

Competitive and Complementary Adsorption of Bisphenol A and 17 α -Ethinyl Estradiol on Carbon Nanomaterials

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Competitive adsorption between organic chemicals is an important process affecting their environmental behavior and risk. Overlapping of adsorption sites between solutes was often emphasized in the literature. However, chemicals with different properties may complementarily occupy different sorption sites. The objective of this study was to test this hypothesis by collecting detailed information on competitive and accumulative adsorption of different chemicals on carbon nanomaterials (CNMs). Bisphenol A (BPA) and 17 α -ethinyl estradiol (EE2) are different with regard to their hydrophobicity and molecular structures, and they were selected as model chemicals. The cumulative adsorption of both BPA and EE2 in bisolute adsorption experiments resulted in much higher total adsorption than in single-solute adsorption experiments. A new competitive–complementary adsorption concept was proposed. This information indicates that the modeling concept of competitive adsorption should be improved to better understand the fate and risk of both CNMs and organic chemicals.

KEYWORDS: Cumulative; co-adsorption; ideal adsorbed solution theory; multiple pollutants; model; nanotechnology

INTRODUCTION

The presence of multiple pollutants is common in contaminated aqueous environments and wastewater treatment systems. Therefore, recent research interests have been focused on the co-adsorption of various adsorbates (1, 2). The coexistence of two or three organic chemicals in an aqueous–solid particle adsorption system generally resulted in competitive adsorption, such as decreased adsorption capacity, increased isotherm linearity, and decreased adsorption coefficient (1, 3–7). In addition, the presence of competitor could inhibit the formation of a slowly desorbing fraction (8) and increase the desorption rate (9). Thus, the mobility and toxicity could be greatly enhanced. Therefore, understanding the mechanisms of competition is essential for establishing a proper modeling scheme and consequently for environmental risk assessment of organic contaminants in real environmental conditions.

Ideal adsorbed solution theory (ISAT)-based models were proposed to quantitatively describe competitive adsorption (3, 5, 7, 10). These models are based on the same general assumption: the effective sorption potential is dependent on the total adsorbed volume and independent of single-solute system or multisolute system. Sander and Pignatello (11) investigated competitive adsorption among benzene, toluene, and nitrobenzene on charcoal. They observed that these molecules could replace each other in molar ratio of 1:1:1, indicating 100% overlapping of adsorption sites. However, Morelis et al. (12) observed that some

high-energy sites in a sediment were still available for secondary adsorbate among phenanthrene, chrysene, and 2,5-dichlorobiphenyl. This line of research indicates that compounds dissimilar in chemical properties do not fully compete for adsorption sites. It is reasonable to imagine that different types of chemicals could be preferentially adsorbed on different types of adsorption sites. For example, Xing et al. (3) stated that azo and amino nitrogens on triazines could form H-bond with $\equiv\text{Si}-\text{OH}$ on silica. However, TCE is incapable of H-bonding, but the IAST model could not identify their difference in adsorption sites and predict competitive adsorption between TCE and atrazine, which actually did not occur in their experiments. Therefore, the adsorption mechanisms of multiple pollutants are still unclear and extended study is needed.

Carbon nanomaterials (CNMs) are unique model adsorbents to study adsorption mechanisms because of their definite structure (7, 13). The adsorption properties of 17 α -ethinyl estradiol (EE2) and bisphenol A (BPA) on CNMs were systematically studied and compared previously (13). Our sorption study and dynamic molecular modeling results showed that BPA has a unique structure to fit into CNM surface adsorption sites. However, EE2 does not have this feature due to a different chemical structure. That is why although the aqueous solubility of EE2 is 50 times lower than that of BPA, which indicates much stronger hydrophobicity of EE2 than BPA, the adsorption affinity of BPA was higher than that of EE2. Therefore, the objective of this work was to examine the applicability of the current concept of competitive adsorption by a detailed study on the competition between EE2 and BPA, which have different

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chemical properties (e.g., chemical structure and hydrophobicity). Theoretical consideration of the adsorption/competition mechanisms is the focus of this study. The concentrations of both primary and secondary adsorbates were measured and processed to investigate the competitive and accumulative adsorption of two adsorbates. Both EE2 and BPA are endocrine-disrupting chemicals (EDCs) and two of the most frequently studied EDCs in environmental research. This line of study could shed light on the mechanisms of competitive adsorption and provide important information in improving the accuracy of adsorption modeling.

MATERIALS AND METHODS

Adsorbents. Various CNMs were used in this study including single-walled carbon nanotubes (SWCNTs with outer diameters of 1–2 nm), multiwalled carbon nanotubes (MWCNTs with outer diameters of 8–15 and 30–50 nm), and fullerene (C_{60}). Fullerene (purity > 99.5%) was obtained from Aldrich Chemical Co., and SWCNT (purity > 90%) and MWCNTs (purity > 95%) were purchased from Chengdu Organic Chemistry Co., Chinese Academy of Sciences. Carbon nanotubes (CNTs, including SWCNTs and MWCNTs) used in this study were synthesized in the CH_4/H_2 mixture at 700 °C by the chemical vapor deposition method. The synthesized CNTs were purified by mixed HNO_3 and H_2SO_4 solutions to reduce the contents of metal catalyst and amorphous carbon. The characterized properties of these CNMs were published previously (13).

Adsorption Experiment. EE2 (at 3.38 g L^{-1}) and BPA (at 100 g L^{-1}) were dissolved in methanol separately as stock solutions. The adsorption experimental procedure was described by Pan et al. (14). Briefly, the stock solutions were diluted sequentially to a series of concentrations distributed evenly on a log scale using 0.01 M $CaCl_2$ and 200 mg L^{-1} $NaNO_3$ solution. The initial concentrations for the adsorption experiments were 100–3000 $\mu g L^{-1}$ for EE2 and 100–40000 $\mu g L^{-1}$ for BPA. The solid/water (w/v) ratios were 1:100–1:200 for fullerene and 1:20000–1:120000 for CNTs. The volume ratio of methanol to water was below 0.001 to avoid cosolvent effect. The vials containing BPA or EE2 solution and CNM were sealed with Teflon-lined screw caps immediately. The same concentration series of adsorbate solution without CNMs was run under the identical condition as control. Headspace was kept minimal to reduce solute vapor loss. According to our preliminary study, adsorption reached equilibrium within 7 days. Thus, the vials were kept in the dark and rotated vertically on a rotator (30 rpm, Glas-Col laboratory rotator) for 7 days and centrifuged at 1000g for 15 min. The supernatant was sampled for HPLC analysis. Sorbed chemicals were calculated by mass difference between original (C_0) and equilibrated aqueous concentrations (C_e). All experiments including the blanks were run in duplicate.

Competition between EE2 and BPA. To study competitive adsorption between EE2 and BPA, 0.1 C_s (solubilities in water at 20 °C) of competitor was added in EE2 or BPA sorption systems. The experimental procedure was identical to that in the above adsorption experiments.

Detection of EE2 and BPA. The supernatants were placed in 1.5 mL vials and were loaded on an HPLC autosampler. The mobile phase for HPLC analysis was 50:50 (v/v) of acetonitrile and deionized water with 1% acetic acid. EE2 was analyzed with a fluorescence detector at 206 nm (excitation wavelength) and 310 nm (emission wavelength). The detection limit was 5 $\mu g L^{-1}$. BPA was quantified on a fluorescence detector at 220 nm (excitation wavelength) and 350 nm (emission wavelength) for the concentration range of 5–4000 $\mu g L^{-1}$ and on a UV detector at 280 nm for the samples with concentrations > 4000 $\mu g L^{-1}$. For the detection of solution containing both adsorbates, the samples were injected twice for EE2 and BPA analysis individually. The wavelength of the fluorescence detector was also adjusted for BPA and EE2 detection separately. In both detection conditions, the peaks for BPA and EE2 could be clearly separated.

Data Analysis. All of the adsorption isotherms were fitted using the Polanyi–Mane model (PMM) with the expression (15)

$$\log S_e = \log S^0 + a[(RT \ln(C_s/C_e)/V_s)]^b$$

where S_e ($\mu g kg^{-1}$) and C_e ($\mu g L^{-1}$) are EE2 or BPA solid-phase and aqueous phase concentrations, respectively. S^0 ($\mu g kg^{-1}$) is adsorption

capacity from PMM, R is the universal gas constant (8.314×10^{-3} kJ $mol^{-1} K^{-1}$), and T is the absolute temperature (K). C_s stands for solubility in water at 20 °C (7600 $\mu g L^{-1}$ for EE2 and 380000 $\mu g L^{-1}$ for BPA according to our measurements in ref 13). V_s ($cm^3 mol^{-1}$) is the molar volume of solute (291 and 221 $cm^3 mol^{-1}$ for EE2 and BPA, respectively, as calculated using Molinspiration property engine v2009.01).

Because the number of data points used in model fitting was not the same for different adsorption isotherms of single-solute and bisolute systems, the coefficient of determination (r^2) could not be compared directly. The adjusted r^2 (r_{adj}^2) was calculated and compared

$$r_{adj}^2 = 1 - [(1 - r^2)(m - 1)/(m - b - 1)]$$

where m is the number of data points used for fitting and b is the number of coefficients in the fitting equation. To compare the adsorption in the concentration range of this study, the single-point adsorption coefficient K_d was calculated at 0.01 C_s , 0.10 C_s , and 0.2 C_s .

Adsorption isotherms were also processed to investigate the cumulative adsorption of EE2 and BPA in bisolute systems. Cumulative adsorption isotherms were established between ($C_e^{BPA} + C_e^{EE2}$) and ($S_e^{BPA} + S_e^{EE2}$) as well as $[(\epsilon/V_s)^{BPA} + (\epsilon/V_s)^{EE2}]$ and $(S_v^{BPA} + S_v^{EE2})$. S_v is the adsorbed volume ($cm^3 g^{-1}$). Superscripts BPA and EE2 represent the values for BPA and EE2, respectively.

In several other studies, adsorbate concentrations were expressed as mole-based concentrations. This method is proper if the adsorption is a site-specific process, and the adsorption could be discussed on the basis of chemical stoichiometry. However, for the adsorption on CNMs, the adsorbed volume is a better measurement to quantify and compare the adsorption. In comparison of molecular weight (MW) and volume (MV) of EE2 and BPA, mass-based adsorption is a proper measurement for adsorption. Thus, most of the discussion is based on mass-based concentrations, but molar-based adsorption capacities are also listed in Table 1 for comparison.

RESULTS AND DISCUSSION

Fitting of Adsorption Isotherms. Different models were used to fit the adsorption isotherms. PMM showed the best fitting performance for adsorption isotherms of EE2 and BPA on CNMs, whereas the Freundlich and Langmuir equations failed to describe the adsorption isotherms (data not shown). PMM was also applied to describe adsorption isotherms with the presence of the competitor. Again, this model showed satisfactory performance as shown in Figures 1 and 2 and Table 1. The adjusted coefficients of determination, r_{adj}^2 , were > 0.95, and no systematic error was observed for standard estimation error. Therefore, the following discussion will be mainly focused on the results obtained from PMM fitting and calculation.

Competition between EE2 and BPA. The first batch of competitive sorption experiment was carried out for MWCNT50 using EE2 as the primary adsorbate (with the concentration of 100–3000 $\mu g L^{-1}$) and BPA as the competitor (with the concentration of 1000 $\mu g L^{-1}$). As illustrated in Figure S2 of the Supporting Information, no obvious change of EE2 sorption was observed in the absence and presence of BPA. However, BPA sorption was significantly inhibited with increased EE2 concentration. At EE2 concentration of 25 $\mu g L^{-1}$, although BPA concentration was much higher than EE2, EE2 adsorption was hardly affected. As EE2 concentration increased to 1700 $\mu g L^{-1}$, BPA adsorption was almost completely inhibited. As measured in our previous study, aqueous solubility (C_s) of BPA is 50 times higher than that of EE2 (13). Thus, the strong competition of EE2 over BPA adsorption and lack of competition of BPA with EE2 at the comparable concentrations could be explained by their difference in hydrophobicity. This conclusion is well recognized in the literature (see, e.g., ref 6). However, competitive adsorption in addition to hydrophobic interaction may present important information to understand competition mechanisms. Therefore,

Table 1. Fitting and Calculating Results of EE2 and BPA Adsorption/Competition on CNMs Based on PMM

	batch ^d	logS ^{0a}		logS ^{0m} ^b		r ² _{adjusted}	K _d and K _d ' ^c			K _d '/K _d ^c			
		μg kg ⁻¹	STE	μmol kg ⁻¹	STE		0.01 C _s	0.10 C _s	0.20 C _s	0.01 C _s	0.10 C _s	0.20 C _s	
EE2	M15 ^e	A	8.14	0.04	5.66	0.04	0.96	6.65 × 10 ⁵	1.22 × 10 ⁵	7.07 × 10 ⁴	0.35	0.60	0.60
		C	7.86	0.05	5.40	0.05	0.97	2.31 × 10 ⁵	7.30 × 10 ⁴	4.26 × 10 ⁴			
	M50	A	7.89	0.01	5.42	0.01	0.99	3.43 × 10 ⁵	7.30 × 10 ⁴	4.26 × 10 ⁴	0.38	0.53	0.59
		C	7.77	0.11	5.30	0.11	0.95	1.30 × 10 ⁵	3.85 × 10 ⁴	2.52 × 10 ⁴			
	S	A	8.49	0.03	6.02	0.03	0.98	2.00 × 10 ⁶	3.49 × 10 ⁵	1.90 × 10 ⁵	0.31	0.63	0.74
		C	8.44	0.06	5.97	0.06	0.98	6.22 × 10 ⁵	2.20 × 10 ⁵	1.40 × 10 ⁵			
	F	A	5.36	0.07	2.89	0.07	0.99	9.51 × 10 ¹	6.11 × 10 ¹	5.16 × 10 ¹	0.66	0.87	1.05
		C	5.82	0.49	3.35	0.49	0.98	6.24 × 10 ¹	5.33 × 10 ¹	5.44 × 10 ¹			
BPA	M15	A	8.09	0.06	5.73	0.06	0.99	1.25 × 10 ⁴	2.72 × 10 ³	1.51 × 10 ³	0.77	0.84	0.86
		C	8.03	0.08	5.67	0.08	0.98	9.63 × 10 ³	2.29 × 10 ³	1.29 × 10 ³			
	M50	A	8.00	0.05	5.65	0.05	0.99	8.16 × 10 ³	1.91 × 10 ³	1.12 × 10 ³	0.76	0.70	0.67
		C	7.80	0.09	5.44	0.09	0.98	6.24 × 10 ³	1.33 × 10 ³	7.46 × 10 ²			
	S	A	8.96	0.15	6.60	0.15	0.98	4.86 × 10 ⁴	1.13 × 10 ⁴	7.17 × 10 ³	0.77	0.76	0.72
		C	8.70	0.11	6.34	0.11	0.99	3.73 × 10 ⁴	8.54 × 10 ³	5.13 × 10 ³			
	F	A	6.37	1.37	4.02	1.37	0.95	6.27 × 10 ⁰	4.89 × 10 ⁰	4.77 × 10 ⁰	1.03	0.63	0.46
		C	5.47	0.37	3.11	0.37	0.98	6.43 × 10 ⁰	3.06 × 10 ⁰	2.22 × 10 ⁰			

^a Adsorption capacity as estimated from PMM fitting. ^b Adsorption capacity based on mole concentration. ^c K_d and K_d' were calculated single-point adsorption coefficients of adsorption and competitive adsorption isotherms, respectively. ^d Batches A and C indicate adsorption and competitive experiments, respectively. Adsorption experiments were conducted for individual adsorbents, EE2 or BPA. Competitive adsorption experiments were conducted with the presence of competitor (0.1C_s, solubility in water at 25 °C). ^e M15, M50, S, and F represent MWCNT15, MWCNT50, SWCNT, and fullerene, respectively.

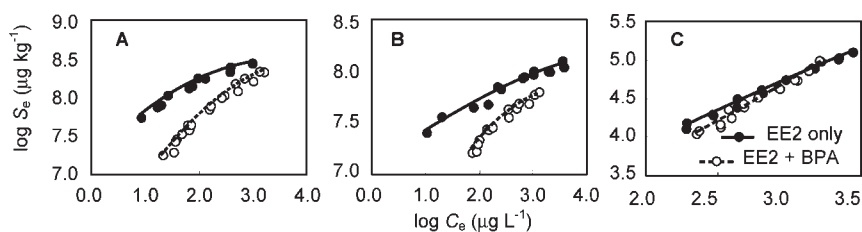


Figure 1. Adsorption of EE2 in the absence (●) and presence (○) of BPA. Panels A, B, and C illustrate sorption isotherms of EE2 on SWCNTs, MWCNT15, and fullerene, respectively. The related information on MWCNT50 is presented in Figure S1A of the Supporting Information. For the competition adsorption experiments, the initial BPA concentration was 0.1C_s (38000 μg L⁻¹).

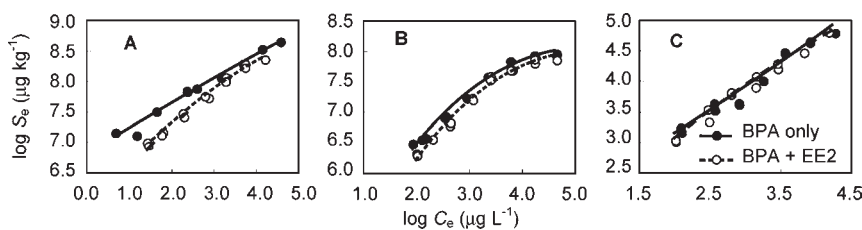


Figure 2. Adsorption of BPA in the absence (●) and presence (○) of EE2. Panels A, B, and C illustrate sorption isotherms of BPA on SWCNTs, MWCNT15, and fullerene, respectively. The related information on MWCNT50 is presented in Figure S1B of the Supporting Information. For the competition adsorption experiments, the initial EE2 concentration was 0.1C_s (760 μg L⁻¹).

the initial concentration of competitor was fixed at 0.1C_s in the rest of the competition experiments in this study.

The competitive adsorption is clearly displayed in **Figures 1** and **2**. The adsorption was generally inhibited in the presence of competitor. According to PMM fitting, S⁰ of EE2 decreased by 11–47% for SWCNTs, MWCNT15, and MWCNT50 because of the competition by BPA (**Table 1**). As noted from **Figure 1**, the adsorption isotherm of EE2 in the presence of BPA generally showed decreased adsorption. Although S⁰ of EE2 on fullerene increased greatly after the addition of BPA, we believe that the comparison between S⁰ values may not be valid at all conditions because of the following two reasons: (1) S⁰ of EE2 (**Table 1**) was much higher than the highest EE2 solid phase concentration in the experiment (**Figure 1**). (2) The aggregation of CNMs may be altered at different adsorbed concentrations (*I*6), which may result in

large uncertainties in comparing the adsorption properties. Thus, comparison based on extrapolated values could be problematic. Single-point adsorption coefficients, K_d, were calculated and compared at 0.01C_s, 0.1C_s, and 0.2C_s and are listed in **Table 1**. K_d' indicates the single-point adsorption coefficient of primary adsorbate in the presence of competitor, and the calculated values are also listed in the table. The effect of competitor on the adsorption of primary adsorbate was described by the ratio between K_d' and K_d (K_d'/K_d in **Table 1**). At C_e = 0.01C_s, EE2 adsorption on SWCNTs, MWCNT15, and MWCNT50 decreased by >60% because of the competition by BPA, and the adsorption on fullerene decreased by 34%. Clearly, the competition was more significant at lower EE2 concentrations as indicated by lower K_d'/K_d values. For example, the EE2 sorption coefficient on SWCNTs decreased by 69, 37, and 26% at 0.01C_s, 0.1C_s, and

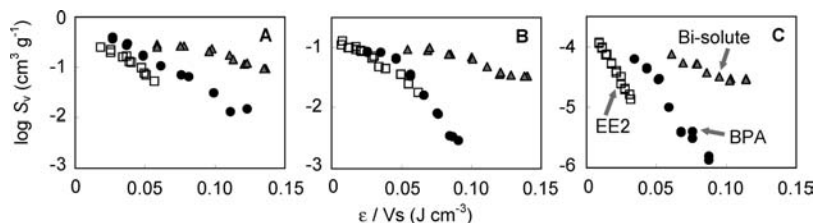


Figure 3. Correlation curves of EE2 and BPA in single-solute and bisolute systems. Open squares and solid circles are correlation curves for EE2 and BPA, respectively. Gray triangles are correlation curves of the sum of BPA and EE2 in bisolute systems. Panels **A**, **B**, and **C** are for SWCNTs, MWCNT15, and fullerene, respectively. The correlation curves for MWCNT50 are presented in Figure S1C of the Supporting Information.

$0.2C_s$, respectively. This observation is consistent with previous studies on competitive adsorption where the Freundlich model was used in adsorption data processing. The nonlinearity factor, n , was observed to increase significantly in competitive experiment in comparison to single-solute sorption experiment (7, 9, 17, 18), which could be visualized as two adsorption isotherms with bigger difference at low concentrations but relatively close at high concentrations in log–log scales. Yu and Huang also calculated single-point adsorption coefficients at different aqueous concentrations (17). Similarly, higher difference at low concentration was observed. The nonlinearity factor, n value, is a measurement of energy distribution heterogeneity of adsorption sites. Therefore, the distribution of adsorption energy is more homogeneous after competition.

The above-mentioned studies mostly focused on the adsorption of primary adsorbates. Because both primary and secondary adsorbates were quantified in this study, the concentration-dependent competition could also be understood and estimated from the adsorption of secondary adsorbate. The adsorption of competitor decreased significantly as the concentration of primary adsorbate increased (Figure S3 of the Supporting Information). This result indicates that the primary adsorbate could overcompete with the competitor as the concentration of primary adsorbate increased.

The adsorption of BPA as affected by EE2 was somehow different from EE2 sorption as affected by BPA. As presented in **Figure 2**, the presence of EE2 resulted in the decrease of BPA adsorption as indicated by a 14–45% decrease of S^0 for SWCNTs, MWCNT15, and MWCNT50. The isotherms of BPA adsorption on fullerene in the absence and presence of EE2 were almost overlapped. A large difference in S^0 (almost 1 order of magnitude) between adsorption and competitive adsorption of BPA on fullerene resulted from unreliable fitting because of data variation. Thus, the discussion regarding the fitting results of BPA adsorption will mostly be focused on SWCNTs, MWCNT15, and MWCNT50. The ratios of K_d'/K_d for BPA were in the range of 67–86% for different concentrations and different CNM combinations and showed less concentration dependence relative to EE2. This phenomenon could also be seen in **Figure 2** as nearly parallel adsorption isotherms with and without the presence of EE2, especially for MWCNT15 (**Figure 2B**).

The strength of the competitive effect for different chemicals was compared in the literature. Yu and Huang reported that phenanthrene is a stronger competitor to EE2 than naphthalene is to EE2 (17). The authors attributed the different competitive behaviors to the closeness of hydrophobicity between primary adsorbate and competitor. The hard carbon in soil organic matter (SOM) possesses hydrophobic adsorption sites (external and internal surfaces) and exhibits strong competitive adsorption among different sorbates. Therefore, in Yu and Huang's study, the higher the hydrophobicity of the competitor, the stronger the competition (17). Wang et al. (6) observed that the strength of

competition with pyrene on chars followed the order phenol < phenanthrene < benzo[*a*]anthracene < 2,2-methylenebis(4-methyl-6-*tert*-butylphenol). They concluded that large size and high hydrophobicity of the competitor resulted in stronger competition and pore blockage. In the current study, the concentration of competitor was fixed at $0.1C_s$. The difference in the degree of competition between BPA and EE2 could not be explained by hydrophobicity. In addition, the molecular size of EE2 is bigger than that of BPA. Thus, pore blockage would not be the case in this study.

Our previous study indicated that CNMs have heterogeneous surface sorption sites and that BPA has a unique butterfly chemical structure and could wedge into high-energy sites (13). However, EE2 does not have this special structural character, and K_{HW} (hexadecane/water distribution coefficient) normalized adsorption coefficients are lower than those of BPA. Therefore, the affinity of BPA to CNMs is stronger than that of EE2 if the hydrophobic effect is excluded. This result is consistent with our current conclusion in this study that BPA is a stronger competitor to EE2 than EE2 is to BPA at competitor concentrations of $0.1C_s$.

Various modeling methods have been proposed to describe competitive adsorption, mostly ISAT-based models, such as the ISAT-based Freundlich model (3), ISAT-based Langmuir model (10), ISAT-based PMM (5), and ISAT-based Dubinin–Ashtakhov (DA) model (7). However, because PMM was shown to be the proper one to describe the adsorption isotherms, only this model is discussed in this competition modeling exercise. The assumptions of ISAT-based PMM competition model were discussed systematically by Xia and Ball (5) and Yang et al. (7). Xia and Ball observed that the correlation curves merged together for liquid adsorbates and that a common value of adsorption capacity for all liquid chemicals could be derived (5). However, for solid adsorbates, the adsorbed volumes were much lower at a given ($\epsilon/(Vs)$) in comparison to liquid chemicals. They used packing efficiencies for individual solid chemicals to calibrate the correlation curves. After this calibration, PMM could be applied for competitive modeling. This concept is applicable and used in this study. As presented in **Figure 3**, the correlation curves for EE2 and BPA did not merge. At the same ($\epsilon/(Vs)$), BPA always had a higher adsorbed volume. This calculation also explains the stronger competitive potential for BPA. A packing efficiency could be applied to calibrate the correlation curves. However, it could be clearly observed in **Figure 3** that the difference between EE2 and BPA adsorption isotherms varied for different adsorbents, indicating that packing efficiency of a given adsorbate could be different on different adsorbents. Because only four adsorbents and two adsorbates were used in this study, the relationship between packing efficiency and properties of adsorbates could not be well addressed. Extended work is needed.

Accumulated Adsorption of EE2 and BPA on CNMs. In most of the competitive adsorption experiments, only the adsorption behavior of primary adsorbate was studied. In this study, because both EE2 and BPA concentrations were measured in the competitive

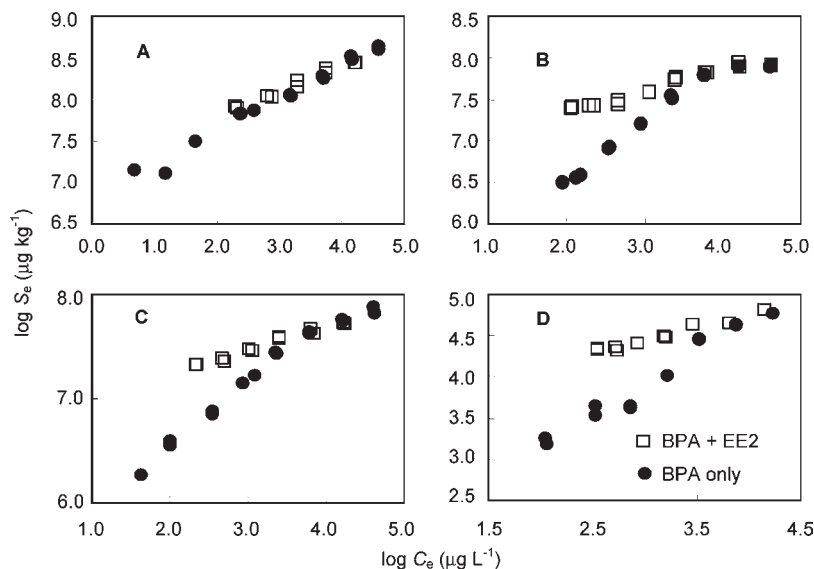


Figure 4. Accumulated adsorption of EE2 and BPA on CNMs. Panels **A**, **B**, **C**, and **D** indicate adsorption of BPA and BPA + EE2 on SWCNTs, MWCNT15, MWCNT50, and fullerene, respectively.

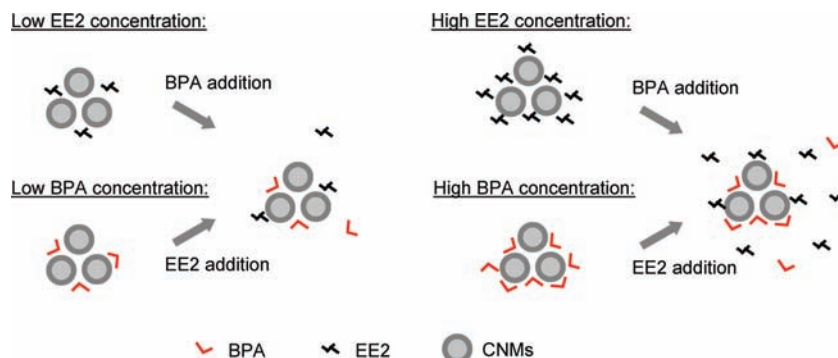


Figure 5. Competitive and complementary adsorption between EE2 and BPA on CNMs. EE2 and BPA may complementarily occupy different adsorption sites, and the apparent adsorption shows both competitive and complementary properties.

adsorption experiments, accumulated EE2 and BPA adsorption could be calculated and compared with individual EE2 and BPA adsorption isotherms. **Figure 4** presents the comparison between BPA adsorption isotherms and BPA/EE2 accumulated adsorption isotherms. Most of the accumulated adsorption isotherms showed higher adsorption than BPA adsorption isotherms, indicating that besides overlapping of adsorption sites, chemicals with different properties may complementarily occupy different adsorption sites. At low concentrations, both BPA and EE2 could be first adsorbed by high-energy sites, such as CNM edges, groove area, and oxygen-containing functional groups (13). Then, competitive interaction was significant. At the same time, chemicals with different properties may have different affinities to different types of adsorption sites, such as BPA to groove area and EE2 to exposed hydrophobic CNM surface. Therefore, the overall adsorption of two chemicals exhibited higher cumulative adsorption than individual ones. As shown in **Figure 4**, for adsorbent with the highest degree of competition (such as SWCNTs), the difference between single-solute adsorption and accumulated bisolute adsorption was small. However, for fullerene, which showed no significant competition, single-solute adsorption and accumulated bisolute adsorption have the most distinct difference.

At high BPA concentrations, the cumulative adsorption was not very significantly different from original adsorption (**Figure 4**). Yang et al. (7) proposed the adsorption of phenanthrene on newly formed pyrene solid particles on the CNM surface. Thus, a big

difference was observed between single-solute adsorption and accumulated bisolute adsorption at high concentrations. Their hypothesis was reasonable because PAHs as well as CNMs comprise benzene rings. The stacking of flat benzene rings is facilitated by π - π interaction and van der Waals forces. However, in this study, the adsorption of secondary chemical (EE2) on adsorbed primary chemical (BPA) is not expected, as confirmed by the result that the adsorption of competitor could be inhibited at high concentration of the primary chemical.

The way that the accumulated adsorption was calculated in **Figure 4** did not distinguish the different properties of EE2 and BPA, such as hydrophobicity and molecular size. In correlation curves, these different properties were considered. Therefore, the accumulated adsorption was also discussed on the basis of the correlation curves. The accumulated adsorbed volumes were much higher than single solutes (**Figure 3**).

Adsorption/Competition Properties and Mechanisms of Different Adsorbents. As compared in **Figures 1** and **2** and in **Table 1**, the significance of competition follows the order SWCNTs > MWCNT15 \approx MWCNT50 > fullerene, whereas the cumulative adsorption showed a reverse sequence: fullerene > MWCNT50 \approx MWCNT15 > SWCNTs. These results are consistent with the hypothesis that different chemicals could compete with each other but, at the same time, occupy different adsorption sites complementarily. As compared for different adsorbents, a higher degree

of competitive adsorption is accompanied by a lower degree of complementary adsorption.

This concept is schematically illustrated in **Figure 5**. At low BPA concentrations, BPA could fit into the groove area with high adsorption energy. Addition of limited concentrations of EE2 could not overcompete with BPA molecules on groove sites. However, the exposed CNM surface is highly hydrophobic and is the adsorption region with high adsorption energy to EE2. Thus, EE2 molecules could be complementarily adsorbed on the CNM surface. As the BPA concentration increases, most of the surface-adsorbed EE2 will also be overcompeted by BPA because of the fit of the BPA butterfly structure on the CNM surface. The overall adsorption does not exceed the BPA adsorption capacity. However, for EE2 adsorption, the competitor BPA would always occupy high adsorption sites, for example, the groove area. Thus, a much stronger competition was observed than in the system where BPA was primary solute and EE2 the competing one.

In competitive adsorption studies, overlapping of adsorption sites has been generally reported in the literature. However, we observed complementary occupation of different adsorption sites by chemicals with different properties. This result indicates that the adsorption sites of a certain adsorbent may be more efficiently used by adsorbate molecules with different structures, especially at low concentrations. Competitive and complementary adsorption should be incorporated into comprehensive modeling for a better description of the behavior of multiple pollutants. However, how to quantitatively describe the overall adsorption is currently unclear, and further study is warranted.

Supporting Information Available: Properties of adsorbates and adsorbents, some complementary information on adsorption, competition and accumulated adsorption. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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