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Carbon nanotubes – the promising adsorbent in wastewater treatment

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Abstract. Carbon materials are a class of significant and widely used engineering adsorbent. As a new member of the carbon family, carbon nanotubes have exhibited great potentials in applications as composite reinforcements, field emitters for flat panel display, sensors, energy storage and energy conversion devices, and catalysts support phases, because of their extraordinary mechanical, electrical, thermal and structural properties. In particular, the large specific surface areas, as well as the high chemical and thermal stabilities, make carbon nanotubes an attractive adsorbent in wastewater treatment. The adsorption properties of the carbon nanotubes to a series of toxic agents, such as lead, cadmium and 1,2-dichlorobenzene have been studied and the results show that carbon nanotubes are excellent and effective adsorbent for eliminating these harmful media in water. The effects of the morphologies and the surface status on the carbon nanotube adsorption capacities are also discussed.

1. Introduction

The search for new and advanced materials is an important task of contemporary research in the environmental protection. In recent years, a great deal of attentions has been focused onto the application of nanostructured materials as adsorbents or catalysts to remove toxic and harmful substances from wastewater and air [1,2]. Various nanometer scale adsorbents, including metals, metal oxides, inorganic and organic carbon nanomaterials in the form of particles, wires and tubes, have been widely used to adsorb CCl_4 , SO_2 , diethyl 4-nitrophenyl phosphate and heavy metals and achieved good effect [3-5]. Recently, fullerenes have been applied to adsorb organometallic complexes [6], naphthalene [7], 1,2-dichlorobenzene [8] and polycyclic aromatic hydrocarbons [1], and their excellent adsorption and desorption properties suggest that they are very promising adsorbent.

Carbon nanotubes (CNTs), a fascinating new member in the carbon family, including single walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) distinguished by their number of layers, have been the research focus due to their unique 1-dimensional structures, exceptional mechanical properties, excellent electronic properties and potential applications. Beside the possibility of making advanced composites [9] and nanoscale electrode devices [10], their high thermal and chemical stabilities of CNTs have also stimulated the applications as catalyst carriers [11]. Structurally, their large specific surface areas, hollow and layered structures make them an ideal adsorption material. In particular, the surface structure of CNTs can be further tuned locally, for example the surface can be functionalized

by oxidation treatment [12] or surfactant treatment [13], the closed tips can be opened, their surfaces can be attached by metals [14], metal oxides [15] or organic ligands [16], which substantially increases the dispersibility and reactivity of the CNTs for the applications in environmental protection.

The high sensitivity to harmful gases indicates that CNTs are good gas sensor materials. The electrical or dielectric variation of the CNTs before and after gas absorption has been the key to gas detection, *e.g.* NO₂ [17], NH₃ [18] and CO [19]. The detection has now been extended to organic vapors, such as methyl ethyl ketone, toluene, dimethyl methylphosphonate, hexane, acetone, chloroform, acetonitrile and methanol [20].

Waste water generally contains lots of toxic and harmful substances, such as heavy metals, organic contaminants, etc., that being discharged from various industrial productions. Drinking water containing these substances causes many chronic or acute diseases, therefore these substances must be eliminated and removed from the wastewater before being discharged into the drainage system. In the paper, we will study the lead, cadmium and organic (1,2-dichlorobenzene) adsorption behavior of CNTs with different morphologies and surface modification.

2. Experimental

Four types of CNTs, named as Xylene-Fe-800 -C-Hor, Propylene-Ni-750 -C-Hor, Benzene-Fe-1150 -C-Vert and Methane-Ni650 -C-Vert, were used to study the morphological effects on lead adsorption. Detailed CNT preparation procedures have previously been described in Ref. [21]. As-grown CNTs were ball milled, dispersed and then refluxed with concentrated nitric acid at 140 °C for 1 h in order to remove the Fe or Ni catalysts and to attach functional groups on the CNT surfaces. After the acid was filtered away using a ceramic filter, and the remaining CNTs were dried at 80 °C, they were used for subsequent adsorption study.

All reagents applied in this study are analytical grade. 0.02 g of the above four oxidized CNT samples were added into 100 ml solutions with initial lead concentrations from 10 to 60 mg/l at a step value of 10 mg/l, and the pH values of the solution were adjusted and kept at 5.0. After equilibrium, the suspensions were filtered through a 0.45 µm membrane filter, and the filtrates were immediately measured by an atomic adsorption spectrometer (Hitachi model Z-6100). The amount of lead adsorbed by CNTs was calculated after subtracting the equilibrium lead content from the initial lead content. This study assesses the CNT morphological effects on lead adsorption. The specific surface areas of the four types of CNTs were measured by nitrogen adsorption/desorption at 77 K using a BET analyzer (Micromeritics ASAP 2000). The attached functional groups on the surfaces were quantitatively evaluated using the Boehm's titration method [21].

Different oxidants, *e.g.* H₂O₂, KMnO₄ and HNO₃, were utilized to oxidize the CNTs (Propylene-Ni-750 -C-Hor), to study the treatment effects on cadmium adsorption. Adsorption isotherms study was carried out by adding 0.05 g of the as-grown and three oxidized CNTs separately into 100 ml solutions with initial Cd (II) concentrations from 1.18 to 9.50 mg/l. The initial and final pH values of the solution were 5.5 and 5.1, respectively. The specific surface areas and the functional groups on the surfaces of the oxidized CNTs were also characterized using methods described above.

pH value effects on organic adsorption properties of the as-grown CNTs (Propylene-Ni-750 -C-Hor) were studied by adding 0.05 g CNTs into 100 ml 1,2-dichlorobenzene (DCB) solutions. The pH was adjusted from 3.6 to 10.7 using 1 M HCl or 1 M NaOH. After equilibrium the solution was centrifuged and the supernatant solution was analyzed using a doubling beam UV/vis spectrophotometer (Hitachi U-3010).

3. Results and discussion

3.1 Morphology effect on the lead adsorption

TEM images show the different morphologies of the four types of CNTs in Fig. 1. Most CNTs in the Xylene-Fe-800°C-Hor sample (Fig. 1a) are fairly straight with an average diameter of 60 nm. CNTs prepared at 1150 °C (Benzene-Fe-1150°C-Vert) have an average diameter of 20–30 nm (Fig. 1b), accompanied with about 20% thick fibers of 120 nm in diameter. The Propylene-Ni-750°C-Hor

sample are usually curved and entangled, with an average diameter of 30 nm (Fig. 1c). The Methane-Ni-650°C-Vert sample exhibits poor crystallinity, Fig. 1d, due to the low temperature (650 °C) and high production rate (500 g/batch).

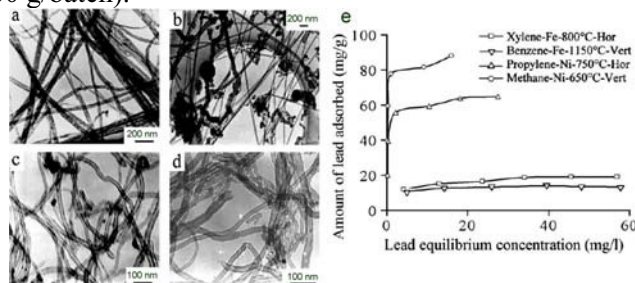


Fig. 1 TEM images of different CNT morphologies and lead adsorption isotherms. (a) Sample Xylene-Fe-800°C-Hor, (b) Sample Benzene-Fe-1150 °C-Vert; (c) Sample Propylene-Ni-750 °C-Hor; (d) Sample Methane-Ni-650 °C-Vert; (e) Adsorption isotherms of lead adsorbed by four kinds of the oxidized CNTs (CNT dosage: 0.02m/100ml; pH=5.0).

The lead adsorption isotherms of the four oxidized CNTs with different morphologies are shown in Fig. 1e. The lead adsorption capability of the sample Benzene-Fe-1150°C-Vert is the weakest, only 11.2 mg/g at the lead equilibrium concentration of 10 mg/l. Sample Xylene-Fe-800°C-Hor reached 14.8 mg/g, greatly improved by sample Propylene-Ni-750°C-Hor to 59.8 mg/g, and maximized by sample Methane-Ni-650°C-Vert to reach 82.6 mg/g. The higher adsorption capability of samples Propylene-Ni-750 °C-Hor and Methane-Ni-650°C-Vert than that of Xylene-Fe-800°C-Hor and Benzene-Fe-1150°C-Vert suggests that the larger specific surface areas are favorable to the lead adsorption, as these areas can effectively increase the active adsorption sites of the CNTs. More importantly, the large quantities of functional groups introduced to the CNT surfaces by nitric acid oxidation (as shown in Table 1) for samples Propylene-Ni-750°C-Hor and Methane-Ni-650°C-Vert may significantly contributed to their adsorption capability. CNTs in sample Methane-Ni-650°C-Vert contains many defects on their tips, lateral surfaces and at the curled places due to low preparation temperature, therefore although their specific surface area is smaller than that of sample Propylene-Ni-750°C-Hor, the functional groups on their surfaces are greater than those of the sample Propylene-Ni-750°C-Hor, leading to the strongest lead adsorption. It can be concluded that CNTs with perfect morphologies tend to have low adsorption capabilities.

Table 1 Specific surface areas and amounts of functional groups on the surfaces of the four types of oxidized CNTs.

Sample no.	S_{BET} (m^2/g)	Carboxyl (mmol/g)	Lactones (mmol/g)	Phenols (mmol/g)
Xylene-Fe-800°C-Hor	47	0.26	0.93	0.46
Benzene-Fe-1150°C-Vert	62	0.27	0.86	0.50
Propylene-Ni-750°C-Hor	154	0.76	1.83	1.45
Methane-Ni-650°C-Vert	145	0.85	1.95	1.51

3.2 Different oxidant treatment effect on the cadmium adsorption by CNTs

It is known that oxidation of carbon surfaces can offer not only a more hydrophilic surface structure, but also a large number of oxygen-containing functional groups, which increase the ion-exchange capability of the CNTs. The Attached functional groups to the CNT surfaces are listed in Table 2, with the carboxyl and lactone groups amount on HNO_3 treated CNTs higher than those oxidized by H_2O_2 and KMnO_4 , and phenol groups being the most on KMnO_4 treated CNTs. The authors have yet to discern the remaining Mn extent to which they contributed to the KMnO_4 treated CNT composites functionality.

Cd (II) adsorption isotherms (Fig. 2) show that the Cd (II) adsorption for as-grown CNTs is low, only 1.1 mg/g at a 4 mg/l Cd (II) equilibrium concentration, whilst the adsorptions increase to 2.6 and 5.1 mg/g for H_2O_2 and HNO_3 oxidized CNTs at identical equilibrium concentration. This indicates that the functional groups introduced by oxidation have improved the CNT ion-exchange capabilities, resulting in enhanced Cd (II) adsorption capacities accordingly. Although the specific surface areas and quantities of the functional groups for KMnO_4 oxidized CNTs are lower than that of HNO_3 oxidized CNTs (Table 2), the Cd(II) adsorption capacity for the former increases sharply compared to the latter, reaching 11.0 mg/g at a Cd (II) equilibrium concentration of 4 mg/l. This may partly be due to the adsorption of the residual MnO_2 particles supported on the CNTs, and the mechanism for Cd (II) adsorption by KMnO_4 oxidized CNTs is still unclear and demands a further exploration [23].

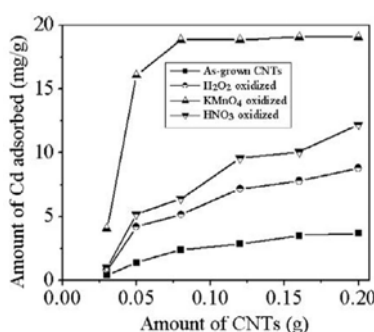


Fig. 2 Adsorption isotherms of Cd (II) adsorbed by CNTs at 0.05 g per 100 ml and initial pH = 5.5, (b) pH effects on the DCB adsorption by as-grown CNTs ($T=25^\circ\text{C}$, $t=24$ h, $C_0=20$ mg/l).

Table 2 A summary of the specific surface areas and amounts of functional groups of the oxidized CNTs.

Sample no.	S_{BET} (m^2/g)	Carboxyl (mmol/g)	Lactones (mmol/g)	Phenols (mmol/g)
H_2O_2 oxidized CNTs	130	0.56	1.10	0.86
KMnO_4 oxidized CNTs	128	0.43	1.34	1.59
HNO_3 oxidized CNTs	154	0.76	1.83	1.45

3.3 DCB adsorption by raw CNTs

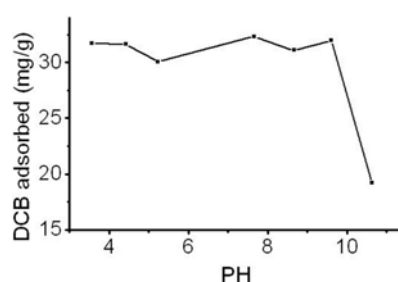


Fig. 3 PH effect on the DCB adsorbed by the as-grown CNTs at different temperatures ($T=25^\circ\text{C}$, $t=24$ h, $C_0=20$ mg/l).

Activated carbon has already been widely used to remove organic substances from wastewater [24]. In this context, we report the DCB adsorptions using as-grown CNTs. Fig. 3 shows the effects of pH value on the adsorptions, demonstrating that the removal of DCB by as-grown CNTs has very little influence in the pH value while ranging from 3 to 10. The adsorption capacity that remains almost constant in such a wide pH range suggests CNTs being excellent adsorbents for DCB removal. When

pH value exceeds 10, the adsorption capacity drops suddenly which may be caused by ionization of some oxygen groups such as carboxylic groups ($-\text{COOH}$) and hydroxylic groups ($-\text{OH}$) on the surface of CNTs. More oxygen groups on the surface of CNTs ionize, more water is adsorbed by these groups at higher pH values. Thus, when water clusters form on these oxygen groups, the adsorption will be affected, in two possible ways. Firstly, since these oxygen groups are located on the CNT surfaces, the formation of water clusters will hinder the DCB diffusion access to the CNT surfaces. Secondly, this water adsorption may interfere with the surface carbonyl groups which adsorb organics through a donor–accepter complex formation, which is believed to block adsorption of DCB on the carbonyl sites [25].

4. Summary

CNTs have exhibited excellent adsorption properties in the removal lead, cadmium and organic 1,2-DCB from water, being a promising candidate in wastewater treatment. The morphologies of the CNTs can affect their adsorption capabilities greatly. CNTs with poor crystallinity and morphology can be easily introduced with much more functional groups, interestingly leading to better adsorption capabilities. Treatment with oxidants not only enhances the dispersibility of the CNTs, but also improves their adsorption capacity.

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