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Communications to the Editor

Carbon Nanotubes as Superior Sorbent for Dioxin Removal

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Dioxins and related compounds (e.g., polychlorinated dibenzofurans and biphenyls) are highly toxic and stable pollutants. Dibenzo-*p*-dioxins are a family of compounds consisting of two benzene rings joined by two oxygen atoms and having from zero to eight chlorine atoms attached around the rings. The dibenzofurans are a similar family differing in which only one of the bonds between the two benzene rings is bridged by oxygen. The toxicity of dioxins varies with the number of Cl atoms, with non- and monochloro dioxins being nontoxic, while being highly toxic with more Cl atoms. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) is a known human carcinogen, and other dioxins are likely human carcinogens. In addition to cancer, dioxins also adversely affect the immune and endocrine systems and the development of fetuses.[1] Dioxins are mainly generated from the combustion of organic compounds in waste incinerators, such as municipal waste, medical waste, hazardous waste, and army stockpiles (chemical agents). They are formed downstream of the combustion zone with typical concentrations of 10−500 ng/m^3. Current regulations on dioxin emissions are complex, depending on the toxic equivalency of the actual compounds and O_2 concentration, and vary in different countries. Nonetheless, removal to well below 1 ng/m^3 is generally required.[2] Since 1991, activated carbon adsorption has been widely adopted for dioxin removal from waste incinerators in Europe and Japan.[2] Because of the higher bond energy between dioxin and activated carbon than other sorbents, the removal efficiency for dioxin by activated carbon is much higher than other sorbents, such as clays, pillared clays, γ-Al_2O_3 and zeolites.[3]

Due to the extreme toxicity of dioxins, it is desirable to have a more efficient sorbent than activated carbon so that the dioxin emissions can be reduced to lower levels. In this communication, we have found that the interactions of dioxins with carbon nanotubes are much stronger than that with activated carbon. The results show that carbon nanotubes are a significantly better sorbent than activated carbon for dioxin removal. Carbon nanotubes include single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). They are hollow nanosize tubes and have attracted intense interest since their recent discovery. Large efforts have been devoted to improving their syntheses, determining their structures, measuring their properties, and finding applications.[4,5] Their unique electronic properties and structure have led to interest in their potential applications. For example, SWNTs were reported to be chemical sensors for NO_2 and NH_3. Upon exposure to gaseous NO_2 or NH_3, the electrical resistance of SWNT was found to change (either increasing or decreasing) significantly.[4] Also, recent reports on hydrogen storage by SWNTs[5a,c,d] and MWNTs[5b] are of great interest. In addition, carbon nanotubes have also been studied as quantum nanowires, electron field emitters, catalyst supports, etc.

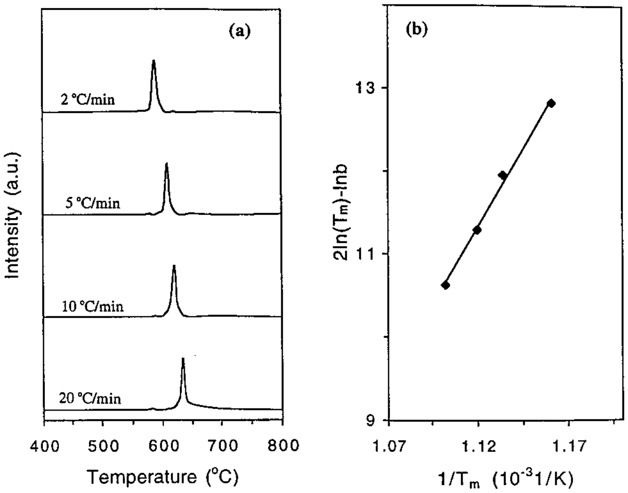

Figure 1. (a) TPD profiles of dioxin on carbon nanotubes at heating rates of 2, 5, 10, and 20 °C/min. (b) Relationship between the maximum desorption temperature (T_m) and the heating rate (b) for dioxin on carbon nanotubes.

In this work, we report first data on MWNTs as sorbent for dioxin removal. A technique based on temperature-programmed desorption (TPD) was used for studying dioxin adsorption.[3] Because of the high melting- and boiling points of dioxins, it is difficult to generate the vapors and control their concentrations. This makes it difficult to directly measure adsorption isotherms for dioxins using conventional techniques. Moreover, the adsorption bonds for these compounds are generally very strong, and the isotherms are very steep. Information in the very low concentration range, in the parts per trillion (ppt) to ppb range, is extremely difficult to obtain. But for dioxins, information in the ppt range is important because removal to the order of ng/m^3 is required. To overcome these difficulties, a simple TPD technique for sorbent screening was developed in our previous work.[3] Since the desorption peak temperature is related to the adsorption bond strength, a stronger bond gives rise to a higher TPD peak. From the different desorption peaks at different heating rates, the activation energy for desorption (or the bond energy)

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[6] In each experiment, 0.1 g of carbon nanotubes was loaded in a stainless steel tubing (1/8-in.) with an inner diameter of 2 mm. The non-chloro dioxin was used as the model compound for dioxins. The dioxin solution in *N,N*-dimethylformamide solution was loaded at the inlet of the sorbent column, and the column was purged with helium (50 mL/min) at room temperature. Subsequently, the sample was heated in the He flow at a constant heating rate. As the temperature was increased, the dioxin at the inlet was vaporized and was subsequently adsorbed in the bed. As the temperature was further increased, the dioxin was eventually desorbed. The effluent or the desorption products were analyzed continuously by both a thermal conductivity detector (TCD) and a flame ionization detector (FID) in a gas chromatograph (Shimadzu, 14A).

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Table 1. Peak Desorption Temperature of Dioxin at Different Heating Rates, Activation Energies for Desorption and Langmuir Constants on Different Sorbents

	peak desorption temp. (°C) at different heating rates						
sorbent	2 °C/min	5 °C/min	10 °C/min	20 °C/min	desorption activation energy (kJ/mol)	Langmuir constant B at 25 °C (1/atm)	ref
carbon nanotubes	588	609	620	634	315	2.7×10^{52}	this work
ZX-4 carbon (Mitsubishi)	481	517	543	?	119	1.3×10^{18}	3
γ-Al_2O_3	306	353	394	?	47.9	4.5×10^{5}	3

is calculated, and then the equilibrium adsorption isotherms for dioxins can be estimated. The experiments were carried out from room temperature to 800 °C at different heating rates from 2 to 20 °C/min.[6] Carbon nanotubes were prepared using catalytic decomposition of methane.[7] The obtained material was treated with nitric acid to dissolve the catalyst particles and then calcined at 400 °C for 1 h in air. Transmission electron microscopy (TEM) image shows that the prepared carbon nanotubes are MWNTs and the ends of some MWNTs are open. The MWNTs have a BET surface area of 155 m^2/g and a pore size distribution from 2.5 to 30 nm (with the first peak at 2.9 nm), obtained from N_2 adsorption isotherms at −196 °C.

Figure 1a shows the TPD spectra of dioxin on carbon nanotubes at different heating rates. The maximum desorption temperature increased from 588 to 634 °C as the heating rate was increased from 2 to 20 °C. According to the following equation[8]

$$2 \ln T_m - \ln b = \frac{E}{RT_m} + \ln ZA \qquad (1)$$

(where T_m is the peak desorption temperature, b is heating rate, E is activation energy for desorption, R is the gas constant, and Z is a constant that depends on the desorption kinetics.), the activation energy for dioxin desorption can be calculated. The plot of [$2 \ln T_m - \ln b$] versus $1/T_m$ is given in Figure 1b. From this plot, the activation energy (E) for desorption of dioxin on the carbon nanotubes is 315 kJ/mol.

For adsorption of low-volatile organic compounds, such as dioxins, the sorbate−surface bond is usually much stronger than the sorbate−sorbate bond. Hence, the adsorption is limited to within a monolayer, and this is particularly the case for low pressures or concentrations. Consequently, the Langmuir isotherm is a meaningful representation for adsorption equilibrium:[9]

$$\theta = \frac{q}{q_m} = \frac{BP}{1 + BP} \qquad (2)$$

where θ is fractional surface coverage, q is the amount adsorbed at absolute temperature T and vapor pressure P, q_m is the monolayer amount, and B is the Langmuir constant. Once the activation energy for desorption (E) is known, the Langmuir constant B can be calculated by[10]

$$B = \frac{\sigma N}{\beta \sqrt{2\pi MRT}} e^{E/RT} \qquad (3)$$

where σ is the molecular area, N is Avogadro's number, β is the vibration frequency of the adsorbate against the surface, and M is the molecular weight. From eq 3, the Langmuir constant for dioxin is

$$B = \frac{3.2 \times 10^{-2}}{\sqrt{T}} e^{E/RT} \text{ (1/atm)} \qquad (4)$$

The value of B at 25 °C is 2.7×10^{52} 1/atm for dioxin on carbon nanotubes. A direct comparison of Langmuir constant B values of dioxin on various sorbents is given in Table 1. It can be seen that desorption temperatures, the desorption activation energy, and the Langmuir constant of dioxin on carbon nanotubes are much higher than those of activated carbon and γ-Al_2O_3. In the Henry's law region, which is the low-concentration regime that is of practical interest, the amount adsorbed on carbon nanotubes is 10^{34} higher that that on activated carbon. Hence, a significantly higher dioxin removal efficiency is expected with carbon nanotubes than that with activated carbon. The strong interaction between dioxin and carbon nanotubes may be attributed to the unique structure and electronic properties of carbon nanotubes. The carbon nanotubes consist of hexagonal arrays of carbon atoms in graphene sheets that surround the tube axis. Strong interactions between the two benzene rings of dioxin and the surface of the carbon nanotubes are expected. Additionally, the dioxin molecule interacts with all surfaces on the walls of the nanotube within the small pore (i.e., 2.9 nm), and these interaction potentials overlap, resulting in enhanced potentials in the pore. In addition, the strong oxidation resistance of carbon nanotubes is also beneficial for regeneration of the sorbent at high temperatures.

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