

Plasma-Induced Grafting of Cyclodextrin onto Multiwall Carbon Nanotube/Iron Oxides for Adsorbent Application

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Received: December 2, 2009; Revised Manuscript Received: April 5, 2010

The magnetic composite of β -cyclodextrin grafted onto multiwalled carbon nanotubes/iron oxides (denoted as MWCNTs/iron oxides/CD) was synthesized using the plasma-induced grafting technique and was developed for the removal of inorganic and organic pollutants from aqueous solutions. The characteristic results of Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), and thermogravimetric analysis (TGA) showed that β -CD was grafted onto the MWCNTs/iron oxides. The grafted β -CD on the MWCNTs/iron oxides contributed to an enhancement of the adsorption capacity because of the strong abilities of the multiple hydroxyl groups and the inner cores of the hydrophobic cavity in β -CD to form complexes with metal ions and organic pollutants. MWCNTs/iron oxides/CD can be separated and recovered from solution by magnetic separation. The adsorption of Pb(II) on MWCNTs/iron oxides/CD was found to be dependent on pH, and the adsorption of 1-naphthol was found to be independent of pH. The results show that the magnetic composite of MWCNTs/iron oxides/CD is a promising composite material for the preconcentration and separation of inorganic and organic pollutants from aqueous solutions in environmental pollution cleanup.

I. Introduction

Inorganic and organic pollution in industrial wastewater has attracted global attention because of its adverse effect on the environment and human health. Various technologies have been used for the treatment of inorganic and organic pollutants, including adsorption,^{1,2} ion exchange,³ biosorption,⁴ electrochemical reduction,⁵ and chemical precipitation.⁶ Adsorption is one of the most cost-effective technologies for the removal of inorganic and organic pollutants. Traditional adsorbent materials have included oxides, clay minerals, and carbon materials, among others. Usually, the adsorption capacities of these adsorbents are not high. Therefore, novel adsorbents with high adsorption capacities and chemical stability are being sought. Carbon nanotubes (CNTs)⁷ have already been investigated as a novel adsorbent for various organic pollutants, metal ions, and radionuclides,^{8–12} and they can be easily modified by chemical treatments to increase their adsorption capacities.⁹ Li et al.¹³ reported that the metal-ion removal capacities on other adsorbents such as granular activated carbon, power activated carbon, fly ash, scolecite, microbeads, and iron-coated sand were lower than those of oxidized CNTs.

However, it is difficult to separate CNTs from aqueous solutions because of their small size. Also, there are serious concerns over the health and environmental risks of CNTs once they have been released into the environment. It should be noted that CNTs have toxicity: they can enter cells, causing damage to plants, animals, and humans.^{14,15} Traditional methods to separate CNTs from aqueous phases have included ultracen-

trifugation and filtration. Centrifugation methods require very high speeds, and traditional filtration methods are prone to filter blockages. In recent years, the application of magnetic adsorbents has received considerable attention because of their easy separation after use. Many techniques have been used for the removal of heavy-metal ions,^{16–20} dyes,²¹ and oil.²² Magnetic iron oxides have been used to fabricate new adsorbents together with other functionalized materials such as alginate capsules,¹⁶ multiwalled carbon nanotubes (MWCNTs),¹⁷ activated carbon,² zeolites,²³ gum arabic,¹⁸ and dimercaptosuccinic acid.¹⁹ The magnetic adsorbents can be separated and recovered from environmental applications by a magnetic process.

Plasma-induced grafting treatment is a useful method for the introduction of functional groups onto material surfaces without altering material bulk properties.^{24,25} It is an environmentally friendly technique for modifying the surface properties of materials because large amounts of chemicals are not needed in grafting processes. Cyclodextrins (CDs) are cyclic oligosaccharides with a characteristic truncated-cone shape that forms a well-defined cylindrical cavity.²⁶ CDs are characterized by a hydrophilic exterior and a hydrophobic interior.²⁷ They are environmentally friendly and are commonly used in the food industry. The identities of encapsulating organic molecules and self-assembly have led to intensive studies of CDs and their inclusion complexes.²⁸ Many nanostructural compounds and composites have been constructed through the self-assembly of CDs, and the hydroxyl groups are also known to mediate compatibility with inorganic-oxide matrixes through hydrogen bonding.²⁹ β -Cyclodextrin (β -CD) is one of the most common CDs, with seven $\alpha(1\rightarrow4)$ glucopyranose units and with a tapered 7.9-Å-deep cavity with top and bottom diameters of 6.0 and 6.5 Å, respectively. β -CD contains a hydrophobic cavity capable of forming inclusion complexes with many organic molecules

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that are otherwise poorly soluble in water.³⁰ The β -CD grafted onto MWCNTs/iron oxides contributes to an enhancement of the adsorption capacity of MWCNTs/iron oxides because of the strong complexation abilities of the multiple hydroxyl groups in β -CD with metal ions²⁶ and of the hydrophobic cavity with organic contaminants. A material consisting of β -CD-grafted MWCNTs/iron oxides (denoted as MWCNTs/iron oxides/CD) has the advantage of a high adsorption capacity and magnetism for separation.

Lead is a toxic cationic metal that can directly and indirectly cause headaches, chills, anemia, diarrhea, and poisoning, leading to the dysfunction of the reproductive system, kidneys, liver, brain, and central nervous system.³¹ Naphthol is an industrial material used in the manufacture of industrial compounds such as dyes, pharmaceuticals, plastics, rubbers, and synthetic fibers.³² It is also an important component of the pesticide napropamide and a principal reaction product of the hydrolysis of the pesticide carbaryl.³³ Naphthol can cause the depolymerization of spindle microtubules and a decrease of protein phosphorylation, thereby disturbing the mitotic processing of cells.³⁴

In this work, the magnetic composite of MWCNTs/iron oxides/CD was first synthesized by a plasma-induced grafting method. MWCNTs/iron oxides/CD was characterized by Fourier transform infrared (FT-IR) spectroscopy, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). The application of MWCNTs/iron oxides/CD for the removals of Pb(II) and 1-naphthol from aqueous solution was investigated by batch experiments in environmental pollution cleanup.

II. Experimental Section

Chemical Materials. All chemicals were of analytical reagent grade and were used as received, and all solutions were prepared with Milli-Q water (resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$) under ambient conditions. Pb(II) stock solution ($1000 \text{ mg} \cdot \text{L}^{-1}$) was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ in Milli-Q water and was further diluted to $60 \text{ mg} \cdot \text{L}^{-1}$ before use. The stock solution of 1-naphthol (purchased from Sinopharm Chemical Reagent Co. Ltd., purity of 99.0%) was prepared at a concentration of $120 \text{ mg} \cdot \text{L}^{-1}$. All chemicals were used without any further purification in the experiments.

Preparation and Characterization of MWCNTs/Iron Oxides/CD. The detailed methods for the preparation of MWCNTs/iron oxides and MWCNTs/iron oxides/CD are described in section SI-1 of Supporting Information. An SEM image of MWCNTs/iron oxides is shown in Figure SI-1 (Supporting Information). MWCNTs/iron oxides (1.0 g) were treated by using N_2 plasma at a pressure of 10 Pa , a power of 70 W , a voltage of 650 V , and a current of 60 mA in a custom-built grafting reactor for 40 min under continuous stirring. The $\pi (\text{C}=\text{C})$ bonds in the sp^2 -hybridized graphite-like carbon within the carbon nanotube lattice are active and chemically unstable because of the lack of rotation around the $\text{C}=\text{C}$ bonds and the unsaturation of the $\text{C}=\text{C}$ bonds, and therefore, they more susceptible to plasma attack.³⁵ It is believed that active sites are generated on the dissociated π bonds in $\text{C}=\text{C}$, which then further react with β -CD. After the plasma-induced treatment process, β -CD solution ($2 \text{ g} \cdot \text{L}^{-1}$) was injected into the grafting reactor, and the mixture was heated to $80 \text{ }^\circ\text{C}$ for 1 day under continuous stirring. The obtained sample was repeatedly washed with Milli-Q water until no β -CD was detected in the supernatant using high-performance liquid chromatography–mass

spectrometry (HPLC–MS). Finally, the magnetic composite of MWCNTs/iron oxides/CD was dried in an oven at $95 \text{ }^\circ\text{C}$ for 12 h .

The specific surface areas of MWCNTs/iron oxides/CD, MWCNT/iron oxides and MWCNTs were measured by the N_2 Brunauer–Emmett–Teller (BET) method. The MWCNTs/iron oxides/CD composite was characterized by FT-IR spectroscopy, XRD, TGA, XPS, and vibrating sample magnetometry (as described in detail in section SI-1 of the Supporting Information).

Batch Adsorption and Desorption Experiments. The adsorption and desorption of Pb(II) were investigated using a batch technique in a 10 mL polyethylene centrifuge tube. The stock suspensions of adsorbent ($2.00 \text{ g} \cdot \text{L}^{-1}$) and NaClO_4 ($0.10 \text{ mol} \cdot \text{L}^{-1}$) were pre-equilibrated for 24 h , and then Pb(II) ($60.0 \text{ mg} \cdot \text{L}^{-1}$) stock solution was added to achieve the desired concentrations of the various components. The pH of the system was adjusted by adding a negligible volume of 0.10 or $0.01 \text{ mol} \cdot \text{L}^{-1}$ HClO_4 or NaOH . After the suspensions had been shaken for 2 days to obtain equilibrium, the solid and liquid phases were separated by a magnetic process using a permanent magnet. After adsorption, desorption was carried out by washing the adsorbent with HClO_4 ($\text{pH} \sim 4$); then, the MWCNTs/iron oxides/CD was dried at $95 \text{ }^\circ\text{C}$. The residual concentration of Pb(II) was analyzed by using Pb chlorophosphonazo III complex at a wavelength of 616 nm . The concentration of 1-naphthol was analyzed using a UV-2550 spectrophotometer at a wavelength of 332 nm . To enhance the determination sensitivity, the residual concentration of 1-naphthol was basified to a pH of 12 with $0.15 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution to ensure that the 1-naphthol was present in the dissociated state.

All reported experimental data are the averages of duplicate or triplicate determinations. The relative error in the data is about 5% .

III. Results and Discussion

Characterization of MWCNTs/Iron Oxides/CD. The specific surface area of MWCNTs/iron oxides/CD, $63.95 \text{ m}^2 \cdot \text{g}^{-1}$, is lower than those of both oxidized MWCNTs, $197.00 \text{ m}^2 \cdot \text{g}^{-1}$, and MWCNT/iron oxides, $88.53 \text{ m}^2 \cdot \text{g}^{-1}$. Although the specific surface area of MWCNTs/iron oxides/CD is lower than that of MWCNT/iron oxides, the adsorption capacity of MWCNTs/iron oxides/CD is higher than that of MWCNT/iron oxides, indicating that the multiple hydroxyl groups of CD play an important role in the enhancement of the adsorption capacity. The specific surface area of iron oxides is $15.34 \text{ m}^2 \cdot \text{g}^{-1}$, which is much lower than that of MWCNTs/iron oxides/CD. Figure 1 shows FT-IR spectra of oxidized MWCNTs, MWCNTs/iron oxides, and MWCNTs/iron oxides/CD. The peak at 3432 cm^{-1} is assigned to the $-\text{OH}$ stretching vibration arising from surface hydroxyl groups on the adsorbent and water. The two characteristic bands at 2847 and 2922 cm^{-1} can be assigned to $\text{C}-\text{H}$ stretching,³⁶ and the peak at 1042 cm^{-1} can be assigned to $\text{CH}-\text{O}-\text{CH}_2$. The strong $\text{Fe}-\text{O}$ adsorption bands at 576 cm^{-1} corroborates that MWCNTs/iron oxides and MWCNTs/iron oxides/CD contain magnetite.^{16,37} In addition, the adsorption bands at 1631 and 2311 cm^{-1} correspond to the vibration of the remaining H_2O and adsorbed CO_2 , respectively.²⁹ Compared to that on oxidized MWCNTs, the relative intensity of the peak at 3432 cm^{-1} is weaker on MWCNTs/iron oxides (spectrum B) and stronger on MWCNTs/iron oxides/CD (spectrum C). It can be explained that the $-\text{OH}$ groups in MWCNTs/iron oxides bind iron metal, but in MWCNTs/iron oxides/CD, the $-\text{OH}$ groups of β -CD are on the surface of the MWCNTs/iron oxides.

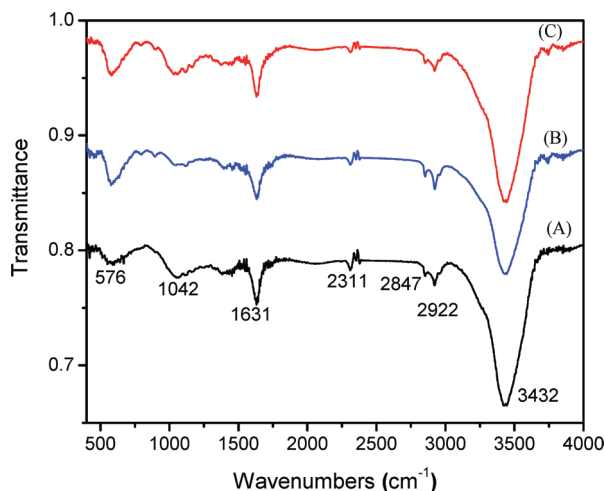


Figure 1. FT-IR spectra of (A) oxidized MWCNTs, (B) MWCNTs/iron oxides, and (C) MWCNTs/iron oxides/CD. The relative intensity of the peak at 3432 cm^{-1} is weaker on MWCNTs/iron oxides (spectrum B) and stronger on MWCNTs/iron oxides/CD (spectrum C). The increase in the band intensity at around 1042 cm^{-1} in spectrum C can be attributed to β -CD.

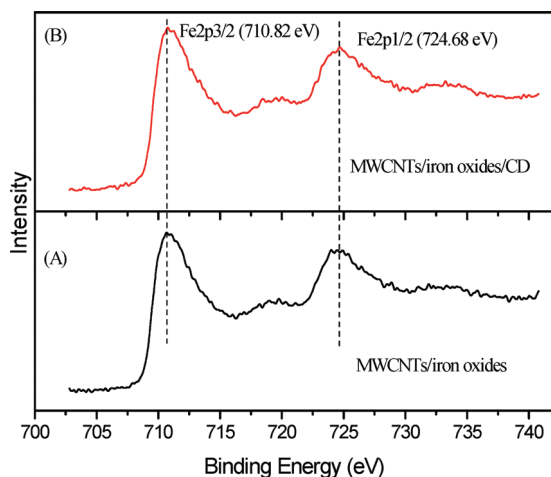


Figure 2. XPS Fe 2p spectra of MWCNTs/iron oxides/CD and MWCNTs/iron oxides. Fe 2p_{3/2} at 710.82 eV and Fe 2p_{1/2} at 724.68 eV correspond to the Fe 2p electron peaks of Fe₂O₃ and Fe₃O₄, respectively.

The relative intensity of the peak at 1042 cm^{-1} in spectrum C is stronger than that in spectrum B, so this peak can be attributed to β -CD. These oxygen-containing functional groups are attached on the surfaces of MWCNTs/iron oxides/CD, which can provide numerous adsorption sites for the adsorptions of Pb(II) and 1-naphthol. The XPS spectra of Fe $2p_{3/2}$ at 710.82 eV and Fe $2p_{1/2}$ at 724.68 eV in MWCNTs/iron oxides and MWCNTs/iron oxides/CD (Figure 2) correspond to electron peaks of Fe $2p$ of Fe_2O_3 and Fe_3O_4 , respectively.³⁸ The C/O/Fe atomic ratio is 5.75:1.67:1 in MWCNTs/iron oxides and 7.23:1.97:1 after the grafting of β -CD. The increase in carbon and oxygen atoms is attributed to the β -CD grafted onto the MWCNTs/iron oxides. The peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ or MWCNTs/iron oxides/CD are deconvoluted into two peaks at 711.3 and 724.9 eV for Fe_2O_3 and two peaks at 710.5 and 724.0 eV for Fe_3O_4 , as shown in Figure SI-3 (Supporting Information).³⁸ The composition ratio of Fe_2O_3 and Fe_3O_4 is 14:1.

Figure 3 presents the XRD patterns of MWCNTs/iron oxides/CD, MWCNTs/iron oxides, and oxidized MWCNTs. The diffraction peaks assigned to MWCNTs at $2\theta = 26.2^\circ$ can be clearly seen for three samples, indicating that the MWCNT

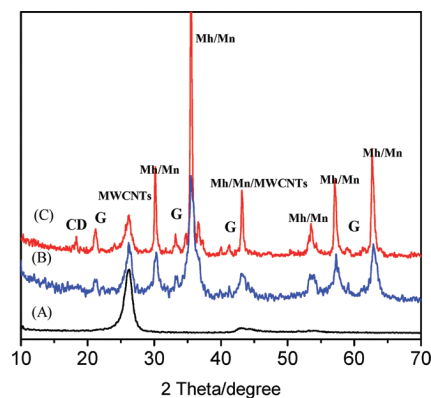


Figure 3. XRD patterns of (A) oxidized MWCNTs, (B) MWCNTs/iron oxides, and (C) MWCNTs/iron oxides/CD. 2θ at 26.2° in the three samples indicates the MWCNT structure; 2θ at 18.30° in MWCNTs/iron oxides/CD can be related to β -CD; and Mn, Mh, and G indicate magnetite, maghemite, and α -FeO(OH), respectively.

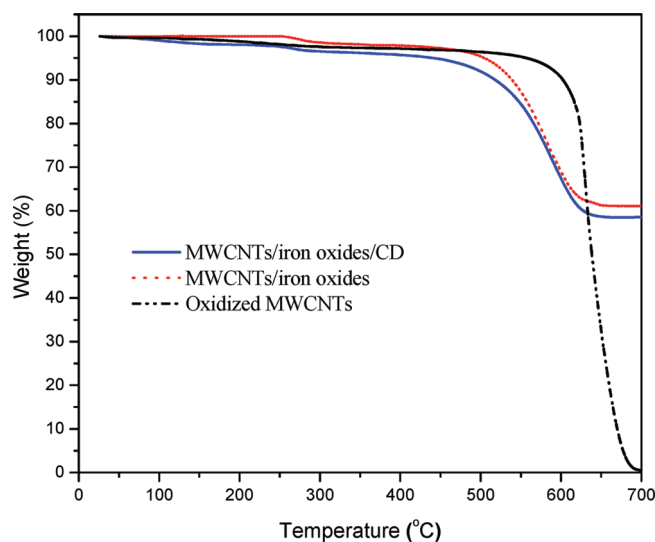


Figure 4. TGA of oxidized MWCNTs, MWCNTs/iron oxides, and MWCNTs/iron oxides/CD. The weight percentage of iron oxides in MWCNTs/iron oxides is 60.93%, and the grafted β -CD content in MWCNTs/iron oxides/CD is 16.6 mg \cdot g $^{-1}$.

structure is not destroyed after the chemical coprecipitation of iron oxides and plasma grafted with β -CD. Six characteristic peaks reveal a cubic iron oxide phase ($2\theta = 30.17^\circ, 35.53^\circ, 43.16^\circ, 53.51^\circ, 57.27^\circ$, and 62.77°), which are close to JCPD standards for Fe_3O_4 (magnetite; card no. 89-3854, $2\theta = 30.088^\circ, 35.439^\circ, 43.07^\circ, 53.432^\circ, 56.958^\circ$, and 62.546°) or $\gamma\text{-Fe}_2\text{O}_3$ (card no. 89-5892, $2\theta = 30.266^\circ, 35.651^\circ, 43.332^\circ, 53.766^\circ, 57.319^\circ$, and 62.949°). Other peaks ($2\theta = 21.18^\circ, 33.29^\circ, 41.16^\circ$, and 59.01°) might be related to the presence of $\alpha\text{-FeO(OH)}$ (goethite),² and the peak at $2\theta = 18.30^\circ$ might be related to $\beta\text{-CD}$.³⁹

TGA was used to calculate the grafted β -CD content.²⁹ Figure 4 shows the TGA curves of MWCNTs/iron oxides/CD, MWCNTs/iron oxides, and oxidized MWCNTs. The TGA curve of oxidized MWCNTs shows that the oxidized MWCNTs decompose at 464.79–700.40 °C. The 2.21% weight loss of MWCNTs/iron oxides at 221.80–350.12 °C should be due to the dehydration of the MWCNTs/iron oxides. The 36.86% weight loss at 369.49–664.07 °C corresponds to MWCNT decomposition,⁴⁰ and the 60.93% weight remaining is attributed to iron oxides. Therefore, the weight ratio of MWCNTs to iron oxides is 1:1.65 in MWCNTs/iron oxides. The 3.76% weight loss of MWCNTs/iron oxides/CD at 40.10–355.58 °C corre-

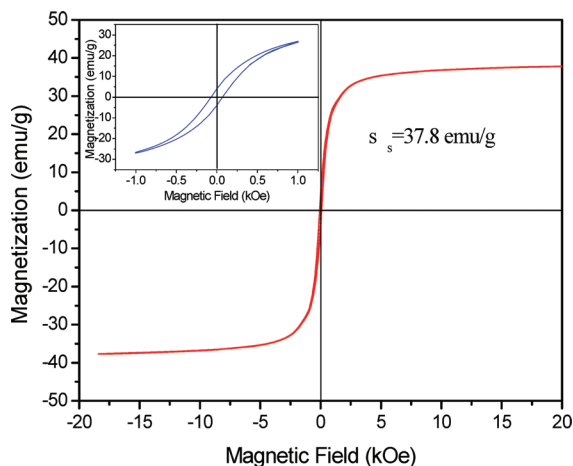


Figure 5. Room-temperature magnetization curve of MWCNTs/iron oxides/CD, indicating that MWCNTs/iron oxides/CD has high magnetism.

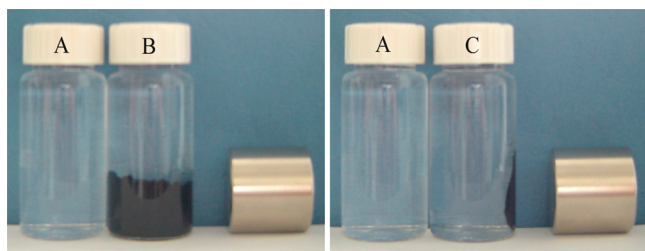


Figure 6. Photographs of magnetic separation. (A) Pb(II) solution, (B) oxidized MWCNTs, and (C) MWCNTs/iron oxides/CD. The particles of MWCNTs/iron oxides/CD can be separated easily with a magnet.

sponds to the dehydration of MWCNTs/iron oxides/CD; the 37.31% weight loss at 387.74–657.22 °C corresponds to MWCNTs and β -CD decomposition;³⁹ and therefore, the 58.93% weight remaining is iron oxides. Because the weight ratio of MWCNTs to iron oxides in MWCNTs/iron oxides/CD is the same as that in MWCNTs/iron oxides, the weight of MWCNTs in MWCNTs/iron oxides/CD is 35.65%. The weight percentage of β -CD in MWCNTs/iron oxides/CD is 1.66%, and therefore, the grafted β -CD content in MWCNTs/iron oxides/CD is 16.6 mg·g⁻¹. TGA thus provides further evidence that β -CD is successfully grafted onto MWCNTs/iron oxides.

The magnetization properties of MWCNTs/iron oxides/CD was investigated at room temperature by measuring magnetization curves (Figure 5). The saturation magnetization, M_s , of MWCNTs/iron oxides/CD is 37.8 emu·g⁻¹ (magnetic field = ± 20 kOe), indicating that MWCNTs/iron oxides/CD has a high magnetism. Figure 6 shows that the particles of MWCNTs/iron oxides/CD are attracted quickly toward a magnet, and the clear solution can be easily removed by pipet or decanted off. This simple magnetic separation experiment confirms that MWCNTs/iron oxides/CD are magnetic and can be used as a magnetic adsorbent to remove pollutants from aqueous solutions.

Adsorption Isotherms. To evaluate the adsorption capacity of MWCNTs/iron oxides/CD, the adsorptions of Pb(II) and 1-naphthol on MWCNTs/iron oxides/CD, MWCNTs/iron oxides, oxidized MWCNTs, and iron oxides were studied. The Freundlich model assumes that different sites with several adsorption energies are involved, and in cases where the intermolecular interactions between adsorbed solute particles are negligible and where only one monolayer of solute can potentially adsorb, the Langmuir model fits quite well.

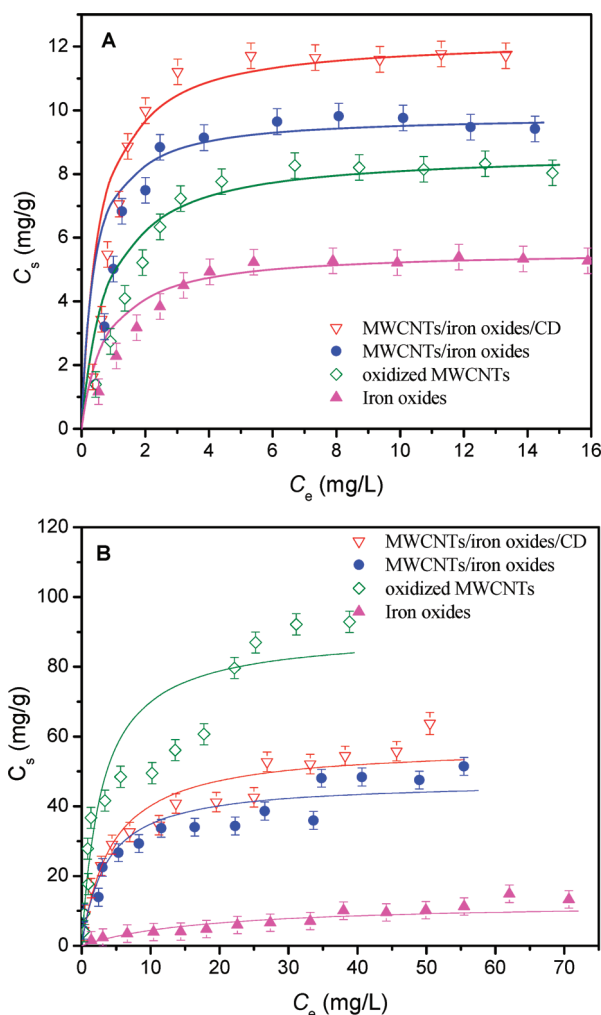


Figure 7. Langmuir isotherms for the removals of (A) Pb(II) and (B) 1-naphthol from MWCNTs/iron oxides/CD, MWCNTs/iron oxides, oxidized MWCNTs, and iron oxides. $\text{pH}_{\text{Pb(II)}} = 5.50 \pm 0.05$, $\text{pH}_{1\text{-naphthol}} = 6.50 \pm 0.05$, $C_{\text{NaClO}_4} = 0.01 \text{ mol}\cdot\text{L}^{-1}$, $m/V = 0.4 \text{ g}\cdot\text{L}^{-1}$, $T = 20 \pm 1$ °C, and equilibrium time = 48 h.

The adsorption of Pb(II) from aqueous solution was studied at pH 5.50 with 0.4 g·L⁻¹ adsorbent and various metal concentrations (1.0–18.0 mg·L⁻¹) (Figure 7A). The experimental data fit the Langmuir model better than the Freundlich model, with correlation coefficients (R^2) in the range of 0.995–0.998 (close to 1) (Table SI-1, Supporting Information), which indicates that monolayer adsorption occurs and that adsorbate interactions are weak and can be neglected. The Langmuir model is expressed as follows

$$C_s = C_{s,\text{max}} b C_e / (1 + b C_e) \quad (1)$$

where C_s is the amount adsorbed per unit mass of adsorbent at equilibrium (mg·g⁻¹), C_e is the equilibrium concentration (mg·L⁻¹), $C_{s,\text{max}}$ is the maximum adsorption capacity corresponding to complete monolayer coverage (mg·g⁻¹), and b is the equilibrium constant (L·mg⁻¹). From the Langmuir model, we can obtain the maximum adsorption capacity. At pH 5.50, the maximum adsorption capacities ($C_{s,\text{max}}$) of Pb(II) are 12.29 mg·g⁻¹ for MWCNTs/iron oxides/CD, 9.85 mg·g⁻¹ for MWCNTs/iron oxides, 8.70 mg·g⁻¹ for oxidized MWCNTs, and 5.60 mg·g⁻¹ for iron oxides. These results indicate that the adsorption capacity of MWCNTs/iron oxides/CD for the

removal of Pb(II) is the highest. For MWCNTs/iron oxides/CD, multiple hydroxyl groups of β -CD are introduced onto the surface of the MWCNTs/iron oxides. These hydroxyl groups can form strong complexes with Pb(II) on the surface of the MWCNTs/iron oxides/CD and, therefore, strongly enhance the adsorption capacity of MWCNTs/iron oxides/CD.

The adsorption of 1-naphthol from aqueous solution was studied at pH 6.50 with $0.4 \text{ g} \cdot \text{L}^{-1}$ adsorbent and various contaminant concentrations ($2.0\text{--}76.0 \text{ mg} \cdot \text{L}^{-1}$) (Figure 7B). The data fit the Langmuir model better than the Freundlich model, with correlation coefficients (R^2) in the range of $0.963\text{--}0.996$ (Table SI-1, Supporting Information). In the case of high adsorption capacity, because of van der Waals forces of adsorbed naphthol molecules, adsorption might not be monolayer and adsorbate interactions might not be negligible, and therefore, there is a break between the experimental data and the Langmuir model line. The maximum adsorption capacities ($C_{s,\text{max}}$) of 1-naphthol are $57.47 \text{ mg} \cdot \text{g}^{-1}$ for MWCNTs/iron oxides/CD, $47.17 \text{ mg} \cdot \text{g}^{-1}$ for MWCNTs/iron oxides, $90.09 \text{ mg} \cdot \text{g}^{-1}$ for oxidized MWCNTs, and $12.48 \text{ mg} \cdot \text{g}^{-1}$ for iron oxides. It can be seen that the maximum adsorption capacity for the removal of 1-naphthol is the highest for oxidized MWCNTs. The reason for this finding is that the surfaces of oxidized MWCNTs have a large number of benzene rings, which can provide effective adsorption sites for the removal of 1-naphthol. The adsorption of 1-naphthol on MWCNTs/iron oxides/CD is lower than that on oxidized MWCNTs, but MWCNTs/iron oxides/CD can be separated with a magnet after adsorbing a pollutant. The adsorption capacity of MWCNTs/iron oxides/CD for 1-naphthol is ~ 1.22 times higher than that of MWCNTs/iron oxides and ~ 4.60 times higher than that of iron oxides. The inner cores of β -CD molecules, with their hydrophobic cavities, easily adsorb 1-naphthol, which enhances the adsorption capacity of MWCNTs/iron oxides/CD (see Figure SI-10, Supporting Information).

The effect of the iron oxide content in MWCNTs/iron oxides/CD on the adsorption capacities of Pb(II) and 1-naphthol was studied (described in section SI-2 of the Supporting Information). No evident effect of iron oxide content on the adsorption capacities of Pb(II) and 1-naphthol on MWCNTs/iron oxides/CD was observed (shown in Figure SI-5, Supporting Information).

The effect of the grafted β -CD content in MWCNTs/iron oxides on the adsorptions of Pb(II) and 1-naphthol was also investigated. From Figure SI-7 (Supporting Information), the grafted β -CD content increased with increasing added β -CD content. The effects of the grafted β -CD content on the adsorption capacities on MWCNTs/iron oxides/CD of Pb(II) at a concentration of $14 \text{ mg} \cdot \text{L}^{-1}$ and of 1-naphthol at a concentration of $36 \text{ mg} \cdot \text{L}^{-1}$ are shown in Figure 8. The results show that the adsorption capacities first increased as the grafted β -CD content increased from 0 to $39.4 \text{ mg} \cdot \text{g}^{-1}$ and then decreased as the grafted β -CD content increased from 39.4 to $63.5 \text{ mg} \cdot \text{g}^{-1}$. Huq and Mercier⁴¹ reported that the adsorption capacity of aromatic molecules on CD-incorporated mesostructured silica increased with increasing content of grafted CD. Phan et al.⁴² reported that the adsorption capacity of organic pollutions onto CD-grafted silica increased with increasing CD content, but it is unnecessary to have an overly high CD content to improve adsorption, because some of the CD molecules are buried in the network or hamper each other when they are present in excess, and the optimum content of β -CD is $66 \mu\text{g} \cdot \text{g}^{-1}$ for

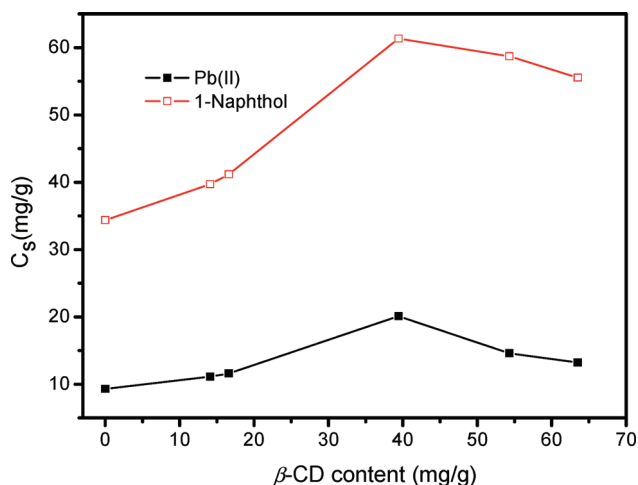


Figure 8. Effect of grafted β -CD content on the removal of Pb(II) and 1-naphthol. $C_{\text{Pb(II),initial}} = 14 \text{ mg} \cdot \text{L}^{-1}$, $C_{\text{1-naphthol,initial}} = 36 \text{ mg} \cdot \text{L}^{-1}$, $\text{pH}_{\text{Pb(II)}} = 5.50 \pm 0.05$, $\text{pH}_{\text{1-naphthol}} = 6.50 \pm 0.05$, $C_{\text{NaClO}_4} = 0.01 \text{ mol} \cdot \text{L}^{-1}$, $m/V = 0.4 \text{ g} \cdot \text{L}^{-1}$, $T = 20 \pm 1^\circ \text{C}$, and equilibrium time = 48 h.

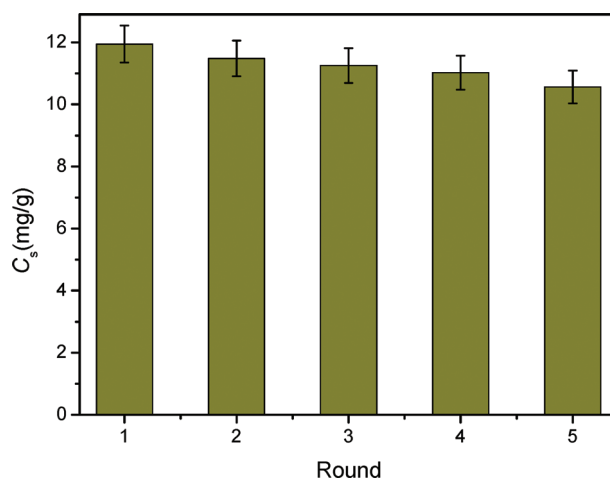


Figure 9. Recycling of MWCNTs/iron oxides/CD in the removal of Pb(II). $\text{pH}_{\text{Pb(II)}} = 5.50 \pm 0.05$, $C_{\text{NaClO}_4} = 0.01 \text{ mol} \cdot \text{L}^{-1}$, $m/V = 0.4 \text{ g} \cdot \text{L}^{-1}$, $T = 20 \pm 1^\circ \text{C}$, and $C_{\text{Pb(II),initial}} = 10 \text{ mg} \cdot \text{L}^{-1}$.

grafted silica. In our work, the optimum content of β -CD was found to be about $39.4 \text{ mg} \cdot \text{g}^{-1}$ for the grafted MWCNTs/iron oxides.

Reusability. The repeated availability of MWCNTs/iron oxides/CD for Pb(II) adsorption through adsorption–desorption cycles is quite crucial for the application of MWCNTs/iron oxides/CD in the removal of Pb(II) from wastewater in real work. Herein, the recycling of MWCNTs/iron oxides/CD in the removal of Pb(II) was investigated. From Figure 9, it can be observed that the adsorption capacity of Pb(II) decreased slightly from 11.94 to $10.56 \text{ mg} \cdot \text{g}^{-1}$ with increasing numbers of times of reuse and that the decline in efficiency was not more than 5% after reuse five times, which indicates that MWCNTs/iron oxides/CD has a good reusability. In a previous report,⁴⁰ the loss of adsorption capacity of powdered activated carbon was found to be up to 70% upon recycling five times. The repeated availability is an important factor for an advanced adsorbent. An advanced adsorbent not only has a higher adsorption capability, but also shows better desorption properties, which will significantly reduce the overall cost for the adsorbent.

In general, the removal of a contaminant from aqueous solution is dependent on the solution pH, ionic strength, and

adsorbent content. Therefore, it is important to study whether the variance of these parameters affects the removal of a contaminant by MWCNTs/iron oxides/CD. (Results and discussion for such an investigation are described in section SI-5 and shown in Figures SI-8–SI-12 of the Supporting Information). The adsorption of Pb(II) on MWCNTs/iron oxides/CD was found to be dependent on pH, whereas the adsorption of 1-naphthol was found to be independent of pH. The adsorption of Pb(II) on MWCNTs/iron oxides/CD was found to increase with increasing adsorbent content and to decrease with increasing ionic strength at low NaClO₄ concentration. To evaluate the chemical changes in the surfaces of the MWCNTs/iron oxides/CD and the molecular-level information of Pb(II) adsorption on MWCNTs/iron oxides/CD, a complementary description was obtained by XPS analysis (described in section SI-6 and shown in Figures SI-13 and -14 in the Supporting Information).

IV. Conclusions

A composite consisting of MWCNTs/iron oxides/CD was synthesized by using the plasma-induced grafting technique. The analysis results obtained by FT-IR spectroscopy, XRD, TGA, and XPS indicate that β -CD was successfully grafted onto MWCNTs/iron oxides. The MWCNTs/iron oxides/CD material has very high adsorption capacities in the removal of Pb(II) and 1-naphthol, and MWCNTs/iron oxides/CD can be separated and recovered from solution by magnetic separation. The magnetic composite of MWCNTs/iron oxides/CD is a very suitable material for organic and inorganic pollution cleanup in the natural environment. The work described in this article is relevant and important for the application of the plasma technique, magnetic separation method, and carbon nanotubes in environmental pollution cleanup.

Acknowledgment. Financial support from the National Natural Science Foundation of China (20971126, 20907055) and 973 projects from the Ministry of Science and Technology of China (2007CB936602) is acknowledged.

Supporting Information Available: More detail on the preparation and characterization of oxidized MWCNTs, MWCNTs/iron oxides, and MWCNTs/iron oxides/CD; characterization methods; proposed mechanisms of Pb(II) and 1-naphthol adsorptions on MWCNTs/iron oxides/CD; relative proportion of species distribution of Pb(II); adsorptions of Pb(II) and 1-naphthol as iron oxide content, pH, adsorbent content, and ionic strength; and XPS analysis of Pb(II) adsorption. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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JP911424K