Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes

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Abstract

Carbon nanotubes (CNTs) were oxidized with H_2O_2 , KMnO_4 and HNO_3 . Their physicochemical properties were investigated by BET N_2 adsorption, laser particle examination, Boehm's titration, zeta potential measurement and cadmium(II) adsorption. The experimental results suggest that cadmium(II) adsorption capacities for three kinds of oxidized CNTs increase due to the functional groups introduced by oxidation compared with the as-grown CNTs. The cadmium(II) adsorption capacity of the as-grown CNTs is only 1.1 mg g^{-1} , while it reaches 2.6, 5.1 and 11.0 mg g^{-1} for the H_2O_2 , HNO_3 and KMnO_4 oxidized CNTs, respectively, at the cadmium(II) equilibrium concentration of 4 mg l^{-1} . Adsorption of cadmium(II) by CNTs was strongly pH-dependent and the increase of adsorption capacities for HNO_3 and KMnO_4 oxidized CNTs is more obvious than that of the as-grown and H_2O_2 oxidized CNTs at lower pH regions. The experiments of CNT dosage effect on the cadmium(II) adsorption show that the adsorption capacity for KMnO_4 oxidized CNTs has a sharper increase at the CNT dosage from 0.03 to 0.08 g per 100 ml than the as-grown, H_2O_2 and HNO_3 oxidized CNTs and its removal efficiency almost reaches 100% at CNT dosage of 0.08 g per 100 ml. Analysis revealed that the KMnO_4 oxidized CNTs hosted manganese residuals, and these surely contributed to cadmium sorption to a yet-undefined extent.

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1. Introduction

Currently there is increasingly interest in removing cadmium from drinking water due to its supreme toxicity to human health in small concentration. According to the World Health Organization guidelines, the permissible concentration of cadmium in drinking water is less than 0.005 mg l^{-1} [1]. Long term drinking water containing cadmium higher than this level can cause nausea, salivation, diarrhea, muscular cramps, renal degradation, lung insufficiency, bone lesions, cancer and hypertension in humans [1,2].

Cadmium contamination in drinking water can naturally occur in zinc, lead and copper ores through diffusion. But its major sources come from industrial process such as electroplating, smelting, alloy manufacturing, pigments, nickel–cadmium and solar battery production. Many methods including chemical precipitation, ion-exchange, reverse osmosis and adsorption have been used to remove cadmium from wastewater. One of these methods, adsorption is a cost-effective, simple and widely used method. A number of adsorbents such as activated carbon [3–7], waste egg shell [8], hematite [9], and holly oak [10] have been explored and expressed good cadmium adsorption property.

CNTs, a fascinating new member in carbon family, have been the worldwide hotspot of study since their discovery [11] due to their unique morphologies and various po-

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tential applications. Their high mechanical strength makes them good candidates for advanced composites [12]. They can be either semiconducting, semimetallic, or metallic, depending on the tube helicity and diameter [13], which open up an promising field in nanoscale electrodevice applications. Their large specific surface area, hollow and layered structures indicate they can be an ideal hydrogen storage material [14]. Recently CNTs have been found an efficient adsorbent for dioxin adsorption which their adsorption capacity is superior to that of activated carbon attributed to the stronger interactions between dioxins and CNTs [15]. Li et al. [16] reported that CNT supported amorphous alumina had higher fluoride adsorption capacity which was about 13.5 times higher than that of AC-300 carbon and four times higher than that of γ - Al_2O_3 . After oxidation with nitric acid, CNTs also showed exceptional adsorption capability and high adsorption efficiency for lead removal from water [17]. The previous studies suggested that CNTs may be an promising adsorption material used in environmental protection.

Here we oxidized CNTs with H_2O_2 , KMnO_4 and HNO_3 and characterized their physicochemical properties in terms of BET N_2 adsorption, laser particle examination, Boehm's titration, zeta potential measurement. The cadmium(II) adsorption isotherms of the as-grown and three kinds of oxidized CNTs were studied, at the same time, the pH and CNT dosage effects on the cadmium(II) adsorption were also evaluated.

2. Experimental

CNTs were prepared by using thermal decomposition of the methane in hydrogen flow at temperature 750 °C using Ni nanoparticles as catalysts. The as-grown CNTs (3 g) were added into the solutions of H_2O_2 , KMnO_4 , and nitric acid, respectively. The suspensions of CNTs mixed with H_2O_2 and KMnO_4 were heated at 80 °C for 3 h. The mixture of CNTs and nitric acid was refluxed at 140 °C for 1 h. The three suspensions were washed five times with 1000 ml deionized water to remove free oxidants. Then the CNTs oxidized with different oxidants were dried at 100 °C and stored for further studies.

The specific surface area and pore size distributions of the as-grown and oxidized CNTs were measured by nitrogen adsorption/desorption at 77 K using BET method.

Particle size distributions of the as-grown and oxidized CNTs were analysed by laser light scattering with a Malvern Mastersizer 2000. The results are volume based and expressed in terms of equivalent spheres. The suspensions of four kinds of CNTs were prepared by dispersing 0.2 g CNTs into 100 ml deionized water. The suspensions were supersonicated for 4 h to make CNTs scatter in water sufficiently. They were then added to the measurement cell under stirring until an obscuration between 10 and 20% were reached. The particle size distribution results were obtained.

The functional groups on oxidized CNTs were quantitatively measured by Boehm's titration method [18]. The Boehm's titration method involved dispersing 0.2 g of the three kinds of oxidized CNTs in 50 ml deionized water. The suspensions were then mixed with 10 ml of 0.1 M base solutions of sodium hydroxide, sodium hydrogen carbonate and sodium carbonate and stirred in a sealed vessel for 48 h. After this time, the suspensions were filtrated and 20 ml filtrates were added to 15 ml of 0.1 M hydrochloric acid, which neutralized the unreacted bases. The solutions were then back-titrated with 0.1 M sodium hydroxide using a Automatic Potential Titrator 716 (Metrohm, Switzerland) which recorded the volume of sodium hydroxide used to titrate the pH values of the solutions to 7.0.

Zeta potentials of the as-grown and oxidized CNTs were measured by a Malvern zetameter (Zetasizer 2000). The pH values of CNT solution were adjusted from 2.0 to 12.0 by adding 0.1 M hydrochloric acid or sodium hydroxide solution to the glass beaker at 25 °C. By measuring the zeta potential as function of pH, the acidity or basicity of the CNT surface and the isoelectric point (IEP) can be determined.

Analytical grade cadmium(II) chloride was used to prepare a stock solution of 1000 mg l^{-1} of Cd(II), which was further diluted to the required concentrations before used. All experiments were carried out at 25 °C.

Adsorption isotherms were studied by adding 0.05 g of the as-grown and three kinds of oxidized CNTs into 100 ml solutions with initial concentrations of Cd(II) from 1.18 to 9.50 mg l^{-1} . The initial and final pH values of the solution were 5.5 and 5.1, respectively. After the suspensions were shaken for 4 h, they were filtered through a 0.45- μm membrane filters. The filtrates were immediately measured by an atomic adsorption spectrometer. The amount of Cd(II) adsorbed on CNTs was calculated by subtracting the equilibrium Cd(II) content from the initial Cd(II) content.

To study the effects of pH on Cd(II) adsorption, 0.05 g of the as-grown and oxidized CNTs were dispersed into 100 ml solutions containing 9.50 mg l^{-1} of Cd(II). The initial pH values of the solutions were adjusted from 2.0 to 12.0 using 0.5 M hydrochloric acid and 0.5 M sodium hydroxide.

The CNT dosage effects on Cd(II) adsorption were carried out by adding 0.03, 0.05, 0.08, 0.12, 0.16 and 0.20 g of the as-grown and oxidized CNTs in 100 ml solution with Cd(II) concentration of 9.50 mg l^{-1} at pH value of 5.5.

3. Results and discussion

Transmission electron microscopy images (Fig. 1) show 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 images of the as-grown carbon nanotubes.

The specific surface area and pore specific volume of the as-grown and oxidized CNTs are listed in Table 1. It can be seen that the specific surface area of the H_2O_2 and KMnO_4 oxidized CNTs increase slightly from 122 to 130 and 128 $\text{m}^2 \text{g}^{-1}$, respectively, after oxidation. While it has a larger increase for nitric acid oxidized CNTs from 122 to 154 $\text{m}^2 \text{g}^{-1}$. This suggests that oxidation of CNTs with nitric acid is an effective method to remove the amorphous carbon, carbon black and carbon nanoparticles introduced by CVD preparation process and probe inner cavities of the CNTs, which expose their internal surface area.

Fig. 2 shows the pore size distributions of the as-grown and oxidized CNTs. The main pore diameter of all kinds of CNTs is about 3.6 nm. The peaks of the H_2O_2 and KMnO_4 oxidized CNTs improve slightly compared with as-grown CNTs. However, it increases greatly after oxidation with nitric acid. This can be easily comprehended considering the structure change of CNTs. Oxidation with nitric acid can open the tips, probe the holes through the CNTs and break up CNTs into smaller pieces at where defects such as pentagon and heptagon exit. So the pore volume of CNTs increased greatly. Whereas the oxidation abilities of H_2O_2 and KMnO_4 are weak and only very little amount of the tips were opened and few CNTs were broken up, so the increase of pore volume is not obvious. The pore specific surface areas listed in Table 1 also consist with the above results.

Particle size distribution can affect the suspensibility and adsorption property of the adsorbents. Fig. 3 shows the

Table 1

Porosity and specific surface areas of as-grown and oxidized CNTs

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$)
As-grown CNTs	122	0.28
H_2O_2 oxidized CNTs	130	0.36
KMnO_4 oxidized CNTs	128	0.32
HNO_3 oxidized CNTs	154	0.58

S_{BET} =BET surface area; V_p =pore specific volume.

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

comparable results of particle size distributions of the as-grown and oxidized CNT obtained by laser light scattering. There are two peaks at 15 and 310 μm for the as-grown CNTs, while for the H_2O_2 oxidized CNTs the peaks decrease to 12 and 200 μm , for the KMnO_4 oxidized CNTs the major peak appears in 12 μm , the other part of the curve suggests that most of CNT diameters are less than 150 μm . The particle diameter of HNO_3 oxidized CNTs is about 8 μm . The phenomenon indicates that oxidation with H_2O_2 and KMnO_4 can partially break up CNTs into small pieces, while oxidation with HNO_3 can cut short most of CNTs. The better suspensibility of HNO_3 oxidized than that of as-grown, H_2O_2 and KMnO_4 oxidized CNTs also prove this result.

It is known that oxidation of carbon surface can offer not only a more hydrophilic surface structure, but also a larger number of oxygen-containing functional groups, which increase the ion-exchange capability of carbon material [19]. The functional groups on the surfaces of

Fig. 3. Particle size distribution of the as-grown and oxidized CNTs.

oxidized CNTs can be quantitatively measured by Boehm's method. According to this method, sodium hydrogen carbonate only neutralizes carboxyl groups, sodium carbonate neutralizes carboxyl groups and lactones, sodium hydroxide can neutralize carboxyl groups, lactones and phenols. So the different kinds of functional groups can be calculated through the known volume of used acid and bases. From the Table 2, it can be seen that the amounts of carboxyl and lactone groups on the CNTs treated with HNO_3 are higher those of CNTs oxidized with H_2O_2 and KMnO_4 . The quantity of phenol groups on CNTs treated with KMnO_4 is most. The authors have not yet discerned the extent to which manganese that remained on the KMnO_4 -treated CNT surface contributed to this composited material's functionality.

Zeta potential is a physical parameter, which can be used to quantify the electrical potential of the solid particle surface. By measuring the zeta potential as function of pH, the acidity or basicity of the CNT surfaces and the isoelectric point ($\text{IEP}=\text{pH}$ value for zeta potential=0) can be determined. The variation of the zeta potential of the as-grown and oxidized CNTs dependence of pH is shown in Fig. 4. The IEP of the as-grown CNTs is 5.0. After oxidation with different oxidants, the IEP shifts to lower pH values due to the acid surface groups introduced by oxidation. At the same pH value, the zeta potential for three kinds of oxidized CNTs follows the order of $\text{H}_2\text{O}_2 < \text{KMnO}_4 < \text{HNO}_3$. This indirectly suggests the amounts of acid functional groups increase following above order. The result is also confirmed by the data obtained from Boehm's titration.

Cadmium(II) adsorption capacities of the as-grown and oxidized CNTs are given as a function of the equilibrium concentration of cadmium(II) ions in Fig. 5. It is clear that the cadmium(II) adsorption capacity of the as-grown CNTs is low and only 1.1 mg g^{-1} at cadmium(II) equilibrium concentration of 4 mg l^{-1} . While the adsorption capacities increase and reach 2.6 and 5.1 mg g^{-1} for the H_2O_2 and HNO_3 oxidized CNTs at the same cadmium(II) equilibrium concentration. This indicates that the functional groups introduced by oxidation improve the ion-exchange capabilities of the CNTs and thus make cadmium(II) adsorption capacities increase correspondingly. The result is consistent with the previous report reported [20] that the adsorption capacity of Cd(II) was maximum for the activated carbon modified by concentrated nitric acid due to both ion-exchange with the surface acidic groups and

Fig. 4. Zeta potential curves vs. pH of the as-grown and oxidized CNTs.

Fig. 5. Adsorption isotherms of Cd(II) adsorbed by CNTs (CNT dosage: 0.05 g per 100 ml; initial pH: 5.5).

forming the surface complex chelate type with humic acids present on the carbon surface. But the Cd(II) adsorption capacity of the activated carbon is 2 mg g^{-1} at cadmium(II) equilibrium concentration of 4 mg l^{-1} . An et al. [21] reported that the Cd(II) adsorption capacities of the granular and powdered activated carbon were only 1.12 mg g^{-1} at cadmium(II) equilibrium concentration of 11.2 mg l^{-1} and pH value of 5.0. The comparison shows that

Table 2

The amount of functional groups on the surfaces of oxidized CNTs determined by Boehm's method

Sample	Carboxyl (mmol g ⁻¹)	Lactones (mmol g ⁻¹)	Phenols (mmol g ⁻¹)
H_2O_2 oxidized CNTs	0.56	1.10	0.86
KMnO_4 oxidized CNTs	0.43	1.34	1.59
HNO_3 oxidized CNTs	0.76	1.83	1.45

CNTs have higher Cd(II) adsorption capability than activated carbon under the same treatment conditions.

An interesting phenomenon in Fig. 5 is the abrupt increase of the adsorption capacity for KMnO_4 oxidized CNTs. Its cadmium(II) adsorption capacity reaches 11.0 mg g^{-1} at cadmium(II) equilibrium concentration of 4 mg l^{-1} . This may be due to the adsorption role of the residual MnO_2 particles supported on the CNTs. The mechanism of cadmium(II) adsorption by KMnO_4 oxidized CNTs is still unclear and needs to be explored further.

Fig. 6 shows the dependence of the cadmium(II) adsorption capability of different CNTs on the pH values of the solutions. It is known that cadmium species can present in deionized water in the forms of Cd^{2+} , CdOH^+ , $\text{Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})_{2(s)}$, etc. [22]. According to the equations in Ref. [20], at pH 5.5, the solubility, $C_{T, \text{Cd}}$, of the $\text{Cd}(\text{OH})_{2(s)}$ is great and reaches about $10^{3.45} \text{ M}$, so the $\text{Cd}(\text{II})^{2+}$ is the main species. At pH 9.0, the $C_{T, \text{Cd}}$ of $\text{Cd}(\text{OH})_{2(s)}$ is only about $2.56 \times 10^{-4} \text{ M}$. With the increase of the pH value, the $C_{T, \text{Cd}}$ of $\text{Cd}(\text{OH})_{2(s)}$ decreases further and reaches 3.23×10^{-5} at pH 12. At this time, the main species in the solution is $\text{Cd}(\text{OH})_{2(s)}$. It is obvious from Fig. 6 that the adsorption of cadmium(II) is higher at alkaline range. But at this region precipitation plays main role in removing the cadmium(II) ions attributed to the formation of precipitate of $\text{Cd}(\text{OH})_{2(s)}$ as the results discussed above. This can also be proved by very lower adsorption capacity of the as-grown CNTs at acidic condition and sharp increase at basic region. The cadmium(II) adsorption capacities of HNO_3 and KMnO_4 oxidized CNTs are more sensitive to pH changes at lower pH region and reach 8.0 and 12.6 mg g^{-1} at pH value of 6.0, while for the as-grown and H_2O_2 oxidized CNTs they are only 2.0 and 3.3 mg g^{-1} , respectively.

Fig. 6. pH effect on the Cd(II) adsorption by CNTs (CNT dosage: $0.05 \text{ g per } 100 \text{ ml}$).

Fig. 7. CNT dosage effect on the Cd(II) adsorption (initial $\text{Cd}(\text{II})^{2+}$ concentration: 9.50 mg l^{-1} and pH 5.5).

It was reported that for all cation adsorption onto oxide surfaces the fraction bound increased from zero to one over a narrow pH range, typically one pH unit, and pH edge shifts from left to right with increasing adsorbate/adsorbent ratio [23]. Fig. 6 shows that adsorption of cadmium(II) by CNTs also abides by such a rule and reaches the highest adsorption capacity in a narrow pH range. The pH edge for cadmium(II) adsorption by the KMnO_4 , HNO_3 and H_2O_2 oxidized and the as-grown CNTs, shifted from left to right suggests that the adsorption sites on the CNTs decrease gradually and this phenomenon is just like the results of increasing adsorbate/adsorbent ratio.

As seen in Fig. 7, the adsorption capacities of all adsorbents increase with increasing of the CNT dosages. But it increases very slow for the as-grown CNTs and is only 3.5 mg g^{-1} at CNT dosage of $0.2 \text{ g per } 100 \text{ ml}$. The increasing trend for H_2O_2 and HNO_3 oxidized CNTs is almost identical and the adsorption capacities are 8.4 and 11.8 mg g^{-1} , respectively, at CNT dosage of $0.2 \text{ g per } 100 \text{ ml}$. The obvious increase takes place at the CNT dosages from 0.03 to $0.08 \text{ g per } 100 \text{ ml}$ for KMnO_4 oxidized CNTs. The removal efficiency for KMnO_4 oxidized CNTs almost arrives at 100% at the CNT dosage of $0.08 \text{ g per } 100 \text{ ml}$, which suggests that the treatment of CNTs with KMnO_4 is an effective method to improve their Cd(II) adsorption capabilities.

4. Conclusions

The specific surface area and pore specific volume of CNTs increase after oxidation with H_2O_2 , KMnO_4 and HNO_3 . Their particle sizes decrease due to the fracture at where defects exit. With deepening of the oxidation degree,

the IEP shifts to the lower pH value and functional groups on the surfaces of CNTs increase correspondingly.

The results of pH and CNT dosage effect on the cadmium(II) adsorption show that the increase of cadmium(II) adsorption capacity for KMnO_4 oxidized CNTs is greater than that of the as-grown, H_2O_2 and HNO_3 oxidized CNTs. The manganese deposition on the KMnO_4 oxidized surfaces surely contributed to the Cd(II) adsorption, to a yet-unquantified extent.

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