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ADSORPTION OF BISPHENOL A ON CARBON NANOTUBES

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Abstract—**The potential of adsorptive removal of bisphenol A was investigated for two commercial carbon nanotubes including: single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs). The surface area, elemental analyses and pH_{zpc} of the carbon nanotubes (CNTs) were determined and the adsorption isotherms were measured. Adsorption isotherms indicate that the adsorption of bisphenol A on carbon nanotubes belongs to type L of the Giles classification. This follows from the textural and chemical characteristics of these carbons and essentially hydrophobic nature of bisphenol A. The adsorption capacity and relative affinity of SWCNTs are higher than that of MWCNTs with SWCNTs having about 12.7 times the adsorption capacity of MWCNTs. This suggests that SWCNTs have higher potential for removing bisphenol A from contaminated water. The weak ion strength dependence and strongly pH dependence of the adsorption process indicate that chemicomplexation is strong while physical sorption on carbon nanotubes surfaces is weak.**

Keywords—Carbon nanotubes, bisphenol A, adsorption

I. Introduction

Bisphenol A is widely used in the production of polycarbonates, epoxy resin, and other plastics. Due to the weak oestrogen-like effect of Bisphenol A, it is designated as one of the endocrine-disrupting chemicals that may pose risks to human health [1, 2]. Furthermore, Bisphenol A appears to be resistant to biodegradation, and is highly resistant to chemical degradation which can lead to high concentrations of Bisphenol A being found in surface water and industrial wastes.

Carbon nanotubes were first proposed following arc-discharge synthesis of C_{60} in 1991 [3]. Due to the unique morphologies, large specific area, remarkable electronic, mechanical and chemical properties, both single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) have attracted much attention since their discovery [4-6]. Many applications such as hydrogen storage, quantum nanowires, catalyst supports, chemical sensors and other technical applications have been developed [7]. Because of the large surface areas of carbon nanotubes, their use as adsorbent for adsorption of trace pollutant from water or air is increasingly of interest. For example, CNTs have already proven good adsorbents for removal of trihalomethanes [8], fluoride [9], 1,2-dichlorobenzene are investigated [10].

The objective of this study is to determine the efficacy of two different types of carbon nanotubes for adsorption of Bisphenol A from water. Characteristics of carbon nanotubes and surface chemistry in solution as a function of pH and ionic strength were also determined.

II. MATERIALS AND METHODS

Materials

Bisphenol A used in the experiments was supplied by Aldrich. The commercial carbon nanotubes samples used in this study were SWCNTs and MWCNTs purchased from Conyuan Biochemical Technology company in Taiwan. The samples used in this study were prepared without modification or conditioning.

Characterization of the Carbon Nanotubes Samples

The BET equation [11] together with N_2 adsorption isotherm data were used to determined specific surface area of the carbon nanotubes. Prior to adsorption experiments, the carbon nanotubes samples were outgassed at 378 K under pressure $<10^{-4}$ Pa for at least 15 hours. Elemental analyses of the carbon nanotubes were determined by an elementary analyzer (Elementar vario EL III) which measured the C, H and N contents. The O content was calculated by difference. A pH shift analysis method of Newcombe [12] and Ferro- García et al. [13] was used to measured the pH of the zero charge (pH_{pzc}).

Bisphenol A Adsorption

Prior to the adsorption experiments, CNT samples were washed with distilled water and then dried at 378 K for 8 hours. Adsorption isotherms of bisphenol A on carbon nanotubes were determined by adding 0.1 g of carbon nanotubes to flasks containing 100 cm^3 of bisphenol A solution. Flasks were kept in a thermostatic bath (Firstek-B610D) at 288, 298 or 308 K with constant agitation for reaction times ranging from 10 minutes to 8 hours. The effect of ionic strength on adsorption were also determined by making measurements at different ionic strengths by adding NaCl to reach concentrations of 0.01 or 0.1 M. The effect of pH ranging from 3 to 11 was measured by adjusting pH using 1M HCl or 1M NaOH. Concentrations of bisphenol A were detected by spectrophotometry (Hitachi, U-1500) at 275.5 nm.

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III. RESULTS AND DISCUSSION

Carbon Nanotubes

Elemental analyses and ash content for the two types of CNTs used in this study are shown in Table 1. Both types of CNTs contain >94 wt% of C, but the SWCNTs yield ten times the ash content compared to MWCNTs. It is noted that a low ash content has been shown to be an important feature of CNTs for predicting the efficacy of its application to water treatment [14].

The pHpzc of SWCNTs and MWCNTs are 8.36 and 9.01, respectively. It indicates a positive charge density on its surface for a solution pH <8.36 and <9.01 and a negative charge density for a solution pH>8.36 and >9.01 for SWCNTs and MWCNTs, respectively. When they are used as adsorbent, the MWCNTs has higher adsorption capacity for positively charge pollutants.

Bisphenol A Adsorption isotherms

The adsorption isotherms of bisphenol A on both types of CNTs are shown in Figure 1. Clearly, the adsorption isotherms reach a plateau amount adsorbed for SWCNTs and MWCNTs at about 171.3 and 36.7 mg/g, respectively. It is due to the textural and chemical characteristics of these carbons and essentially hydrophobic nature of bisphenol A. Adsorption of bisphenol A on CNTs may involve different combinations of chemical, electrostatic and physical interactions. Isotherms shown in Figure 1 indicate that the adsorption of bisphenol A on carbon nanotubes belong to type L of the Giles classification [13]. It shows that as more sites in the carbon nanotubes are filled, it becomes increasingly difficult for the bisphenol A to find an available vacant site to be adsorbed. This phenomenon can be attributed to two factors. First, the bisphenol A is more likely to be adsorbed flat. The second factor is there is no strong competition in the solution.

On the other hand, the adsorption capacity of the carbon samples were determined from isotherms using Langmuir's equation. The adsorption capacity, X_m, the constant, B, and the bisphenol A-carbon nanotubes relative affinity, BX_m, in the adsorption process were determined. Normalized adsorption capacities of the carbon nanotubes are listed in Table 2. It is apparent that the adsorption capacity and relative affinity of SWCNTs are higher than those of MWCNTs, with SWCNTs having about 12.7 times the adsorption capacity of MWCNTs. However, there is only 4.67 times the amount of bisphenol A adsorption on SWCNTs compared to MWCNTs. This may be explained by the fact that the diffusion mechanisms control the adsorption process. Since the adsorption is base on π-π dispersion interactions between the aromatic ring electrons in the bisphenol A molecules and those on the carbon nanotubes basal plane [15], the MWCNTs with a pH_{pzc} (9.01) similar to that of the solution, will show a surface charge density close to zero. In addition, the bisphenol A is in molecular form at pH=9. On the other hand, the SWCNTs with a pH_{pzc} of 8.36< the pH of solution, will show a negative charge density under working condition. Their dispersion interactions with bisphenol A molecules will be increased respect to MWCNTs. Thus, the bisphenol A-carbon nanotubes dispersion interactions will be enhanced. The B value for adsorption of bisphenol A on SWCNTs is greater than that for MWCNTs. It indicates stronger interaction between bisphenol A and SWCNTs surfaces than that for the MWCNTs.

Effects of contact time, temperature and pH

Figure 2 shows the effect of contact time on the adsorption of bisphenol A on CNTs. The bisphenol A adsorption on CNTs rises quickly within the first thirty minutes and then reaches an apparent equilibrium level. Figure 3 shows that increasing the temperature by 20 ℃ has only a small influence on decreasing the adsorption of bisphenol A on carbon nanotubes. Reasonably, the adsorption capacity is slightly decreased with the increasing temperature. It is because of elevated temperature makes the bisphenol A molecules more energetic. The desorption rate is higher than that of adsorption rate.

The capacity of CNTs to adsorb bisphenol A fundamentally depends on the chemical nature of the carbon surface and the pH of the solution. Chemical and electrostatic interactions may also affected by water chemistry, such as pH or ionic strength [16]. The solution pH is an important parameter in adsorption process because it decides the charge of both the carbon nanotubes and the adsorbate and thus affects the adsorbent-adsorbate electrostatic interactions [17]. Figure 4 shows the effect of solution pH on the adsorption of bisphenol A on carbon nanotubes in the bisphenol A of 100 mg/l. Clearly, the adsorption of bisphenol A on both carbon nanotubes fluctuates very little in pH=3-9. At pH>9, the amount adsorbed decreased quickly with increasing pH. It may be due to at least two possibilities: (1) This is because of the net signs of the surface charge of the carbon nanotubes and of the bisphenol A species at different pH. Therefore, the carbon nanotubes appear a net positive charge at pH< their pHpzc and a net negative charge at pH > their pHpzc. At pH<8, bisphenol A is observed in its molecular form and deportonation bisphenolate monoanion sets in to a considerable extent at around pH=8. Thus, the decresed adsorption capacity of the carbon nanotubes at basic pH is due to the repulsive electrostatic interactions between the negatively charged carbon nanotubes surface and bisphenolate anion [14]. (2) It is possible that oxygen-containing groups on the carbon nanotubes surface were ionized at higher pH and they adsorbed more water to block the access of bisphenol A molecules to the adsorption sites [9].

Effect of electrolytes

The effects of adding an electrolyte (0.1 and 0.01 M NaCl) was also investigated (Table 3). It is apparent that the adsorption of bisphenol A on carbon nanotubes was inhibited in the presence of electrolyte. However, the adsorption capacity was slighter decreased with the increasing concentration of NaCl. It is due to the presence of NaCl may cause a salting-out effect that decreases the solubility of bisphenol A and increases the ion strength of the solution. Na+ ions may form electrical double layer complex with CNTs, which favor the adsorption when the concentration of the bisphenol A is decreased. The ions may compete with bisphenol A in the adsorption sites that inhibits the bisphenol A adsorption on carbon nanotubes.

On the other hand, the influence of ion strength on the activity coefficients of BPA+ and HBPA- ions, which limit their transfer to CNT cavities [18]. Summarizing the ionic strength and pH effects on the adsorption of bisphenol A on carbon nanotubes, the weak ionic strength dependence and strong pH dependence on the adsorption indicate that the adsorption mechanism is surface complexation, and it suggests that the chemicomplexation is strong while physical sorption on the carbon nanotubes surfaces is weak.

IV. CONCLUSIONS

Two types of CNTs obtained from commercial sources, including SWCNTs and MWCNTs, were used to study adsorption of bisphenol A from water. The adsorption isotherms indicate that the adsorption of bisphenol A on carbon nanotubes belong to type L of the Giles classification. The SWCNTs have about 12.7 times more adsorption capacity than MWCNTs per unit mass, suggesting that SWCNTs have greater potential for removing bisphenol A from water.

The bisphenol A adsorption on CNTs increases quickly in thirty minutes and then reaches equilibrium. Between 208 and 308 K, temperature has only a small effect on the adsorption of bisphenol A on CNTs. The adsorption of bisphenol A on both carbon nanotubes fluctuates very little between pH=3-9. However, at pH>9, the amount adsorbed decrease quickly with increasing pH. The adsorption of bisphenol A on carbon nanotubes was inhibited in the presence of electrolyte. The adsorption capacity was slighter decreased with the increasing concentration of NaCl. The weak ionic strength dependence and strong pH dependence on adsorption process suggest that chemicomplexation is strong while physical sorption on carbon nanotubes surfaces is weak.

TABLE 1. ELEMENTAL ANALYSIS AND ASH CONTENT OF THE CARBON NANOTUBES (WT%)

	SWCNTs	MWCNTs
C	94.9	98.2
H	1.5	0.9
N	1.9	0.1
O (by diff.)	1.8	0.8
Ash	7.8	0.76

Table 2. Results obtained from the Langmuir equation applied to the adsorption of Bisphenol A on carbon nanotubes.

Sample	BET, m^2/g	X_m, mg/g	X'_m, mg/m^2	B, L/mg	BX_m, L/g
SWCNTs	890.3	1428.6	13.15	0.0057	0.641
MWCNTs	108.6	112.4	0.13	0.00093	1.329

Table 3. The effect of ion strength on the adsorption of Bisphenol A on carbon nanotubes.

Sample	0	0.01 M NaCl	0.1 M NaCl
SWCNTs (mg/g)	171.3	96.9	87.7
MWCNTs (mg/g)	36.7	32.6	32.1

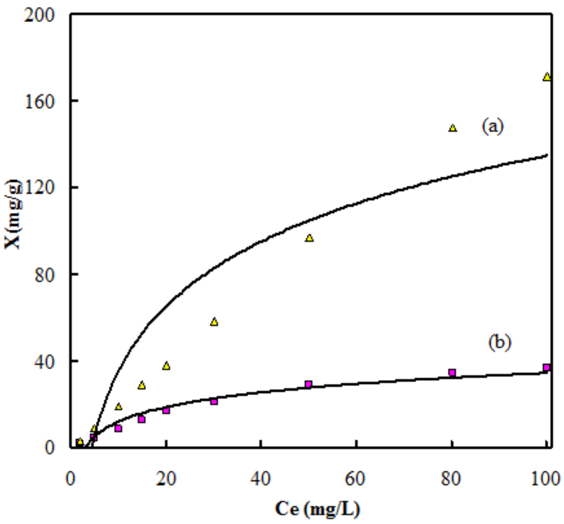

Figure 1. Adsorption isotherms of bisphenol A on (a) SWCNTs and (b) MWCNTs.

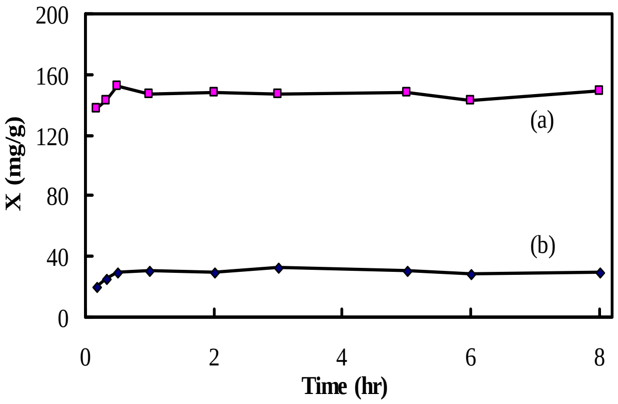

Figure 2. Effect of contact time on the adsorption of bisphenol A on (a) SWCNTs and (b) MWCNTs.

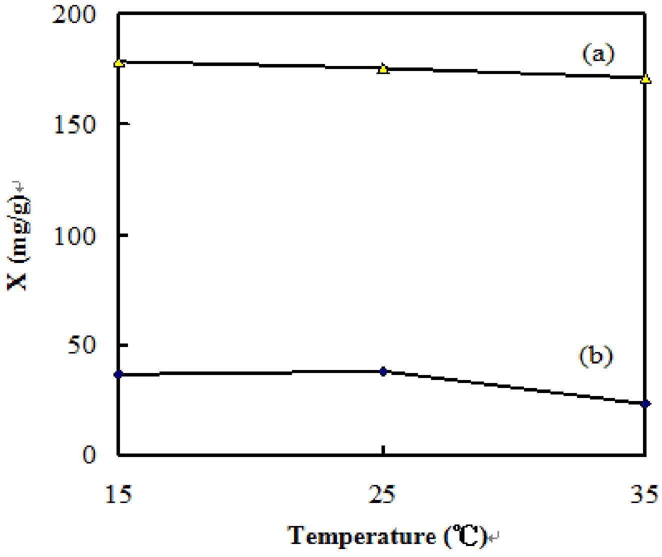

Figure 3. Effect of temperature on the adsorption of bisphenol A on (a) SWCNTs and (b) MWCNTs.

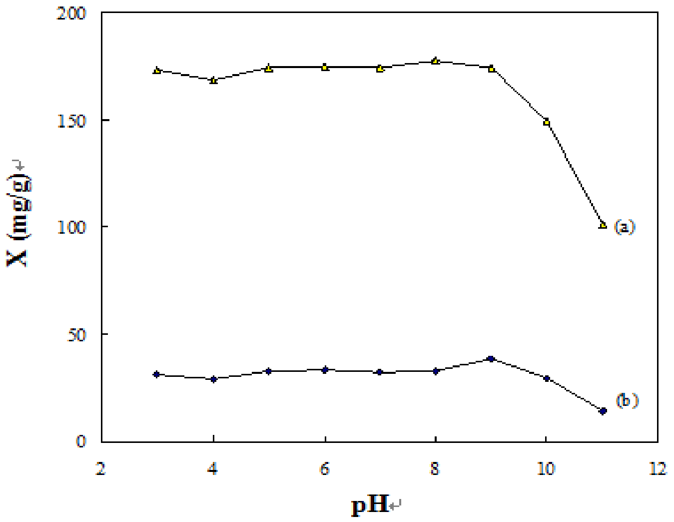

Figure 4. Effect of solution pH on the adsorption of bisphenol A on (a) SWCNTs and (b) MWCNTs.

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