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羧基化多壁碳纳米管/ Fe_3O_4 磁性复合材料对水中铜(II)的吸附性能

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摘要: 羧基化多壁碳纳米管(c-MWCNT)/ Fe_3O_4 磁性复合材料(c-MWCNTMCs)通过六水合三氯化铁、乙酸钠、乙二醇、二乙二醇和c-MWCNT混合,然后超声处理,在200℃下加热10h而制得。结果表明c-MWCNTMCs在去离子水中表现出良好的分散性、酸碱稳定性和磁性,可以作为去除铜(II)的吸附剂。c-MWCNTMCs易被磁铁从水中分离,并对铜(II)具有较高的吸附容量。c-MWCNTMCs对铜(II)的吸附较快,并成拟二级吸附动力模型。c-MWCNTMCs和Cu(II)之间的吸附力是一种化学键,在pH < 2的条件下吸附剂可以再生。具有磁性的 Fe_3O_4 只对快速分离有利,而对吸附几乎没有影响。基于这种新型复合材料从水中去除的铜(II)的检测限可达1.29 μg/L。

关键词: 羧基化磁性多壁碳纳米管; 羧基化多壁碳纳米管; 吸附; 铜(II); 化学吸附

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Adsorption performance of carboxylated multi-wall carbon nanotube- Fe_3O_4 magnetic hybrids for Cu(II) in water

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Abstract: Carboxylated multi-wall carbon nanotube (c-MWCNT)- Fe_3O_4 magnetic hybrids (c-MWCNTMCs) were prepared by mixing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium acetate, ethylene glycol and diethylene glycol with c-MWCNTs, followed by sonicating and heat treatment at 200 °C for 10 h. Results indicated that the c-MWCNTMCs showed a good dispersion stability, an acid and alkali resistivity, and magnetic properties in deionized water, and can be used as adsorbents for Cu(II) removal. The c-MWCNTMCs could be easily separated from water by a magnet and showed a high adsorption capacity for Cu(II). The adsorption of Cu(II) on the c-MWCNTMCs was quick and followed a pseudo-second-order model. The adsorption force between the c-MWCNTMHs and Cu(II) was of a chemical type and the saturated adsorbents can be regenerated at pH < 2.0. The magnetic Fe_3O_4 favored only the quick separation and had little contribution to adsorption. The low limit of Cu(II) in water that was removable with the hybrids was 1.29 μg/L.

Keywords: Carboxylated magnetic multi-walled carbon nanotube composites; Carboxylated multi-walled carbon nanotube; Adsorption; Cu(II); Chemical adsorption

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1 Introduction

A large quantity of copper is discharged annually worldwide, causing environmental problems since copper is one of the important class of inbiodegradable heavy metals^[1]. Therefore, the restriction of copper emissions has become an important task. Many conventional methods have been employed to remove copper ions from solutions, such as oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption^[2]. Adsorption is the most promising method for the removal of copper ions from wastewater due to its regenerability, high efficiency and economy.

Because of the unique physical and chemical properties such as high mechanical properties, unique electronic performance, large length-diameter ratio, high chemical stability and gigantic specific surface area, carbon nanotubes (CNTs) have the potential to be applied as the adsorbents for organic^[3] and inorganic substances^[4] in the analytical sciences. And CNTs have shown excellent adsorption ability and stable physical and chemical structures compared with other traditional adsorption materials, such as activated carbon (AC)^[5], fly ash^[6], chitin^[7] and resins^[8]. Moreover, many researchers^[9-12] have also reported that CNTs modified with various agents, such as nitric acid, hydrogen peroxide, ammonium persulfate, ethylenediamine and so on, have a higher cation adsorption capacity than the pristine CNTs.

However, the difficulty of separating CNTs from the solution is a long-standing problem. And the traditional magnetic materials bear some drawbacks, such as small surface area and limited adsorption capacity, which limit their applications. To solve the inconvenience of separating CNTs from liquid phases and the poor adsorption capacity of magnetic materials, researchers have made some improvements by introducing magnetic elements into CNTs^[13,14]. And this technology has received considerable attention in solving environmental problems these years with its primary advantage of purifying a large amount of wastewater within a short time^[15]. Gupta et al.^[16] discovered that CNTs coated with magnetic iron oxide could dispose Cr(III) with a high removal rate of about 90.0%. Gong et al.^[17] prepared magnetic multi-walled carbon nanotube composites (MMWCNTs), which displayed the advantage of separating cationic dyes compared with other adsorbents. However, the CNTs detached from the composites during the dispersion in solution by sonication due to the weak binding force (e. g. electrostatic attraction) between CNTs and magnetic ion oxides, leading to a loss of CNTs in

the composites. Therefore, developing new magnetic carbon nanotube adsorbents with acid and alkali resistance, high bond strength, high adsorption capacity and easy separation from solution is for a high efficient and economic wastewater disposal.

Based on our previous study^[18] on the preparation and characterization of new carboxylated magnetic multi-walled carbon nanotube composites (c-MWCNTMCs), the adsorption behavior of Cu(II) on c-MWCNTMCs was investigated as a function of pH, temperature and ionic strength and compared with carboxylated multi-walled carbon nanotubes (c-MWCNTs). Also, Cu(II) adsorption mechanism was discussed.

2 Experimental

2.1 Materials

MWCNTs with outer diameters of 40-60 nm and lengths of 5-15 μm were purchased from Shenzhen Nanotechnologies Port Co., Ltd., China. Ferric chloride hexahydrate was obtained from Yufeng Chemical Reagents Company (Changsha, China). Sodium diethyldithiocarbamate (DDTC), as the chelating agent, was supplied by Tingxin Chemical Reagents Company (Shanghai, China). Pentahydrate copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was used to prepare Cu(II) stock solutions. All chemicals used in the experiments were in analytical purity.

2.2 Synthesis of c-MWCNTMCs

c-MWCNTs was obtained according to the works reported previously^[10,19] and c-MWCNTMCs was prepared with reference to our previous work^[18]. Briefly, the c-MWCNTMCs was blended with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium acetate and a mixture of ethylene glycol and diethylene glycol together and then sonicated for 1 h. The homogeneous yellow solution obtained was transferred to a Teflon-lined stainless-steel autoclave, sealed and heated at 200 $^\circ\text{C}$ for 10 h. After cooled to room temperature, c-MWCNTMCs were isolated from the mixture by an external magnetic field, washed several times with ethanol and deionized water sequentially, and then dried in vacuum at 65 $^\circ\text{C}$ for 10 h.

2.3 Analytical method of Cu(II)

DDTC is selected as the chelating reagent for the higher stability constant of Cu(II)-DDTC complex than that of the other metal-DDTC complexes^[20]. Cu(II)-DDTC complex, with a low water-solubility, can be adequately dissolved and extracted from aqueous medium with non-polar organic solvents^[21]. Since a lot of emphases have been placed on green chemistry, spectrophotometric analysis of the

Cu(II)-DDTC complex without a consumption of harmful substances is advocated and has successfully been used by many researchers in aqueous medium^[22-25]. In this work, the absorbance of solution containing Cu(II)-DDTC complex was directly measured with a UV1800 UV-Vis spectrophotometer (Shimadzu Corporation, Japan) at 454 nm in aqueous phase and a nonionic surfactant PEG-1500 was added to increase the solubility of Cu(II)-DDTC complex. The blank absorbance of reagents was determined for correction.

The calculation of the concentration of Cu(II) in solutions can be expressed by the Eq. (1) below:

$$\rho = \frac{(A - A_0) - b}{a \times V} \quad (1)$$

Where ρ is the concentration of Cu(II) in solution (mg/L), A the absorbance of the stock solution, A_0 the absorbance of the blank control, b the interception of the regression equation, a the slope of the regression equation and V the sample volume (L).

2.4 Batch adsorption experiment

The adsorption of Cu(II) on adsorbents was investigated in batch mode. The suspensions of different adsorbents were pre-equilibrated with 0.01 mol/L NaCl for 24 h, to which the Cu(II) stock solutions were added. HCl or NaOH was added to adjust pH values. The suspensions were shaken for 4 h to reach equilibrium, and a fixed amount of supernatant solutions was taken to determine the absorbance. The adsorbents in suspension were separated by centrifugation for c-MWCNTs at 15000 r/min for 30 min or by using a magnet for c-MWCNTMCs. The separated adsorbents were slightly washed with deionized water to remove un-adsorbed Cu(II) ions, then put into conical flask and added with acid or base to adjust the pH values to release Cu(II) from c-MWCNTMCs. The released Cu(II) was measured as the above-mentioned method after the flask was shaken for one day.

All batch experiments were carried out at ambient temperature ($25 \pm 2^\circ\text{C}$) and all the suspensions were shaken on a constant-temperature shaker (SHZ-82) at 150 r/min. To minimize the adsorption by wall of the container, all the apparatus were immersed in the concentrated nitric acid for 24 h before use.

c-MWCNTMCs and c-MWCNTs were characterized with 8400 s Fourier transform infrared spectrometer (FTIR, Shimadzu Corporation, Japan), and their morphologies were characterized by H-800 transmission electron microscopy (TEM, Hitachi Corporation, Japan).

3 Results and discussion

3.1 Dispersion stability, acid and alkali resistivity, and magnetic performance of c-MWCNTMCs and c-MWCNTs

Fig. 1a shows the dispersion stability of the two adsorbents in deionized water after sonication for 5 min and holding for one day. The results indicated that both kinds of adsorbents could be well dispersed in deionized water. Moreover, c-MWCNTs displayed a better dispersion stability in deionized water for at least one week than that of c-MWCNTMCs with a much shorter dispersion stability of one day. The longer dispersion stability of c-MWCNTs might be ascribed to the smaller density and the better solubility increased by carboxyl groups.

To determine the acid and alkali resistivity of two kinds of adsorbents, pH values of the solutions were increased from 1.0 to 14.0. And it was obvious that the obtained supernatants were pellucid when the adsorbents were immersed in the different pH solutions, indicating that they were stable at different pH values.

The separation of mobile-solid phase is challenging. As is known to all, CNTs are difficult to separate from liquid for their tiny size. Fig. 1b shows the magnetic performance of the two adsorbents in deionized water. The c-MWCNTMCs, which possessed magnetism, could be easily separated in a few seconds and the supernatant was almost transparent, indicating that c-MWCNTMCs could completely be separated from the solution. But the c-MWCNTs, which exhibited a slight paramagnetism, cannot be separated in this way. And the traditional way of separating c-MWCNTs was filtration or centrifugation. Although filtration was suitable for the separation of a large amount of mixtures, the process is time consuming and causes mass loss of adsorbents. Meanwhile, centrifugation could only dispose a relatively small amount of mixtures. Therefore, the novel magnetic separation method is promising for separating solid material at a high speed and high efficiency.

3.2 Characterization of Cu(II)

All of the untreated CNTs were curled and entwined^[26] and the c-MWCNTs were seen with more open ends that joint the tubes together^[19]. After oxidation, the c-MWCNTs appeared exfoliated with a shorter length than the pristine CNTs. According to the previous work in our laboratory^[18], SEM image of the c-MWCNTMCs depicted an entangled network of the c-MWCNTs with clusters of iron oxides attached to their surfaces. TEM image (Fig. 1c) of the c-MWCNTMCs further confirmed the combination of c-MWCNTs and Fe_3O_4 particles.

Fig. 1d shows the surface functional groups of the pristine CNTs, the c-MWCNTs and the c-MWCNTMCs obtained by FT-IR. Compared with the pristine CNTs, the presence of C=O at 1700 cm⁻¹ and OH at 3400 cm⁻¹ in the c-MWCNTs indicated that the carboxylic groups had been successfully introduced into CNTs by oxidation. Peaks at 1400 cm⁻¹ and 920 cm⁻¹ were bending vibration absorption peaks of OH in carboxyl group, which further evidence the

presence of carboxyl group. The IR spectra of the c-MWCNTMCs showed absorptions at 3400 cm⁻¹ for OH, 1740 cm⁻¹ for C=O, and 600 cm⁻¹ for Fe₃O₄, indicating that the c-MWCNTMCs were composed of the c-MWCNTs and magnetic ion-oxides. A blue shift of C=O in the c-MWCNTMCs, as compared with the c-MWCNTs might be caused by the inductive effect from Fe₃O₄.

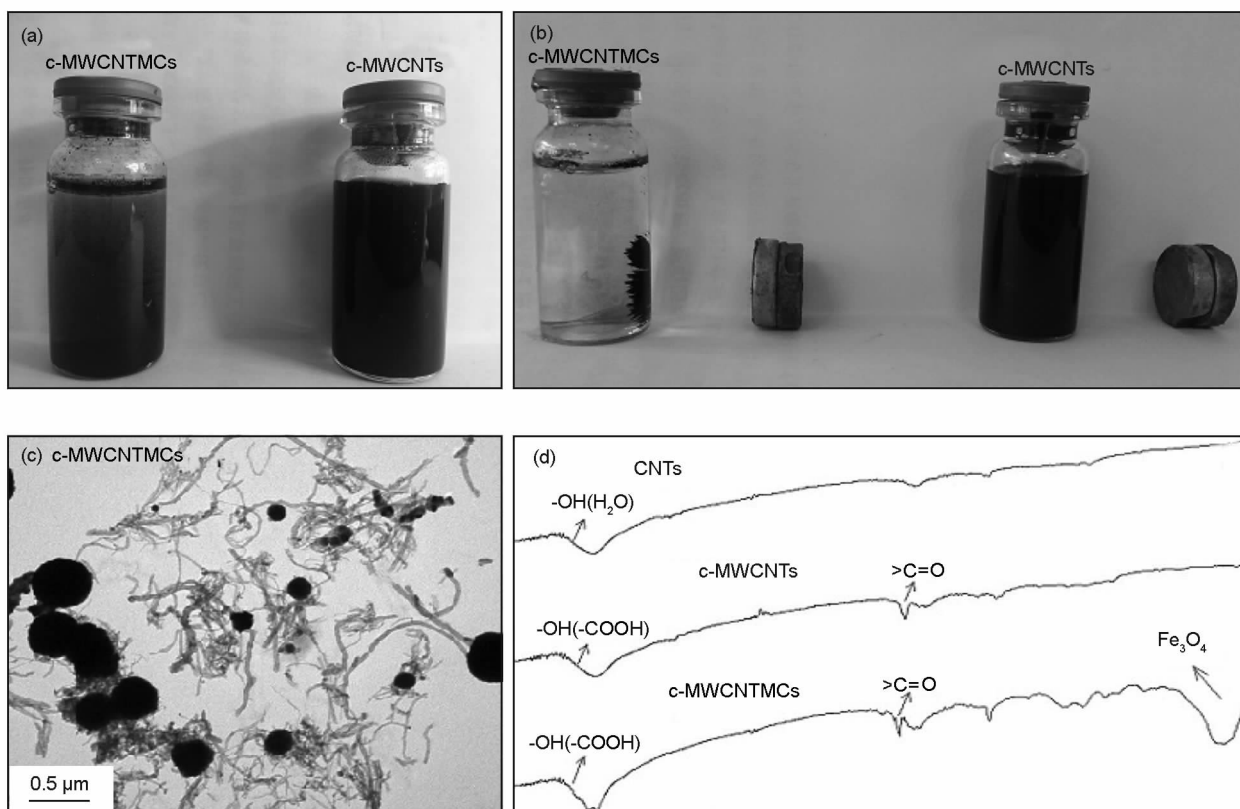


Fig. 1 (a) Dispersion state, (b) magnetic performance, (c) TEM image and (d) FT-IR spectra of the adsorbents.

3.3 The content analysis of Cu(II)-DDTC complex

Fig. 2a shows that maximum absorption peaks of Cu(II)-DDTC complex are located at 435 and 454 nm in carbon tetrachloride (non-polar organic phase) and deionized water (polar inorganic phase), respectively. Molar adsorption coefficients obtained in water and carbon tetrachloride are 7.5×10^3 and 7.9×10^3 , respectively, indicating that water phase method is feasible. Fig. 2b shows the absorption curve of the complex in water phase. The absorptions in Fig. 2b agree well with the Lambert-Beer law from 2.5 to 7.0 mg/L ($R > 0.999$, $N = 6$). The relative standard deviations (RSD) at the concentrations of 3.5, 5.0, 6.5 mg/L were all less than 1.0%, which was negligible.

3.4 Adsorption efficiency

The amount of Cu(II) adsorbed was calculated by the following equation Eq. (2):

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (2)$$

Where q_t (mg/g) is the amount of Cu(II) adsorbed, C_0 (mg/L) is the initial concentration of Cu(II), C_t (mg/L) is the concentration of Cu(II) at time t , V (L) is the solution volume, and m (g) is the mass of adsorbents.

The static equilibrium adsorption experiments were conducted to compare the adsorption performance of Cu(II) on the two adsorbents. From Fig. 3, it was found that the c-MWCNTs exhibited a slightly higher adsorption efficiency and capacity than the c-MWCNTMCs. The adsorption efficiency of Cu(II) decreased from 88.97 to 44.10% for the c-MWCNTMCs, from 93.10 to 49.70% for the c-MWCNTs. The adsorption capacity of Cu(II) increased from 8.90 to 52.9 mg/g for the c-MWCNTMCs, from 9.31 to 59.6 mg/g for the c-MWCNTs with the in-

crease of Cu(II) concentration from 1 to 12 mg/g. The phenomenon might be explained by the following two reasons. Since the c-MWCNTs had a slightly bigger specific area (167m²/g) than the c-MWCNTMCs (109m²/g) , the amount of active sites on the surface of the c-MWCNTs might be slightly more than those of the c-MWCNTMCs , and therefore , the adsorption capacity of the c-MWCNTMCs was slightly lower

than that of the c-MWCNTs. The oxygen-containing groups , mainly carboxyl and hydroxyl groups increased the solubility of adsorbents in polar media^[27] , part of which were negatively charged at pH = 6.0 by ion exchange ,leading to an increase of the adsorption for positively charged Cu(II) through electrostatic attraction.

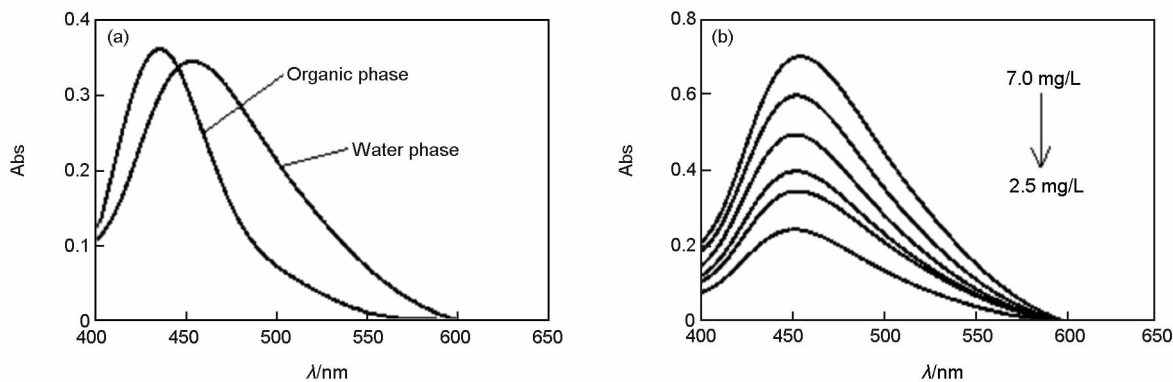


Fig.2 UV-vis adsorption spectra of Cu(II)-DDTC complex (a) in different phases and (b) that with different concentrations in water phase.

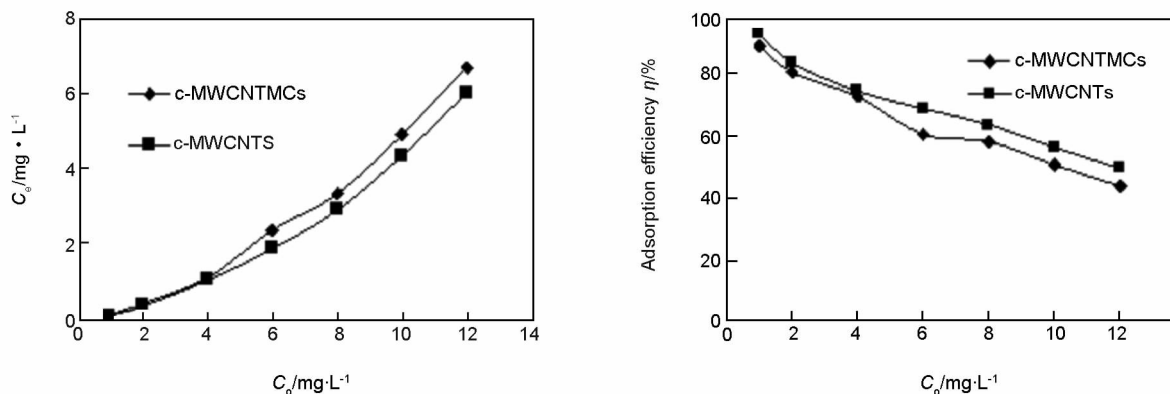


Fig.3 (a) A comparison of C_e and (b) adsorption efficiency of Cu(II) on the c-MWCNTMCs with those on the c-MWCNTs. ($V = 25.00\text{ mL}$, $m_{c\text{-MWCNTs}} = 2.5\text{ mg}$, $m_{c\text{-MWCNTMCs}} = 2.5\text{ mg}$, $t = 25\text{ }^\circ\text{C}$, $\text{pH} = 6.0$, $t = 240\text{ min}$) .

3.5 Adsorption isotherms

Fig. 4 shows the adsorption isotherms of Cu(II) on the c-MWCNTMCs and the c-MWCNTs at 25 °C. The data obtained from Fig. 4 were evaluated by Freundlich , Langmuir and Dubinin-Radushkevich (D-R) isothermal models. The Freundlich model is based on adsorption on surface active-binding sites with varied affinities. The stronger binding sites are occupied first and the binding strength decreases with the increment of site occupation. The Freundlich equation can be expressed as Eq. (3) :

$$\lg q_e = \lg K_F + \frac{1}{n} \lg C_e \quad (3)$$

The Langmuir equation , which is suitable for monolayer adsorption on surface , is expressed as Eq. (4) :

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 K_L} \quad (4)$$

In Eq. (3) and Eq. (4) , q_e (mg/g) is Cu(II) concentration on adsorbent at equilibrium , C_e (mg/L) is the Cu(II) concentration in solution at equilibrium , q_0 (mg/g) represents the maximum adsorption capacity , K_F and n represent the adsorption capacity and the adsorption driving force respectively. The bigger is the K_F , the greater is the adsorption capacity. The adsorption strength increases with the increment of n . And there is a general statement that the values of n in the range of 2 to 10 stand for good , 1 to 2 for moderate , and less than 1 for poor adsorption. K_L is the Langmuir constant related to the adsorption energy.

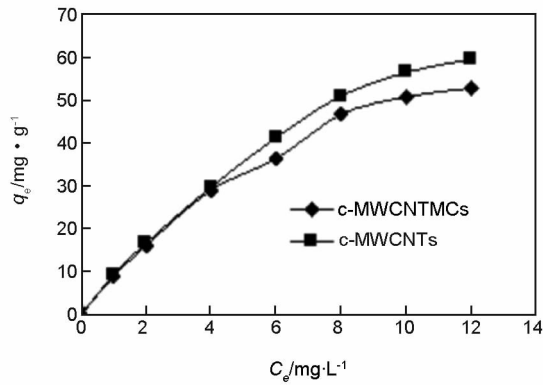


Fig. 4 Adsorption isotherm of Cu(II) on c-MWCNTs and c-MWCNTMCs. $V = 25.00 \text{ mL}$, $m_{\text{c-MWCNTs}} = 2.5 \text{ mg}$, $m_{\text{c-MWCNTMCs}} = 2.5 \text{ mg}$, $t = 25^\circ\text{C}$, $\text{pH} = 6.0$, $t = 240 \text{ min}$.

The D-R model is usually applied at low concentrations and is valid to depict the adsorption behavior on both homogeneous and heterogeneous surfaces^[28]. The D-R equation can be expressed in the linear form as Eq. (5):

$$\ln q_e = \ln q_0 - \beta \varepsilon^2 \tag{5}$$

Where, q_e (mg/g) and q_0 (mg/g) have the same meaning defined above, β (mol^2/kJ^2) is the adsorption free energy, and ε is the Polanyi potential, which is represented by Eq. (6)

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{6}$$

Where C_e (mg/L) has the same meaning defined above, R (8.314 J/mol K) is the universal gas constant, and T (K) is the adsorption temperature.

All the correlation coefficients and constants extracted from the data in Fig. 4 are listed in Table 1. The correlation coefficients of Freundlich model and

D-R model were no less than 0.99, indicating that Freundlich model and D-R model gave a better fitness than Langmuir model for the adsorption of Cu(II) on the two adsorbents. The relative adsorption capacity of the c-MWCNTs was higher than that of the c-MWCNTMCs based on K_F values, which was consistent with the results from the adsorption efficiency experiments. And the large value of K_F (>20) indicated that both adsorbents had a high adsorption affinity towards copper ions. The values of Freundlich exponent n further confirmed that the c-MWCNTs had a slightly stronger adsorption strength for Cu(II) than the c-MWCNTMCs. And the values of Freundlich exponent n of the c-MWCNTs and the c-MWCNTMCs were greater than 2, indicating that these two types of adsorbents had excellent adsorption for Cu(II). Meanwhile, adsorption activation energy $\beta E = (2\beta)^{-1/2}$ could be calculated from β obtained from D-R model^[29]. When E_a is from 1 to 8 KJ/mol, adsorption is a physical type. When E_a is from 8 to 16 KJ/mol, adsorption is an ion-exchange type. When E_a is from 20 to 40 KJ/mol, adsorption is a chemical type^[30]. The calculated E_a for the c-MWCNTMCs and the c-MWCNTs were 17.48 and 17.93 KJ/mol, implying that the adsorption of Cu(II) on the two adsorbents might be ion-exchange and chemical types.

3.6 Adsorption kinetics

In order to analyze the adsorption mechanism of Cu(II) on the c-MWCNTMCs and the c-MWCNTs, two kinetic models including the pseudo-first-order and the pseudo-second-order models were employed to assess the experimental data obtained at an initial Cu(II) concentration of 20 mg/L.

Table 1 Constants and correlation coefficients of Freundlich, Langmuir and D-R models for the adsorption of Cu(II) on adsorbents at 25 °C

Materials	Freundlich isotherm model			Langmuir isotherm model		
	$K_F / \text{mg}^{1-n} \text{ L}^n / \text{g}$	n	R^2	$q_0 / \text{mg/g}$	$K_L / \text{l/mg}$	R^2
c-MWCNTMCs	25.08	2.23	0.988	60.60	0.95	0.987
c-MWCNTs	29.56	2.27	0.992	68.03	1.05	0.984
Materials	D-R isotherm model					
	$q_0 / \text{mg/g}$	$\beta (\times 10^{-3}) / \text{mol}^2 / \text{kJ}^2$	R^2	$E_a / \text{kJ/mol}$		
c-MWCNTMCs	306.4	1.64	0.993	17.48		
c-MWCNTs	320.6	1.56	0.990	17.93		

The pseudo-first-order kinetic model [2] is expressed in linear form as Eq. (7):

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \tag{7}$$

The pseudo-second-order kinetic model [2] is described as Eq. (8):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

In Eq. (7) and Eq. (8), k_1 (min^{-1}) and k_2 ($1/\text{mg min}$) are the adsorption rate constants of first and second order kinetic models, respectively; q_e (mg/g) and q_t (mg/g) represent adsorption uptakes at equilibrium and at time t , respectively.

A plot of $\log(q_e - q_t)$ versus t according to the pseudo-first-order kinetic model should give a straight line, however, the experimental data of Cu(II) adsorption onto the two adsorbents did not follow the pseudo-first-order model. The experimental data of Cu(II) adsorption onto the two adsorbents obeyed the pseudo-second-order kinetic model as shown in Fig. 5a. The rate constants were calculated from the slope and the intercept of each linear plot in Fig. 5a. The calculated kinetics parameters for adsorption of Cu(II) on c-MWCNTMCs and c-MWCNTs were listed in Table 2. As it can be observed, the correlation coefficients (R^2) of the pseudo-second-order kinetics

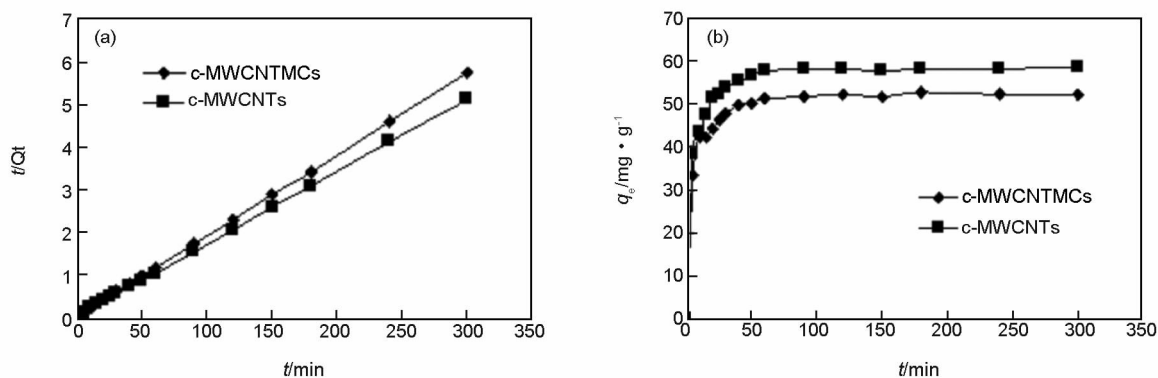


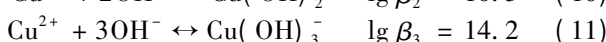
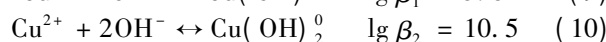
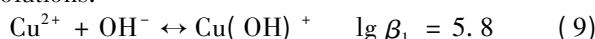
Fig. 5 (a) Pseudo-second-order kinetic models and (b) kinetic curves for adsorption of Cu(II) onto the c-MWCNTMCs and the c-MWCNTs.

Table 2 Parameters of the pseudo-second-order kinetic model for adsorption of Cu(II) onto the c-MWCNTMCs and the c-MWCNTs ($C[\text{Cu(II)}] = 20 \text{ mg/L}$)

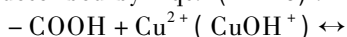
Materials	Pseudo-second-order kinetic model		
	$q_0/\text{mg/g}$	$k_2/\text{g/mg/min}$	R^2
c-MWCNTMCs	52.91	6.64×10^{-3}	0.9999
c-MWCNTs	59.17	5.94×10^{-3}	0.9999

3.7 Effect of pH values on adsorption

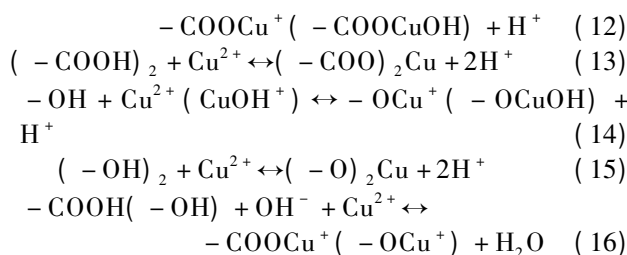
Copper can be present in deionized water in the forms of Cu^{2+} , $\text{Cu}(\text{OH})^{1+}$, $\text{Cu}(\text{OH})_2^0$, and $\text{Cu}(\text{OH})_3^-$. Equilibrium constants ($\log\beta$) for Cu(II) hydrolysis reactions^[31] are shown in Eqs. (9-11). $\text{Cu}(\text{OH})_2$ ($K_{\text{sp}} = 2.2 \times 10^{-20}$) might begin to precipitate beyond pH value of 7 at the initial concentration of Cu(II) 20 mg/L in the present study. Thus, the optimized pH value of the present system should be selected at 6.0 to ensure the free copper ions in the solutions.



There are mainly three kinds of functional groups on the surfaces of the two kinds of adsorbents. The interaction between the adsorbents and Cu(II) may be described by Eqs. (12-16).



model were approximate 0.9999. Also, the experimental q_e values were consistent with q_e values calculated from pseudo-second-order kinetic model. The small values of k_2 also indicated that the adsorption processes reached equilibrium very quickly. The adsorption kinetics of Cu(II) adsorbed on both adsorbents were presented in Fig. 5b. The curves demonstrated that the adsorption rates of Cu(II) on both adsorbents at the initial stage of adsorption was relatively rapid, then slowly decreased and both reached equilibrium at about 50 min. And the result of the adsorption rate at the initial stage of adsorption was in accordance with the result of k_2 values.



In Eqs. (12-15), there is a competition between H^+ and Cu^{2+} ($\text{Cu}(\text{OH})^+$) at the same sorption sites of adsorbents. With the decreasing pH value, Cu^{2+} ($\text{Cu}(\text{OH})^+$) adsorption will decrease along with the increasing competition between H^+ and Cu^{2+} ($\text{Cu}(\text{OH})^+$). Eq. (16) represents the increasing of Cu^{2+} adsorption through electrostatic attraction according to an anionic exchange mechanism at high pH.

The amount of Cu(II) loaded on the c-MWCNTMCs and the c-MWCNTs at different pH values is shown in Fig. 6a. The adsorption capacity of Cu(II) on the c-MWCNTMCs and the c-MWCNTs increased from 2.95 to 52.46 mg/g and 3.35 to 59.58 mg/g respectively with increasing pH values from 1.0 to 6.0. We found that Cu(II) adsorbed on the two adsorbents increased synchronously with pH values, suggesting that the adsorption efficiencies of the c-MWCNTMCs and the c-MWCNTs to Cu(II) were highly pH dependent. One of the main contributions was the electrostatic attraction between the negatively charged adsorbent surface

and the positively charged cationic ions.

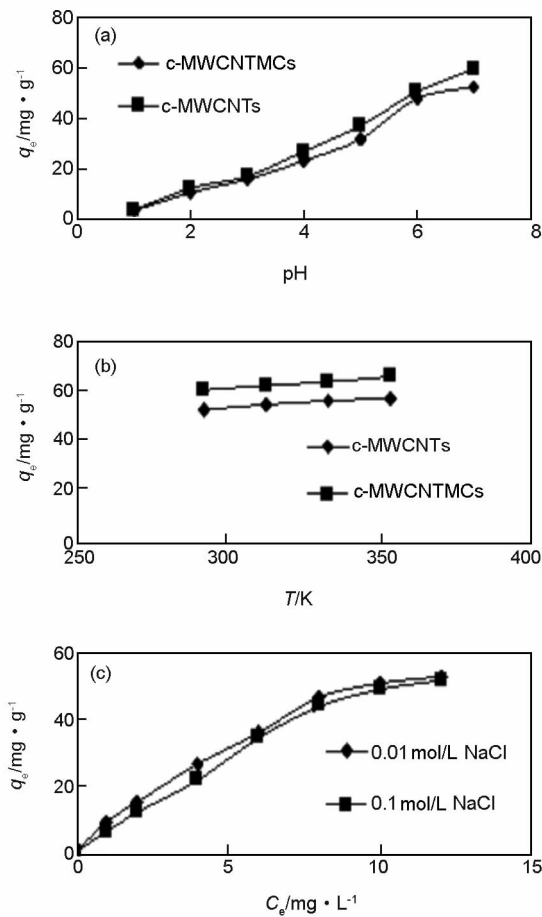


Fig. 6 Effect of pH , temperature and ionic strength on the adsorption capacity of Cu(II) on adsorbents.

3.8 Effect of temperature on adsorption

Adsorption capacity of Cu(II) on adsorbents as a function of temperature is shown in Fig. 6b. The adsorption capacity of Cu(II) on the c-MWCNTMCs and the c-MWCNTs increased from 52.46 to

57.01 mg/g and from 60.57 to 66.12 mg/g respectively with temperature from 293 to 353 K , suggesting that the adsorption were endothermic.

In order to evaluate the thermodynamics of Cu (II) adsorption on the c-MWCNTMCs and the c-MWCNTs , the data shown in Fig. 6b was analyzed by the following equations^[32]:

$$K_D = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (17)$$

$$\ln K_D = -\frac{\Delta H^\theta}{RT} + \frac{\Delta S^\theta}{R} \quad (18)$$

Where K_D is the distribution coefficient , C_0 (mg/L) is the initial concentration of Cu(II) , C_e (mg/L) is Cu(II) concentration in solution at equilibrium , V (L) is the solution volume and m (g) is the mass of adsorbents , R (8.314 J/mol/K) is the gas constant , and T (K) is the absolute temperature. ΔH^θ and ΔS^θ are standard enthalpy change , and standard entropy change , respectively.

Gibbs free energy changes (ΔG^θ) can be calculated from Eq. (19) :

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \quad (19)$$

Relevant parameters calculated from Eq. (18) and (19) are given in Table 3. The positive value of ΔH^θ represented an endothermic adsorption. ΔG^θ was negative as expected for a spontaneous process under our experimental conditions. The decrease of ΔG^θ with the increase of temperature indicated more efficient adsorption at high temperature. The positive values of entropy change (ΔS^θ) reflected the affinity of adsorbents towards Cu(II) ions in aqueous solutions. Moreover , the result could be supported by the previous study^[33-35]. Thus , it could be referred that the presumed mechanism between Cu(II) and adsorbents was ion-exchange , followed by chemical adsorption.

Table 3 Thermodynamic parameters for Cu(II) adsorption on the c-MWCNTMCs and the c-MWCNTs

	Temperature T/K	ΔH^θ /kJ·mol ⁻¹	ΔS^θ /J·mol ⁻¹ ·K ⁻¹	ΔG^θ /kJ·mol ⁻¹
c-MWCNTMCs	293	2.17	24.6	-5.02
	313			-5.51
	333			-6.01
	353			-6.50
c-MWCNTs	293	2.58	28.1	-5.65
	313			-6.21
	333			-6.77
	353			-7.33

Note: C [Cu(II)]_{initial} = 12 μg/mL , V = 25.0 mL , m = 2.5 mg , pH = 6.0 , t = 240 min

3.9 Effect of ionic strength

To investigate ionic strengths effect on Cu(II) adsorption on the two adsorbents , ionic strengths of 0.01 and 0.1 mol/L NaCl were adopted in our experiment. Fig. 6c shows that Cu(II) adsorptions decreased slightly with the increase of ionic strength.

This might be explained by two reasons. One is the high activity coefficient^[34] of metal ions caused by high ionic strength , retarding ion transfer to the adsorbent surfaces sites , the other is a competition between the cationic ions^[36] of the solute and Cu(II) , restraining Cu(II) from ion exchange with H⁺. However ,

it could be found out that the effect of ion strengths decreased with the increase of Cu(II) concentration. This might be attributed to the competition between the cationic ions of the solute and copper ions. Also, it could be inferred that the competition between the cationic ions of the solute and Cu(II) was the main reason for the effect of ionic strength.

3.10 Effect of the coexisting ions on the recovery of Cu(II)

In order to study the influences of the coexisting ions on the recoveries of Cu(II) on the c-MWCNT-MCs, a fixed amount of Cu(II) (0.2 mg/L) was determined with different amounts of foreign ions. The recovery of Cu(II) in deionized water are all above 90% at the concentration of the foreign ions given in Table 4.

3.11 Desorption of Cu(II)

A promising adsorbent should not only possess a high adsorption capability, but also can be regenerated for repeated usage, which can remarkably save the overall cost in the industrial application. Fig. 7 shows the Cu(II) desorption from the c-MWCNTs and the c-MWCNTMCs as a function of time and at various pH values. It was evident that Cu(II) desorption can be promoted by decreasing pH and completed in about 60 min. The amount of desorbed Cu(II) was low (about 5%) at pH > 5.0, then increased sharply at pH < 5.0, and eventually reached about 90% at pH < 2.0. Results showed that Cu(II) adsorbed by the c-MWCNTs and the c-MWCNTMCs could be easily desorbed at low pH values. However, there was no obvious difference between the desorption curves of the c-MWCNTs and the c-MWCNTMCs. Thus, it can be speculated that the minor differences of the adsorption and desorption curves might be caused by the minor differences of their specific areas. In other words, Fe₃O₄ might show only benefit for magnetic separation but little for adsorption capacity in the adsorption.

The recovery of Cu(II) on the c-MWCNTMCs remained above 90.0% after a repeated use for five adsorption and desorption cycles, indicating that the c-MWCNTMCs is promising candidate for repetitive adsorption/desorption of heavy metal ions in environmental water samples. This result was supported by the research conducted by Chen et al.^[37], which had reported that the c-MWCNTMCs for solid-phase extraction remained 95.0% recovery after runs for 50 adsorption and desorption cycles.

3.12 Addition/recovery tests and detection limit

Tap water and lake water taken from our school were collected as water samples. Tap water was used directly, while lake water was filtrated by 0.45 μm

microporous membrane (Millipore) and digested by HNO₃ (65%) for 24 h before use. The samples were operated according to section 2.4 and the supernatant was filtered through a microporous membrane (Millipore) with 0.45 μm pore size before detection. Various amounts of Cu(II) were also added to these water samples. The determination results can be seen in Table 5. The c-MWCNTMCs can enrich and determine trace copper with the recovery of 97.0% – 108.0%, indicating that the c-MWCNTMCs is an effective and fast absorbent for enriching trace copper in environmental water.

Table 4 The maximum of coexisting ions concentrations under which ones'interferences are insignificant

Ions	Added as	Concentration C /mg·L ⁻¹	Recovery /%
Na ²⁺	NaCl	10000	98.9 ± 2.0 ^a
k ⁺	KCl	10000	95.3 ± 0.7 ^a
Cl ⁻	NaCl	10000	94.1 ± 2.1 ^a
NO ₃ ⁻	NaNO ₃	5000	96.1 ± 1.4 ^a
Ca ²⁺	CaCl ₂	500	93.7 ± 4.2 ^a
SO ₄ ²⁻	Na ₂ SO ₄	500	92.5 ± 2.3 ^a
Al ³⁺	Al ₂ (SO ₄) ₃	50	94.1 ± 2.5 ^a
Fe ³⁺	FeCl ₃	10	92.9 ± 1.6 ^a

Note: ^a mean ± standard deviations. C [Cu(II)] = 0.2 mg/L, V = 250 mL, m_{c-MWCNTs} = 20 mg, T = 25 °C, N = 4.

Table 5 Determination of trace amount of Cu(II) in tap water, lake water taken from our campus and Xuanwu Lake

Water	Added /μg	Found /μg	Recovery /%
Tap Water (1 l)			
Cu	0	0.55 ± 0.3 ^a	-
	25	25.3 ± 0.7 ^a	97.0
	50	51.5 ± 0.9 ^a	102.0
Lake water (Campus, 1 l)			
Cu	0	14.6 ± 1.3 ^a	-
	25	39.4 ± 1.3 ^a	99.0
	50	65.7 ± 2.6 ^a	102.0
Lake water (Xuanwu Lake, 1 l)			
Cu	0	5.2 ± 0.4 ^a	-
	25	31.0 ± 2.2 ^a	103.0
	50	59.5 ± 0.6 ^a	108.0

Note: ^a Uncertainty is the standard deviation for four duplicated runs. V = 500 mL, m_{c-MWCNTMCs} = 20 mg, T = 25 °C, N = 4.

The limit of detection (LOD) of the proposed method was studied under the optimal experimental conditions. The detection limit is defined by the equation LOD = 3S₀, where S₀ is the standard deviation of blank measurements^[38]. The LOD of Cu(II) is 1.29 μg/L (N = 12).

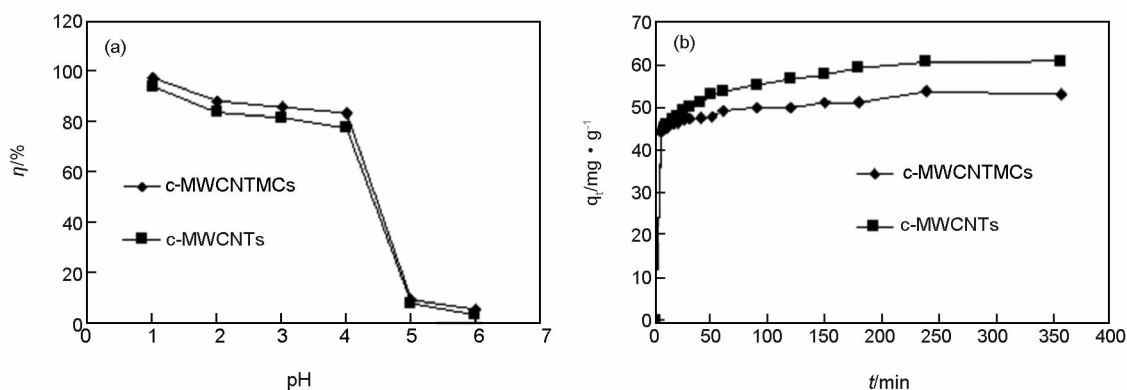


Fig.7 Release of Cu(II) from the c-MWCNTMCs at different (a) pH values and (b) times.

4 Conclusions

The c-MWCNTMCs had a high adsorption capacity for Cu(II) and were easy to separate from solution, which showed great potential for removing heavy metal ions from solutions. The good regenerability and easy separation of the c-MWCNTMCs made c-MWCNTMCs an economic adsorbent for fast extraction of heavy metal ions from polluted water. The adsorption mechanism between heavy metal ions and surface functional groups of the c-MWCNTMCs was a chemical type. And adsorption kinetics followed a pseudo-second-order kinetic model.

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