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Adsorption of 17 α-ethyl estradiol with the competition of bisphenol A on the marine sediment of Hong Kong

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ABSTRACT

The present experimental study was to characterize the adsorption behavior of 17 α-ethyl estradiol (EE2) onto marine sediment in both the single and binary solute systems. Stepwise spiking was innovatively performed to better understand the competition effects. Adsorption of EE2 on the marine sediment can be well fitted by the Freundlich model with an affinity coefficient (K_F) varying from 15.8 to 39.8 L/kg. It was significantly influenced by SOM and the particle properties. Co-presence of BPA brought about a significant competition effect on the adsorption of EE2, leading to a reduced EE2 adsorption. The competitive effect imposed by EE2 to BPA, however, was even more serious owing probably to the large molecular structure and high hydrophobicity of EE2. The sediment sample with the highest SOM and SSA presented a mild competition effect, while the sediment with the lowest SOM and largest particle size exhibited the most serious competition effect.

1. Introduction

Endocrine disrupting chemicals (EDCs) have attracted growing attentions from the academic community and general public in recent years, for their chronic harm to the reproduction of organisms in the ecosystem (Colborn et al., 1993; Collins, 2008). 17 α-ethyl estradiol (EE2) is one of common EDCs found in the aquatic environment. EE2 is generally used in our daily life as contraceptive pills. Owing to its long half-life in living organisms such as fish, the toxicity of EE2 was reported to be significantly greater than many other similar hormones, e.g. estrone and β-estradiol (Li et al., 2014). Bisphenol A (BPA) is another typical EDC that had been widely employed previously as a plasticizer in industrial production. Due to releases from various sources and insufficient removal from wastewater, EE2, BPA and other EDCs have entered rivers, lakes, soils and marine waters (Li et al., 2013b). Occurrence of EE2 in high abundance has been found in surface water (Peng et al., 2008), agricultural soil (Azzouz and Ballesteros, 2012), river and coastal sediment (Azzouz and Ballesteros, 2012; Zhang et al., 2009).

For hydrophobic compounds such as EE2, strong adsorption onto soil or sediment is expected to greatly affect their fate and transport in the environment (Sun et al., 2012; Voice and Weber, 1983). However, compared to the numerous studies on the occurrences and toxicities of EE2 and other EDCs, limited research has been conducted on their adsorption behavior, especially in the marine water-sediment system. Recently, adsorption of EE2 has been reported on engineered materials such as biochars (Sun et al., 2011) and carbon nanotubes (Pan et al., 2008), as well as on natural solids including minerals (Shareef et al., 2006) and soil samples (Li et al., 2013a; Sun et al., 2012). According to the experimental studies, the properties of the absorbents, including the particle size, surface feature and the organic matter content, all affect the adsorption of EE2. Most of these investigations, however, were focused on the adsorption of EE2 only under the single-solute condition, which is rather different from the multi-solute system in the natural environment. Compared to single-solute EE2 adsorption, multi-solute adsorption with the competition of other EDCs remains to be investigated. Pan and Xing (2010) reported the competitive adsorption of BPA and EE2 on carbon nanomaterials. Similar tests on the co-adsorption of BPA and EE2 were conducted by Li et al. (2013b) on soils and Yu and Huang (2005) and Li et al. (2014) on river sediments. In general, research on the competitive adsorption of EDCs on natural materials is largely limited. There is no report of experimental studies on the adsorption of EE2, either individually or competitively, in marine sediment.

In the present study, the adsorption behavior of EE2 on marine sediment was investigated in both single and binary solute systems. Natural marine sediment samples with varied particle properties and organic matter contents were collected for the experimental studies. To

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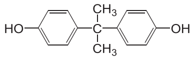
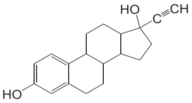
Table 1

Chemical properties of the selected EDCs: BPA and EE2 (Sun et al., 2010).

	BPA	EE2
Molecular structure		
Molecular diameter (Å)	4.3	6.0
Water solubility, S_W (mg/L)	380	7.6
Octanol-water distribution coefficient, logK_{ow}	2.2	4.2

further illustrate the competitive effects, the tests were conducted not only in the way of simultaneous spiking of the two solutes (EE2 and BPA) but also by the approach of stepwise spiking of the competing agent and the target compound. The experimental findings are important to the better understanding of (1) the influences of the marine sediment properties on the adsorption of EE2 and (2) the competitive effect imposed by BPA to EE2 or EE2 to BPA during the sediment adsorption in the binary-solute system.

2. Materials and methods

2.1. Chemicals

Pure EE2 and BPA used in the present study were of analytical grade provided by Sigma-Aldrich. The main physicochemical properties of EE2 and BPA are given in Table 1. EE2 are more hydrophobic than BPA, with a lower water solubility (S_w) and higher octanol-water partition coefficient (K_{ow}). Other reagents and solvents, including hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), calcium chloride ($CaCl_2$), sodium azide (NaN_3), and acetonitrile, used in the experimental study were of analytical grade purchased from Sigma-Aldrich. The stock solution of either EE2 or BPA was firstly prepared in methanol, which was then diluted to working concentrations before use. The organic solvent in the working solutions after purged by pure N_2 was $< 0.1\%$ to avoid co-solvent effects (Plaza et al., 2009).

2.2. Marine sediment

Natural marine sediment samples were collected from 5 sites in Victoria Harbour, Hong Kong, marked as #1–#5. The latitudes/longitudes of sites #1–#5 are 22°14.800/114°16.000, 22°17.500/114°13.500, 22°17.470/114°11.180, 22°18.400/114°06.500, and 22°18.142/114°03.051, respectively (Fig. 1). The sediment samples were collected from the top 30 cm surface of the sediment by Peterson grab. After shells and gravels were removed, the sediment was stored below 4 °C in refrigerator and transferred to laboratory as soon as possible before the experimental use. The sediments were air-dried, homogenized and then ground to pass through 60-mesh sieve (Xu et al., 2008). The sediment samples from different sites were expected to have different organic contents and particle sizes distribution, as site #1 is closer to the mouth of Pearl River on its left, #5 is closer to the open ocean to its right, and site #4 is at the middle of Victoria Harbour that receives stormwater runoffs from the urban areas of both sides of the Harbour (Fig. 1).

The fraction of organic matter in the sediment (f_{OM}), or sediment organic matter (SOM), was measured by the means of ignition at 550 °C (Beaudoin, 2003; Fei et al., 2011). To determine the content of black carbon in sediment (f_{BC}), the raw sediment was treated first by HCl and then by H_2O_2 to remove the carbonates and labile organic matter, respectively. The organic residual in the treated sediment was then measured and its fraction was recorded as f_{BC} (Xu et al., 2008; Zhao et al., 2001). The particle size distributions of the sediment samples were measured by a particle size analyzer (Coulter LS 13320, Beckman, USA). The specific surface area (SSA) was determined for the sediments by a surface analyzer (Coulter SA 3100, Beckman, USA) using the multipoint Brunauer–Emmett–Teller (BET) nitrogen adsorption method. The physicochemical characteristics of the marine sediment samples are summarized in Table 2.

2.3. Adsorption of EE2 on the marine sediments

Tests on the adsorption of EE2 by the 5 sediments were conducted following the batch equilibration approach (OECD, 2000). The laboratory tests on the adsorption isotherms were performed using 12-ml amber glass screw-cap vials (minimal headspace) with Teflon-lined septa (Xing and Pan, 2010; Xing and Pignatello, 1997). Briefly, for each sediment sample, the sediment was placed in a series of vials, each with 0.4 g dry sediment. The vials were filled with 10 mL of the background solution containing 0.01 M $CaCl_2$ for the basic ionic strength and 200 mg/L NaN_3 for microbial inhibition (Xing and Pan, 2010). EE2 solution was then added into the vials to different concentrations from 0.5 to 8.0 mg/L. If not stated otherwise, the pH of the solutions was 7.2 for the sediment adsorption tests.

The sealed vials were placed in a temperature-controlled shaking incubator (Polyscience, USA) for adsorption at 25 °C. According to the preliminary tests, the equilibrium of EE2 adsorption by the sediment could be reached within 24 h. Upon completion of the adsorption tests, the sediment mixtures from the test vials were centrifuged to remove the solids. The EE2 concentrations in the aqueous phase were measured using a high-performance liquid chromatography (HPLC). Concentration loss caused by adsorption of EE2 to the glass walls or by other reasons was found to be $< 3\%$. Thus, from the difference between the initial and final EE2 concentrations in the aqueous phase, the amount of EE2 adsorbed by the sediment in each test vial could be calculated. The results from a series of initial concentrations were then used to determine the adsorption isotherm of EE2 for each sediment sample.

2.4. Adsorption of EE2 by the sediment with the competition of BPA

The EE2 adsorption experiments also were conducted in the presence of BPA as a competitor chemical. The batch isotherm tests followed the similar procedure as described above, except for the extension of the equilibration time to 2 days. As a competing compound, BPA was dosed at 40 mg/L (about 10% of its solubility in water). The competitive adsorption tests were carried out in 3 sub-groups: (1) adsorption of EE2 only as the reference, (2) synchronous competitive adsorption of EE2 and BPA when both chemicals were simultaneously spiked initially, and (3) lag-competitive adsorption which had EE2 spiked 1 day after BPA to have the competing agent adsorbed onto the sediment before the competition. Upon the completion of the tests, both EE2 and BPA were analyzed for their equilibrium concentrations in the aqueous phase.

In addition, the effect of the EE2 presence on the adsorption of BPA also was investigated. For the tests, EE2 as a competitor had a fixed concentration at 3 mg/L (about 10% of its solubility in water), while the BPA concentration varied from 5 to 50 mg/L for adsorption by the sediment. Similarly, the competitive adsorption tests were conducted in 3 sub-groups: (1) adsorption of BPA alone as the reference, (2) synchronous competitive adsorption of BPA and EE2, and (3) lag-competitive adsorption which had BPA spiked 1 day after EE2. The equilibrium concentrations of BPA and EE2 in the aqueous phase were measured after the adsorption tests.

2.5. Chemical analysis

The EE2 and BPA concentrations in water were measured by an HPLC (Waters 2695) with a C18 column (5 μm, 2.1 × 150 mm) for