



Preparation and characterization of MWCNTs/LDHs nanohybrids for removal of Congo red from aqueous solution

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Abstract: The assembly of layered double hydroxides (LDHs) and multi-walled carbon nanotubes (MWCNTs) nanohybrids was prepared as MWCNTs/LDHs by co-precipitation. The synthesized nanoparticles were characterized by using XRD, FT-IR, SEM/EDX, TGA and BET. XRD and SEM studies proved that MWCNTs phases did not enter into the interlayers of LDHs, they dispersed over the LDHs surface homogeneously. BET results showed that MWCNTs/LDHs possessed hierarchically porous nanostructure with large surface area (124.974 m²/g) and great pore volume (0.604 cm³/g). Batch experiments were conducted to study the adsorption efficiency of Congo red (CR). It was worthy to note that MWCNTs/LDHs exhibited excellent adsorption performance with the maximum CR adsorption capacity of 595.8 mg/g in weak acidic environment. The adsorption kinetics and isotherm parameters can be well described by the pseudo-second-order and the Langmuir isotherm models, respectively. The thermodynamic studies indicated that the adsorption process was spontaneous and endothermic.

Key words: layered double hydroxide; multi-walled carbon nanotube; Congo red; kinetic; thermodynamic; isotherm

1 Introduction

Nowadays, the disposal of dyes and pigments wastewater discharged from factories has received great attention. The deep color, low biodegradability and complex aromatic structures of dyes caused severe consequences such as aesthetic pollution, toxicity and disturbance in aquatic life [1,2]. Recently, various methods have been applied to removing the dyes in wastewater, such as adsorption, membrane separation, ion exchange, photocatalytic degradation and biological treatments [3–7]. Among these methods, adsorption has attracted much attention due to its low cost, easy design, recycle of adsorbents and few harmful secondary pollution. So, to find the low-cost, easily obtained and highly effective adsorbents has been crucial during the application of adsorption.

Layered double hydroxides (LDHs) are known as a general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A_{x/n}]^{n-} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations on layers, and the incorporated anions (A^{n-}) are

in the interlayer space for charge balancing [8]. On account of the advantages like compositional diversity, ease of synthesis and low cost, LDHs have been widely used as adsorbents for the treatment of polluted water [9–11]. On the other hand, multi-walled carbon nanotubes (MWCNTs) with large specific surface area, high thermal and chemical stability, and good mechanical flexibility, have played an important role in many fields [12,13].

The integrated MWCNTs/LDHs nanohybrids tend to present larger specific surface area and better disperse ability. It can be believed that the removal rate of dyeing effluents by MWCNTs/LDHs composites would be improved. What is more, very few similar studies had been found out according to the survey.

In this work, we synthesized the composites of negatively charged oxidized MWCNTs and positively charged LDHs compounds via electrostatic interaction between the two materials. Congo red (CR), a typical discarded anionic azo dye in aqueous environment [14,15], was selected as a model pollutant. Various conditions like pH, contact time, sorbent dosage,

and initial CR concentration were optimized for maximum sorption capacity. Furthermore, the adsorption kinetics, isotherms, and thermodynamic studies of CR adsorption process have been estimated systematically.

2 Experimental

2.1 Chemicals and materials

All chemicals used in this study were commercially available and used as-received without additional purification. $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and Congo red (CR, $\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$, CAS Registry No. 573-58-0) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., HNO_3 , HCl , Na_2CO_3 , NaOH , and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.. MWCNTs with a diameter of 20–40 nm were purchased from Shenzhen Nanotech Port Co., Ltd.. The deionized water was used for preparing the sample solutions.

2.2 Synthesis of MWCNTs/LDHs

A certain amount of pristine MWCNTs were interacted with appropriate amount HNO_3 under continuous stirring accompanied reflux condensation at 120 °C for 24 h to form negatively charged MWCNTs [16]. Then, the modified MWCNTs were washed with deionized water and ethanol alternately several times by filtering until pH was equal to about 7. Finally, the collected powder was dried under vacuum at 80 °C overnight, and the as-prepared materials were signed as O-MWCNTs.

The MWCNTs/LDHs composites were prepared by conventional co-precipitation method [17]. The modified MWCNTs with different doses were ultrasonically dispersed into 50 mL salt solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with $\text{Mg}^{2+}/\text{Al}^{3+}$ mole ratio of 2:1 at room temperature, the solution was added dropwise with an alkali solution including NaOH and Na_2CO_3 under vigorous stirring at room temperature until the pH value of the slurry was equal to 10. The concentrations of NaOH and Na_2CO_3 were settled according to the concentrations of Mg^{2+} and Al^{3+} ions as follows: $[\text{NaOH}] = 1.6[\text{Mg}^{2+} + \text{Al}^{3+}]$ and $[\text{Na}_2\text{CO}_3] = 2[\text{Al}^{3+}]$. Then, the suspension was aged in an autoclave at 80 °C for 16 h. The obtained solid denoted as MWCNTs(*x*)/LDHs (*x* represents different dosages of modified MWCNTs) was centrifuged and washed with deionized water and finally dried at 80 °C overnight. For comparison, pristine LDHs were prepared following the same procedure in aqueous solution without MWCNTs.

2.3 Characterization methods

The morphologies analyses of LDHs and MWCNTs/LDHs composites were taken on the scanning

electron microscope (SEM) (JEOL, Japan). Energy dispersive X-ray (EDX) analysis was aimed to identify the actual elemental incorporation contents of adsorbents. This analysis was aimed to identify the actual elemental incorporation contents of the adsorbents. The surface area and porosity of the adsorbents were derived on ASAP 2400 analyzer (Micro meritics, USA). The surface area, pore distribution and pore volume of the adsorbents were obtained using the adsorption isotherm branch of nitrogen gas according to the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models. X-ray diffraction (XRD) patterns were obtained by using Rigaku D/MAX 2500 X-ray diffractometer with Cu K_α radiation (40 kV, 250 mA, $\lambda = 0.154$ nm) to confirm the structure of the adsorbents. Data were obtained at 2θ from 5° to 70° with a scan speed of 8 (°)/min. Fourier transform infrared spectra (FT-IR) were recorded on an AVATAR 360 in the spectral range of 400–4000 cm^{-1} . Thermogravimetric analysis (TGA) was taken from 30 to 800 °C under nitrogen atmosphere on the instrument with the temperature increasing linearly by a rate of 8 °C/min. The zeta potentials of the particles were determined with a Malvern Zetasizer ZEN3600 according to the manufacturer's recommendations.

2.4 Adsorption methods

The adsorption equilibrium experiment was performed by adding 25 mg MWCNTs/LDHs nanocomposite adsorbents into 200 mL of CR solution with the concentration fixed at 150 mg/L. The dispersed suspension was agitated in a homoiothermal water bath shaker at a fixed speed of 200 r/min and 298 K for 5–480 min. Approximately, 5 mL of sample was taken out from the suspension at certain time intervals and then filtered with a 0.45 μm membrane for analysis.

The UV–Vis spectrophotometer (UV–2600) was used to determine the concentrations of CR dye stayed in the solution at the maximum wavelength of 485 nm. The adsorption quantity at any given time (q_t), the adsorption quantity reaching the equilibrium (q_e) and the dye removal rate (R , %) were obtained by calculating from the following equations:

$$R = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1)$$

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (2)$$

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (3)$$

where c_0 (mg/L) is the initial concentration of CR; c_t (mg/L) is the concentration of CR solution at any time t (min); c_e is the concentration of dye at the time close to equilibrium; V is the volume of dye solution (L); and m is the dosage of adsorbent (g).

3 Results and discussion

3.1 Characterization of adsorbents

X-ray diffraction patterns of LDHs, pristine MWCNTs (P-MWCNTs), oxydic MWCNTs (O-MWCNTs) and MWCNTs(x)/LDHs composites were shown in Fig. 1. The P-MWCNTs and O-MWCNTs had similar crystal structures (Figs. 1(b) and (c)). The diffraction pattern peak at around 26° was ascribed to the (002) reflection of MWCNTs (JCPDS card No. 003-4477) [18]. The peaks at 11.56° , 23.34° , 34.54° , 60.86° and 62.10° fitted well to planes (003), (006), (012), (110) and (113) of LDHs composites [8]. Notably, the characteristic peaks of MWCNTs(x)/LDHs, shown by Figs. 1(d) and (e), were the same with the pure LDHs and MWCNTs materials. The plane (002) peak intensity of MWCNTs(x)/LDHs composites increased obviously according to the increasing dose of MWCNTs. MWCNTs(x)/LDHs were formed on account of surface electrostatic attraction between LDHs and MWCNTs. Moreover, no other characteristic peaks were discovered in Fig. 1, the baseline was quite low and stable. So, it could be illustrated that the synthesized MWCNTs/LDHs materials were equipped with high crystallinity and purity.

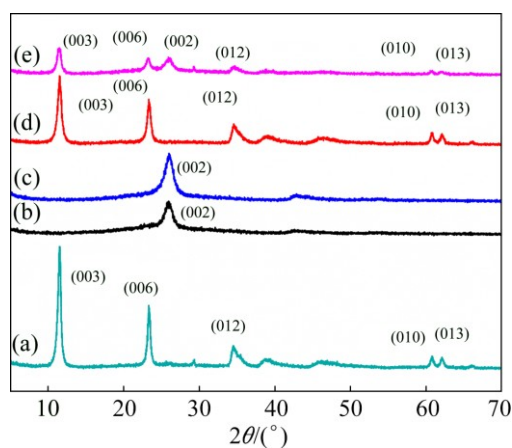


Fig. 1 XRD patterns of LDHs (a), P-MWCNTs (b), O-MWCNTs (c), MWCNTs (0.1 g)/LDHs (d) and MWCNTs (0.5 g)/LDHs (e)

The lattice parameters of LDHs and MWCNTs/LDHs were shown in Tables 1 and 2. The d_{003} and d_{006} of LDHs phases were kept around 0.76 nm and 0.38 nm in LDHs and MWCNTs/LDHs, respectively, which agreed with the reported literature [19]. The cell parameter c , calculated from d_{003} ($c=3d_{003}$), matched the distance from the hydroxide layer to the adjacent; parameter a ($a=2d_{110}$), matched the average distance between the two metal ions within the layers. Obviously,

the structure of the brucite-like layers and the distance among the layers had not changed. In other words, the MWCNTs phases did not enter into the interlayers of LDHs, but they dispersed over the LDHs surface homogeneously.

Table 1 Crystal cell parameters of samples

Sample	$a=2d_{110}/\text{nm}$	$c=3d_{003}/\text{nm}$
LDHs	0.30	2.29
MWCNTs/LDHs	0.31	2.31

Table 2 Basal spacing values of samples

Characteristic reflection	LDHs		MWCNTs/LDHs		MWCNTs	
	$2\theta/^\circ$	d/nm	$2\theta/^\circ$	d/nm	$2\theta/^\circ$	d/nm
(003)	11.56	0.76	11.48	0.77	—	—
(006)	23.34	0.38	23.24	0.38	—	—
(002)	—	—	26.18	0.34	26.18	0.34
(009)	34.54	0.26	34.5	0.26	—	—
(110)	60.86	0.15	60.66	0.15	—	—

As shown in Fig. 2, the strong and broad absorption bands at around 3424 cm^{-1} were due to the O—H stretching vibration from water molecules on the layer surfaces and in interlayers. The bands at around 1360, 784 and 676 cm^{-1} were corresponding to the stretching and bending vibration of carbonate anions in the layers, which were similar to the literature reported [8]. The bands at around 2363, 1702, 1566 and 1082 cm^{-1} were attributed to stretching of carbon-oxygen and carboxylate groups [18].

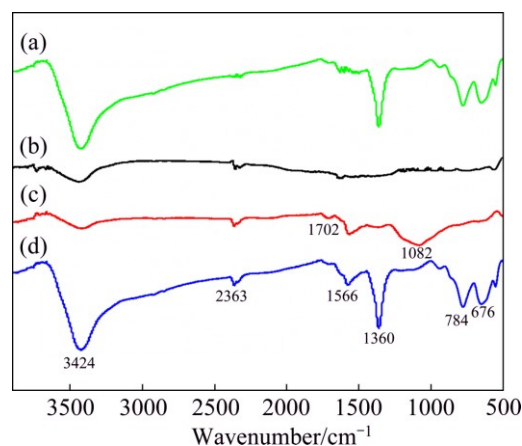


Fig. 2 FT-IR spectra of LDHs (a), P-MWCNTs (b), O-MWCNTs (c) and MWCNTs/LDHs (d)

As seen from Fig. 3, the LDHs particles and the MWCNTs were tangled together to form agglomerated particles, the morphology of MWCNTs/LDHs was much rougher than that of LDHs. The dispersivity of LDHs was obviously improved because of the input of MWCNTs. Besides, LDHs kept the layer structure [20].

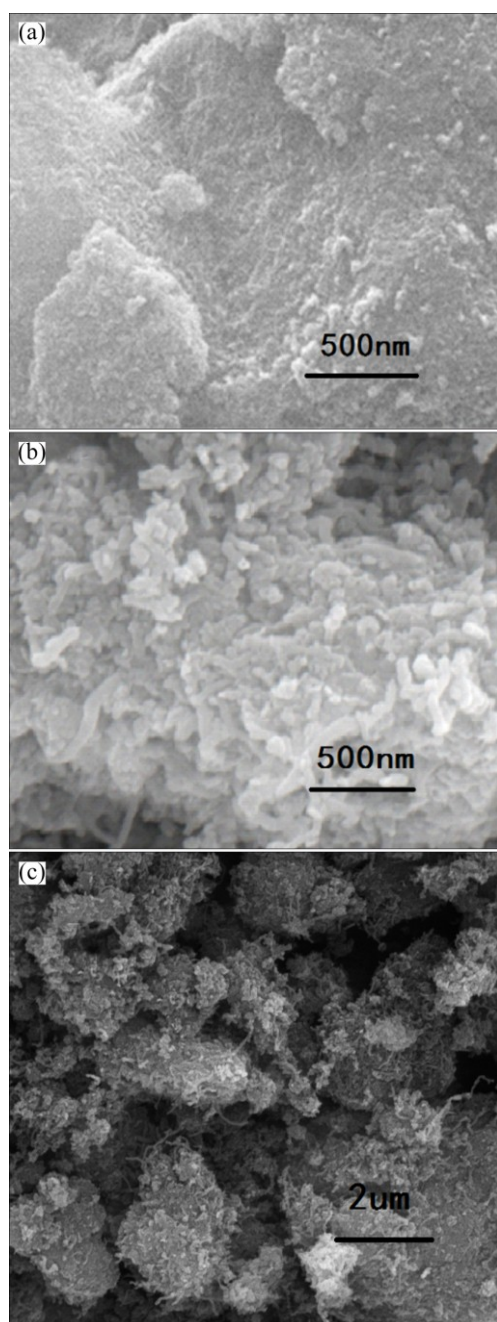


Fig. 3 SEM images of LDHs (a) and MWCNTs/LDHs with varied magnifications (b, c)

Table 3 showed that mainly four elements (C, O, Mg and Al) existed in the MWCNTs/LDHs composites, and the Mg/Al mole ratio was kept at 2:1. It was also illustrated that the density of metal elements in LDHs layers had not changed during the reaction process. The high density of carbon was due to the MWCNTs.

Table 3 Element analysis of MWCNTs/LDHs by EDX (mass fraction, %)

Mg	Al	C	O
5.72	2.87	58.20	33.21

Figure 4(a) showed that two significant mass losses appeared in LDHs: the temperature range of 20–280 °C was the first mass loss (about 16.8%), which was attributed to the removal of surface-adsorbed and layer-intercalated water. The major loss (about 27.1%) at 280–480 °C could be assigned to the decomposition of carbonate anions between the layers and the removal of hydroxylation in LDHs layers [21]. As seen from Fig. 4(b), the thermal decomposition process of MWCNTs/LDHs also consisted of two main mass losses. It was noted that MWCNTs/LDHs showed less mass loss in each stage compared to the original LDHs. Obviously, the thermostability of MWCNTs/LDHs composites was improved in comparison with LDHs.

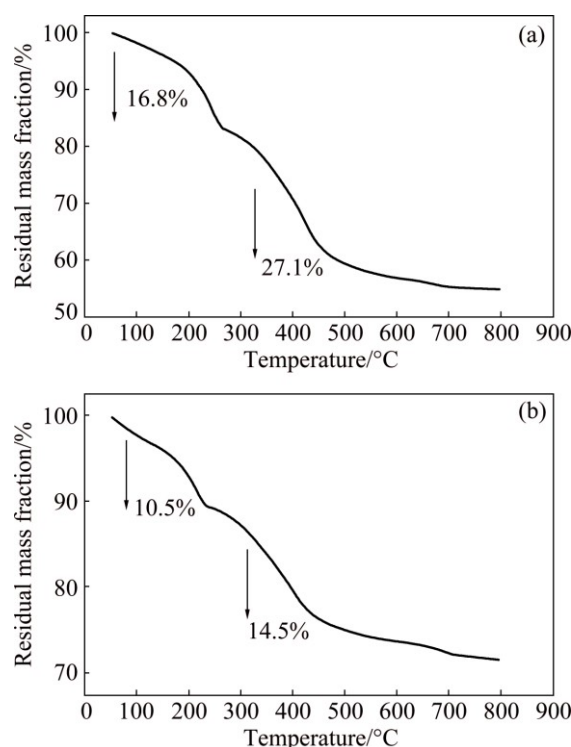


Fig. 4 TGA curves of LDHs (a) and MWCNTs/LDHs (b)

Figure 5 showed the nitrogen adsorption–desorption isotherm of O-MWCNTs, P-MWCNTs, LDHs and MWCNTs/LDHs composites. All the samples exhibited type IV nitrogen adsorption isotherms (IUPAC) with H3-type hysteresis loops for the desorption isotherms [19]. It was illustrated that the pore structure characteristics of the composites were the same. Parameters in Table 4 showed the surface areas, pore volumes and pore diameters of samples. Obviously, the dispersion of LDHs increased due to the addition of MWCNTs. The pore diameters of samples were distributed to the range of 2–50 nm, which fitted to the mesoporous materials.

The results from the XRD, FT-IR, SEM/EDX, N₂-sorption isotherm and TGA demonstrated that the MWCNTs/LDHs composites were obtained successfully.

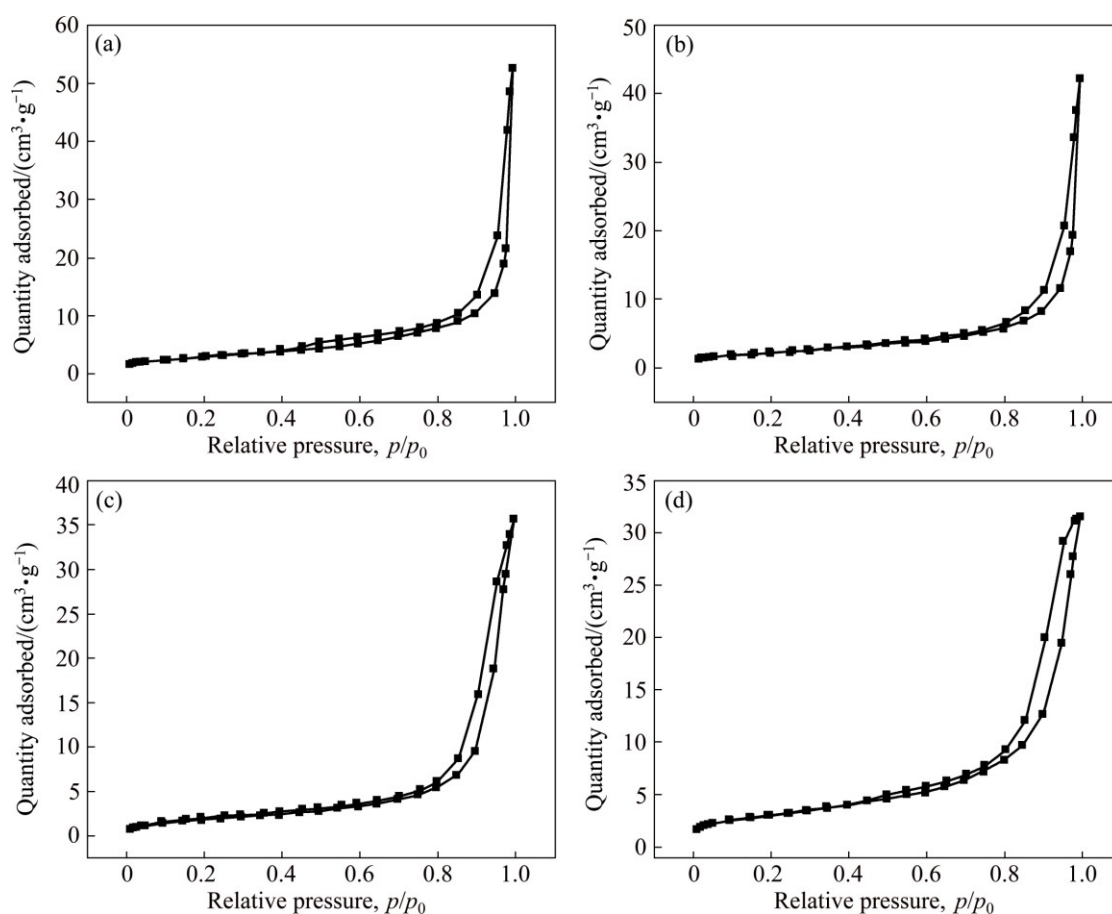


Fig. 5 Nitrogen adsorption-desorption isotherms of O-MWCNTs (a), P-MWCNTs (b), LDHs (c) and MWCNTs/LDHs (d)

Table 4 Pore structure parameters of samples

Sample	Surface area/(m ² ·g ⁻¹)	Pore volume/(mL·g ⁻¹)	Pore diameter, D _v /nm
P-MWCNTs	70.476	0.627	3.775
O-MWCNTs	104.818	0.900	3.812
LDHs	59.956	0.580	18.042
MWCNTs/LDHs	124.974	0.604	3.805

3.2 CR dye removal by MWCNTs/LDHs

3.2.1 Effects of contact time

As seen from Fig. 6(a) that MWCNTs/LDHs had strong adsorption ability (595.8 mg/g). The adsorption rate of MWCNTs/LDHs was fast at the first beginning 70 min. Soon after, the adsorption rate slowed down gradually, and the adsorption finally reached the equilibrium 3 h later.

3.2.2 Effects of solution pH

To explore the effect of solution pH value on the adsorption performance of the MWCNTs/LDHs nanocomposites, the initial pH of the CR solution was adjusted to the range of 4–9 by using 0.10 mol/L HNO₃ and 0.10 mol/L NaOH solutions. Figure 6(b) showed that the adsorption performance became poor with increasing

the pH value. Obviously, the removal of CR solution by MWCNTs/LDHs preferred lower pH value. To analyze the adsorption mechanism, zeta potentials of MWCNTs/LDHs in CR solution with variable pH were measured at room temperature and the results were presented in Fig. 7. As in conjunction with Fig. 6(b), the optimal removal rate was achieved when zeta potential was near zero. This study proved that the adsorption system was mostly dominated by charge neutralization [22].

3.2.3 Effects of initial dye concentration

To explore the influence of initial CR concentration on CR removal, simulative wastewater solution was obtained by diluting the dye stock solution in distilled water to get various desired concentrations (50–250 mg/L). As shown in Fig. 6(c), the CR adsorption sites grew with increasing the concentration of CR solution, and the removal rate of CR also increased gradually. It could be seen that the unsaturated adsorption sites on the surface of MWCNTs/LDHs decreased with the increase of initial concentration. When $c_0=50$ mg/L, the adsorption rate reached the peak value of 99.7%.

3.2.4 Effects of adsorbent dosage

The effect of adsorbent dosage on CR removal was studied by adding various dosages of MWCNTs/LDHs

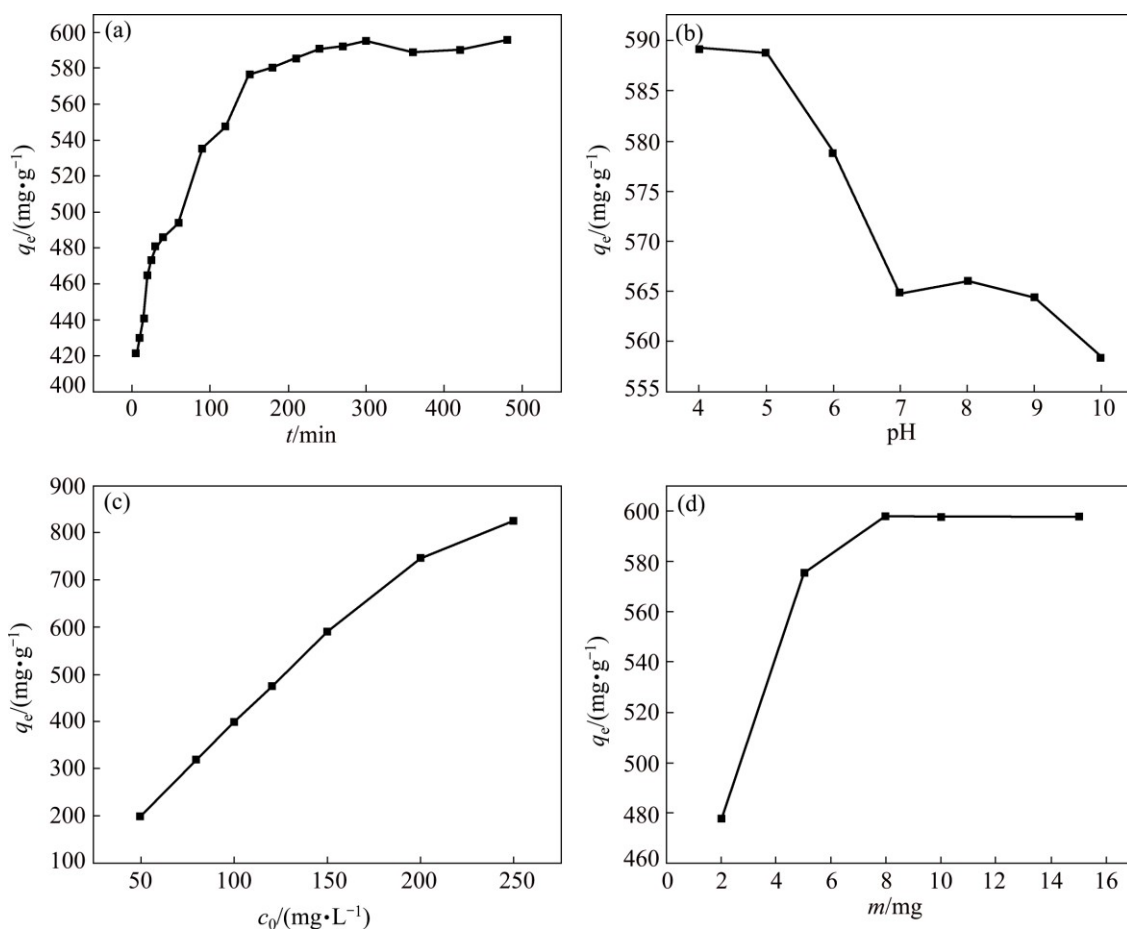


Fig. 6 Effects of different factors on CR dye adsorption by MWCNTs/LDHs: (a) Contact time; (b) pH; (c) Initial dye concentration; (d) Adsorbent dosage

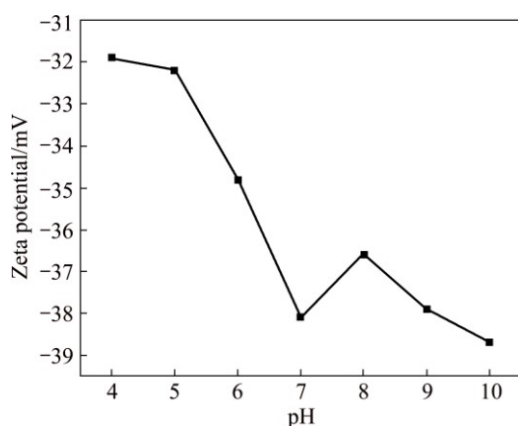


Fig. 7 Zeta potential of MWCNTs/LDHs with pH in CR

nanocomposites (2–15 mg) into 20 mL CR solution with a concentration of 150 mg/L and a fixed pH value of 7. The effect of adsorbent dosage on CR removal was shown in Fig. 6(d). It was observed that the removal rate increased with an increase in adsorbent dosage from 2 to 8 mg. The removal rate did not change with increasing the dosage of the adsorbents from 2 to 8 mg.

3.2.5 Comparison of materials

The removal rates of different materials for CR

from aqueous solution were determined in the same condition of contact time, pH, adsorbent dosage, initial dye concentration, rotation speed and temperature. As shown in Fig. 8, the removal rate of the MWCNTs (0.5 g)/LDHs composites was the highest. Significantly, the removal rate of the MWCNTs/LDHs composites rose with increasing the amount of MWCNTs, which illustrated that the addition of MWCNTs could improve the removal rate for anionic azo dye pollutants by LDHs.

Furthermore, there were few reports about the use of MWCNTs/LDHs materials for the adsorption of azo dye. The comparison of the results from this study and literature survey was illustrated in Table 5. As can be seen from Table 5, compared with all of adsorbents used, MWCNTs/LDHs may be a good option for wastewater treatment.

3.2.6 Adsorbent recyclability

After the adsorption reaction, the used adsorbents were ultrasonic washed by ethanol and deionized water alternately until the solution became colorless. The solid powders were collected and dried in vacuum oven under 80 °C overnight. As shown in Fig. 9, the adsorption removal rate of the recycled materials gradually

declined, but the reuse removal rate was still above 68% after five cycles. It was proved that the MWCNTs/LDHs were efficient adsorbents for the treatment of dye wastewater with good recyclability.

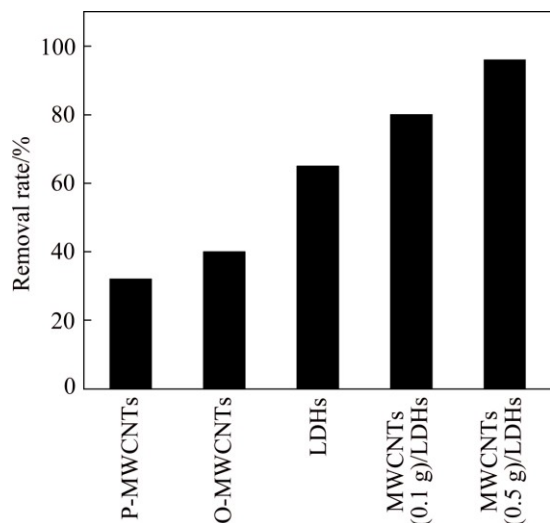


Fig. 8 Comparison of CR removal effect by different materials

Table 5 Comparison of adsorption capability of CR with literature

No.	Adsorbent	$q_e/(\text{mg} \cdot \text{g}^{-1})$	Ref.
1	NiO–SiO ₂	204.1	[23]
2	Sr ₅ (PO ₄) ₃ (OH)/Fe ₃ O ₄	396	[24]
3	MWCNTs	352.11	[25]
4	Activated carbon	32.85	[14]
5	MnFe ₂ O ₄ /PW	86.96	[26]
6	Fe ₂ O ₃ –Al ₂ O ₃	498	[27]
7	Pd NPs–AC	76.9	[28]
8	Ag NPs–AC	66.7	[28]
9	ZnO–NRs–AC	142.9	[28]
10	MWCNTs/LDHs	598.5	This study

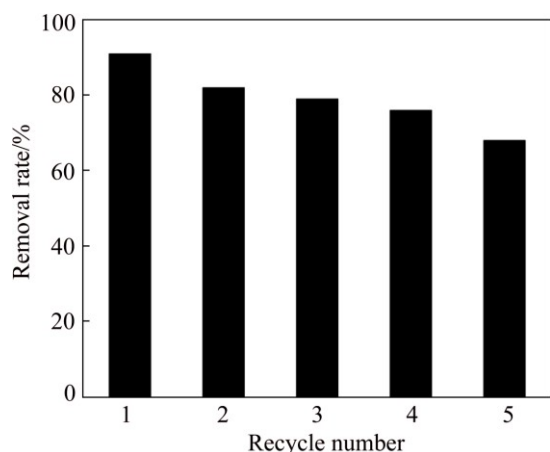


Fig. 9 Recyclability of MWCNTs/LDHs on CR adsorption with five cycles

3.3 Adsorption isotherms

In order to analyze the distribution of adsorbates between the liquid and adsorbents at certain temperature, two models including Langmuir and Freundlich were used to describe the adsorption processes.

The non-linearized form of Langmuir isotherm model could be described as the following equation:

$$q_e = \frac{q_m k_L c_e}{1 + k_L c_e} \quad (4)$$

where k_L (L/mg) is the Langmuir adsorption constant related to the energy of adsorption, q_m and q_e (mg/g) are the maximum and equilibrium adsorption capacities, respectively.

The non-linearized form of Freundlich isotherm model is given as the following equation:

$$q_e = k_F c_e^{1/n} \quad (5)$$

where k_F and n are the Freundlich constants related to the capacity and intensity of adsorption, respectively.

The adsorption isotherms of CR onto MWCNTs/LDHs were shown in Figs. 10(a) and (b). The correlation coefficient values of CR dye adsorption isotherms by MWCNTs/LDHs were listed in Table 6. It could be assumed that the Langmuir model was much more correlated to the experimental data for adsorbents. And the adsorption took place at specific homogeneous sites within the adsorbents.

3.4 Adsorption thermodynamics

The thermodynamic parameters including the changes of Gibbs free energy (ΔG), entropy (ΔS) and enthalpy (ΔH) were determined by the adsorption isotherms at different temperatures. The changes in ΔG , ΔH and ΔS were calculated by following equations:

$$\Delta G = -RT \ln k_d \quad (6)$$

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

where R (8.314 J/(mol·K)) is the mole gas constant, k_d is obtained from q_e/c_e equation, and T (K) is the temperature.

The thermodynamic data for the adsorption of dyes onto MWCNTs/LDHs composites were listed in Table 7. The negative values of ΔG and positive values of ΔH indicated that the adsorption of CR onto MWCNTs/LDHs composites was spontaneous and endothermic. The positive values of ΔS illustrated that the randomness increased at the solid/solution interface during the adsorption of CR on the MWCNTs/LDHs composites.

3.5 Kinetics of adsorption

Two kinetic models, pseudo-first-order and pseudo-second-order, were used to investigate the kinetics of the adsorption of CR onto MWCNTs/LDHs.

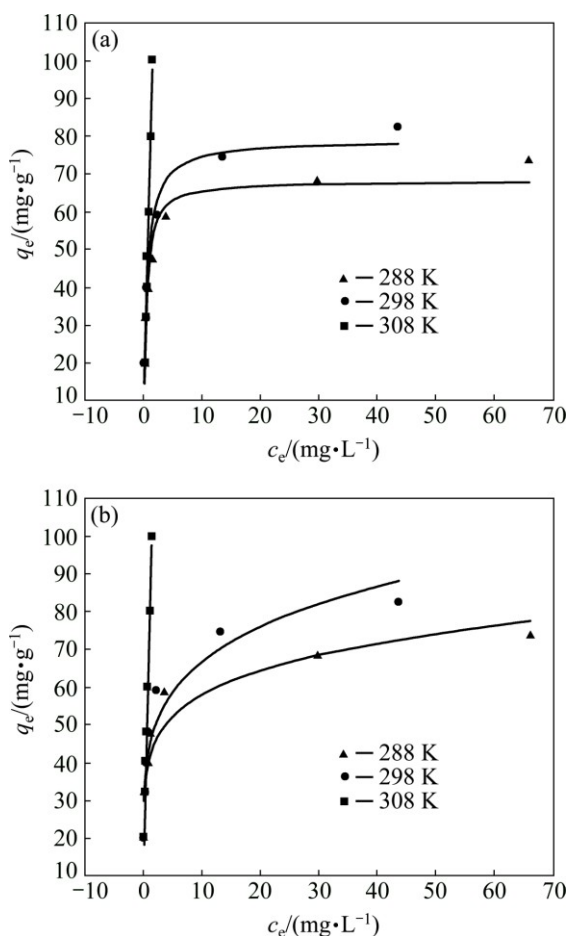


Fig. 10 Adsorption isotherms fitted with Langmuir (a) and Freundlich (b) models of CR removal on MWCNTs/LDHs at different temperatures

Table 6 Parameters calculated by Langmuir and Freundlich isotherm models for CR removal onto MWCNTs/LDHs

<i>T</i> /K	Langmuir isotherm model		Freundlich isotherm model		
	$k_L/(\text{L} \cdot \text{mg}^{-1})$	R^2	k_F	n	R^2
308	0.13	0.988	664.25	1.14	0.993
298	1.64	0.964	403.46	5.27	0.908
288	2.28	0.902	405.3	6.49	0.886

Table 7 Thermodynamic data for adsorption of dyes onto MWCNTs/LDHs composites

<i>T</i> /K	$\Delta G^\ominus/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S^\ominus/(\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$\Delta H^\ominus/(\text{kJ} \cdot \text{mol}^{-1})$
288	−12.07		
298	−13.71	0.233	52.44
308	−16.57		

The pseudo-first-order and pseudo-second-order kinetic models were shown in following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

$$t/q_e = 1/(k_2 q_e^2) + t/q_e \quad (9)$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at adsorption time t (min) respectively, k_1 (min^{-1}) and k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

Figure 11 showed the first-order (a) and second-order (b) kinetics of CR adsorption. All the values along with correlation coefficients were given in Table 8. Obviously, the experimental data were closer to the pseudo-second-order kinetic model. And the R^2 value for the pseudo-second-order kinetic model was higher than that calculated with the pseudo-first-order kinetic model. So, the CR adsorption onto MWCNTs/LDHs was suited for the pseudo-second-order kinetic model at 25 °C.

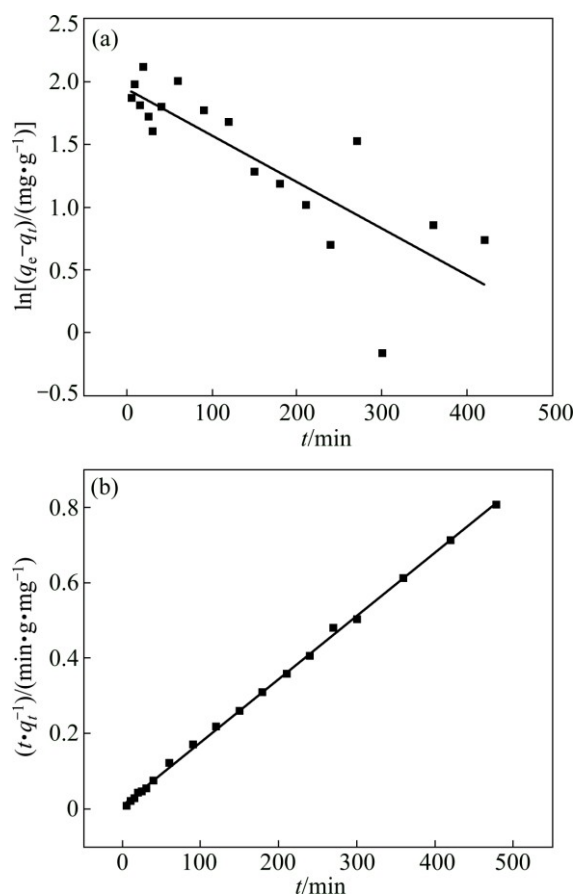


Fig. 11 CR adsorption kinetics by MWCNTs/LDHs: (a) Pseudo-first-order model; (b) Pseudo-second-order model

Table 8 Kinetic parameters of CR adsorption in MWCNTs/LDHs

<i>T</i> /K	$q_{e,\text{exp}}/(\text{mg} \cdot \text{g}^{-1})$	Pseudo-first-order		
		$q_{e,\text{cal}}/(\text{mg} \cdot \text{g}^{-1})$	k_1/min^{-1}	R^2
298	595.8	87.72	8.54	0.653
<i>T</i> /K	$q_{e,\text{exp}}/(\text{mg} \cdot \text{g}^{-1})$	Pseudo-second-order		
		$q_{e,\text{cal}}/(\text{mg} \cdot \text{g}^{-1})$	$k_2/(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	R^2
298	595.8	598.8	1	0.999

4 Conclusions

1) The composites of negatively charged oxidized multi-walled carbon nanotubes and positively charged layered double hydroxides compounds were synthesized via electrostatic interaction between the two materials. The structural characteristics of MWCNTs/LDHs nanohybrids were characterized by SEM/EDX, FT-IR, BET, XRD, TGA and N₂-sorption isotherm. The results showed that the dispersivity of LDHs was obviously improved due to the addition of MWCNTs.

2) MWCNTs/LDHs were effective adsorbents with an adsorption capability of 595.8 mg/g for the removal of CR in aqueous solution. The dye adsorption by MWCNTs/LDHs depended on various parameters such as adsorbent dosage, contact time, pH, and initial dye concentration. The adsorption percentage was maximal in weak acidic environment.

3) The experimental data were best fitted to Langmuir isotherms, which could be assumed that the sorption process was monolayer. And the adsorption kinetic followed pseudo-second-order kinetics. Furthermore, thermodynamic studies showed that the adsorption process was spontaneous and endothermic. It could be expected that the adsorbents with good recyclability were potential materials in wastewater treatment.

References

- [1] SURESH P, VIJAYA J J, KENNEDY L J. Photocatalytic degradation of textile dyeing wastewater through microwave synthesized Zr-AC, Ni-AC and Zn-AC [J]. Transactions of Nonferrous Metals Society of China, 2015, 25(12): 4216–4225.
- [2] BELTRÁN-HEREDIA J, SÁNCHEZ-MARTÍN J, DELGADO-REGALADO A. Removal of carmine indigo dye with moringa oleifera seed extract [J]. Industrial & Engineering Chemistry, 2009, 48(14): 6512–6520.
- [3] HU Q H, QIAO S Z, HAGHSERESHT F, WILSON M A, LU G Q. Adsorption study for removal of basic red dye using bentonite [J]. Industrial & Engineering Chemistry, 2006, 45(2): 733–738.
- [4] SANTHY K, SELVAPATHY P. Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon [J]. Bioresource Technology, 2006, 97(11): 1329–1336.
- [5] ZAPATA A, OLLER I, SIRTORI C, RODRÍGUEZ A, SÁNCHEZ-PÉREZ J A, LÓPEZ A, MEZCUA M, MALATO S. Decontamination of industrial wastewater containing pesticides by combining large-scale homogeneous solar photocatalysis and biological treatment [J]. Chemical Engineering Journal, 2010, 160: 447–456.
- [6] LIU C H, WU J S, CHIU H C, SUEN S Y, CHU K H. Removal of anionic reactive dyes from water using anion exchange membranes as adsorbents [J]. Water Research, 2007, 41(7): 1491–1500.
- [7] HUSAIN Q. Potential applications of the oxidoreductive enzymes in the decolorization and detoxification of textile and other synthetic dyes from polluted water: A review [J]. Critical Reviews in Biotechnology, 2006, 26(4): 201–221.
- [8] ZHANG Fen, ZHANG Chang-lei, SONG Liang, ZENG Rong-chang, LIU Zhen-guo, CUI Hong-zhi. Corrosion of in-situ grown MgAl-LDH coating on aluminum alloy [J]. Transactions of Nonferrous Metals Society of China, 2015, 25(10): 3498–3504.
- [9] LI Chang-ming, WEI Min, EVANS D G, DUAN Xue. Recent advances for layered double hydroxides (LDHs) materials as catalysts applied in green aqueous media [J]. Catalysis Today, 2015, 247: 163–169.
- [10] WANG Qiang, O'HARE D. Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets [J]. Chemical Reviews, 2012, 112(7): 4124–4155.
- [11] GUO Xiao-xiao, ZHANG Fa-zhi, EVANS D G, DUAN Xue. Layered double hydroxide films: Synthesis, properties and applications [J]. Chemical Communications, 2010, 46(29): 5197–5210.
- [12] YANG Wei-jie, DING Ping, ZHOU Lei, YU Jin-gang, CHEN Xiao-qing, JIAO Fei-peng. Preparation of diamine modified mesoporous silica on multi-walled carbon nanotubes for the adsorption of heavy metals in aqueous solution [J]. Applied Surface Science, 2013, 282: 38–45.
- [13] LIU Yan, CUI Gui-jia, LUO Chao, ZHANG Li, GUO Yao-peng, YAN Shi-qiang. Synthesis, characterization and application of amino-functionalized multi-walled carbon nanotubes for effective fast removal of methyl orange from aqueous solution [J]. RSC Advances, 2014, 4(98): 55162–55172.
- [14] CHONG K Y, CHIA C H, ZAKARIA S, SAJAB M S. Vaterite calcium carbonate for the adsorption of Congo red from aqueous solutions [J]. Journal of Environmental Chemical Engineering, 2014, 2(4): 2156–2161.
- [15] ABBAS M, TRARI M. Kinetic, equilibrium and thermodynamic study on the removal of Congo red from aqueous solutions by adsorption onto apricot stone [J]. Process Safety and Environmental Protection, 2015, 98: 424–436.
- [16] PANAHIAN S, RAISI A, AROUJALIAN A. Multilayer mixed matrix membranes containing modified-MWCNTs for dehydration of alcohol by pervaporation process [J]. Desalination, 2015, 355: 45–55.
- [17] AHMED I M, GASSER M S. Adsorption study of anionic reactive dye from aqueous solution to Mg-Fe-CO₃ layered double hydroxide (LDH) [J]. Applied Surface Science, 2012, 259: 650–656.
- [18] LI Qing-hua, ZHOU Qin-hua, DENG Dan, YU Qiao-zhen, GU Li, GONG Ke-da, XU Ke-hang. Enhanced thermal and electrical properties of poly (D, L-lactide)/multi-walled carbon nanotubes composites by in-situ polymerization [J]. Transactions of Nonferrous Metals Society of China, 2013, 23(5): 1421–1427.
- [19] TAKEI T, MIURA A, KUMADA N. Soft-chemical synthesis and catalytic activity of Ni-Al and Co-Al layered double hydroxides (LDHs) intercalated with anions with different charge density [J]. Journal of Asian Ceramic Societies, 2014, 2(3): 289–296.
- [20] AN Yang, HOU Juan, LIU Zhi-yong, PENG Bang-hua. Enhanced solid-phase photocatalytic degradation of polyethylene by TiO₂-MWCNTs nanocomposites [J]. Materials Chemistry and Physics, 2014, 148(1–2): 387–394.
- [21] FAHAMI A, BEALL G W. Mechanochemical synthesis and characterization of hydrotalcite like Mg-Al-SO₄-LDH [J]. Materials Letters, 2016, 165: 192–195.
- [22] ORIEKHOVA O, STOLL S. Investigation of FeCl₃ induced coagulation processes using electrophoretic measurement, nanoparticle tracking analysis and dynamic light scattering: Importance of pH and colloid surface charge [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014, 461: 212–219.
- [23] LEI Chun-sheng, ZHU Xiao-feng, ZHU Bi-cheng, YU Jia-guo, HO Wing-kei. Hierarchical NiO-SiO₂ composite hollow microspheres with enhanced adsorption affinity towards Congo red in water [J]. Journal of Colloid and Interface Science, 2016, 466: 238–246.

- [24] ZHANG Fan, YIN Xiao-ju, ZHANG Wei-hua. Development of magnetic $\text{Sr}_5(\text{PO}_4)_3(\text{OH})/\text{Fe}_3\text{O}_4$ nanorod for adsorption of Congo red from solution [J]. Journal of Alloys and Compounds, 2016, 657: 809–817.
- [25] ZARE K, SADEGH H, SHAHRYARI-GHOSHEKANDI R, MAAZINEJAD B, ALI V, TYAGI I, AGARWAL S, GUPTA V K. Enhanced removal of toxic Congo red dye using multi walled carbon nanotubes: Kinetic, equilibrium studies and its comparison with other adsorbents [J]. Journal of Molecular Liquids, 2015, 212: 266–271.
- [26] AKKAYA SAYGILI G. Synthesis, characterization and adsorption properties of a novel biomagnetic composite for the removal of Congo red from aqueous medium [J]. Journal of Molecular Liquids, 2015, 211: 515–526.
- [27] MAHAPATRA A, MISHRA B G, HOTA G. Adsorptive removal of Congo red dye from wastewater by mixed iron oxide-alumina nanocomposites [J]. Ceramics International, 2013, 39: 5443–5451.
- [28] GHAEDI M, BIYAREH M N, KOKHDAN S N, SHAMSALDINI S, SAHRAEI R, DANESHFAR A, SHAHRIYAR S. Comparison of the efficiency of palladium and silver nanoparticles loaded on activated carbon and zinc oxide nanorods loaded on activated carbon as new adsorbents for removal of Congo red from aqueous solution: Kinetic and isotherm study [J]. Materials Science and Engineering C, 2012, 32(4): 725–734.

多壁碳纳米管/层状双金属氢氧化合物杂化材料的制备和表征及其对刚果红废水的吸附性能

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摘 要: 通过共沉淀法将多壁碳纳米管组装到层状双氢氧化物表面, 得到新型杂化材料多壁碳纳米管/层状双金属氢氧化合物(MWCNTs/LDHs)。采用 XRD、FT-IR、SEM/EDX、TGA 和 BET 对合成材料进行表征。XRD 与 SEM 研究表明, MWCNTs 未进入 LDHs 层内, 而是均匀地分布在 LDHs 层状表面。BET 结果表明, MWCNTs/LDHs 是具有高比表面积($124.974 \text{ m}^2/\text{g}$)和大孔体积($0.604 \text{ cm}^3/\text{g}$)的多孔材料。采用批次实验法研究 MWCNTs/LDHs 对染料刚果红的吸附效果。值得注意的是, 在弱酸溶液环境下 MWCNTs/LDHs 对刚果红的最大吸附量达到 595.8 mg/g , 表现出优异的吸附性能。通过对吸附所得数据进行热力学及动力学拟合, 发现吸附过程符合 Langmuir 吸附, 且符合准二级动力学模型; 由所得热力学数据可知, 吸附过程为自发及吸热过程。

关键词: 层状双金属氢氧化合物; 多壁碳纳米管; 刚果红; 动力学; 热力学; 等温线

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