

Article

Single and Competitive Adsorption of 17 α -Ethinylestradiol and Bisphenol A with Estrone, β -Estradiol, and Estriol onto Sediment

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Abstract: The competitive adsorption of bisphenol A (BPA) and 17 α -ethinylestradiol (EE2) with different endocrine disrupting compounds (EDCs), such as estrone (E1), β -estradiol (E2), and estriol (E3) was investigated in the water-sediment system. The primary and interaction effects of coexisted EDCs on the adsorption of BPA and EE2 were studied in binary and multiple systems. The adsorption selectivity of sediment at different initial concentrations of EDCs was also considered, based on the distribution coefficient (β). In binary systems, coexisted EDCs exhibited a positive effect on the adsorption of BPA, while E3 showed a negative effect on the adsorption of EE2. In ternary systems, the interaction of E1*E3 and E2*BPA showed a synergistic effect on the sorption of BPA and EE2, respectively. In quaternary systems, the interaction of E1*E2*E3 showed a synergistic effect on the adsorption of both BPA and EE2. In the quinary system, coexisted EDCs all showed an antagonistic effect on the adsorption of BPA and EE2, which indicated that the coexisted EDCs competed for adsorption with BPA and EE2. EDCs in the E2-EE2-BPA system presented a superior selectivity of sediment with β values of 43.48–87.86. The order of sediment selectivity (E1 > EE2 > E2 > E3 > BPA) in binary systems was in agreement with EDCs' adsorption capacity, which suggested that the adsorption was dominated by partition adsorption.

Keyword: bisphenol A; 17 α -ethinylestradiol; competitive adsorption; sediment; selectivity

1. Introduction

EDCs are compounds that disrupt wildlife's reproductive system by imitating and blocking the activity of natural hormones [1]. The synthetic EDCs 17 α -ethinylestradiol (EE2) and bisphenol A (BPA) are frequently found in wastewater, marine water, and sediments [2,3]. EE2 is generally used in contraceptive pills [4]. Because of the long half-life, the toxicity of EE2 in fish was determined to be 10–50 times greater than estrone (E1) and β -estradiol (E2) [5]. EE2 usually finds its way into the surface water via the wastewater. After entering the water, EE2 is absorbed by sediments until equilibrium is achieved and, then, the excess EE2 is again released into the water. Previous investigations observed high concentrations of EDCs in sediments and to a lesser extent in air and drinking water [6]. BPA is mainly used as a synthetic plasticiser in the chemical industry and exhibited estrogenic active even at micrograms per litre concentrations [7]. E1, E2, and E3 are mainly released by excreta of human and livestock, and were able to reverse the gender of aquatic animals even at low concentrations ($\mu\text{g/L}$) [8,9]. Due to the disorderly discharged sewage and residues from conventional wastewater treatment plants, the EDCs are transferred into the sediment-water system [10]. Furthermore, manure spreading worsens EDC transfer into the sediment-water system [11]. Despite the fact that most of the EDCs in wastewater and manure can be removed via various treatment processes, the remaining concentration still is larger than the maximal theoretical safe concentration.

Increasingly, studies have been conducted that focussed on the behaviour of EDCs in sediment/water [12–14]. To better understand the adsorption in sediment, the distribution and accumulation of EDCs were studied in sediment-water by researchers [15]. Recently, Sun *et al.* [16] studied the adsorption of EDCs onto different size fractions of sediment. Card and co-workers evaluated and predicted the adsorption behaviour of hormones in sediment [17]. The adsorption of four different EDCs was investigated in a sediment-water system, and the environmental fate of EDCs was studied by Li *et al.* [18]. Although the aforementioned studies examined the distribution and adsorption of EDCs in a sediment-water system, competitive adsorption of multiple EDCs in such a system and the selectivity of the sediment were not explored in detail to date.

In the current study, EE2 and BPA were set as the research targets; and the natural EDCs (E1, E2, and E3) were set as the interferents. The objectives of this work were to: (1) determine the primary and interaction effect of coexisting EDCs on EE2 and BPA in binary and multiple competitive adsorption systems; (2) to estimate the adsorption capacity of EDCs in binary systems; and (3) to estimate the selectivity of the sediment for binary and multiple EDCs in the adsorption process. The study aims to provide a theoretical foundation for the adsorption of multiple EDCs in a water-sediment system.

2. Results and Discussion

2.1. Differences in Adsorption Capacity of EE2 and BPA in the Binary System

In the binary-EDCs system, the competitive effects of coexisting EDCs on EE2 and BPA are represented by the included angle ($\tan \theta$) of the linear isotherms. When $\tan \theta > 0$, the adsorption is regarded as promoted by the coexisting EDCs; when $\tan \theta = 0$, there is no competitive effect by the coexisting EDCs; when $\tan \theta < 0$, the adsorption is restrained by the coexisting EDCs. The correlation coefficients of the isotherms were all greater than 0.90, which indicated that the equations were all well fitted.

The specific variations of $\tan \theta$ in both single and binary adsorption systems are shown in Table 1. For BPA, the values for $\tan \theta$ in the binary-EDCs system were all larger than 0, confirming that the coexisting EDCs promote the adsorption of BPA. The adsorption capacity of BPA reached an optimum value in the condition of coexisting with E1. For EE2, the value of $\tan \theta$ is less than 0 when coexisting with E1, E2, and BPA. This result indicated that the presence of E1, E2, and BPA results in a restraining effect on the adsorption of EE2, and E1, E2, and BPA might be competing with EE2 for adsorption binding. The value for $\tan \theta$ was larger than 0 for the condition that EE2 coexisted with E3, which suggests that E3 promoted the adsorption of EE2 and the adsorption reached the optimum value.

Table 1. The effect of coexisting EDCs on EE2 and BPAs in binary adsorption.

EDCs	Parameters	Conditions				
		Single	Coexisted with E1	Coexisted with E2	Coexisted with EE2	Coexisted with E3
BPA	R^2	0.9931	0.9689	0.9658	0.9619	0.9424
	k	0.0072	0.0128	0.0112	0.0083	0.0078
	$\tan \theta_i$	-	0.0057	0.0040	0.0011	0.0006
EDCs	Parameters	Conditions				
		Single	Coexisted with E1	Coexisted with E2	Coexisted with E3	Coexisted with BPA
EE2	R^2	0.9192	0.9687	0.9699	0.9210	0.9340
	k	0.03223	0.0254	0.02705	0.03381	0.03149
	$\tan \theta_i$	-	-0.0068	-0.0052	0.0016	-0.0007

Furthermore, the adsorption capacities of EE2 and BPA in single and binary systems were investigated, and the thermodynamics of EDCs adsorption were fitted according to the Fredilich isotherm (Figures 1 and 2). From the Figure 1, it can be seen that the adsorption capacities of EDCs in the BPA binary system were: BPA < E1, BPA < E2, BPA < EE2, and BPA < E3. For the EE2 binary system, Figure 2 shows that the order of the adsorption capacities of the EDCs in the binary system were: EE2 < E1, EE2 > E2, EE2 > E3, and EE2 > BPA. To explore the order of the adsorption capacities of the EDCs in sediment, the adsorption of E2 and E3 in single and binary system were determined, and the order of the adsorption capacities were: E2 > E3. Liu *et al.* [19] previously regarded the adsorption of EDCs on activated carbon as a physical process in the study of removal methods. In the present study, we equally assumed that the adsorption of EDCs onto sediment was a physical

process and, therefore, the order of adsorption capacities of the EDCs in the binary system would be: E1 > EE2 > E2 > E3 > BPA.

Figure 1. The adsorption capacity of EDCs in the BPA binary system.

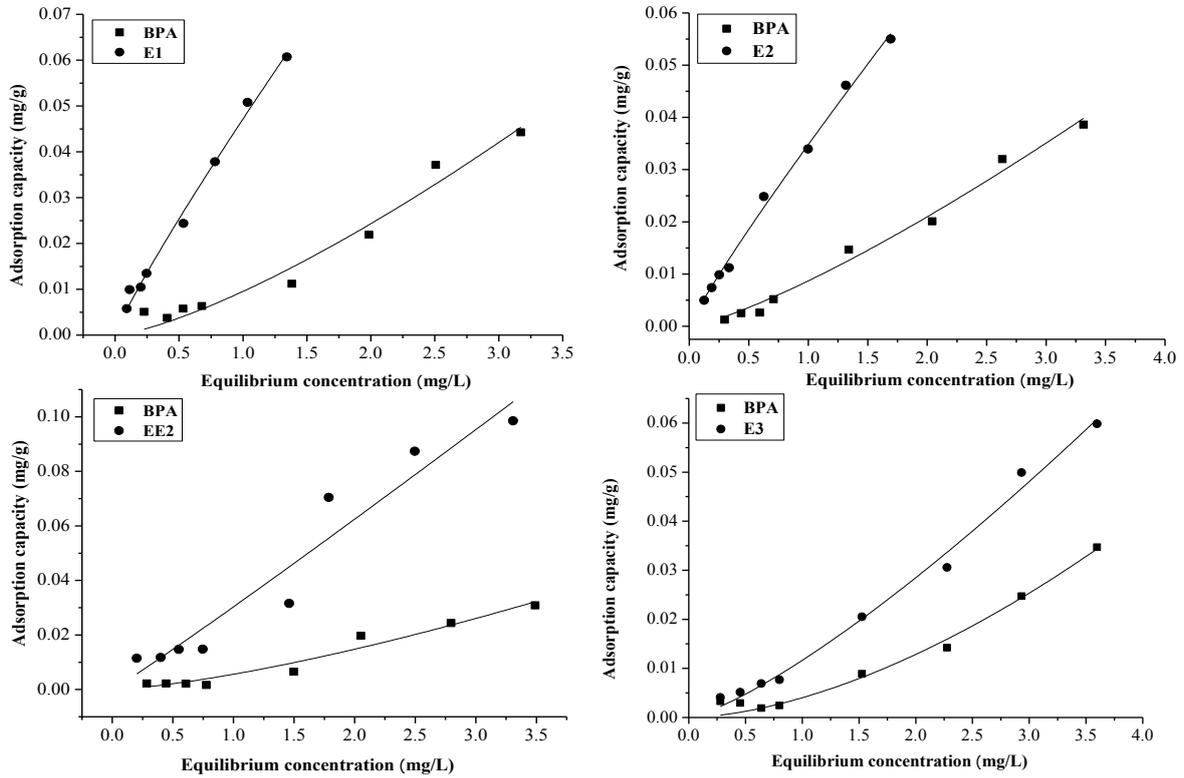
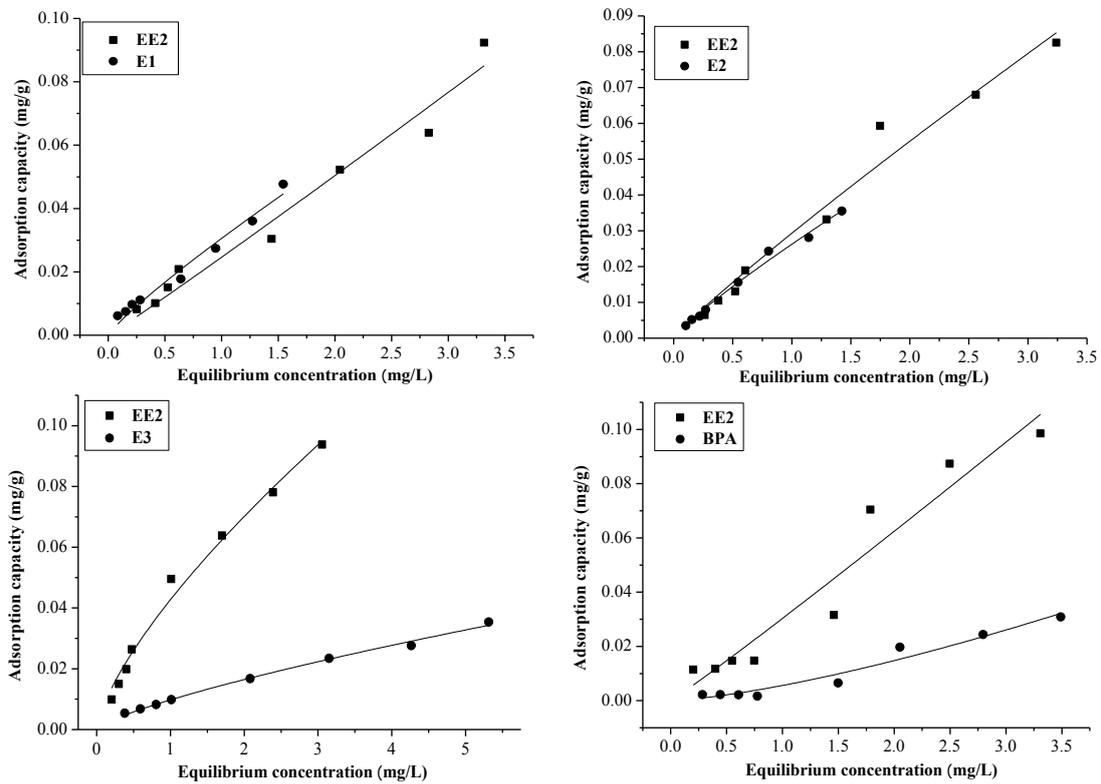


Figure 2. The adsorption capacity of EDCs in the EE2 binary system.



2.2. The Differences of Adsorption Capacity of Multiple EDCs

In multiple-EDCs systems, the competitive effects between EE2 (or BPA) and natural EDCs were equally represented by the included angle ($\tan \theta$) of the isotherms. The difference is: the interactions of coexisting EDCs were the focus of this research. When $\tan \theta > 0$, the adsorption is regarded as promoting synergism between coexisting EDCs; when $\tan \theta = 0$, there is no interaction effect between the coexisting EDCs; when $\tan \theta < 0$, the adsorption is reduced by the antagonistic effect between coexisting EDCs.

2.2.1. The Adsorption of BPA and EE2 in a Ternary EDCs System

The values of $\tan \theta$ are shown in Table 2. The results in Table 2 show that, for BPA, $\tan \theta$ of the ternary EDCs system are all positive, which suggests that the coexisting EDCs synergistically affected the adsorption of BPA. According to the $\tan \theta$ values, this synergistic effect of coexisting EDCs could be induced according to the following sequence: $E1 * E3 > E2 * E3 > E1 * E2$ and $E1 * EE2 > E2 * EE2 > EE2 * E3$. For EE2, the synergistic interaction of coexisting EDCs were in the following order: $E2 * BPA > E1 * E3 > E2 * E3 > E1 * BPA$. The antagonistic effect of coexisting EDCs were as follows: $E1 * E2 > E3 * BPA$, which confirms that $E1 * E2$ and $E3 * BPA$ restrained the adsorption of EE2 and the extent of restraining was: $E1 * E2 > E3 * BPA$.

Table 2. The variation of adsorption capacity of BPA and EE2 in a ternary EDCs system.

EDCs	Parameters	Conditions			
		Single	Coexisted with E1 and E2	Coexisted with E2 and E3	Coexisted with E1 and E3
	R^2	0.9955	0.9868	0.9876	0.9818
	k	0.0072	0.0109	0.0114	0.0122
	$\tan \theta_i$	-	0.0037	0.0042	0.0050
BPA	Parameters	Conditions			
		Single	Coexisted with E2 and EE2	Coexisted with E1 and EE2	Coexisted with EE2 and E3
	R^2	0.9955	0.9909	0.9349	0.9947
	k	0.0072	0.0105	0.0109	0.0094
	$\tan \theta_i$	-	0.0033	0.0037	0.0022
EDCs	Parameters	Conditions			
		Single	Coexisted with E1 and E2	Coexisted with E1 and E3	Coexisted with E2 and E3
	R^2	0.9236	0.9641	0.9922	0.9856
	k	0.0322	0.0241	0.0408	0.0373
	$\tan \theta_i$	-	-0.0081	0.0086	0.0051
EE2	Parameters	Conditions			
		Single	Coexisted with E1 and BPA	Coexisted with E2 and BPA	Coexisted with E3 and BPA
	R^2	0.9236	0.9514	0.9969	0.9884
	k	0.0322	0.0352	0.9029	0.0307
	$\tan \theta_i$	-	0.0030	0.8461	-0.0015

2.2.2. The Adsorption of BPA and EE2 in a Quaternary EDCs System

To better understand the effect of interaction of coexisting EDCs, the adsorption of BPA and EE2 in a quaternary system were studied (Table 3).

Table 3. The variation of adsorption capacity of BPA and EE2 in a quaternary EDCs system.

EDCs	Parameters	Conditions				
		Single	With E1, E2, and EE2	With E1, E2, and E3	With E1, EE2, and E3	With E2, EE2, and E3
BPA	R^2	0.9955	0.9931	0.9952	0.9693	0.9899
	k	0.00715	0.0098	0.0396	0.0058	0.0130
	$\tan \theta_i$	-	0.0026	0.0324	-0.0013	0.0058
EDCs	Parameters	Conditions				
		Single	With E1, E2, and E3	With E1, E2, and BPA	With E1, E3, and BPA	With E2, E3, and BPA
EE2	R^2	0.9236	0.9794	0.9899	0.9965	0.9329
	k	0.0322	0.0396	0.0333	0.0290	0.0255
	$\tan \theta_i$	-	0.0074	0.0011	-0.0032	-0.0067

For the adsorption of BPA and EE2 in the quaternary EDCs system, the influence of ternary interactions by coexisting EDCs was studied. For the adsorption of BPA, the presence of E1*E2*EE2, E1*E2*E3, and E2*EE2*E3 showed synergistic effects, and these ranked according to: E1*E2*E3 > E2*EE2*E3 > E1*E2*EE2. However, the interaction of E1*EE2*E3 showed an antagonistic effect on the adsorption of BPA. For the adsorption of EE2, the presence of E1*E2*E3 and E1*E2*BPA showed a synergistic effect, which was E1*E2*E3 > E1*E2*BPA. Conversely, E1*E3*BPA and E2*E3*BPA showed an antagonistic effect on the adsorption of EE2, and the order was: E2*E3*BPA > E1*E3*BPA.

2.2.3. The Adsorption of BPA and EE2 in a Quinary EDCs System

As it was shown in Table 4, for the adsorption of BPA and EE2, $\tan \theta < 0$ demonstrated that competitive adsorption occurred in the presence of E1, E2, EE2, E3, and E1, E2, E3, BPA, respectively. In the quinary EDCs system, interaction of E1*E2*EE2*E3 showed an antagonistic effect on the adsorption of BPA and E1*E2*E3*BPA antagonistically affected the adsorption of EE2.

Table 4. The variation of adsorption capacity of BPA and EE2 in a quinary EDCs system.

EDCs		BPA		
Parameters	R^2	k	$\tan \theta_i$	
Single	0.9955	0.0072	-	
With E1, E2, EE2, and E3	0.9961	0.0030	-0.0042 (Antagonistic effect)	
EDCs		EE2		
Parameters	R^2	k	$\tan \theta_i$	
Single	0.9236	0.0322	-	
With E1, E2, E3, and BPA	0.9848	0.0212	-0.0110 (Antagonistic effect)	

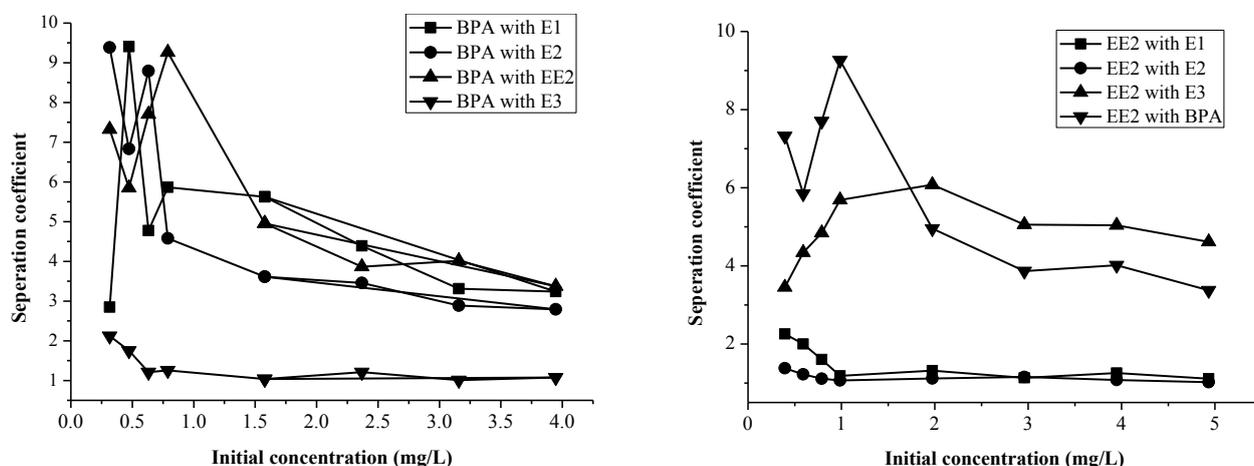
2.3. Selectivity of Sediment for EDCs

2.3.1. Selectivity of Sediment for EDCs in a Binary System

The adsorption of pollutants not only depends on the adsorption capacity and coexisting contaminants, but also on the selectivity of the sediment. The separation coefficients ($\beta_{a/b}$) of the EDCs in binary systems were studied at initial concentrations of 1.0–5.0 mg/L (Figure 3).

In the binary system of BPA, the $\beta_{a/b}$ of the EDCs was in the order of: $\beta_{E1/BPA} > \beta_{EE2/BPA} > \beta_{E2/BPA} > \beta_{E3/BPA}$. In the binary system of EE2-BPA, $\beta_{EE2/BPA}$ was larger than $\beta_{E1/EE2}$, $\beta_{EE2/E2}$, and $\beta_{EE2/E3}$ when the initial concentration was in the range of 0–1 mg/L. When the initial concentration was 1–5 mg/L, $\beta_{EE2/BPA}$ was larger than $\beta_{EE2/E3}$ and the value of $\beta_{E1/EE2}$ was close to $\beta_{EE2/E2}$. Figure 3 infers that the initial concentration of EE2 has a major impact on the selectivity of the sediment. The order of sediment selectivity of EDCs is accordance with the adsorption capacity, which was $E1 > EE2 > E2 > E3 > BPA$. These results show that the higher the selectivity of the sediment, the stronger the adsorption capacity of the EDCs. Furthermore, the results indicate that the adsorption of EDCs onto surface sediment is dominated by partition adsorption.

Figure 3. The separation coefficients ($\beta_{a/b}$) of BPA and EE2 in a binary system.

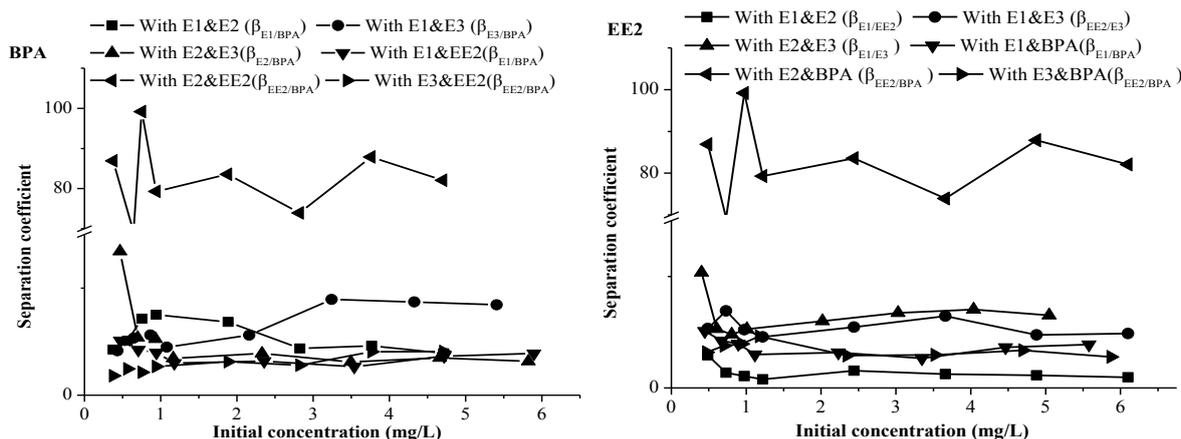


2.3.2. The Selectivity of Sediment for EDCs in a Ternary System

A series of ternary EDCs systems were chosen to analyze the sediment selectivity of adsorption and the adsorption selectivity was measured via $\beta_{a/b}$ (Figure 4).

Figure 4 shows that $\beta_{E1/BPA}$ was in the range of 43.48–87.86 in the E2-EE2-BPA system, which suggest that the selectivity of the sediment for EDCs in the E2-EE2-BPA system was superior to other ternary systems. For the adsorption of BPA, the selectivity of sediment was minimal in the BPA-E3-EE2 system and is in agreement with the results for E3*EE2, which has a weakly promoting effect on the adsorption. For the adsorption of EE2, the selectivity of the sediment showed a minimum value in the EE2-E1-E2 system. This can be attributed to the antagonistic effect of E1 *E2 in the system.

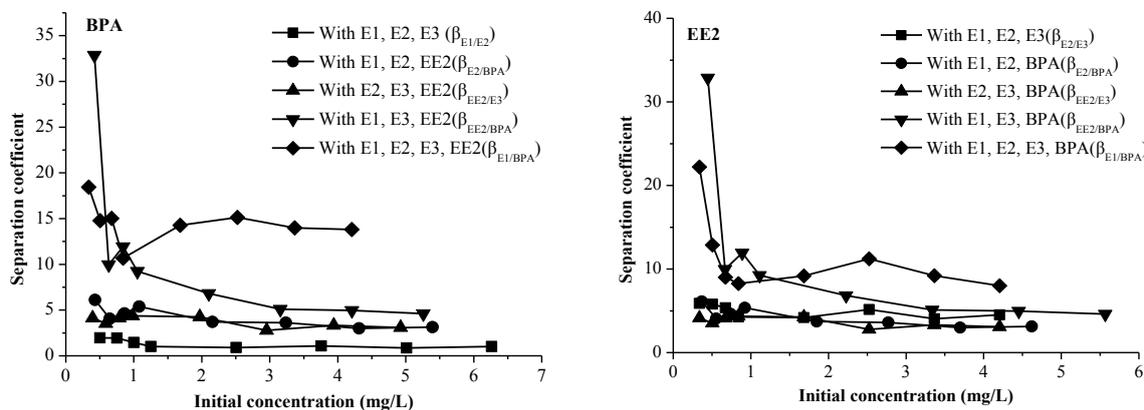
Figure 4. The separation coefficient ($\beta_{a/b}$) of BPA and EE2 in a ternary adsorption system.



2.3.3. The Selectivity of Sediment for EDCs in a Quaternary and Quinary System

To simulate the behaviour of the EDCs in natural water, the adsorption selectivity of BPA and EE2 in both quaternary and quinary system were studied at different initial concentrations (Figure 5). At the initial concentration of 0–1 mg/L, the adsorption selectivity of BPA and EE2 in the E1-E2-EE2-BPA system was obviously superiority and decreased sharply as the initial concentration increased. In the range of 1–5 mg/L, the adsorption selectivity of the EDCs in the quinary system reached its maximum. The selectivity of all EDCs decreased with increasing initial concentration, which suggests that higher concentrations of substrate has a negative effect on the selectivity of the sediment.

Figure 5. The separation coefficient ($\beta_{a/b}$) of BPA and EE2 in a quaternary and quinary adsorption system.



3. Experimental and Methods

3.1. Physicochemical Properties of Sediment

The sediment samples used in this study were directly collected from a depth of 0–5 cm near the Songhua River in Jilin City, China.

3.2. Materials and Chemicals

E1, E2, EE2, and E3 (purity > 97%) were purchased from Sigma-Aldrich (Munich, Germany). Methanol and acetonitrile (HPLC grade) were obtained from Burdick & Jackson (Honeywell, Morristown, NJ, USA). NaOH (AR) and HCl (AR) were purchased from the Beijing Chemical Engineering Factory (Beijing, China). CaCl₂ was purchased from the Xilong Chemical Plant of Shantou, Guangdong. NaN₃ (AR) was obtained from the Tianjin Fuchen Chemical Reagents Factory. Sediments were collected from the Songhua River in the Jilin Province, China.

A 1200-HPLC (Agilent Company, Santa Clara, CA, USA), equipped with two model pumps (G1312A), an in-line degasser (G1322A), a column oven (G1316A), and a fluorescence detector (G1321A), was used for HPLC analysis. The injection loop volume was 20.0 µL, and a Zorbox SB-C18 column (250 mm × 4.6 mm; 5 µm) was used for the separations. A 2-16K centrifuge (Sigma, Munich, Germany), a FA-1004 analytical balance (Shanghai Hengping Science Instrument Company, Shanghai, China), and Milli-Q ultrapure water (Millipore, Billerica, MA, USA) were also used.

3.3. Sorption Isotherms of EDCs

A 5.0 mg/L standard solution of E1, E2, EE2, E3, BPA, and two co-existing EDCs was prepared. Batch experiments were conducted to investigate the adsorption behaviour of the EDCs. For each determination, 0.7 ± 0.0001 g of the surface sediments (SSs) was mixed with 40 mL of the EDCs solution at different concentrations; the concentrations of the EDCs were 0.4, 0.6, 0.8, 1.0, 2.0, 3.0, 4.0, and 5.0 mg/L, respectively. The solutions contained different EDCs and 200 mg/L of NaN₃ to minimise biological activity. NaOH and HCl (both 0.1 mol/L) were used to set the pH to 6.70 ± 0.03 . The conical flask was placed in a shaker for 24 h at room temperature. Each sample was filtered with a 0.45 µm membrane filter and transferred into 2 mL amber vials for high performance liquid chromatography (HPLC) analysis. Duplicate experiments were conducted to account for experimental error and to investigate the reproducibility of the results. A blank experiment was performed as a control.

3.4. Analysis of EDCs

The EDCs were separated and quantified using a gradient elution procedure. The mobile phase was composed of water (A) and methanol (B). The procedure for E1 was 20% A and 80% B; the procedure for E2, EE2, E3, and BPA was 25% A and 75% B. The UV wavelength for compound detection was $\lambda = 280$ nm. The elution procedure for the EDCs was all 30% A and 70% B in binary, ternary, and quaternary systems. The elution procedure settings for all the EDCs were as follows: 0–5 min, 70% B; 5–10 min, 70%–85% B; and 10–18 min, 85% B. The flow rate of the mobile phase was 1.0 mL/min. The column temperature was maintained at 30 °C. The excitation wavelength of the fluorescence detector was fixed at 230 nm, and the emission wavelength was set to 315 nm.

3.5. Variation of Adsorption Capacity

The thermodynamics isotherm of EDCs was simulated via the following linear isotherm:

$$Q_e = kC_e \quad (1)$$

where Q_e is the concentration of the solid-phase (mg/g), C_e is the concentration of the equilibrium solution phase (mg/L), and k is the Langmuir fitting parameter (L/mg). Figure 6 showed the differences of EDCs adsorption.

Figure 6. The included angle of isotherms 1 and 2.

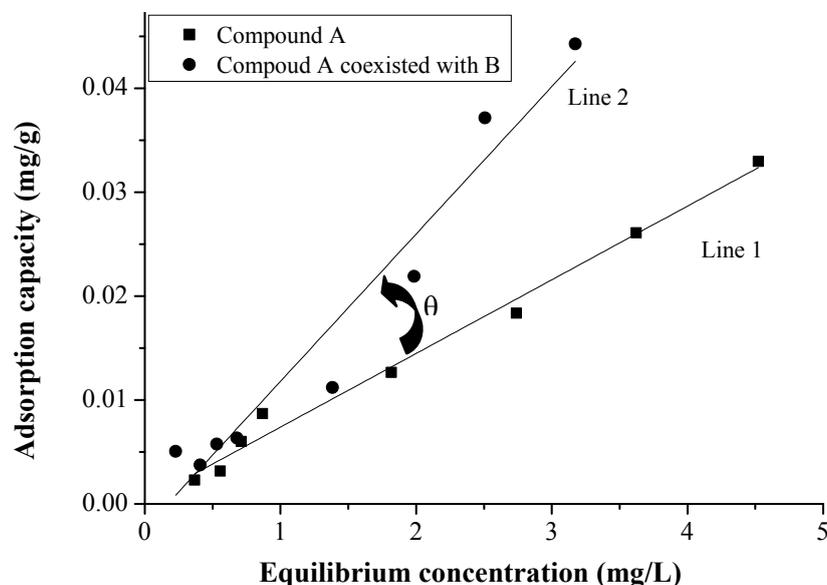


Figure 6 describes the isotherms for two conditions: line 1 is the isotherm of compound A in a single adsorption system, and line 2 is the isotherm of compound A coexisting with B in the binary system. There is an acute angle between line 1 and line 2. To quantify the differences between EDCs under a variety of conditions, the acute angle was calculated using the following equation.

$$\tan \theta = (k_2 - k_1) / (1 + k_1 \times k_2) \quad (2)$$

where k_1 , k_2 are the gradients of line 1 and 2, respectively. Theta (θ) is the angle between line 1 and 2, which indicates the changes in adsorption capacity under two different adsorption conditions. The results show that $\tan \theta$ was in the range of -1 to 1 . The negative value of $\tan \theta$ shows the competitive effect of coexisting compounds on the target compound, whereas positive values of $\tan \theta$ show the advanced effect of coexisting compounds on the target compound.

3.6. The Selectivity of Sediment for EDCs

$$D = V/m (\rho_0/\rho_t - 1) \quad (3)$$

$$B = D_a/D_b \quad (4)$$

where D is partition ratio between the sediment and water, V is the volume of EDCs solution (L), ρ_0 is the concentration of original solution (mg/L), and ρ_t is the solvent concentration when the adsorption reached equilibrium (mg/L), m is the quality of sediment (g). B is the partition coefficient between two components.

4. Conclusions

The interaction effect of coexisted EDCs on BPA and EE2, and the order of adsorption capacity of BPA and EE2 in binary and multiple adsorption systems were investigated. Additionally, the adsorption selectivity of sediment for EDCs and the influence of different initial concentrations was determined, based on the distribution coefficient (β). The following conclusion can be drawn:

(1) The order of selectivity is accordance with the adsorption capacity ($E1 > EE2 > E2 > E3 > BPA$) showed the adsorption of EDCs in sediment is dominated in physical adsorption.

(2) The EDCs in ternary and quinary system shows a high selectivity of sediment.

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Author Contributions

Yu Li, experimental design and manuscript organization; Cheng Zhang, experimental design, sample analysis, data processing and manuscript preparation; Shanshan Li, language improvement; Changzhi Zhou and Xiaopeng Li, sample analysis. All authors read and approved the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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