Removal of Copper Ions from Water Using Chemical Modified Multi-walled Carbon Nanotubes

Yu-Jun Zhang, Jun Yang, Bo-Liang Liu and Yuan-Dong Xu*

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou, China
ydx11@126.com*

Summary: Multi-walled carbon nanotubes (CNTs) were modified by oxidation with sodium hypochlorite (NaClO) solutions and were employed as adsorbents to study the adsorption characteristics of copper ions from water. The results show that adsorption capacity of CNTs treated by NaClO solution can be greatly enhanced. The adsorption capacity of Cu^{2+} on as received and modified CNTs increased with the increase of pH and CNTs mass, but it decreased with the temperature. Experimental data also indicated that the adsorption process could achieve equilibrium within 40 min. Both Langmuir and Freundlich isotherm models fitted the experimental data very well. According to the Langmuir model the maximum copper ions adsorption uptake onto modified CNTs was determined as 40.00 mg/g. Our results suggest that CNTs have profound potential application in environmental protection.

Key Words: Carbon nanotubes; Chemical modification; Adsorbent; Copper ion; Adsorption model.

Introduction

Industrial effluents that carry heavy metal ions into natural water systems have become an increasingly serious environmental concern. Heavy metals are prominent contaminations in aquatic environment and soils, whose main source are metallurgical, tannery, mining, battery manufacturing industries, etc. As they do not degrade biologically like organic pollutants, their presence in drinking water or industrial effluents is a public health problem due to their absorption and therefore possible accumulation in organisms [1]. Because of the toxicity of heavy metals and their detrimental effect on living species, including humans, standards that govern the emission of these metals to the aquatic environment are becoming increasingly stringent. Removing toxic heavy metals from industrial wastewater is an urgent environmental issue. In wastewater treatment, various approaches have been adopted to remove heavy metals, such as precipitation, electrochemical treatment, chemical oxidation or reduction, solvent extraction, ion exchange and adsorption. Adsorption is cost-effective, simple and widely used techniques [2, 3].

Carbon nanotubes, a novel kind of carbon material, have come under intense multidisciplinary research since their discovery by Iijima [4] and batch production [5]. They have exceptional mechanical properties, unique electrical property, high chemical and thermal stability, and thus have vast potential applications in many fields [6]. Due to their large specific surface area, and layered structures, CNTs have attracted researchers' interest as a new type of adsorbent and offer an attractive option for the removal of trace pollutants. CNTs have been proven to possess great potential as superior adsorbents for removing many kinds of organic and inorganic pollutants such as dioxin [7], volatile organic compounds [8, 9] from air stream or fluoride [10], 1,2-dichlorobenzene [11], trihalomethanes [12], soil organic matters [13] and various heavy metal ions from aqueous solution [14-20]. The present study aims at investigating adsorption characteristics of Cu^{2+} onto CNTs. The effects of adsorbent mass, adsorption temperature, initial pH, contact time and initial Cu^{2+} concentrations on the adsorption behaviour were investigated. Langmuir and Freundlich models were applied to fit the experimental data.

Results and Discussion

Characterization of CNTs

Fig. 1a and b show the SEM images of as received and modified CNTs, respectively. It is seen that the isolated CNTs are tortuous and their length range is from hundreds of nanometers to micrometers. The TEM images demonstrated that the as-produced and modified CNTs were cylindrical with average inner diameters of 10 nm, outer diameters of 30 nm (Fig. 2). The as received CNTs contain a large amount of metal catalysts and amorphous carbon. These metal catalysts and amorphous carbon were removed after modification. After oxidation with NaClO, lots of the tips for CNTs were opened and fracture took place at positions where defects such as pentagons and heptagons existed.

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*To whom all correspondence should be addressed.
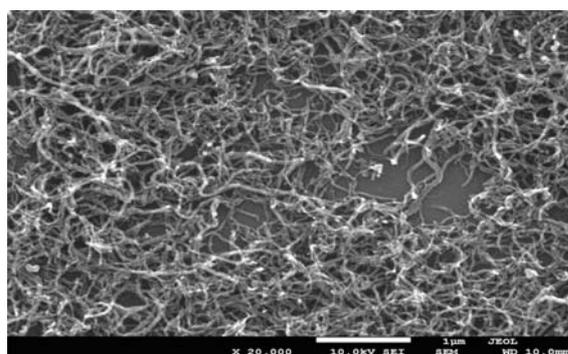
(a)
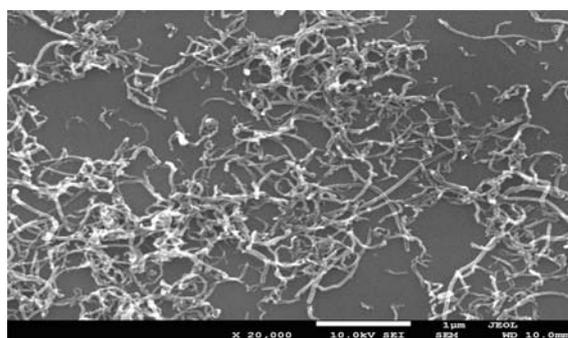
(b)

Fig. 1: Scanning electron microscope images of CNTs: (a) as received CNTs, (b) modified CNTs.
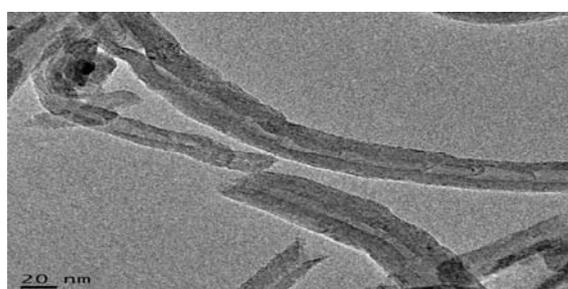
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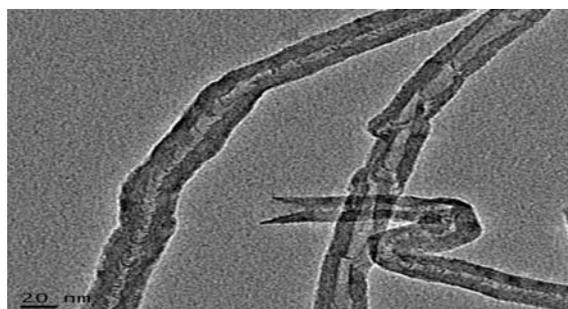
(b)

Fig. 2: Transmission electron microscope images of CNTs: (a) as received CNTs, (b) modified CNTs.

Fig. 3a and b show the Fourier-transformed infrared spectra of as received and modified CNTs, respectively. It is seen that the as received CNTs exhibit insignificant peaks. In contrast, the NaClO-modified CNTs yielded three major peaks at wavenumbers near 1400, 1700 and 3500 cm^{-1}, which were associated with aromatic $-C=C$ groups, carbonyl groups ($-C=O$) from carboxylic acids ($-COOH$), and hydroxyl groups ($-OH$) from carboxylic acids or alcoholic groups ($-COH$) [12, 21], respectively. Evidently, many oxygen-containing functional groups were generated on the surface of modified CNTs, providing various adsorption sites, and increasing the adsorption capacity [22].
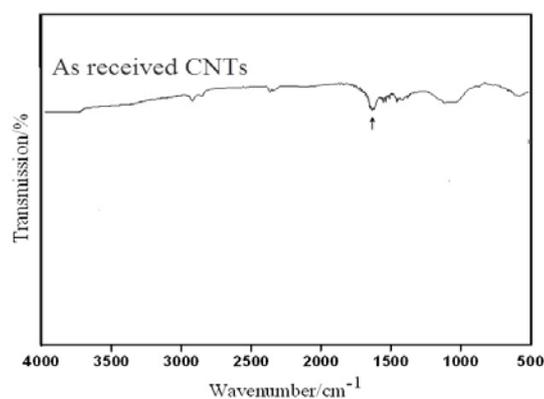
(a)
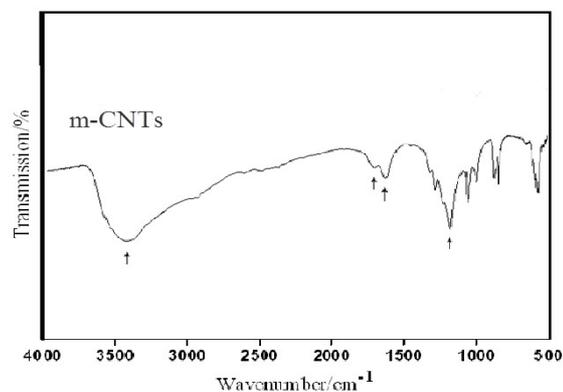
(b)

Fig. 3: FTIR spectra of as received (a) and modified CNTs (b).

Effect of CNTs Mass

Fig. 4 shows the effect of the CNT mass on the adsorption of Cu^{2+} by as received and modified CNTs. The adsorption capacities of both as received and modified CNTs increase with increasing of CNTs

mass. But it increases very slow for as received CNTs and its adsorption is only 23.8% at CNTs mass of 100 mg per 100 mL. However, the obvious increase takes place at the CNTs mass from 20 to 100 mg per 100 mL for NaClO-modified CNTs. The adsorption percentage for NaClO-modified CNTs boosts from 28% to 48%, which may be that the modification to the CNTs on one hand increased the adsorption active sites and on the other hand improved the interaction between the adsorbent and the adsorbate [23]. From the experiment result it is obvious that the treatment of CNTs with NaClO is an effective method to improve their Cu^{2+} adsorption capabilities.
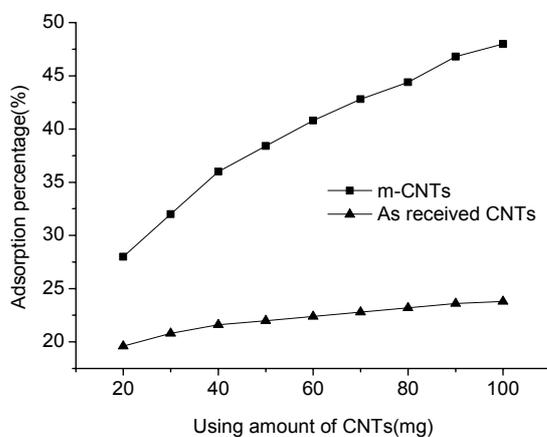
Fig. 4:   Effect of the CNTs mass on the adsorption of Cu^{2+}.

Effect of the Temperature

In practical application, temperacture is one of the most important factors affecting adsorption of metal ions. The effect of temperature on the adsorption of Cu^{2+} by modified CNTs is shown in Fig. 5. It can be seen that the adsorption capacity decreases with increasing temperature. A fall in temperature would be propitious to the adsorption, indicating that the adsorption process is exothermic [24].

Effect of the pH

The pH value plays an important role with respect to the adsorption of metal ions on CNTs. It can affect the site dissociation of CNTs and the hydrolysis, complexation, and precipitation of metal ions. Fig. 6 shows that as the pH increases, the adsorption capacity of Cu^{2+} increases for both as

received and modified CNTs, but more sharp increase was observed for modified CNTs. At lower pH (pH **<** 3.0), the CNTs surface is expected to have a net positive charge, and Cu^{2+} adsorption onto such a surface is extremely difficult; moreover, Cu^{2+} and protons compete for binding sites on CNTs, resulting in low adsorption capacity. At higher pH values, a net negative charge is present on the surface of the CNTs, promoting the adsorption of Cu^{2+}, because of the electrostatic force of attraction between Cu^{2+} and the surface of the CNTs. At pH over 6, insoluble copper hydroxide begins to precipitate from the solution, making true adsorption studies impossible. Hence, the pH of Cu^{2+} solution should be very well controlled during adsorption studies. The adjustment of pH in this experiment is confined at only acidic condition.
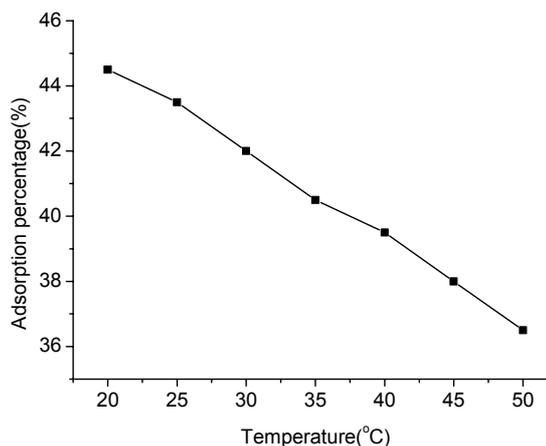
Fig. 5:   Effect of temperature on the adsorption of Cu^{2+}.
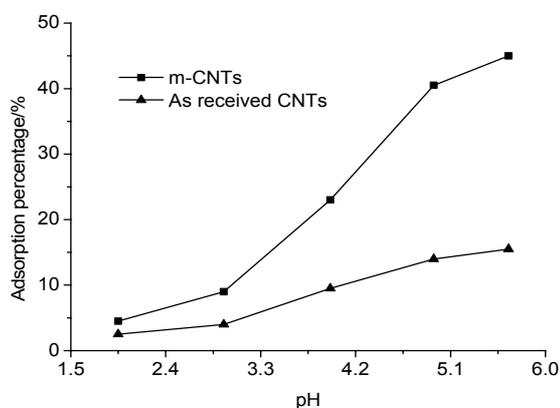
Fig. 6:   Effect of pH on the adsorption of Cu^{2+}.

Effect of the Contact Time

Fig. 7 shows the effect of contact time on the adsorption of Cu^{2+} onto modified CNTs at different initial concentrations. It is noted that the adsorption amount of Cu^{2+} increased quickly with time at the first 20 min and then reached equilibrium within approximately 40 min. At first the adsorbent possessed more adsorption active sites, so the adsorption rate was high and with more and more adsorption vacancies were occupied the adsorption rate decreased and ultimately reached the equilibrium. The results indicate that modified CNTs are adsorbent of high efficiency, which have strong potential for wastewater treatment.
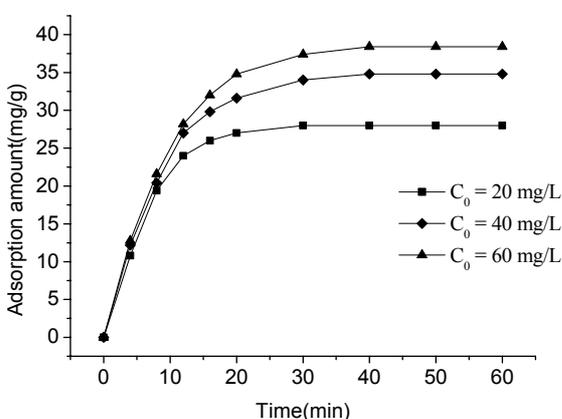
Fig. 7:   Effect of contact time on the adsorption of Cu^{2+} with modified CNTs.

Adsorption Isotherms

Fig. 8 presents the adsorption isotherms of Cu^{2+} on modified CNTs at pH 5.65, as a relationship between the amount of Cu^{2+} adsorbed per unit mass of CNTs (Q_e) and the equilibrium concentration of Cu^{2+} solution (C_e). The adsorption capacities increased with concentration, reaching a plateau, which represents the maximum adsorption capacity. The adsorbed Cu^{2+} onto modified CNTs was 38.4 mg/g at an equilibrium concentration of 40.8 mg/L.

The analysis of isotherm data is important in developing an equation that accurately describes the results and which can be used in design. The experimental data for equilibrium adsorption were analyzed using Langmuir and Freundlich isotherm models. The Langmuir model assumes that there is no interaction between the adsorbate molecules and

the adsorption is localized in a monolayer, and The Freundlich model assumes that different sites with several adsorption energies are involved. The expression for the Langmuir and Freundlich adsorption models [25] are as follows:

$$Q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{1}$$

$$Q_e = K_F C_e^{1/n} \tag{2}$$

Equations 1 and 2 can be rearranged as

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{3}$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where Q_e is the amount of Cu^{2+} that is adsorbed per gram of CNTs (mg/g); C_e denotes the equilibrium concentration of Cu^{2+} in solution (mg/L); Q_0 is the theoretical saturation capacity of the monolayer (mg/g); b represents the Langmuir constant (L/mg) that relates to the affinity of the binding sites, and K_F and n are the Freundlich constants. The Langmuir and Freundlich constants were obtained from fitting the isotherm models to the sorption equilibrium data, by plotting C_e/Q_e versus C_e and $\ln Q_e$ versus $\ln C_e$, respectively. The simulations of Langmuir and Freundlich model for Cu^{2+} adsorption are shown in Fig. 9 and Fig. 10, respectively.
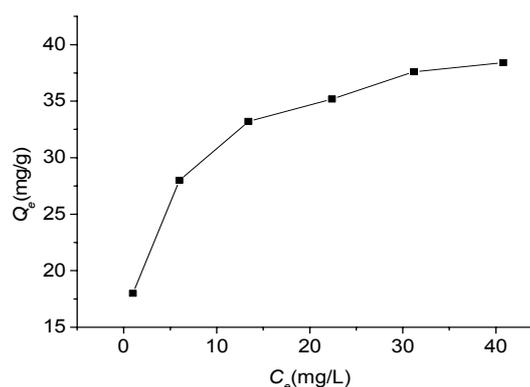
Fig. 8:   Adsorption isotherm of Cu^{2+} onto modified CNTs.
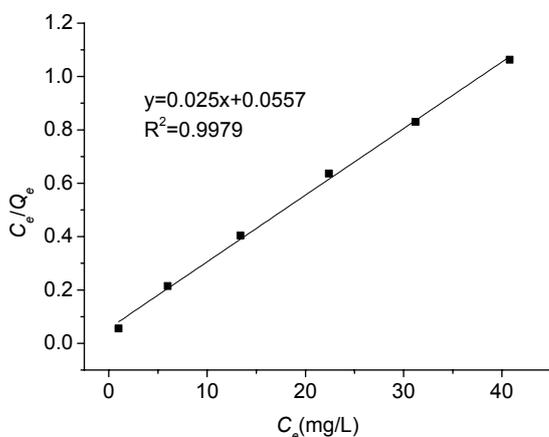
Fig. 9: Langmuir isotherm model simulation for Cu^{2+} adsorption on modified CNTs.
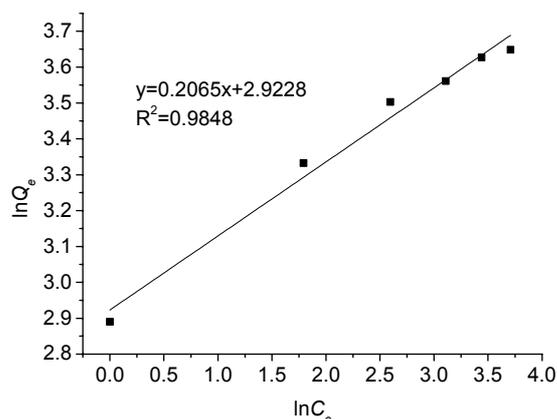
Fig. 10: Freundlich isotherm model simulation for Cu^{2+} adsorption on modified CNTs.

As can be noticed, the correlation coefficients of Langmuir and Freudlich models are 0.9979 and 0.9848, respectively, indicating that both Langmuir and Freundlich isotherm models fit the experimental data very well, and Langmuir model dose better. The maximum adsorption capacity of Cu^{2+} calculated by the Langmuir model is 40.00 mg/g with modified CNTs.

Experimental

Preparation of Modified CNTs

Multi-walled carbon nanotubes (produced by catalytic vapor decomposition) purchased from

Shenzhen Nanotech Port Co. Ltd. (NTP), with 20~40 nm in outer diameter, were selected as adsorbents to study adsorption characteristics of Cu^{2+} from water. The length of CNTs was in the range of 5~15 μm and their purity was above 95%.

As received CNTs (1.5 g) were heated at 350 °C for 30 min to remove amorphous carbon. After thermal treatment, these CNTs were dispersed into a flask containing 150 mL of 70% sodium hypochlorite solution (45 mL of H_2O + 105 mL of NaClO). The solution was then shaken in an ultrasonic cleaning bath (Model KQ100E, Ultrasonic Instruments Co. Ltd., Kunshan, China) for 30 min and was then continuously stirred at 65 °C in a water bath for 3 h. After cooling, the CNTs were filtered and then washed with deionized water until neutral pH. This type of carbon nanotubes were named as m-CNTs. The treated CNTs were dried at 60 °C and stored for further use.

Preparation of Cu^{2+} Solution

Analytical-grade copper sulfate (Reagent chemical Co. Ltd., Tianjin, China, 99% purity) was used to prepare a stock solution containing 1000 mg/L of Cu^{2+}, which was further diluted with deionized water to the desired concentrations before use.

Adsorption Experiments

All adsorption experiments were performed in a closed 150 mL glass conical flask, containing predetermined mass of as received or modified CNTs; 100 mL of Cu^{2+} solution. Agitation was performed for a predetermined time at a certain temperature in a constant temperature shaker (THZ-82). The suspensions were filtered through 0.45 μm membrane filters and the concentration of residual Cu^{2+} in the filtrates was measured. The effect of CNTs on Cu^{2+} adsorption were carried out by adding 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg of as received and modified CNTs to 100 mL Cu^{2+} solution with initial concentration of 50 mg/L at a pH value of 5.65. The adsorption temperature was 25 °C and adsorption time was 6 h. In the experiments related to the temperature effect, the control conditions were an initial Cu^{2+} concentration of 40 mg/L, a m-CNTs mass of 50 mg and adsorption time of 6 h. Then, the temperature was held at 20, 25, 30, 35, 40, 45 and 50 °C and the pH was fixed at 5.65 during experiments. In the experiments refered to the pH effect, the control conditions were same as those of temperature.

Then, the pH of the solution was adjusted to between 1.9 and 5.7, using 0.1 M HNO$_3$ and 0.1 M NaOH and the temperature was maintained at 25 ^{o}C during experiments. The experiment of contact time effects on Cu^{2+} adsorption were carried out by adding 50 mg of m-CNTs to 100 ml Cu^{2+} solution with initial concentration of 20, 40 and 60 mg/L at a pH value of 5.60. The adsorption process was kept for 4, 8, 12, 16, 20, 30, 40, 50 and 60 min, respectively and the temperature was maintained at 25 ^{o}C. For the equilibrium study, a known mass of m-CNTs (50 mg) was added to 100 mL of Cu^{2+} solution (initial concentration ranging from 10 to 60 mg/L, 10 mg/L interval, pH 5.65). The temperature was also held at 25 ^{o}C.

The percentage and amount of Cu^{2+} adsorbed was calculated as follows:

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (5)$$

$$Q = \frac{(C_0 - C_t) \times V}{W} \qquad (6)$$

where R is the adsorption percentage of Cu^{2+} (%), Q is the amount of Cu^{2+} adsorbed by CNTs (mg/g), C_0 is the initial copper ion concentration (mg/L), C_t is the final Cu^{2+} concentration after a certain period of time (mg/L), V is the volume of Cu^{2+} solution (L), and W is the mass of the adsorbent (g).

Analytical Methods

The concentration of Cu^{2+} was determined by a flame atomic absorption spectrometer (FAAS, Model TAS-986, Purkinje General Instrument Co. Ltd., Beijing, China).The size and morphology of CNTs were observed by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700, Tokyo, Japan) and a high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010, Tokyo, Japan). The functional groups on the surface of CNTs were detected by Fourier Transform Infrared Spectroscopy (FTIR, Model Prestige-21, Shimadzu Instrument Co., Japan).

Conclusion

Multi-walled carbon nanotubes were modified by oxidation with NaClO solution and the adsorption characteristics of Cu^{2+} onto as received and modified CNTs were investigated. The results revealed that the adsorption capacity of CNTs has increased markedly after modification treatment because functional groups appeared on the modified CNTs surface. The adsorption capacity of Cu^{2+} onto as received and modified CNTs both increased with the increase of the pH and the mass of adsorbents, especially for modified CNTs. However, there was a decline in the adsorption capacity of modified carbon nanotubes with the increase of temperature. The adsorption of Cu^{2+} onto modified CNTs could reach equilibrium in merely 40 min. Both Langmuir and Freundlich models fitted the adsorption isotherm data well. The short time needed to reach equilibrium as well as the high adsorption capacity of Cu^{2+} suggests that modified CNTs are effective adsorbents for the removal of heavy metals from aqueous solution in water treatment and have profound prospect in environment protection.

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