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Sorption characteristics and factors affecting the adsorption behavior of bisphenol A and 17β-estradiol/ethinyl estradiol in river- and farmland-based artificial groundwater recharge with reclaimed water

Weifang Ma[a,*], Chao Nie[a], Xiaoqi Gao[a], Dan Qu[a], Xiaoxiu Lun[a], Bin Chen[b]

[a] *College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China, emails: mpeggy@163.com (W. Ma), niechao1205@126.com (C. Nie), gaoxiaoqi36@sina.com (X. Gao), qudana@163.com (D. Qu), lunxiaoxiu@bjfu.edu.cn (X. Lun)*

[b] *School of Environment and Natural Resource, Renmin University of China, Beijing 100872, China, email: chenbin@163.com*

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ABSTRACT

Endocrine-disrupting chemicals (EDCs) in river- and farmland-based natural groundwater recharge using reclaimed municipal wastewater pose a major threat to groundwater-based drinking water supplies in Beijing, China. The sorption characteristics of three selected typical EDCs, bisphenol A (BPA), 17β-estradiol (E2), and ethinyl estradiol (EE2) were investigated in river sediment– and farmland soil–water systems to simulate the sorption process and the factors influencing sorption during reclaimed water recharge. The results showed that the two-compartment first-order model fitted the kinetics of sorption very well ($R^2 > 0.99$). The fast sorption rates for E2 and EE2 onto soil were higher than those onto sediment, while the rate was different for BPA. The partitioning and π–π bonds might be a relatively more important mechanism for the sorption of BPA onto sediment, while surface adsorption contributed significantly to E2 and EE2 sorption onto soil. The fast sorption rate was negatively correlated to the ΔG values in all adsorption media. The average removal rate (η) of the three EDCs was in the order $\eta_{(\mathrm{BPA})} < \eta_{(17\beta-\mathrm{E2})} < \eta_{(\mathrm{EE2})}$ and soil < sediment which showed that E2 was easily adsorbed onto sediment, while BPA was more mobile in the farmland-based artificial groundwater recharge system. The absolute free energy values of ΔG were less than 40 kJ/mol, indicating that the adsorption process consisted primarily of physical sorption. With an increase in pH value, the adsorption capacity and partition coefficient clearly decreased, especially when the pH value was higher than the pKa values of the EDCs. The amounts of BPA, E2, and EE2 that were adsorbed increased with an increase in ionic strength, especially for the E2 and EE2, because the amount of ion exchange and polar sorption would increase. However, these values decreased with an increase in temperature. These results could be useful for predicting a potential pathway for removal and the ecological risks of EDCs when using reclaimed municipal wastewater for aquifer recharge.

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*Corresponding author.

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1. Introduction

China has been suffering from water shortages, especially in the arid northern areas. The reclaimed water can transfer Endocrine-disrupting chemicals (EDCs) into soil and groundwater when it is used for irrigation and groundwater recharge. For instance, approximately 8.2×10^8 cubic meters of reclaimed water is currently reused in Beijing for the purposes of agricultural and landscape irrigation, river, and industry reuse. The occurrence of EDCs in reclaimed water, river, and groundwater has recently raised a serious public concern. The release of EDCs from reclaimed wastewater treatment plants (RWWTPs) and the subsequent occurrence of EDCs in receiving rivers and farmland soils can impact groundwater quality. Worldwide concern about the presence and fate of EDCs in the environment has increased in recent years due to their toxicity, even at low concentrations [1,2]. Various studies have reported on the occurrence of many types of contaminants with an endocrine-disrupting function in the aquatic and terrestrial environment [3,4]. EDCs accounted for 27% of the priority organic compounds detected during groundwater recharge in China [5]. EDCs are difficult to completely remove from reclaimed water [6–8], meaning that some of them are introduced into the groundwater, thereby posing risks to the groundwater and thus humans. Over the last two decades, the concentration of nonylphenol (NP), with an average value of 947.79 ng/L, was the highest for the priority organic compounds, with NP being ranked before bisphenol A (47.6 ng/L) and EE2 (87.4 ng/L) [9].

The sorption of EDCs onto river sediment or farmland soil plays a crucial role in the process of recharge with reclaimed water. It has been reported that the hydrophobic organic contaminants are mostly distributed on suspended solids and particularly in the bottom sediment rather than in the aqueous phase [10–12]. Previous research has shown that the adsorption of selected EDCs is proportional to the fraction of organic matter (OM) in sediment or soil [3]. Sweeney et al. [13] have identified the affinity for sorption of 17β-estradiol (E2) in soil–water systems appeared to be associated with the specific surface area and/or the cation-exchange capacity (CEC) of the soil with correlations to mineral particle size and OM content [14]. Several studies have shown that the π–π bonds formed between BPA and nonhydrolyzable carbon (NHC) or black carbon (BC) may be stronger than those between ethinyl estradiol (EE2) and either NHC or BC [15]. The comparison of the K_{HW} (hexadecane–water partition coefficient) normalized adsorption coefficient between EDCs and several poly-aromatic hydrocarbons indicated that the π–π electron donor–acceptor system is an important mechanism for the adsorption of benzene ring containing chemicals on carbon nanomaterials. BPA has a unique ability to adsorb because of its "butterfly" structure of two benzene rings [1,16]. The adsorption behavior and biodegradation have been studied in many countries, but studies are rare regarding the sorption characteristics and the factors influencing EDCs in river- and farmland-based artificial groundwater recharge with reclaimed water [17].

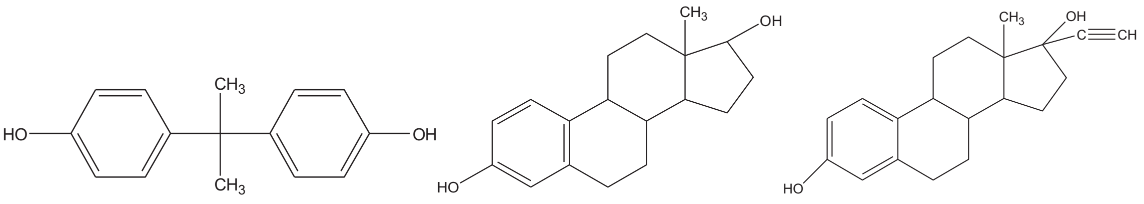
The adsorption characteristics of EDCs varied greatly in different sediment and soils, usually being affected by environmental conditions, which increased the uncertainty of the risk associated with the application of reclaimed water to irrigation and groundwater recharge. The purpose of the present study was to investigate the kinetics and thermodynamic properties of BPA, E2, and EE2 sorption onto sediment and soil; and to evaluate the factors affecting the adsorption behaviors (such as temperature, pH, and ionic strength); thus, supporting the development of EDC pollution prevention and control measures during river- or farmland-based artificial groundwater recharge using reclaimed water in China.

2. Materials and methods

2.1. Soils and chemicals

Sediment and farmland soil were collected from the Chaobai River and farmland at depths of 0–30 cm in Beijing (Table 1), China. The samples were freeze-dried for 48 h and passed through a 2-mm sieve. The standards for bisphenol A (BPA), 17β-estradiol (E2), and ethinyl estradiol (EE2) were obtained from Sigma-Aldrich (USA). Some of their physicochemical properties are shown in Table 2, and their structures are provided in Fig. 1.

The specific surface areas and micropore volume were determined by an Autosorb-iQ-C (Quantachrome, Boynton Beach, FL, USA) using the multi-point and HK (Horvath–Kawazoe) methods. The identities of the functional groups present were obtained on a Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer (Thermo Fisher Scientific, Inc.,



BPA 17β-E2 EE2

Fig. 1. Chemical structures of the three EDCs.

USA). CEC was determined following the procedures defined by Chapman [18]. Total organic carbon (TOC) was determined using a solid TOC analyzer (SCSH, TOC-VCPH, Japan) [19].

A stock solution of EDCs was prepared in MeOH and stored at −18°C in the dark. Ultra performance liquid chromatography grade methanol (MeOH), acetonitrile (ACN), and acetone were purchased from Fisher (USA). Stock solutions (0.5 g/L) of each standard were prepared in MeOH and stored at −18°C in the dark. To obtain a standard curve with different concentrations (5–500 μg/L) before instrumental analysis, the stock solutions were diluted using MeOH as solvent.

Before instrumental determination, the EDCs in the samples required concentration and purification. The cartridges Oasis HLB (200 mg, 6 mL) from Waters Corporation (USA) were used for solid phase extraction. The sorption equilibrium water sample was filtered through a 0.45-μm glass filter membrane (Whatman, UK), and acidified to pH 3 by adding a few drops of 1 M HCl within 12 h of sampling. Afterward, the acidified water sample was introduced to an Oasis HLB cartridge (Waters, 6 mL × 200 mg), which was activated by acetonitrile, methanol, and ultrapure water for solid phase extraction at a flow rate of 5 cm/min. High-purity water was produced using a Milli-Q Plus system (Millipore, USA).

2.2. Sorption experiments

The artificial reclaimed water used for lab-scale experiments was tertiary effluent from the YinWenJiChao Reclaimed Water Treatment Plant in Beijing. In this plant, the process stages are ozone oxidation, a membrane bioreactor, chemical phosphorus removal, disinfection, and constructed wetland flow through a constructed wetland. The water samples for this study were collected and stored in the dark for a maximum of 3 d. The main chemical characteristics of the artificial recharge water were as follows: COD 21 mg/L, NH_4^+ 0.3 mg/L, Ca^{2+} 56 mg/L, Mg^{2+} 21 mg/L, TN 3.7 mg/L, TP 0.3 mg/L, SO_4^{2-} 29 mg/L, HCO_3^- 56 mg/L, and Cl^- 68 mg/L.

Batch equilibrium sorption studies were used to identify the sorption of the three EDCs onto sediment and soil. Soil (or sediment) and reclaimed water (containing 200 mg/L NaN_3 as a biocide) were added to a 500-mL bottle at a ratio of 1:50 (w/v). A total of 300 mL of solutions of the individual compounds with different concentrations (50–500 μg/L for BPA, E2, and EE2) were added to the soil–water system at the beginning of each experiment. A preliminary study showed that adsorption of the EDCs reached equilibrium within 24 h at 20 and 40°C. The soil–water systems were shaken in a mechanical shaker for 24 h at 150 rpm. The bottles were centrifuged at 3,000 rpm for 20 min after equilibration. The supernatants were filtered through Whatman glass fiber filters (GF/C, 0.45 mm). All of the sorption tests as well as the blanks were performed in triplicate.

2.3. Factors affecting the adsorption behavior of sediment and soil

The effects of different values of pH, ionic strength, and temperature on the adsorption ability of BPA, E2, and EE2 onto sediment and soil were studied. The pH of the sediment mixture was adjusted from 2 to 12 using 0.1 mol/L HCl and 0.1 mol/L NaOH to investigate its influence on equilibrium adsorption. Ionic strength (0.01–0.1 mol/L) was changed by adding different amounts of $CaCl_2$ to the water–sediment solution. Temperatures of 20 and 40°C were selected to evaluate the influence of temperature on the adsorption characteristics of EDCs onto the sediment.

2.4. Data analysis

The two-compartment first-order kinetic model (Eq. (1)) was used to describe the sorption kinetics of BPA, E2, and EE2.

$$q_t/q_e = f_1(1 - e^{-k_1 t}) + f_2(1 - e^{-k_2 t}) \tag{1}$$

where t(h) is the reaction time, and q_t and q_e (μg/g) are the concentrations at time t and the equilibrium concentration of EDCs absorbed on the sorbent matrix, respectively. K_1(1/h) and k_2(1/h) represent the sorption rate constants of the fast and slow sorption compartments, respectively; and f_1 and f_2 represent the fractions of the fast and slow compartments, respectively, with $f_1 + f_2 = 1$.

The Freundlich model is an empirical equation, which was used to fit measured sorption isotherm data as follows:

$$\log q_e = \log K_f + n \log C_e \tag{2}$$

where C_e (μg/L) is the equilibrium BPA, E2, and EE2 aqueous concentration, K_f [(μg/g)/(μg/L^{-1})^n] is the Freundlich sorption coefficient, and n is the isotherm linearity index. The single-point distribution coefficient (K_d) at ($C_e = 500$ μg/L) was calculated from the Freundlich parameters:

$$K_d = q_e/C_e \tag{3}$$

According to the Gibbs equation, the relationship of K_d and 1/T at different temperatures can be described by Eq. (4):

$$\ln K_d = \Delta G/RT \tag{4}$$

3. Results and discussion

3.1. The kinetics of sorption of the three EDCs and the contribution of fast sorption

To obtain the adsorption mechanism of BPA, E2, and EE2 onto sediment and soil, the relationship between the adsorption time and amount was investigated (Fig. 2). The results showed that the adsorption amount increased quickly in the first 10 min and rose slowly up to equilibrium concentration. The fast sorption was primary throughout the entire sorption process. The two-compartment first-order model fitted the kinetics of sorption quite well ($R^2 > 0.990$) (Fig. 2, Table 3). The physicochemical properties of the sediment and soil are summarized in Table 1. The fast sorption rate constants of BPA, E2, and EE2 were 2.61, 2.28, and 1.99 h^{-1} for sediment and 2.04, 2.31, and 2.68 h^{-1} for farmland soils, respectively. The fast sorption rate k_1 was much greater than k_2. Fast sorption dominated the sorption process for the initial 5 h. Then, the slow sorption compartment gradually increased until the adsorption equilibrium was reached. The fast sorption rates onto soil, k_1 for E2 and EE2 were higher onto soil (OM 2.5%) and were higher than those onto sediment (OM 4.5%), while the situation is different for BPA, indicating that the fast sorption rates for E2 and EE2 were related to the specific surface area rather than the amount of OM. The various functional groups such as aromatic C–O, hydroxyl group, and methylene C–H were detected by FT-IR absorption spectra (Fig. 3) in the sediment. For sediment, the high content of soil OM promoted the adsorption process, especially for BPA, because BPA has two benzene rings that promote the formation of π–π bonds which then contribute greatly to surface adsorption. The fast sorption was ascribed to the partitioning function and surface sorption, while slow sorption was due to pore filling [20].

The average amount of adsorption of BPA, E2, and EE2 onto sediments was higher than the amounts adsorbed onto soils. Furthermore, the ratios between the different compartment fractions (f_1/f_2) for the three EDCs were also comparable among the samples, indicating the predominant role of the fast sorption compartment process during the sorption process. The total sorption amount of the three EDCs on soil and sediment was in the order of EE2 > E2 > BPA. A similar order of the sorption of EDCs onto soil has been reported by Li et al. and Ying [21,22]. Hydrophobicity was considered to be the major mechanism for the sorption of EDCs onto soil, which was responsible for the same order of sorption affinity and log K_{OW} (EE2 > E2 > BPA) [16]. The f_1 values for BPA, E2, and EE2 in soil were all 0.97, while the values were 0.97, 0.98, and 0.99 in sediment. These results indicated that the sorption was influenced by the physicochemical properties of the EDCs, and the TOC and amorphous structure of OM in the soil. Liu et al. proposed that the different sorption behaviors correspond to the organic fraction of the soil with amorphous and condensed structures [23].

3.2. The sorption isotherms of the three EDCs

Adsorption plays an important role in the fate of BPA, E2, and EE2 in the soil–water system during reclaimed water recharge [14,24]. The sorption isotherms of these three compounds fitted the Freundlich model well (Fig. 4 and Table 4). As shown in Table 4, the average removal rate (η) of the three EDCs in the soil–water system was in the order $\eta_{(BPA)} < \eta_{(17\beta-E2)} < \eta_{(EE2)}$ and soil < sediment. E2 is

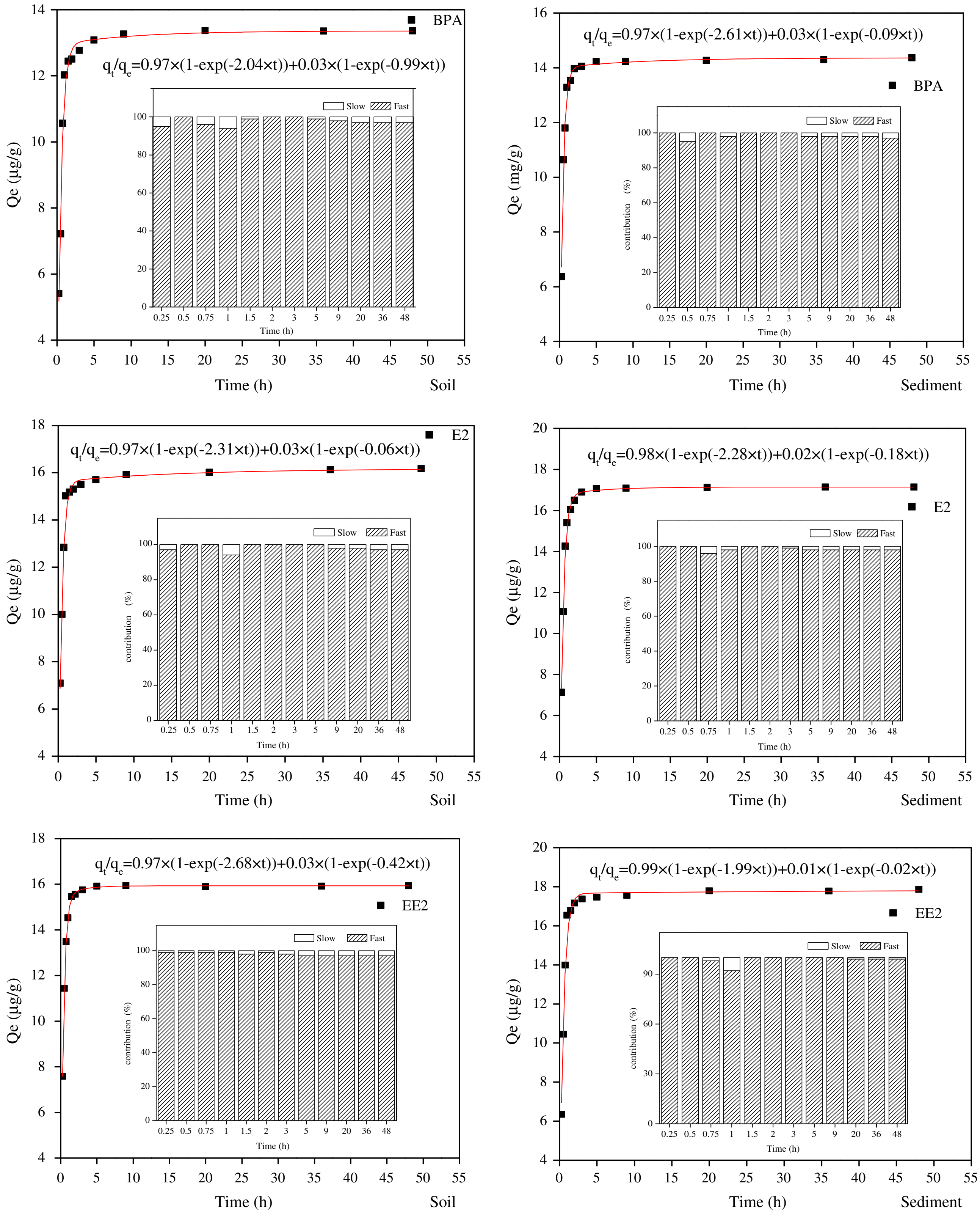


Fig. 2. Sorption kinetics of BPA, E2, and EE2 in soil and sediment, and the fitting results for the two-compartment first-order model.

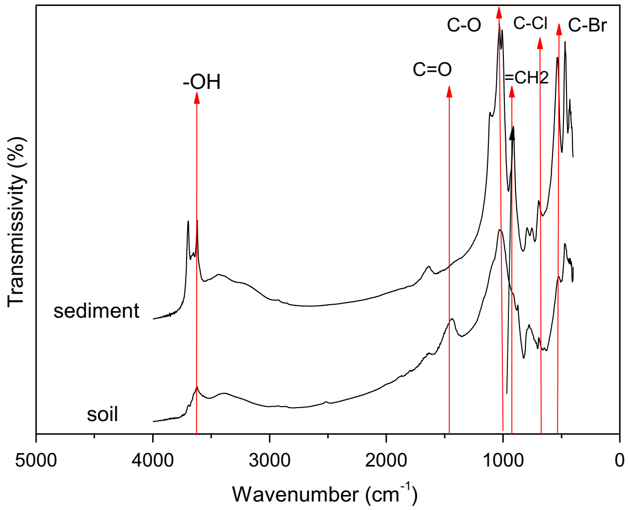


Fig. 3. FT-IR spectra of sediment and soil.

easily adsorbed onto soil, while BPA is more mobile. The soil showed a stronger sorption affinity for both E2 and EE2 than for BPA. Similar orders for the sorption of EDCs sorption on soil from South Australia have been reported by Ying and Kookana [22], but E2 showed a weaker adsorption than that of EE2 in the result of Li et al. [17]. This finding indicated that the order of sorption of these compounds was consistent with the physicochemical properties of the chemicals and the prosperities of the soil (Tables 1 and 2; Fig. 1).

The sediment exerted a nonlinear sorption of EDCs, especially for BPA with a value of n of 0.729, which was ascribed to surface sorption and concurrent partitioning into the residual OM phase. In contrast, the specific surface area of sediment was lower than that of farmland soil, which suggested that partitioning and π–π bonds may be a relatively more important mechanism for the sorption of BPA onto sediment. The K_d value was in the order of $K_{d(BPA)} < K_{d(17\beta-E2)} < K_{d(EE2)}$ and $K_{d(soil)} < K_{d(sediment)}$ which represented the partitioning coefficient. The higher hydrophobicity of the EDCs might account for their stronger affinity for soil and sediment. The pore-filling mechanism was not a major mechanism for BPA, E2, and EE2 sorption because the total pore volume was only 0.0039 and 0.0043 cm^3/g and the pores were macroporous in size. The results agreed well with the research of Li et al. [21]. Furthermore, the sorption ability was depended on the aqueous concentration of the EDCs. The total adsorption amount increased slowly with an increase in concentration due to site limitation in the binding of organic pollutants on the rigid surfaces. A positive correlation between the organic carbon content and soil or sediment sorption capacity was observed. The diverse functional groups such as hydroxyl, methyl C–H, aromatic C=O and C=C, C–$(CH_3)_3$, and aromatic C–H were detected by FTIR spectra and were correlated with K_{oc} (affinity parameter normalized to TOC). The BPA molecule has two benzene rings which promoted the formation of π–π bonds that then contributed greatly to surface adsorption. Several studies refer to the observation that the normalized K_{oc} depends on the organic content of the soil and the specific characteristics of the OM [25–27].

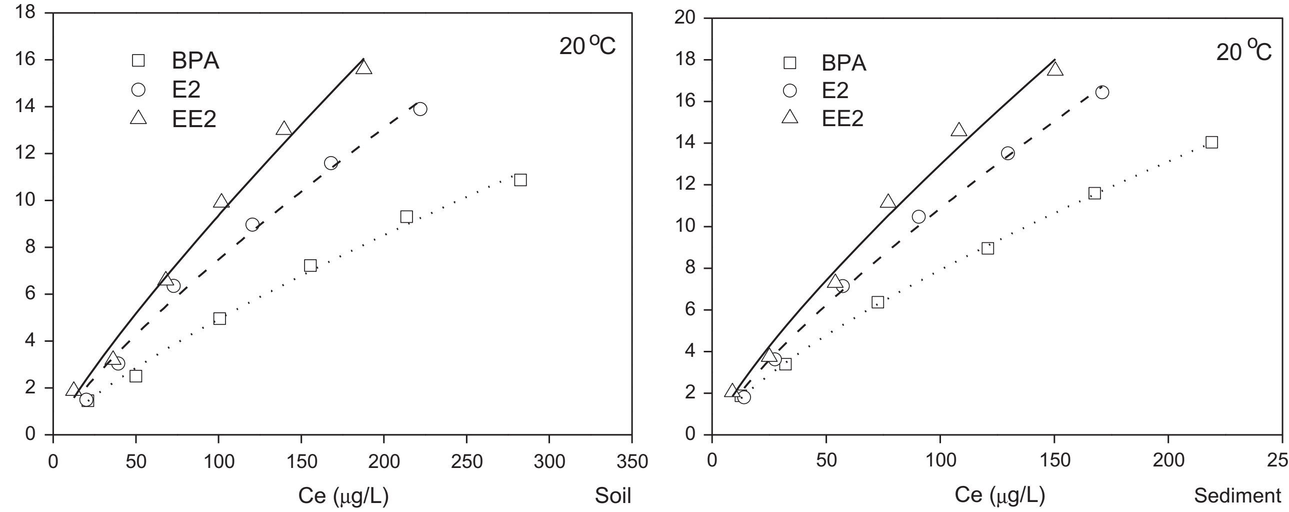


Fig. 4. The sorption isotherms of BPA, E2, and EE2 onto sediment and soil at 20˚C.

Table 1
The physicochemical properties of sediment and soil

	Site	CEC (cmol/kg)	Organic matter (g/kg)	Sand: silt:clay (%)	Total phosphorus (g/kg)	Total nitrogen (g/kg)	Specific surface area (m^2/g)	Pore volume (cm^3/g)
Sediment	N40.13° E116.67°	18.58	44.63	49:33:18	0.789	44.63	11.6482	0.0043
Farmland soil	N39.55° E116.33°	24.90	25.29	50:27:23	1.042	25.29	13.4548	0.0039

Table 2
The properties of the three EDCs

	Molecular formula	Molecular weight (g/mol)	CAS no.	Water solubility (mg/L)	Vapor pressure (Pa)	log K_{ow}	pKa
BPA	$C_{15}H_{16}O_2$	228.29	80–05–7	120–300	4×10^{-8}	3.6	9.6–10.2
17β-E2	$C_{18}H_{24}O_2$	272.38	50–28–2	13.0	3×10^{-8}	3.9	10.71
EE2	$C_{20}H_{24}O_2$	296.40	57–63–6	4.8	6×10^{-9}	4.1	10.4

Table 3
Summary of the model-fitting results for BPA, E2, and EE2 for the studied samples

		Two-compartment first–order kinetic						
Sample	EDCs	f_1	f_2	f_1/f_2	K_1	K_2	K_1/K_2	R^2
Sediment	BPA	0.974	0.025	39.0	2.606	0.0896	29.1	0.990
	17β-E2	0.977	0.023	42.5	2.282	0.1803	12.7	0.993
	EE2	0.989	0.011	89.9	1.99	0.0222	89.6	0.977
Farmland soil	BPA	0.968	0.032	30.3	2.036	0.0992	20.5	0.975
	17β-E2	0.966	0.034	28.4	2.308	0.0601	38.4	0.981
	EE2	0.967	0.033	29.3	2.677	0.4283	6.3	0.999

Table 4
The model-fitting parameters for adsorption isotherms

Sample	Temperature (℃)	EDC	Average removal rate/η	K_d	K_{oc}	K_f	n	R^2
Farmland soil	20	BPA	0.4930	0.0373	1.4749	0.1201	0.8027	0.9978
		E2	0.5956	0.0614	2.4278	0.1803	0.8088	0.9885
		EE2	0.6641	0.0824	3.2582	0.1815	0.8561	0.9887
Sediment	20	BPA	0.6334	0.0587	1.3153	0.2757	0.7291	0.9995
		E2	0.6979	0.0930	2.0838	0.2704	0.8022	0.9956
		EE2	0.7452	0.1141	2.5566	0.3162	0.8070	0.9860
Farmland soil	40	BPA	0.376	0.0219	0.8659	0.0843	0.7680	0.9478
		E2	0.498	0.0459	1.8149	0.1304	0.8193	0.9815
		EE2	0.501	0.0535	2.1154	0.1004	0.8840	0.9817
Sediment	40	BPA	0.4708	0.0313	0.7013	0.1124	0.8029	0.9981
		E2	0.6265	0.0691	1.5483	0.1973	0.8116	0.9879
		EE2	0.6328	0.0713	1.5976	0.1782	0.8354	0.9849

The ΔG values calculated with the Gibbs equation are listed in Table 5. The negative ΔG value was between −3.80 and −4.80, indicating a spontaneous adsorption of BPA, E2, and EE2 from solution to the soil and sediment surface. The ΔG value for BPA was lower in the sediment than in farmland soil, which

Table 5
Sorption free energy of the EDCs in soils

ΔG (kJ/mol)	BPA	E2	EE2
Sediment	−4.44	−4.39	−4.77
Farmland soil	−3.80	−4.79	−4.80

was in the same order as the fast sorption rate. In contrast, the Δ*G* for E2 and EE2 was in the opposite order in sediment and soil, which was in the same order as fast sorption rate. The result showed that the fast sorption rate was negatively correlated to the Δ*G* values in different adsorption media. The standard Gibbs free energy value increased with the increasing temperature, which meant that the sorption reaction decreased. However, the Δ*G* values were favorable because the enthalpy release overcame the unfavorable entropic change [28].

3.3. Effect of temperature on the sorption of three EDCs

The adsorption capacity of BPA, E2, and EE2 onto sediment and soil at 500 μg/L decreased by 29.15, 11.51, and 14.59%; and 28.16, 12.47, and 14.46%, respectively, when temperature increased from 20 to 40℃, because the adsorption process is an exothermic reaction (Fig. 5). It can be clearly seen that the sorption of BPA, E2, and EE2 in sediment and soil well fitted the Freundlich model in the temperature range between 20 and 40℃ and that the range of the sorption saturation amount of the EDCs decreased when the temperature increased. The K_d and K_f for the sorption of BPA, E2, and EE2 onto sediment decreased 47, 27, and 38%; and 59, 27, and 44% at a temperature of 40℃ compared to 20℃, respectively, which showed that the partitioning function and the adsorption capacity decreased. The same decreasing trend of K_d and K_f for the sorption of BPA, E2, and EE2 onto soil was observed. When the temperature increased, the ion exchange and polar sorption would decrease, while the solubility of the EDCs would increase [29]. With the temperature increasing, the amount of soluble TOC increased and the diversity of functional groups decreased, which reduced the *π*–*π* bonding of the BPA onto the sediment. Therefore, the equilibrium adsorption capacity of the BPA onto sediment decreased more than that for soil. As a result, the amount of EDCs entering the sediment phase would decrease at the equilibration point at a higher temperature.

3.4. The effect of pH on the adsorption of the three EDCs

The equilibrium adsorbed quantities of BPA, E2, and EE2 decreased with an increase in pH (2–12). When the pH values changed from 2 to 4, both the Q_e and K_d remained almost unchanged, but when the pH was increased above six, both Q_e and K_d were apparently decreased at different initial concentrations (Fig. 6). The adsorption amounts of BPA, E2, and EE2 decreased 17.58, 12.52, and 18.15% when the pH increased from 4 to 10 because pH changes can affect the surface charge of the sediment. The surface charge of the sediment was predominantly negative when the pH was higher than 9. BPA, E2, and EE2 can be expected to become negatively charged ions above pH 10.0 because the pKa values for BPA, E2, and EE2

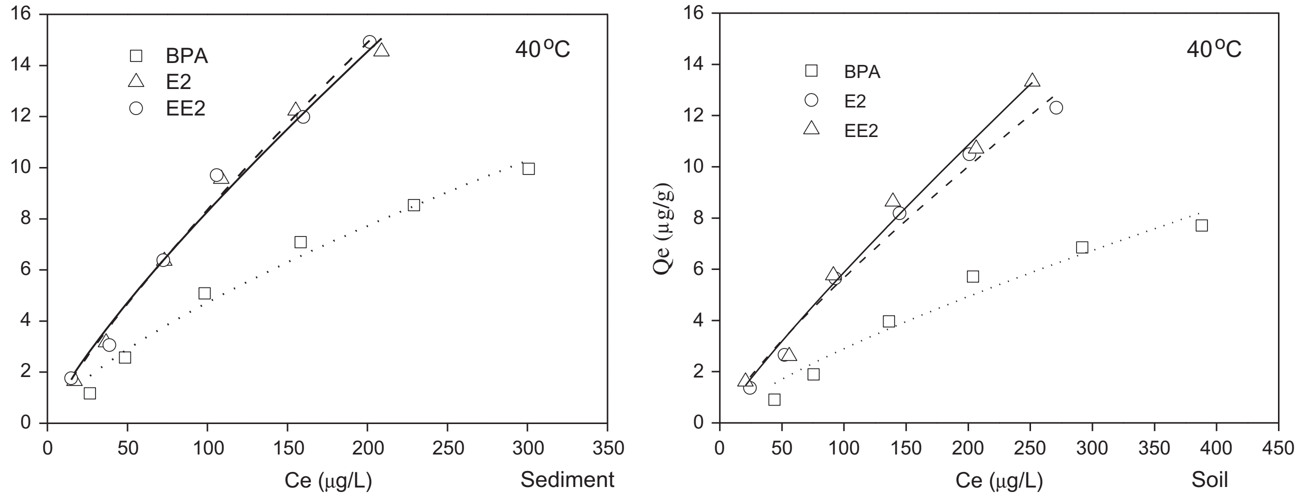


Fig. 5. The sorption isotherms of BPA, E2, and EE2 onto sediment at 40℃.

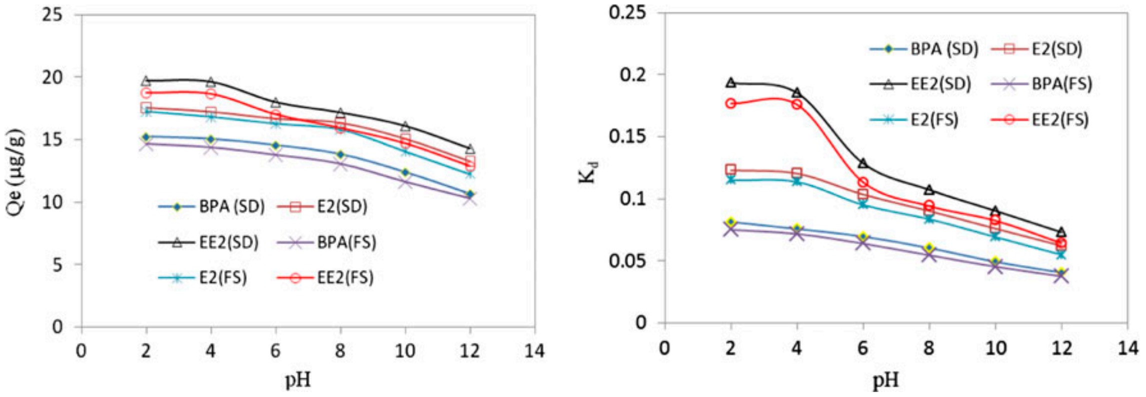


Fig. 6. The effect of pH on amounts adsorbed and the distribution coefficients of EDCs. (SD samples referred as sediment. FS samples referred as farmland soil).

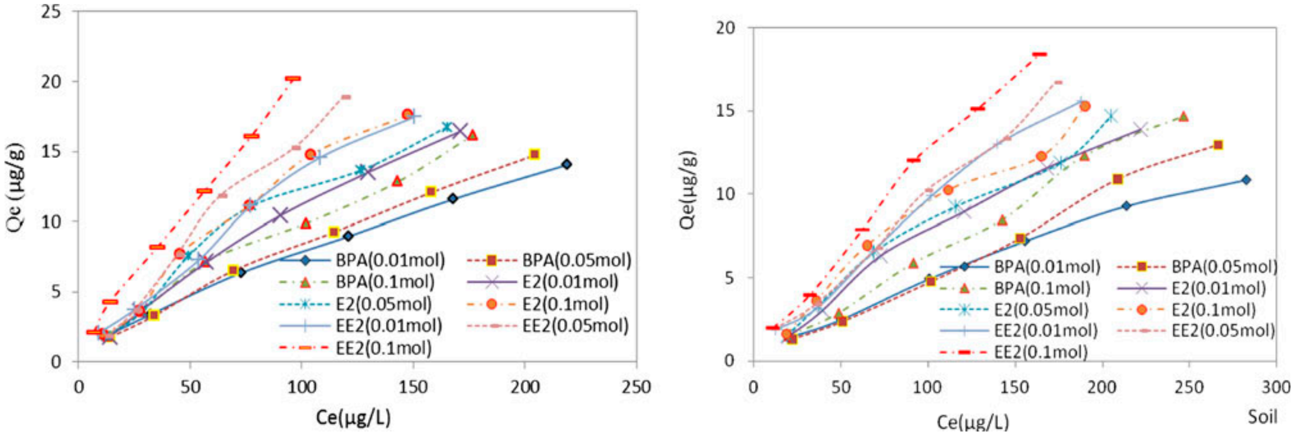


Fig. 7. Effects of ionic strength on the amounts of EDCs adsorbed onto sediment and soil.

molecules are 10.3 ± 0.2, 10.4 ± 0.03, and 10.5 ± 0.01, respectively [30]. At a lower pH, the hydrogen bonding between functional groups (such as the hydroxyl group and carboxyl group) of the EDCs might play a certain role in the adsorption of the EDCs. The siloxane (Si–O) group might be converted to Si–OH, and the surface of the sediment would also be surrounded by the hydronium ions which enhance the interaction of the unionized BPA, E2, and EE2 molecules with the binding sites of the sediment by more attractive forces [28,31,32]. However, BPA, E2, and EE2 all remain neutral molecules when the pH of the water–soil system went below their pKa values. Although the sediment surface was negatively charged with OH^- ions, the negative charge produced a weaker force on the neutral molecular form. When the pH was higher than the pKa, the EDCs tended to have the deprotonated form and thus were negatively charged ions. The repulsive electrostatic interactions decreased the adsorption of the EDCs onto the sediment [33]. The combined effects resulted in the greatest reduction of EE2 adsorbed onto the sediment. Because the aromatic and π–π bonds were less affected than other functional groups, the reduction in the Q_e and K_d values for BPA was at a minimum.

3.5. The effect of ionic strength on the adsorption of the three EDCs

The ionic strength was adjusted using $CaCl_2$ from 0.01 to 0.1 mol/L to investigate the effect of ionic strength on the adsorption behavior of the EDCs. The amounts of BPA, E2, and EE2 adsorbed onto sediment and soil increased with the increasing ionic strength, especially for E2 and EE2 because the amount of ion exchange and polar sorption would increase (Fig. 7). The variation between sediment and soil was insignificant. With an increase in the ionic strength, the electric double layer usually became compressed, which might result in a closer approach of the EDCs and adsorbent and enhance the adsorptive capacity [34,35]. With the increasing ionic strength, the charge on the soil surface changed from negative to positive charge due to the Ca^{2+}. This promoted the adsorption of the EDCs onto the sediment and soil. The negatively charged sediment directly adsorbed too many positive-charged ions with the increase in $CaCl_2$ concentration. It has been reported that several mechanisms could contribute to excessive adsorption of cation on a negative sediment surface, such as hydrophobic interactions, hydrogen bonding, and Van der Waals' force [28,36]. However, with a further increase of ionic strength, the salting-out effect of $CaCl_2$ on the EDCs would be much more evident and would decrease the concentration of EDCs in the aqueous solution, which would result in the reduction of the EDCs adsorbed onto the sediment in the water–sediment system [37]. Moreover, the competitive adsorption effects between the EDCs and cations onto the available adsorption sites might decrease the number of active sites for the adsorption of EDCs with the increasing ionic strength.

4. Conclusion

The adsorption of BPA, 17β-E2, and EE2 on sediment and farmland soil is due mainly to physical adsorption and is a spontaneous process with a value of ΔG between −3.80 and −4.80 kJ/mol. The adsorption process fitted the two-compartment first-order model very well. Both fast and slow adsorption occurred simultaneously, and the fast sorption rate constants and fast sorption compartments were much higher than those of slow sorption. Both partitioning and π–π bonds may be a relatively more important mechanism for the adsorption of BPA onto sediment, while surface adsorption contributed significantly to the sorption of E2 and EE2 onto the soil. The average removal rate (η) of the three EDCs was in the order $\eta_{(\mathrm{BPA})} < \eta_{(17\beta\text{-E2})} < \eta_{(\mathrm{EE2})}$ and soil < sediment which showed that the E2 was easily adsorbed onto sediment, while BPA was more mobile in the farmland-based artificial groundwater recharge system. The isotherm linearity index (K_f) indicated that the adsorption capacity of the sediment was higher than that of the soil.

The pH value, ionic strength, and temperature were found to influence the adsorption ability for EDCs onto sediment and soil. The adsorption capacity and partition coefficient clearly decreased with an increase in pH value. The adsorption amounts of BPA, E2, and EE2 increased with an increase in ionic strength, but decreased with the increased temperature. These results could be useful for predicting a potential pathway for removal of EDCs, thus optimizing reclaimed water treatment and enhancing the ecological purification function of rivers.

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