

ADSORPTION OF ORGANIC CHEMICALS ON CARBON NANOTUBES IN AQUATIC ENVIRONMENT

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Introduction

Carbon nanotubes (CNTs), a novel carbon material, have been proposed for a wide range of commercial application due to their distinct structure and outstanding properties [1]. However, previous study has shown that CNTs would enter into cells easily and be biologically active because of their nanosize, which made them likely to react with tissues and cause cellular damage [2]. Furthermore, the toxicity of CNTs is not only from their own harmful nature but also may come from toxic substances adsorbed by them. CNTs have been demonstrated to act as strong adsorbents, due to their highly hydrophobic surfaces, for organic compounds in aqueous solution [3, 4]. Thus, a fundamental understanding of factors controlling adsorption of organic contaminants by CNTs is critical for both environmental risk assessment of CNTs and toxic organic chemicals as well as for evaluating their potential use as adsorbents in water and wastewater treatment applications.

In the present work, adsorption of three synthetic organic compounds (SOCs) by both single-walled CNTs (SWNTs) and multi-walled CNTs (MWNTs) has been investigated in aqueous solutions. The major objective of this study was to explore the roles of CNT physicochemical properties, SOC properties and background solution chemistry (pH, ionic strength, and the presence of natural organic matter (NOM)) on SOC adsorption by CNTs.

Experimental

Three SOCs, phenanthrene (PNT), 2-phenylphenol (2PP) and biphenyl (BP), were employed as adsorbates. The selected properties of SOCs are summarized in Table 1. Three SWNTs (pristine [SWNT], carboxyl functionalized [SWNT-COOH], and hydroxyl functionalized [SWNT-OH]) and three MWNTs (MWNT, MWNT-COOH and MWNT-OH) were used as received. The specific surface area (S_{BET}) and total pore volume (V_{total}) of the six CNTs obtained from nitrogen adsorption are summarized in Table 2 along with the oxygen contents obtained from EA and XPS analyses.

Table 1. Selected Physicochemical Properties of SOCs

SOC	Planarity	MW ^a g/mol	S_w^b mg/L	pK _a	log K _{ow} ^c
PNT	Planar	178.23	1.1	n.a.	4.68 ± 0.17
BP	Nonplanar	154.21	6.1	n.a.	3.98 ± 0.23
2PP	Nonplanar	170.21	700	9.6	2.94 ± 0.25

^a molecular weight; ^b water solubility; n.a.: not applicable; ^c simulated with ACDLABS11.0

Adsorption isotherms of SOCs by CNTs were obtained by constant carbon dose experiments in completely mixed batch reactors (255 mL glass bottles). The bottles containing 1 mg of CNTs and SOC solution were placed into a rotary tumbler for one week to reach equilibrium. After one week, the supernatants were analyzed using a high performance liquid chromatography (HPLC) analyzer. The isothermal data were analyzed with the Freundlich model. Solution pH was adjusted to three level of 4, 7, 10(11) with HCl and NaOH solution, while ionic strength was adjusted with NaCl (0.001-0.1 M). Two types of NOM effect experiments were conducted: 1) NOM (4 mg DOC/L) and SOC solution spiked simultaneously adsorption; and 2) NOM one-week preloading experiment.

Table 2. Selected Characteristics of CNTs

CNT	S_{BET} m ² /g	V_{total} cm ³ /g	R_{open}^a %	d_e^b nm	Length (μm)	O(w/w)% EA	XPS
SWNT	486	0.722	7-10	1-2	5-30	1.8	3.7
SWNT-OH	420	0.739	7-10	1-2	5-30	4.1	5.4
SWNT-COOH	386	0.680	7-10	1-2	5-30	3.2	4.4
MWNT	164	0.664	54-100	8-15	10-50	0.0	1.5
MWNT-OH	192	0.765	54-100	8-15	10-50	2.8	6.4
MWNT-COOH	134	0.589	54-100	8-15	10-50	1.1	6.7

^a the proportion of open ends in CNTs; ^b outer diameter

Results and Discussion

For the liquid phase adsorption, as shown in Table 3, the adsorption capacities obtained from Freundlich model (K_F) indicate that the adsorption affinities of the SWNTs to SOCs were about 5 and 3 times to those of the MWNTs. Considering the higher specific surface areas of SWNTs than those of MWNTs, the adsorption affinities of CNTs were normalized by their surface areas (S_{BET} , Table 2). The Q values (Table 3) indicate that even normalized with surface area, the adsorption affinities of the SWNTs to SOCs were still higher than those of MWNTs, which suggested that surface area was the major but not only factor determining the adsorption difference between them.

As shown in Table 3, surface functionalization of the CNTs led to a reduction in the adsorption capacity of SOCs. This reduction was correlated with the oxygen-containing functional group contents on the surface of CNTs. Only a slight reduction was observed, which was attributed to the small increase in oxygen contents as measured with EA and XPS (Table 2). Surface functionalization can improve the dispersion of CNTs in aqueous solution, which might increase the access to adsorption sites. However, due to formation of water clusters around the oxygen-containing functional groups, some of the adsorption sites might be blocked for the access of SOCs. The overall decrease in the adsorption of SOCs indicated that water cluster formation played a more important role than the increase in the adsorption sites on the adsorption of hydrophobic SOCs.

Table 3. Freundlich Isotherm Parameters of SOC

Adsorption on CNTs						
SOC	CNT	K_F^a	n	r^2	K_{F-SW}^b	Q^c
PNT	SWNT	285	0.41	0.967	297	0.61
	SWNT-OH	238	0.39	0.965	246	0.59
	SWNT-COOH	206	0.37	0.945	213	0.55
	MWNT	58	0.29	0.986	60	0.37
	MWNT-OH	48	0.31	0.981	50	0.26
	MWNT-COOH	39	0.27	0.977	40	0.30
BP	SWNT	125	0.43	0.979	273	0.56
	SWNT-OH	104	0.38	0.977	209	0.50
	SWNT-COOH	96	0.37	0.981	186	0.48
	MWNT	30	0.61	0.993	90	0.55
	MWNT-OH	21	0.64	0.985	66	0.34
	MWNT-COOH	22	0.61	0.993	65	0.49

^a adsorption affinity coefficient, (mg/g)/(mg/L)ⁿ; ^b solubility-normalized K_F values, mg/g; ^c specific surface area normalized K_{F-SW} values, mg/m². The isotherm results of 2PP were not listed since they have the same trend with BP.

Fig. 1 compared the uptake of the different SOCs to pristine SWNT and MWNT. Adsorption of three SOCs by all CNTs followed the order: PNT >> BP > 2PP. Considering that the water solubility of 2PP is two to three orders of magnitude higher than those of BP and PNT, hydrophobic interaction was not the only factor determining the adsorption difference among them. The -OH group of 2PP promoted π - π electron donor acceptor (EDA) interaction between 2PP and CNTs, which counterbalanced the decreased sorption of 2PP due to its lower hydrophobicity.

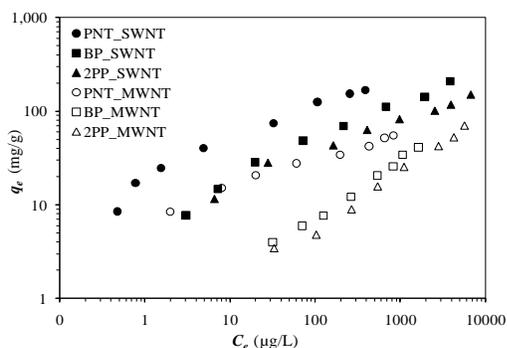


Fig. 1 The adsorption isotherms of three SOCs on pristine SWNT and MWNT.

PNT and BP have similar sizes but different molecular structures, as shown in Table 1. After solubility-normalization, the K_{F-SW} values (Table 3) of PNT and BP sorption on SWNT and MWNT showed the opposite trends. Since the planar PNT molecule is rigid, the longitudinally-parallel external surface and interstitial channels of the SWNTs can provide more accessible adsorption sites for PNT than the short, entangled MWNTs (Table 2). Contrary to PNT, the nonplanar BP is flexible and can adjust its molecular configuration to be better packed in the tubular spaces of the MWNTs with diameter several times larger than their widths. Therefore, in addition to hydrophobic effect, the molecular configuration of SOC

molecules was likely an extra critical factor contributing to the different adsorption behavior of SOCs on SWNTs and MWNTs with different geometry.

Changing the solution pH from 4 to 10 did not affect the adsorption of nonionic PNT on CNTs, but there was an observable reduction effect on the adsorption affinity of 2PP with increasing pH above the pK_a of 2PP (9.6). This may result from the decreased hydrophobic interaction, hindered hydrogen bonding and enhanced electrostatic repulsion between 2PP and CNTs. Increasing ionic strength up to 0.1M exhibited no effect on PNT adsorption by CNTs, but showed a lightly positive effect on ionic 2PP adsorption by MWNT-OH, which may be partly attributed to the decrease of electrostatic repulsion between 2PP and CNTs due to the added salt and partly from increased hydrophobic interaction due to the decreased solubility of 2PP.

The presence of NOM greatly reduced adsorption of SOCs on CNTs, and preloaded NOM exhibited stronger suppression than simultaneously spiked NOM, suggesting that a longer contact time of CNT with NOM resulted in a more negative impact. In addition, the impact of NOM on the SWNTs was higher than that on the MWNTs, especially at low concentration, which might be attributed to the different adsorption site accessibility between them. Furthermore, NOM showed different effects on adsorption of PNT and BP, which indicated that the planarity and hydrophobicity of SOCs may also play important roles in their adsorption by CNTs.

Conclusions

Adsorption of SOCs by CNTs was controlled by their available surface area, suggesting that SWNTs with higher surface area would uptake more SOCs in the environment as compared to MWNTs. Functionalization of CNTs decreased their adsorption capacities, which was attributed to the formation of water clusters. The hydrophobicity and molecular configuration (functional group and planarity) of SOCs appear to be important factors determining their adsorption by CNTs. Among the three background solution characteristics, NOM showed the most significant effect on SOC adsorption, while solution pH and ionic strength exhibited only slight or insignificant impacts on SOC adsorption.

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References

- [1] Baughman RH, Zakhidov AA, De Heer WA. Carbon nanotubes - the route toward applications. *Science*. 2002;297(5582):787-92.
- [2] Oberdorster G, Oberdorster E, Oberdorster J. Nanotoxicology: An emerging discipline evolving from studies of ultrafine particles. *Environmental Health Perspectives*. 2005;113(7):823-39.
- [3] Yang K, Zhu L, Xing B. Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. *Environmental Science & Technology*. 2006;40(6):1855-61.
- [4] Lu CS, Chung YL, Chang KF. Adsorption of trihalomethanes from water with carbon nanotubes. *Water Research*. 2005 Mar;39(6):1183-9.
- [5] Girifalco LA, Hodak M, Lee RS. Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential. *Physical Review B*. 2000 Nov;62(19):13104-10.