumbers indicates that chemical adsorption reaction occurred between AO7 molecules and activated carbon. The spectra of AO7 adsorbed on the composite have very similar trends. Thus, these vibrations can be used as indicators for AO7 adsorbed on activated carbon or the composite.

To a certain extent, the activated carbon can catalyze the degradation of adsorbed AO7 during regeneration. However, the catalysis ability of only activated carbon is limited. CuFe_2O_4 has good catalytic activity (Wu et al., 2004) and its presence could greatly catalyze this azo dye's decomposition. In order to obtain insights into the reaction process, degradation of AO7 on activated carbon and the composite was investigated by means of in situ DRIFT spectroscopy. In the test, about 10 mg AO7 (adsorbed on original activated carbon or the composite) was placed into the reactor. The inert atmosphere was also maintained during the heating up and the cooling-down intervals. The infrared spectra of the AO7 degradation on activated carbon and the composite at different temperature are demonstrated in Fig. 6b and c, respectively.

The AO7 adsorbed on activated carbon was stable at temperatures below 150°C (Fig. 6b). The absorptions at 1504 cm^{-1} , 1120 cm^{-1} , and 1033 cm^{-1} weakened slowly with the increase of temperature. When the temperature increased to 350°C , changes in these peaks became obvious and, after keeping at 400°C for 10 min, these two peaks disappeared, while the peak at 1033 cm^{-1} did not disappear completely. The results indicate that AO7 molecules were easily broken at $\text{N}=\text{N}$ and $-\text{SO}_3$. Nevertheless, complete breaking of the phenyl ring was difficult under the tested condition.

Fig. 6c shows the degradation process of the AO7 adsorbed on the composite. At 150°C , obvious change had occurred in the spectra. The peak at 1037 cm^{-1} ($-\text{SO}_3$) decreased sharply, the peak at 1123 cm^{-1} almost disappeared, while a new peak at 1151 cm^{-1} appeared. This indicated that breaking of $-\text{SO}_3$ away from the phenyl ring had taken place. The peaks at 1508 cm^{-1} , 1151 cm^{-1} , and 1123 cm^{-1} decreased with further increase in temperature, especially at 300°C . After staying at this temperature for 20 min, these peaks disappeared completely, and the intensive adsorption of the aromatic ring vibrations weakened evidently, which indicated that part of aromatic rings had

Fig. 7. Variation of the adsorption capacity of the composite as a function of regeneration cycles.

been cleaved. This suggested that the degradation of AO7 on the composite was easier and needed lower temperature than that on activated carbon, contributing to the higher catalytic activity of CuFe_2O_4 .

3.4. Regeneration of the spent composites

The adsorption capacity of the composite for AO7 after its regeneration has also been studied. The spent composite was regenerated following the process mentioned above. The regenerated samples were again saturated with AO7 with the same initial concentration of 1000 mg l^{-1} , determining their new adsorption capacity. These adsorption–regeneration cycles were carried out up to five times. The results obtained are depicted in Fig. 7. The value of cycle 0 corresponds to the adsorption capacity of the original composite.

Generally, the adsorption capacity of the composite decreases as the number of regeneration cycle increases. The extent of this decrease was not great for the first regeneration cycle and 97% of the initial adsorption capacity was maintained. Thereafter, the reduction was relatively obvious and after the fifth cycle, the adsorption capacity was reduced to 54%, from 199 to 109 mg g^{-1} .

Powdered activated carbon is difficult to thermally regenerate and the regeneration temperature is commonly at or beyond 800°C (Clifford et al., 1983). The good regeneration result and relatively low regeneration temperature (500°C) demonstrated that the composite could offer a much higher catalytic activity than the activated carbon alone.

4. Conclusions

CuFe_2O_4 /activated carbon magnetic adsorbents were successfully prepared by a chemical coprecipitation method. The magnetic phase formed in the composites is spinel CuFe_2O_4 .

No significant decrease in the surface area and in the microporosity of the activated carbon was caused by the presence of the copper ferrite. The composites showed high adsorption capacity for AO7 and more importantly, no reduction in adsorption was produced by the formation of the composite.

The copper ferrite present on the surface of activated carbon plays an important role in catalytic degradation of AO7 adsorbed on the composite. Moreover, the magnetic adsorbent can be used repeatedly.

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