

# Removal of heavy metals from aqueous solution by carbon nanotubes: adsorption equilibrium and kinetics

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**Abstract:** Carbon nanotubes prepared by catalytic chemical vapor deposition of hydrocarbon at 650°C show good adsorption capability of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions from aqueous solution after oxidized with concentrated nitric acid at 140°C for 1 h. The specific surface area and particle size distribution of the as-grown and oxidized CNTs were studied by BET method and laser particle analyzer. Three kinetic models, that is, first-, pseudo second- and second-order, were used to investigate the adsorption data and the pseudo second-order model can represent the experimental data better than two others. The equilibrium data fitted well with the Langmuir model and showed the following adsorption order:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ .

**Keywords:** carbon nanotubes; heavy metals; adsorption

## Introduction

Wastewaters from battery manufacturing, printing, painting, dyeing and other industrial processes often contain considerable amounts of heavy metals that would endanger public health if discharged without adequate treatment. Long-term ingestion of water containing higher concentration of heavy metals can cause many diseases such as stomach ailment, intestinal distress, mental retardation, liver and kidney damage, and anemia (Benguella, 2002; Li, 2002). So they must be removed from polluted streams.

Many methods have been used to remove the excess heavy metals from aqueous solution such as electrochemical treatment, reverse osmosis, precipitation and adsorption (Panayotova, 2001). Among these methods, the most commonly used one for heavy metals removal is adsorption by different adsorbents. Chitin (Benguella, 2002), zeolite (Panayotova, 2001), activated carbon (Kadirvelu, 2001), slag (Dimitrova, 1998), egg shell (Kuhand, 2000), ion exchange resins (Rengaraj, 2001), hematite (Singh, 1998) and silica gel (Park, 1995) have been used as heavy metal adsorbents and shown definite removal capabilities. With the increasingly stringent wastewater draining standard, it is desirable to seek a more efficient absorbent material to remove heavy metals from aqueous solution.

Carbon nanotubes (CNTs), one neonatal material in carbon family, were discovered in 1991 by Iijima of the NEC Laboratory (Iijima, 1991). They are seamlessly concentric cylinders curled from the graphite sheet with honeycomb lattice structures. Their unique nanolayered structures, large surface area, high mechanical strength and remarkable electrical conductivities make them potential applications for a wide range of promising applications, such as field emission (Rinzler, 1995; de Heer, 1995), reinforcing materials in

composites (Ajayan, 1994), nanodevices (Dai, 1996) and chemical sensors (Kong, 2000). Dillon *et al.* first studied the hydrogen adsorption property of CNTs and showed that CNTs may be a promising material for hydrogen storage (Dillon, 1997). Subsequently, Long *et al.* found that CNTs were superior adsorbent for dioxin removal (Long, 2001). Li *et al.* used CNTs as supports to deposit  $\text{Al}_2\text{O}_3$  and found that  $\text{Al}_2\text{O}_3/\text{CNTs}$  exhibited excellent adsorption property for removing fluoride from drinking water (Li, 2001). Very recently, we found that CNTs showed exceptional adsorption capability of lead from water after oxidized with nitric acid (Li, 2002).

In this work, CNTs were prepared and oxidized with nitric acid. Batch adsorption studies were carried out for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$ , then their kinetic adsorption data were fitted with the first-, pseudo second- and second-order rate models. At the same time, the equilibrium data were fitted with the Langmuir isotherm models.

## 1 Experimental methods and materials

### 1.1 Preparation of CNT adsorbent

CNTs were fabricated by catalytic chemical vapor deposition of the propylene-hydrogen ( $\text{C}_3\text{H}_6 : \text{H}_2 = 2 : 1$ ) mixture at about 650°C in a standing furnace with Ni particles as the catalyst. The quantity of a batch of as-grown CNTs can reach 500 g. Transmission electron microscopy images show that the CNTs have an average diameter of about 30 nm and a length ranging from hundreds of nanometers to micrometers. The as-grown CNTs were ground by ball milling to break the CNTs into short pieces and refluxed with concentrated nitric acid at 140°C for 1 h in order to remove the Ni catalyst particles and increase the functional groups on the surfaces of CNTs. Finally they were filtered with a ceramic filter to remove the acid and dried at 80°C for the subsequent

experimental use.

## 1.2 Apparatus of characterizing the adsorbent

The specific surface area of the as-grown and refluxed CNTs were measured by nitrogen adsorption/desorption at 77 K using BET method (Micromeritics ASAP 2000). Particle size distributions of the as-grown and oxidized CNTs were analysed by laser light scattering with a Malvern Mastersizer (Mastersizer 2000).

## 1.3 Metal adsorption

Stock solutions (1000 mg/L) were prepared by dissolving analytical grade reagents of lead nitrate, copper chloride and cadmium chloride in deionized water. The solutions were further diluted to required concentration before use. All adsorption experiments were conducted at 25 °C.

Adsorption kinetics were carried out by adding 1 g of oxidized CNTs in 2000 ml solution with  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  concentrations of 30, 30, and 30 mg/L without any pH adjustment (pH = 4.2). The dependence of kinetic adsorption of different  $Cu^{2+}$  concentrations on time was also studied. At predetermined time intervals, samples were separated with a 0.45  $\mu m$  membrane filter and analyzed by an atomic adsorption spectrometer. The amount of adsorption at time  $t$ ,  $q_t$  (mg/g) was calculated by:

$$q_t = (C_0 - C_t) V / W, \quad (1)$$

where  $C_0$  and  $C_t$  are the solution concentrations of heavy metals at initial and any time  $t$ , respectively,  $V$  is the volume of the solution and  $W$  is the weight of dry adsorbent used.

Adsorption isotherm studies were conducted in 250 ml glass beakers where contained 0.05 g of oxidized CNTs and 100 ml solutions with initial concentrations of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  of 60, 30 to 15 mg/L, respectively. The initial pH value of the solutions was 4.2. After the suspensions were shaken for 5 h, they were filtered and analyzed.

## 2 Results and discussion

### 2.1 Characterization of CNTs

Transmission electron microscopy image (Fig. 1) shows that as-grown CNTs are usually curved with average inner diameters of 10 nm, outer diameters of 30 nm, and length ranging from hundreds of nanometers to micrometers.

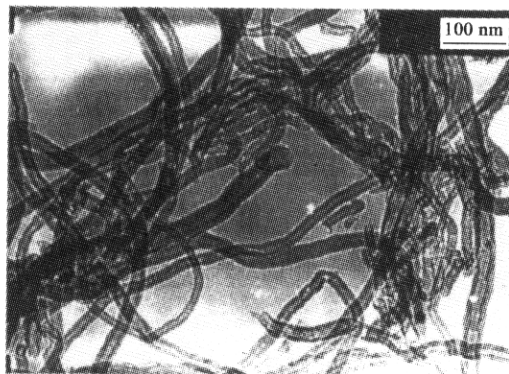


Fig. 1 TEM image of the as-grown CNTs

The specific surface area is 126  $m^2/g$  for the as-grown CNTs and 153  $m^2/g$  for the oxidized CNTs. The enlarged

specific surface area for the oxidized CNTs is mainly due to the opened tips and the rupture of the CNTs at where defects exist, for example, there are many pentagons and heptagons caused the CNTs to curve.

Particle size distribution is a factor to affect the suspensibility and adsorption property of the adsorbents. Fig. 2 shows the comparable particle size distributions of the as-grown and oxidized CNT obtained by laser light scattering. Two curves in Fig. 2 represent the frequency curve, which are useful for displaying the distinct sizes of the particles. There are two peaks at 15  $\mu m$  and 310  $\mu m$  for the as-grown CNTs, while for the oxidized CNTs the peaks decrease to 8  $\mu m$ . This result obviously showed that the sizes of the CNTs become smaller after oxidation and is consistent with the result of increase of the specific surface area. The smaller sizes of CNTs benefit for the CNTs to suspend in the solution and increase the adsorption rate due to the decrease of the diffusion distance.

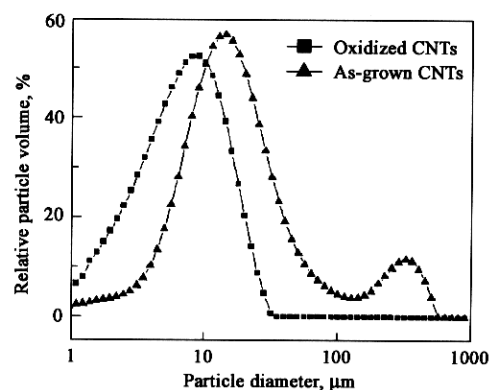


Fig. 2 Particle size distribution of the as-grown and oxidized CNTs

### 2.2 Adsorption kinetics

Kinetics of adsorption describing the solute uptake rate is one of the important characteristics representing the adsorption efficiency of the CNTs and determine their potential applications further. According to Fig. 3, the adsorption rates increase sharply in the first 10 min for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  ions, then they reach equilibrium gradually at the time of 40 min for  $Pb^{2+}$ , 70 min for  $Cu^{2+}$  and 30 min for  $Cd^{2+}$ . The former steeper adsorption curve suggests that the adsorption takes place rapidly on the surfaces of the oxidized CNTs. Subsequently the lower adsorption rate may be due to the longer range diffusion of metal ions into the inner cavities and interlayers of oxidized CNTs (Li, 2002).

To analyze the adsorption rate of three metal ions onto the CNTs, three kinetic models were tested on the experimental data (Benguella, 2002).

First-order rate equation:

$$\log(q_e - q_t)/q_e = K_L t / 2.3. \quad (2)$$

Where  $K_L$  is the Lagergren rate constant of adsorption ( $1/\text{min}$ ),  $q_e$  is the amount of metal ion adsorbed (mg/g) at equilibrium.

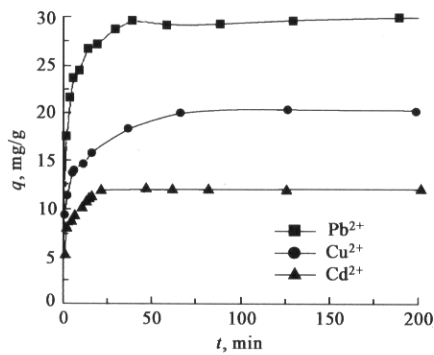


Fig. 3 Effect of contact time on the rate of adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by oxidized CNTs at pH 4.2, temperature 25 °C

Pseudo second-order rate equation:

$$t/q_t = 1/(2K'q_e^2) + t/q_e, \tag{3}$$

where  $K'$  is the pseudo second-order rate constant of adsorption( $\text{g}/(\text{mg} \cdot \text{min})$ ), the initial adsorption rate  $\nu_0 = 2K'q_e^2$  (Redda, 2002).

Second-order rate equation:

Table 1 Kinetic parameters for metal adsorption by the oxidized CNTs

	First-order			$\nu_0$	Pseudo second-order			Second-order		
	$q_e$	$K_L$	$R^2$		$q_e$	$K'$	$R^2$	$q_e$	$k$	$R^2$
$\text{Pb}^{2+}$	7.25	0.012	0.6327	0.033	30.12	0.009	0.9999	6.65	0.0036	0.8727
$\text{Cu}^{2+}$	10.24	0.053	0.9815	0.049	20.45	0.008	0.9954	12.93	0.011	0.9741
$\text{Cd}^{2+}$	1.58	0.036	0.9810	0.096	12.33	0.047	1.000	1.7	0.1632	0.8602

The validity of the pseudo second-order rate model can be checked by studying the kinetics under different initial metal concentrations (Redda, 2002). Fig. 4 shows the dependence of kinetic adsorption of different  $\text{Cu}^{2+}$  concentrations on time. It can be seen that the adsorption rate is quickly in the first 15 min, then it reaches equilibrium gradually at the time of 70 min. The amount of  $\text{Cu}^{2+}$  adsorbed on oxidized CNTs increases with the initial concentrations. Fig.5 shows straight lines were obtained as the experimental data were fitted to the pseudo second-order rate equation. The regression coefficients ( $R^2$ ) of  $\text{Cu}^{2+}$  concentrations of 10, 20 and 30 mg/L are 0.9999, 1.0000 and 0.9995, respectively, which suggested that the pseudo second-order rate model could adequately described the kinetic adsorption of  $\text{Cu}^{2+}$  ions.

2.3 Adsorption isotherm

Equilibrium adsorption studies were performed to determine the maximum metal adsorption capacities of the CNTs. Fig.6 shows the adsorption isotherms of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions by the oxidized CNTs. It can be seen that at the equilibrium metal concentration of 10 mg/g the adsorption capacities of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions by the oxidized CNTs are 64.21, 27.43 and 10.96 mg/g, respectively.

The equilibrium data of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  adsorption by the oxidized CNTs were analyzed in accordance with the Langmuir adsorption isotherm models whose linearized equations was:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m C_e}. \tag{6}$$

$$1/(q_e - q_t) = 1/q_e + kt, \tag{5}$$

where  $k$  is the rate constant ( $\text{g}/(\text{mg} \cdot \text{min})$ ).

Linear plot figures of  $\log(q_e - q_t)$  vs.  $t$ ,  $t/q_t$  vs.  $t$  and  $1/(q_e - q_t)$  vs.  $t$  were drawn and the  $K_L$ ,  $K'$  and  $k$  values calculated from the slopes and intercepts are listed in Table 1. As shown in Table 1, the regression coefficients of the pseudo second-order rate model for the linear plots is higher than that of other two models, so the pseudo second-order rate model can represent the adsorption data even more. The  $q_e$  calculated from the pseudo second-order rate model of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions are 30.12, 20.45 and 12.33 mg/g, respectively, in the order of  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ , which are consistent with the results in Fig.3. The initial adsorption rate( $\nu_0$ ) values of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions are 0.033, 0.049 and 0.096  $\text{mg}/(\text{g} \cdot \text{min})$ , in the order of  $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$ . The differences in the initial adsorption rate of three metal ions may be due to the nature and distribution of active groups on the adsorbent and the affinity between the metal ions and the adsorbent.

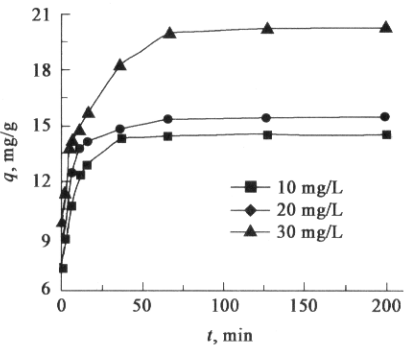


Fig. 4 Effect of contact time on the rate of adsorption of  $\text{Cu}^{2+}$  with different concentrations by oxidized CNTs at pH 4.2, temperature 25 °C

Where  $C_e$  is the equilibrium heavy metal concentration( $\text{mg}/\text{L}$ ),  $q$  is the amount adsorbed( $\text{mg}/\text{g}$ ) and  $q_m$ ,  $b$  are the Langmuir model constants. Fig.7 shows graphical comparison of the experimental and calculated Langmuir isotherm. It can be seen that the agreement is excellent. The correlation coefficients  $R^2$ (Table 2) for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions are very close to 1, which also indicates the good fitness of experimental data and Langmuir isotherm model. The maximum adsorption capacities of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions by the oxidized CNTs calculated from the Langmuir isotherm were 63.29, 28.33 and 11.01, respectively, following the sequence of  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ . Differences in the maximum adsorption capacity of various metal ions have been explained by the differences in the ionic size of metal, the nature and distribution of active groups on the adsorbent, and

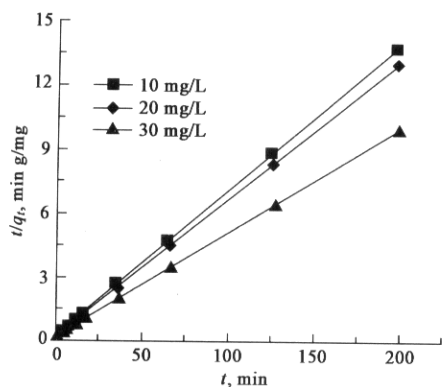


Fig.5 Test of pseudo second-order rate equation for adsorption of different concentrations of Cu<sup>2+</sup> by oxidized CNTs at pH 4.2, temperature 25 °C

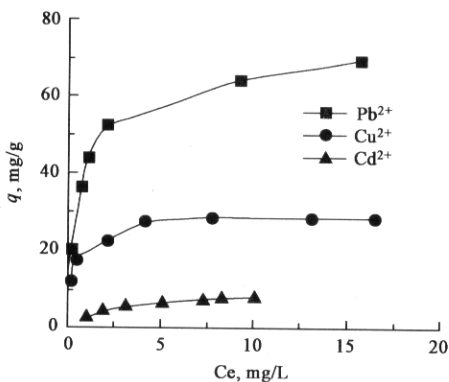


Fig.6 Adsorption isotherms of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> on oxidized CNTs at pH 5.0, temperature 25 °C

the mode of interaction between the metal ions and the adsorbent(Iqbal, 2002)

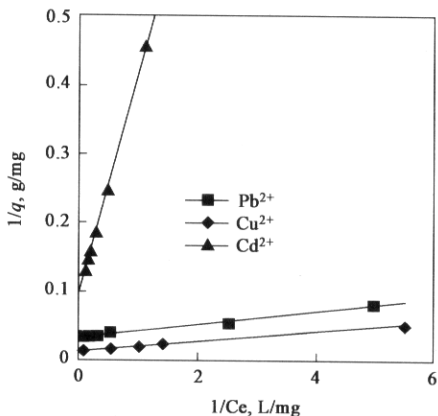


Fig.7 Langmuir isotherms of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> adsorbed on oxidized CNTs at pH 5.0, temperature 25 °C

**Table 2** Langmuir parameters for metal adsorption by the oxidized CNTs

	Langmuir		
	$q_m$	$b$	$R^2$
Pb <sup>2+</sup>	63.29	2.47	0.9877
Cu <sup>2+</sup>	28.33	3.84	0.9809
Cd <sup>2+</sup>	11.01	0.28	0.9926

### 3 Conclusions

The specific surface area of CNTs increase after oxidation with concentrated nitric acid and the particle sizes decrease due to the rupture of the CNTs at where defects exist. Three kinetic models of first-, pseudo second- and second-order rate equations were used to investigate the adsorption data and the pseudo second-order rate model fit the experimental data better than two others. For an 30 mg/L initial metal concentration, the initial adsorption rates( $\nu_0$ ) of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> are 0.033, 0.049 and 0.096 mg/(g·min), respectively, in the order of Cd<sup>2+</sup> > Cu<sup>2+</sup> > Pb<sup>2+</sup>.

The equilibrium data fitted well with the Langmuir model and the maximum adsorption capacities of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> by the oxidized CNTs calculated from the Langmuir isotherm were 63.29, 28.33 and 11.01, respectively, following the sequence of Pb<sup>2+</sup> > Cu<sup>2+</sup> > Cd<sup>2+</sup>.

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