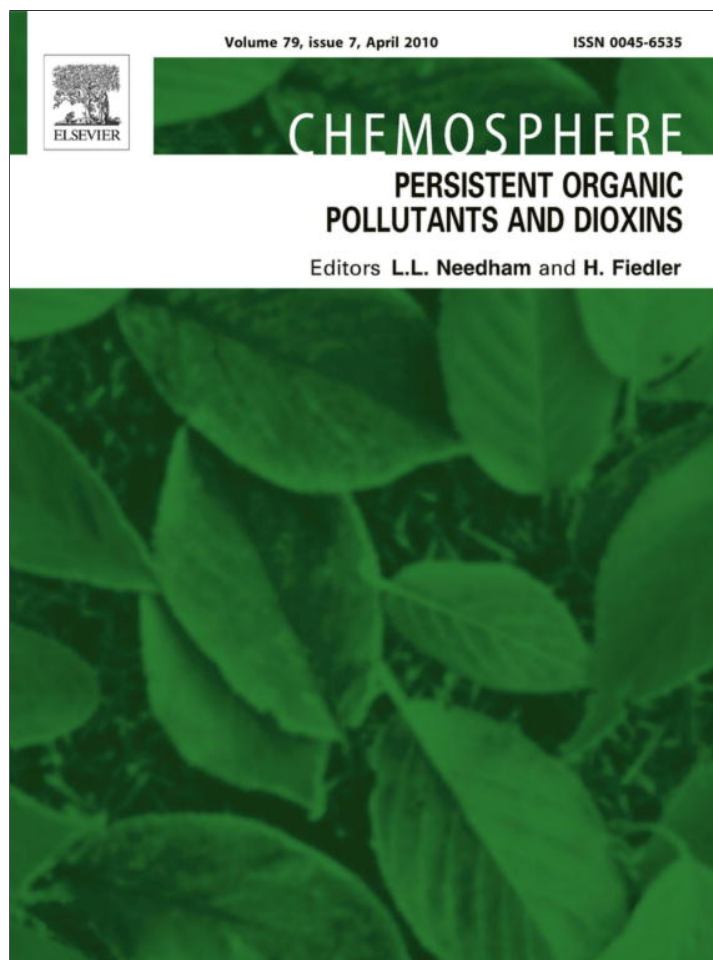


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Removal of polychlorinated biphenyls from aqueous solutions using β -cyclodextrin grafted multiwalled carbon nanotubes

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ABSTRACT

Cyclodextrins have excellent ability in the preconcentration of organic pollutants from aqueous solutions by forming inclusion complexes. Multiwalled carbon nanotubes (MWCNTs) possess high adsorption capacity in the removal of organic pollutants through the formation of conjugated complexes. In this paper, β -cyclodextrin (β -CD) was grafted on the surfaces of MWCNTs by using plasma technique. The β -CD grafted MWCNTs (MWCNT-g-CD) were characterized by using Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, thermo gravimetric analysis-differential thermal analysis, and scanning electron microscopy in detail. The prepared MWCNT-g-CD were used to remove polychlorinated biphenyls (PCBs) from aqueous solutions under ambient conditions. The results suggest that MWCNT-g-CD have much higher adsorption capacity than MWCNTs in the removal of PCBs from aqueous solutions. MWCNT-g-CD are suitable materials in the preconcentration and immobilization of PCBs from large volumes of aqueous solutions in environmental pollution cleanup.

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1. Introduction

The occurrence of polychlorinated biphenyls (PCBs) in soils and water systems is currently a major problem of global concern because of their harmful impact on ecosystem health and on the safety of human food supplies (Sawicki and Mercier, 2006). Moreover, PCBs are the typical persistent organic toxins present in the natural environment ubiquitously, and they are highly toxic and resist to degradation and have high bioaccumulation property. Therefore, the remediation of PCB pollutants from natural environment has become a major global problem of the world. Among all kinds of PCBs, the knowledge on the properties of low chlorinated PCBs in the environment are significant for the evaluation of the transport and overall fate of PCBs because of their relatively high aqueous solubility in wastewater. Among the low chlorinated PCBs, dichlorobiphenyls and trichlorobiphenyls are the primary congeners of PCBs in the natural environment (Adeel et al., 1997). Thereby, 4,4'-dichlorobiphenyls (4,4'-DCB) and 2,3,3'-trichlorobiphenyl (2,3,3'-TCB) herein are selected as the models of PCBs.

Cyclodextrins (CDs) are cyclic oligosaccharides formed from the degradation of starch by bacteria and have hydrophobic interior

cavity and hydrophilic periphery face, which have the tendency to form inclusion complexes with typical organic pollutants, such as PCBs, chlorinated hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and explosives (Wang et al., 1998; Tick et al., 2003; Wu et al., 2004; Sawicki and Mercier, 2006; Villaverde et al., 2006; Galia et al., 2007; Kida et al., 2008). The hydrophilic periphery of CDs increases the apparent aqueous solubility of low polarity organic compounds (such as PCBs, PAHs, and organic solvents) as well as enhancing their desorption properties and transport in soil (Brusseau et al., 1997; Boving et al., 1999; Ko et al., 2000; Villaverde et al., 2005; Field and Sierra-Alvarez, 2008). The hydrophilic periphery is really convenient for the need of carrying out the applications of CDs in the removal of organic molecules from large volumes of aqueous solutions (Wu et al., 2004). Moreover, CDs can decrease the microbial toxicity of organic compounds (such as pesticides, phenanthrene, and polychlorinated biphenyls), which results in the enhancement of the biological detoxification (Bizzigotti et al., 1997; Wang et al., 1998; Field and Sierra-Alvarez, 2008). Due to these favorable physicochemical properties, CDs have recently been used in environmental applications to improve the remediation of contaminated soils and groundwater (Wang et al., 1998; Villaverde et al., 2006). The adsorption behaviors of PCBs on CDs are important for the understanding and evaluation the remediation effect of CDs in the removal of PCB pollution in the environment. Kida et al. (2008) reported that γ -CD was an effective adsorbent to remove chlorinated aromatic compounds (including PCBs) from insulating oil via the formation of inclusion

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complexes. However, few literatures are available to understand the adsorption of PCBs with small molecules by CDs (Hunt et al., 2007).

Carbon nanotubes (CNTs) are relatively new adsorbents and they have been proven to possess excellent adsorption capacity to eliminate many kinds of organic pollutants (Long and Yang, 2001; Gotovac et al., 2006; Chen et al., 2007) and heavy metal ions (Chen and Wang, 2006; Tan et al., 2008; Chen et al., 2009) from large volumes of wastewaters. The results suggested that CNTs are very suitable material in the removal of organic and inorganic pollutants from large volumes of aqueous solutions. However, the inherent insolubility of CNTs in most organic and aqueous solvents limits the manipulation of CNTs in solution phase, which greatly hinders the application of CNTs in real work (Qin et al., 2004; Hong et al., 2006). Therefore, researches have been extended to include the modification of CNTs by introduce special functional groups on the surfaces of CNTs to enhance the adsorption capacity of CNTs and to improve the dispersion property in aqueous solutions. As mentioned above, CDs can remove organic pollutants effectively through the formation of inclusion complexes. However, CDs can not be used directly to remove organic pollutants because of the excellent solubility in aqueous solutions. If the CD molecules are grafted on the surfaces of CNTs, the solubility of CDs in aqueous solutions is negligible because the CD molecules are connected together with the insoluble CNTs. Plasma induced grafting treatment is a promising method to introduce functional groups to CNT surfaces without altering the properties of CNTs, and the plasma grafted functional groups to the substance surfaces can enhance the chemical functionality. Comparing to the chemical modification method, plasma technique is also an environmental friendly method to graft functional groups on CNTs because no chemicals are used in the process (Shao et al., 2009). Therefore, CNTs modified with CDs can improve the compatibility of CNTs and extend the application of CNTs and CDs in the removal of organic pollutants from large volumes of aqueous solutions in the environmental pollution cleanup.

Herein, we firstly synthesized the multiwalled carbon nanotubes (MWCNTs) grafted with β -CD (denoted as MWCNT-g-CD) by N_2 plasma induced grafting technique. The prepared MWCNT-g-CD were applied to remove 4,4'-DCB and 2,3,3'-TCB from aqueous solutions to evaluate their potential application in the removal of PCBs in the environmental pollution cleanup.

2. Experimental procedures

2.1. Chemical materials

The chemicals $NaClO_4$, $HClO_4$, $NaOH$, and β -CD used in the experiments were purchased in analytical grade. 4,4'-DCB and 2,3,3'-TCB (>99% purity) were purchased from AccuStandard Inc. (New Haven, USA). MWCNTs were prepared by using chemical vapor deposition of acetylene in hydrogen flow at 760 °C using Ni-Fe nanoparticle as catalyst (Wang et al., 2005). All chemicals were used without any purification in the experiments. All the solutions were prepared with Milli-Q water under ambient conditions.

2.2. Plasma induced grafting procedures

One gram of MWCNTs was treated under N_2 plasma conditions in a custom-built grafting reactor for 40 min under continuous stirring. The plasma treatment conditions were: N_2 plasma of 10 Pa, power of 70 W, voltage of 650 V, and electrical current of 60 mA. Thus N_2 plasma treated MWCNTs were denoted as MWCNT-treat. After N_2 plasma induced treatment process, the MWCNT-treat in the grafting reactor were heated to 80 °C and 100 mL 1.5 g/L β -

CD aqueous solution was injected into the grafting reactor. Then MWCNT-treat samples were grafted with β -CD at 80 °C for 24 h under continuous stirring. The derived samples were repeatedly washed with Milli-Q water thoroughly until no β -CD was detected in the rinsing solution. At last, the samples were dried in oven at 95 °C for 24 h, and thus MWCNT-g-CD materials were obtained and used in the following experiments.

2.3. Characterization

The MWCNTs and MWCNT-g-CD were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), thermo gravimetric analysis-differential thermal analysis (TGA-DTA), and scanning electron microscopy (SEM) in detail. The Raman spectroscopy analyses of the samples were mounted by using a LabRam HR Raman spectrometry at the excitation of 514.5 nm by Ar^+ laser. The XPS measurements were performed with an ESCALab220i-XL surface microanalysis system (VG Scientific) equipped with an Al $K\alpha$ ($h\nu = 1486.6$ eV) source. The XRD characterization was performed by using X-ray diffraction (Rigaku D/max) with Cu $K\alpha$ radiation at room temperature. TGA-DTA measurements were examined by using a Shimadzu TGA-50 thermogravimetric analyzer from 25 to 800 °C at the heating rate of 10 °C/min with an air flow rate of 50 mL/min. The SEM images were carried out by using a JSM-6320F FE-SEM (JEOL).

2.4. Adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD and on MWCNTs

The adsorption experiments of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD and on MWCNTs were carried out at $T = 20 \pm 1$ °C in 60 mL serum bottles, sealed with rubber septa and aluminum cap. The stock suspension of MWCNTs (or MWCNT-g-CD), $NaClO_4$, $HClO_4$ and 4,4'-DCB (or 2,3,3'-TCB) solution were added to achieve the desired concentrations of different components. The adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNTs and on MWCNT-g-CD were not affected by pH value in the pH range of 2.5–10. Therefore, the adsorption experiments were proceed in acidic solution (i.e., pH = 3.55 ± 0.02) by adding negligible volumes of 0.1 M or 0.01 M $HClO_4$ or $NaOH$.

Yang et al. (2007) reported that the adsorption of 2,4,5-trichlorobiphenyl (2,4,5-TCB) and biphenyl on activated carbon felt reached equilibrium in 20 min. Moreover, in the adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNTs and on MWCNT-g-CD experiments, >95% removal of 4,4'-DCB and 2,3,3'-TCB was achieved during the first 24 h of contact time, and <5% of additional removal was achieved in the following 24 h of contact time. Our kinetic adsorption experiments suggested that the adsorption of 4,4'-DCB and 2,3,3'-TCB occurred mainly in the first contact time of 24 h, and 45 h was enough to achieve the adsorption equilibrium. Therefore, the contact time of 4,4'-DCB and 2,3,3'-TCB adsorption on MWCNT-g-CD and MWCNTs was selected to 50 h in our experiments.

After the suspensions were shaken for 50 h, the solid and liquid phases were separated by centrifugation. The concentration of adsorbates (i.e., 4,4'-DCB and 2,3,3'-TCB) in supernatant was analyzed by gas chromatography equipped with electron capture detector (GC-ECD). GC-ECD was performed on a Hewlett-Packard 5890 chromatograph equipped with a DB-5 column (50 m \times 0.32 mm \times 0.17 mm), using high purity nitrogen as carrier gas. The amount of 4,4'-DCB or 2,3,3'-TCB adsorbed on MWCNTs or on MWCNT-g-CD was calculated from the difference of the initial concentration (C_0) and the final one (C_{eq}) of 4,4'-DCB or 2,3,3'-TCB in supernatant after centrifugation (Adsorption % = $\frac{C_0 - C_{eq}}{C_0} \times 100\%$, and $C_s = \frac{C_0 - C_{eq}}{C_{sorbent}} = \frac{C_0 - C_{eq}}{m_{sorbent}} \times V$, where C_s is the concentration of 4,4'-DCB or 2,3,3'-TCB on solid phase, V is the volume of the

suspension, $C_{\text{adsorbent}}$ is the content of the adsorbent, and $m_{\text{adsorbent}}$ is the mass of the adsorbents (i.e., MWCNTs or MWCNT-g-CD).

2.5. Desorption and decomposition study

In order to study the interaction intensity of MWCNT-g-CD and MWCNTs with PCBs, the TGA-DTA analysis of MWCNTs and MWCNT-g-CD before and after the adsorption of 4,4'-DCB were carried out to study the desorption property of 4,4'-DCB as a function of temperature. The 4,4'-DCB adsorbed on MWCNT-g-CD and on MWCNTs were prepared in 60 mL serum bottles (sealed with rubber septa and aluminum seals) at 20 ± 1 °C. The experimental conditions were: the initial concentration of 4,4'-DCB was 4.14 mg/L, $m/V = 0.03$ g/L, $C[\text{NaClO}_4] = 0.01$ M, equilibration time = 50 h, and $\text{pH} = 3.55 \pm 0.02$. After the adsorption experiments, the solid phases were repeatedly rinsed with Milli-Q water until no free 4,4'-DCB in the supernatant was detected by using GC-ECD methods. At last, the samples were dried in oven at 95 °C for 24 h, and thus MWCNTs and MWCNT-g-CD with adsorbed 4,4'-DCB were obtained, and used for TGA-DTA analysis.

3. Result and discussion

3.1. Characterization of MWCNTs and MWCNT-g-CD

The microstructure transformation of MWCNTs and MWCNT-g-CD are observed by SEM (Fig. 1). The differences of the surface morphology between MWCNTs and MWCNT-g-CD are observed. As can be seen from Fig. 1, after plasma induced grafting with β -CD, the smooth MWCNT surfaces become rough, and the surface defects of MWCNT-g-CD are enhanced. The integrity of MWCNT patterns is not damaged. Moreover, owing to the grafting of β -CD

molecules, the average diameter of MWCNT-g-CD is larger than that of the MWCNTs, which also suggests that β -CD is grafted on MWCNT surfaces.

The Raman spectra of the MWCNTs and MWCNT-g-CD are shown in Fig. 2A. The dominant peaks are observed at 1352 cm^{-1} for the disordered structure of MWCNTs (D mode) and at 1580 cm^{-1} for the graphite structure of MWCNTs (G mode). The I_D/I_G ratios are 0.72 for MWCNTs and 1.08 for MWCNT-g-CD, which reveals that the disorder degree of MWCNT-g-CD surfaces increases after the MWCNTs are grafted with β -CD molecules. The D mode is originated from the defects in MWCNTs curved graphene sheets and tube ends. It reveals that β -CD molecules are grafted on the surfaces of MWCNTs by plasma induced grafting process.

XPS is an effective technique for the analysis and identification of surface groups, which can be used to identify the functional groups attached to the surfaces of MWCNTs. Fig. 2B shows the high resolution XPS C 1s spectra of MWCNTs and MWCNT-g-CD. The C 1s spectra of MWCNTs and MWCNT-g-CD can be deconvoluted into five components (Ago et al., 1999; Okpalugo et al., 2005; Liu et al., 2008): (1) the peak at 284.1 ± 0.2 eV is contributed by the sp^2 -hybridized graphite-like carbon atoms ($-\text{C}=\text{C}-$); (2) the peak at 285.5 ± 0.2 eV is due to the sp^3 -hybridized carbon ($-\text{C}-\text{C}-$); and (3) the peaks at 286.7 ± 0.2 , 287.6 ± 0.2 , and 288.8 ± 0.2 eV are considered to originate in carbon atoms bound to one, two, and three oxygen atoms, respectively, which correspond to the species of $-\text{C}-\text{O}$ (e.g., alcohol, ether), $-\text{C}=\text{O}$ (e.g., ketone, aldehyde), and $-\text{COO}^-$ (e.g., carboxylic, ester), respectively. The quantitative analysis of C 1s spectrum of MWCNTs are 67.5% for $-\text{C}=\text{C}-$, 23.7% for $-\text{C}-\text{C}-$, 5.04% for $-\text{C}-\text{O}$, 0.94% for $-\text{C}=\text{O}$ and 2.83% for $-\text{COO}^-$, whereas those of C 1s spectrum of MWCNT-g-CD are 64.6% for $-\text{C}=\text{C}-$, 21.1% for $-\text{C}-\text{C}-$, 11.6% for $-\text{C}-\text{O}$, 0.93% for $-\text{C}=\text{O}$ and 1.76% for $-\text{COO}^-$. One can see that the peak fractions of $-\text{C}=\text{C}-$, $-\text{C}-\text{C}-$, $-\text{C}=\text{O}$, and $-\text{COO}^-$ decrease, whereas the peak fraction of $-\text{C}-\text{O}$ increases after MWCNTs are grafted with β -CD under the plasma conditions. It is reasonable because β -CD is a cyclic oligosaccharide, which contains large amounts of hydroxyl groups. The grafted β -CD molecules on MWCNT-g-CD increase the peak fraction of $-\text{C}-\text{O}$ obviously and thereby decrease the other peak fractions simultaneously and reasonably. Moreover, all of the peak fractions of $-\text{C}=\text{C}-$, $-\text{C}-\text{C}-$ and $-\text{COO}^-$ decrease after plasma induced grafting with β -CD molecules, which suggests that β -CD molecules are grafted on the defect positions of MWCNTs (corresponding to the decreasing of the peak fraction of $-\text{COO}^-$ group) or grafted on the framework of MWCNTs (corresponding to the decreasing of the peak fractions of $-\text{C}=\text{C}-$ and $-\text{C}-\text{C}-$ groups) directly. Furthermore, the grafted β -CD molecules on MWCNT-g-CD can also improve the disorder degree of MWCNT-g-CD surfaces. This is consistent with the results of Raman analysis (Fig. 2A) and SEM images (Fig. 1).

Fig. 2C presents the XRD patterns of MWCNTs and MWCNT-g-CD. The peaks at $2\theta = 26.2$, 43.0 , and 53.7° are related to the characteristics of MWCNTs observed. The XRD patterns of MWCNTs and MWCNT-g-CD are very similar, which suggests that little alteration in the structures of MWCNTs occurs in the plasma grafting process with β -CD molecules. The plasma grafting process only occurs on the surfaces of MWCNTs and does not destroy the frameworks of MWCNTs. The microstructure transformation of MWCNTs and MWCNT-g-CD also shows that β -CD molecules are grafted on the surfaces of MWCNTs (see Fig. 1).

In order to calculate the amount of β -CD grafted on MWCNT-g-CD, MWCNTs and MWCNT-g-CD were characterized by TGA-DTA methods (Fig. 2D). According to the TGA-DTA curves of MWCNTs, the carbon impurity (such as amorphous carbon) in MWCNTs is negligible, and MWCNTs are decomposed at 477.6 – 682.7 °C (endothermic). Comparing with MWCNTs, MWCNT-g-CD are less ther-

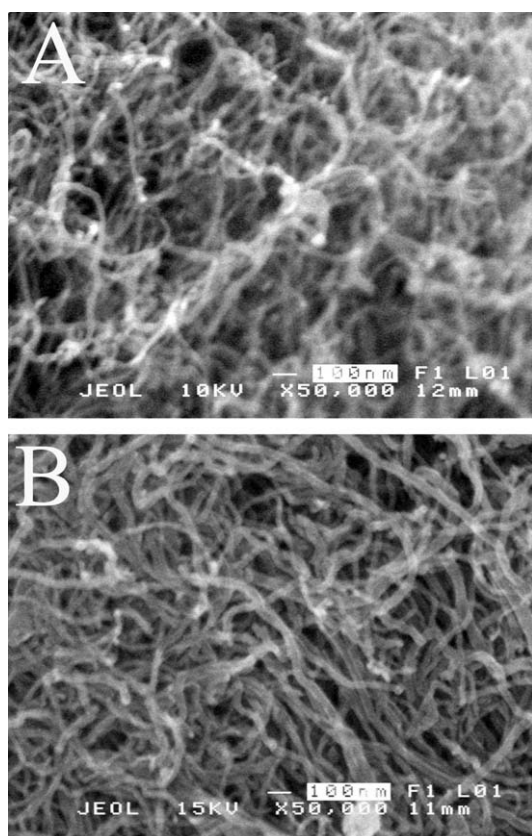


Fig. 1. SEM images of MWCNTs (A) and MWCNT-g-CD (B) samples.

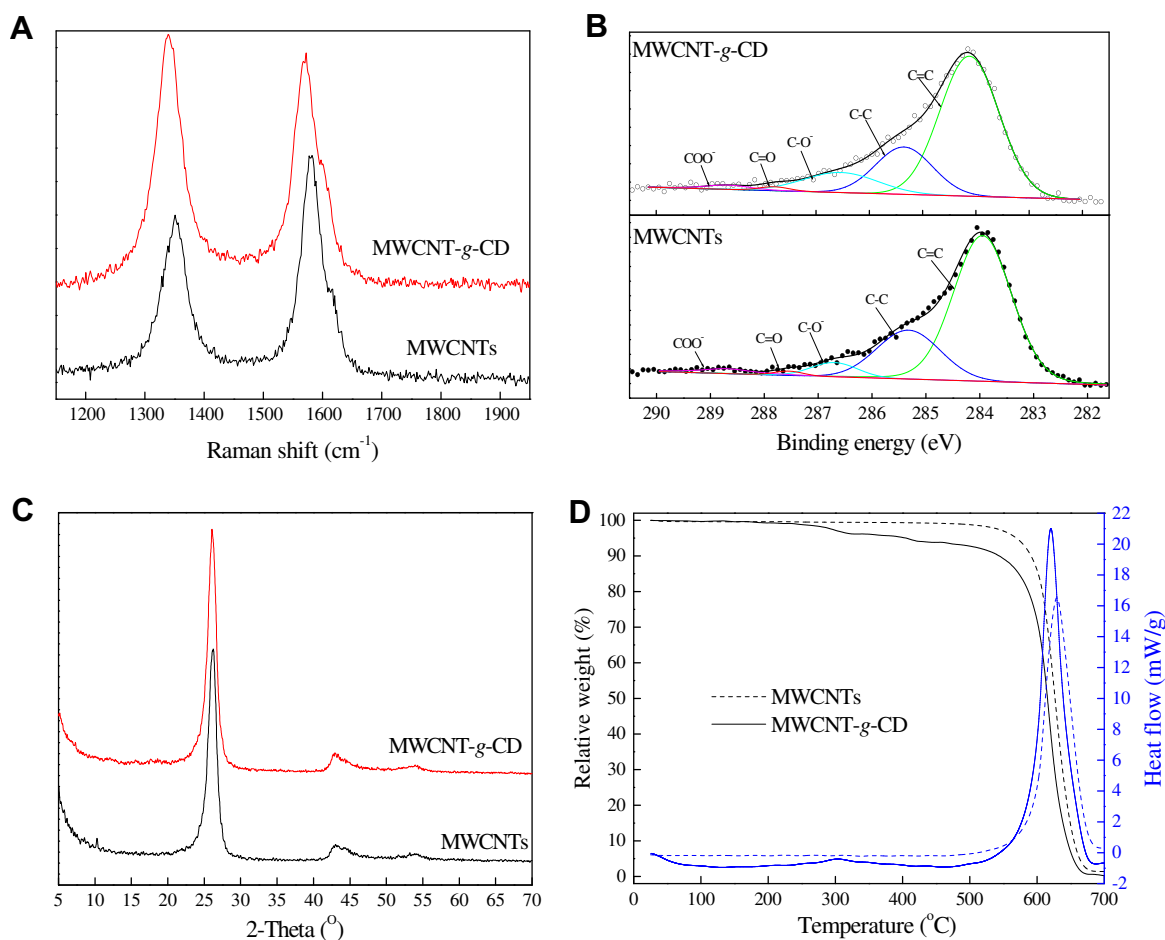


Fig. 2. Characterization of MWCNTs and MWCNT-g-CD. (A) Raman spectra; (B) XPS C 1s spectra; (C) XRD patterns; and (D) TGA–DTA curves.

mal stable responding for the presence of the grafted β -CD on the surfaces of MWCNTs. The TGA–DTA curves of MWCNT-g-CD show the characteristic decomposition stages of β -CD. The 6.03% weight loss at 200–444 °C (exothermic) corresponds to the decomposition of β -CD (Cruz et al., 2008; Choi et al., 2009). As it is well known, the final decomposition temperature (FDT) of CDs is above 500 °C, the residual of CDs is \sim 15% in air atmosphere (Wang et al., 2007; Choi et al., 2009) and \sim 20% (Lu et al., 2000; Li et al., 2004; Su et al., 2005; Uyar et al., 2005; Wei et al., 2005) in nitrogen atmosphere from room temperature to 450 °C. Therefore, the 94.0% weight loss at 453.6–711.7 °C (exothermic) corresponds to the combustion of MWCNTs and the residues of β -CD. From the TGA–DTA analysis, the weight percentage of grafted β -CD on MWCNT-g-CD is calculated to be \sim 7.1%. Considering the amounts of MWCNTs (1.0 g) and β -CD (0.15 g) in the plasma grafting process, the results suggest that plasma technique is an effective method to graft β -CD molecules on the surfaces of MWCNTs.

3.2. Adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD and on MWCNTs

In order to evaluate the application of MWCNT-g-CD in the removal of organic pollutants from the natural environment, the adsorption of 4,4'-DCB and 2,3,3'-TCB from aqueous solutions on MWCNT-g-CD and on MWCNTs was studied under ambient conditions using batch technique. In the removal of PCBs from aqueous solutions, the amount of adsorbent used in the cleaning process is crucial for the economic application. Under the effective removal percentage uncertainties, the less amount of adsorbent is used,

the lower cost is applied. Thereby, the effect of adsorbent dosage on the adsorption of PCBs was first carried out.

The effect of adsorbent content on the adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNTs and on MWCNT-g-CD is shown in Fig. 3. As can be seen from Fig. 3, the adsorption data of 4,4'-DCB and 2,3,3'-TCB on MWCNT-treat are a little higher than those of 4,4'-DCB and 2,3,3'-TCB on MWCNTs, which is due to the enhancement of surface defects on MWCNT-treat after N_2 plasma treat-

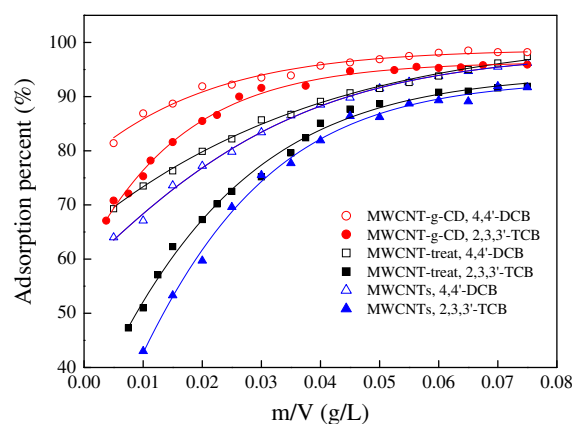


Fig. 3. Effect of adsorbent content on the removal of 4,4'-DCB and 2,3,3'-TCB from solution on MWCNTs, on MWCNT-treat and on MWCNT-g-CD. $T = 20 \pm 1$ °C, equilibrium time 50 h, $pH = 3.55 \pm 0.02$, $C[NaClO_4] = 0.01$ M, $C[PCBs]_{initial} = 4.14$ mg/L.

ment process. It is reasonable that the adsorption percent of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD are much higher than those of 4,4'-DCB and 2,3,3'-TCB on MWCNTs and on MWCNT-treat. The enhancement of the adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD is attributed to the van der Waals and hydrophobic interactions of 4,4'-DCB and 2,3,3'-TCB with grafted β -CD on the surfaces of MWCNT-g-CD (Bojinova et al., 2003; Galia et al., 2007). More than 96% 4,4'-DCB and 95% 2,3,3'-TCB is removed from aqueous solution to MWCNT-g-CD at the adsorbent content of 0.04 g/L, which indicates that MWCNT-g-CD have very high adsorption capacity in the preconcentration and immobilization of PCBs from large volumes of aqueous solutions. Comparing the adsorption curves of 4,4'-DCB and 2,3,3'-TCB on MWCNTs, on MWCNT-treat and on MWCNT-g-CD, respectively, one can see that the adsorption data of 4,4'-DCB is always higher than those of 2,3,3'-TCB on the same adsorbent, which can be due to the negative influence of steric hindrance. The adsorption sites on the adsorbent surfaces are mainly composed of external surfaces, groove areas, and interstitial and inner pores (Pan and Xing, 2008). External surfaces and groove areas are usually available for adsorption, while interstitial and inner pores are uncertain if the molecules of persistent organic pollutants (POPs) are too large to fit into the area (Pan and Xing, 2008). From the structures of 4,4'-DCB and 2,2,3'-TCB, the 4,4'-DCB molecule is ~ 1.01 nm in length and ~ 0.43 nm in width, whereas the 2,3,3'-TCB molecule is ~ 0.89 nm in length and ~ 0.49 nm in width. β -CD molecule has a tapered cavity 0.79 nm deep with top and bottom diameters of 0.60 nm and 0.65 nm. The 4,4'-DCB and 2,2,3'-TCB can form inclusion complexes with β -CD, and can also enter into the inner channels of β -CD and MWCNTs. The steric hindrance in the molecules resulting in their three-dimensional structure influences the adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNTs and on MWCNT-g-CD (Chin et al., 1997; Prosen et al., 2007). The width of 4,4'-DCB is smaller than that of 2,3,3'-TCB, and it is reasonable that the adsorption of 4,4'-DCB is higher than that of 2,3,3'-TCB on MWCNTs and on MWCNT-g-CD. Cornelissen et al. (2005) reported that the adsorption capacity of organic compounds on black carbon was: atrazine < hexachloroethane < butylate < diuron, and the sequence was due to the steric hindrance effect. Wodarg et al. (2004) reported that particulate organic carbon had higher adsorption capacity for lower chlorinated PCBs than for higher chlorinated PCBs. Sun and Ghosh (2008) reported that the removal percentage of low chlorinated PCBs was much higher than that of high chlorinated PCBs by using activated carbon. Herein, it is reasonable that the adsorption curve of 4,4'-DCB is higher than that of 2,3,3'-TCB on MWCNTs and on MWCNT-g-CD under the same experimental conditions.

The adsorption isotherms of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD are shown in Fig. 4. The experimental data are well simulated by Langmuir model ($C_s = \frac{bC_{smax}C_{eq}}{1+bC_{eq}}$, C_s is the concentration of 4,4'-DCB or 2,3,3'-TCB adsorbed on solid phase, C_{eq} is the concentration of 4,4'-DCB or 2,3,3'-TCB in solution after adsorption experiments, C_{smax} is the maximum adsorption capacity, and b is Langmuir constant). The C_{smax} values of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD calculated from the Langmuir model are ~ 261 mg/g and ~ 235 mg/g, respectively, under the experimental conditions. The high adsorption abilities of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD indicates that MWCNT-g-CD are very suitable materials in the removal of 4,4'-DCB and 2,3,3'-TCB and maybe extended to other PCBs from large volumes of aqueous solutions. The high adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD is also attributed to the strong π - π interactions between MWCNT-g-CD and PCBs (Pan and Xing, 2008) and the van der Waals and hydrophobic interactions of PCBs with grafted β -CD molecules on the surfaces of MWCNT-g-CD (Bojinova et al., 2003; Galia et al., 2007). As can be seen from Fig. 4, the adsorption

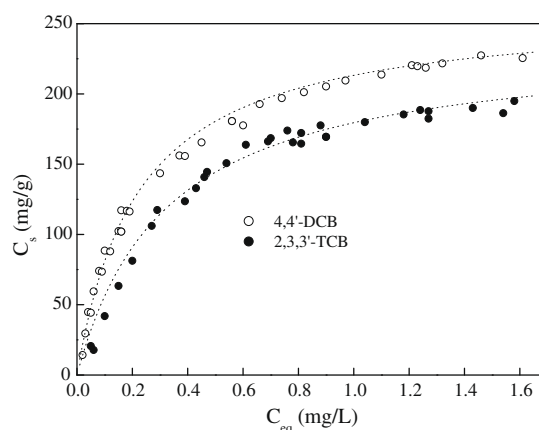


Fig. 4. The adsorption isotherms of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD. $T = 20 \pm 1$ °C, equilibrium time 50 h, $\text{pH} = 3.55 \pm 0.02$, $C[\text{NaClO}_4] = 0.01$ M, $m/V = 0.03$ g/L.

isotherm of 4,4'-DCB on MWCNT-g-CD is higher than that of 2,3,3'-TCB on MWCNT-g-CD, which is attributed to the steric hindrance effect because the interaction of chlorinated aromatics and CDs is affected by the shape and size of the chlorinated aromatics (i.e., PCBs) (Kida et al., 2008).

The effect of pH and NaClO_4 concentration on the removal of 4,4'-DCB from aqueous solution to MWCNT-g-CD is also studied, and the results indicate that the adsorption of 4,4'-DCB is independent of pH at pH 2–10. When pH exceeds 10, the adsorption percentage of 4,4'-DCB on MWCNT-g-CD decreases with increasing pH values. This can be due to the fact that more oxygen containing groups on MWCNT-g-CD surfaces are ionized (carrying negative charge) at high pH values and thus adsorb more water molecules. The formation of water cluster on oxygen containing groups blocks the access of PCBs to the adsorption sites of MWCNT-g-CD and thereby results in less adsorption of 4,4'-DCB. The adsorption of 4,4'-DCB on MWCNT-g-CD is independent of NaClO_4 concentrations at the concentration ranging from 0.001 to 0.05 M. 4,4'-DCB is nonionic chemical and the properties of 4,4'-DCB is not affected by pH and ionic strength of aqueous solutions. Although the surface properties of MWCNT-g-CD change with varying ionic strength, the adsorption of 4,4'-DCB is independent of ionic strength.

3.3. Desorption and decomposition analysis

As it is well known, the desorption property of PCBs from solid phase is related to the bond strength of organic pollutants and adsorbents. Stronger bond generally gives rise to a higher desorption temperature (Long and Yang, 2001). From Fig. 3, it is clear that the amount of 4,4'-DCB adsorbed on MWCNT-g-CD is much higher than that of 4,4'-DCB adsorbed on MWCNTs. Hence, it is expected that the interaction of 4,4'-DCB with MWCNT-g-CD is stronger than that of 4,4'-DCB with MWCNTs. As can be seen from the TGA-DTA curves of MWCNTs and MWCNT-g-CD before and after the adsorption of 4,4'-DCB (Fig. 5), the 4,4'-DCB adsorbed on MWCNTs was desorbed (including possible oxidization) step by step in the temperature programming process in TGA-DTA experiments. The desorption of 4,4'-DCB adsorbed on MWCNT-g-CD was very difficult and restrained the decomposition of MWCNT-g-CD, which is due to the strong interaction of 4,4'-DCB with MWCNT-g-CD. We also studied the desorption of 4,4'-DCB from MWCNT-g-CD in Milli-Q water and in organic reagents (such as methanol, ethanol, hexamethylene, and hexane), and the adsorbed 4,4'-DCB was very difficult to be desorbed from MWCNT-g-CD in our desorption

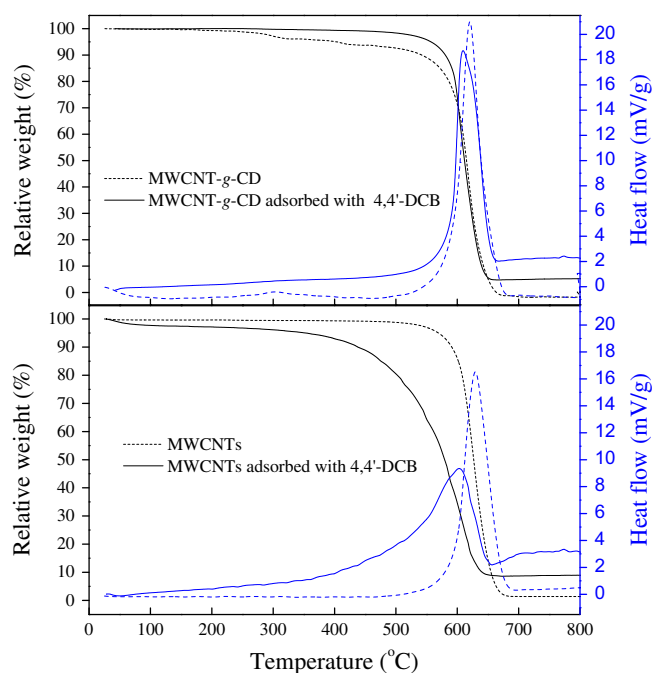


Fig. 5. TGA-DTA curves of MWCNTs and MWCNT-g-CD before and after adsorption of 4,4'-DCB.

experimental study, which was in consistent with the TGA-DTA analysis. Yang et al. (1999) reported that CuCl_2 modification can significantly enhance the adsorption of dioxins on carbon for the π -complexation of CuCl_2 and dioxin. The desorption temperature of dioxin increased markedly. The results of the TGA-DTA analysis of 4,4'-DCB adsorbed on MWCNT-g-CD are very interesting because the pollution of PCBs caused by the desorption of PCBs from MWCNT-g-CD is negligible, which means that MWCNT-g-CD are very suitable materials for the preconcentration of PCBs in PCB pollution cleanup. It is not necessary to worry about the desorption of PCBs from MWCNT-g-CD under ambient conditions in the application of MWCNT-g-CD in the removal of PCBs from large volumes of aqueous solutions in real work.

4. Conclusions

In this paper, we reported a simple method to graft β -CD molecules on MWCNT surfaces by using plasma technique. The plasma induced grafting method is an environmental friendly technique and the chemicals are avoided to be used in the grafting process. The grafted CD molecules on MWCNTs can enhance the adsorption of PCBs on MWCNT-g-CD because of the strong interaction between CD and PCBs. The adsorption of 4,4'-DCB and 2,3,3'-TCB on MWCNT-g-CD are high and independent of pH and ionic strength. MWCNT-g-CD are very promising materials in the preconcentration and immobilization of aqueous soluble PCBs from large volumes of aqueous solutions in environmental pollution cleanup.

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