



Study on the sorption behaviour of estrone on marine sediments



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ABSTRACT

The sorption behaviour of estrone (E1) on marine sediments treated by different methods was systematically investigated. About 22 h was required for sorption equilibrium of E1. Sorption isotherms of E1 were well fitted with Freundlich model. The sorption behaviour of E1 on HCl-treatment and H₂O₂-treatment sediments related significantly with the sediment organic carbon contents. Additionally, clay minerals and surface areas of sediments played dominant roles in the sorption of E1 on H₂O₂-treatment sediments. Some external factors which could affect sorption behaviour of E1 were also investigated. Our results showed that the sorption capacity of E1 on the sediments increased with the increasing concentrations of cationic surfactant cetyltrimethylammonium bromide (CTAB), nonionic surfactant polyoxyethylene (80) sorbitan esters (Tween 80) and salinity of seawater. In contrast, the sorption capacity of E1 decreased with the increasing concentration of anionic surfactant sodium dodecylbenzene sulfonate (SDBS), pH value and temperature of seawater.

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1. Introduction

Recently there has been increasing evidence of estrone (E1) having endocrine-modulating characteristic, which is defined as endocrine disrupting chemicals (EDCs). EDCs are the focus of current environmental concern, as they can cause adverse health effects in an intact organism, or its progeny, subsequent to endocrine function. Adverse effects already observed include hormone-dependent cancers, reproductive tract disorders, and reduction in reproductive fitness. Numerous studies on the effects of estrone on a range of wildlife species have been reported, including intersex in wild roach and vitellogenin induction in rainbow trout caused by estrone (Rodger-Gray et al., 2001), intersex in lobster in Nova Scotia and abnormal sex ratios in harpacticoid copepods near sewage discharge in the Firth of Forth (Matthiessen and Gibbs, 1998). Estrone, as the natural female hormone, is excreted by women, and is therefore ubiquitous in the aquatic environment receiving sewage inputs. It is among the most potent of all EDCs which are implicated in causing adverse effects in fish adjacent to sewage outfalls. Such steroid is sufficiently stable to survive sewage treatment processes and is reactivated during those processes through deconjugation. As a result of the importance of EDCs such as estrone, its occurrence and environmental behaviour has been widely studied. In a study of several sewage

treatment works (STW) in the UK, STW effluents contained estrone at a concentration of 1–80 ng/L (Desbrow et al., 1998). Effluents from three Dutch STW also contained estrone at concentrations of 0.4–47 ng/L (Belfroid et al., 1999). In 16 German municipal STW effluents, estrone was measured at concentrations up to 80 ng/L, and in 10 Canadian STW effluents corresponding values of 48 ng/L of estrone was reported (Ternes et al., 1999). In Sweden, a minor STW discharged 5.8 ng/L of estrone (Larsson et al., 1999).

The overall objective of this study was to investigate different sorption properties of various types of sediments treated by different procedures, and to examine the effects of sediment ingredients and external factors on the sorption of E1. This aspect of research under seawater conditions will fill gaps in the literature. Meanwhile, this research may provide convincing evidence of the migration pattern of E1 in marine environments, and will contribute to the future protection and pollution control of marine systems.

2. Materials and methods

2.1. Chemicals

E1 was purchased from Sigma Chemical Co. with purity of >99%. One gram of E1 was first dissolved into methanol to make up solution concentration of 1.0 g/L, and then 1.0 ml E1-methanol solution was added into 999 ml seawater to make up a final standard solution concentration of 1.0 mg/L (3.70 μmol/L). Nonionic surfactant polyoxyethylene (80) sorbitan esters (Tween 80) and cationic surfactant cetyltrimethylammonium bromide (CTAB) were all purchased from Sigma Chemical Co. with purity of >99%. Anionic

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surfactant sodium dodecylbenzene sulfonate (SDBS) was obtained from Kasei Kogyo Co. (Tokyo, Japan) with purity of >99%. All other chemicals used in this study were analytical grade and obtained from Shanghai Chemical Reagent Co., China.

2.2. Seawater

Natural seawater (NSW), collected from the Jiaozhou Bay, China, was filtered through 0.45 μm filter and irradiated with strong ultraviolet light for 24 h to eliminate the effects of natural dissolved organic matter and microorganisms as far as possible (Yang and Zhang, 1997). The salinity and pH value of the seawater were 33.4‰ and 8.03‰, respectively. In order to study how the ion strength influenced the sorption behaviour of E1, two kinds of diluted seawater (DSW) were prepared from NSW and deionized water (salinity 0) with the volume proportions of 2:1 (DSW1) (salinity 22.2‰) and 1:1 (DSW2) (salinity 16.7‰), respectively. The pH values of all of solutions were adjusted to 8.00 ± 0.03 with sodium acetate and acetic acid solutions to simulate natural marine condition.

2.3. Sediment collection and treatment

The sediment samples were collected from the Yellow Sea. At each location, surface sediment was collected by a grab sampler and then sealed in plastic bags to be kept at -20°C . Before the use, frozen sample was thawed at room temperature and air-dried. Then the sediment sample was treated by H_2O , HCl and H_2O_2 according to Yang and Zhang (1997) and Zhao et al. (2001), as shown as follows.

- A. *H₂O-treatment*. Sediment samples were washed with only a small volume of distilled water, air-dried, and then ground. The part that could pass 60–80 mesh sieves was chosen as experimental material.
- B. *HCl-treatment*. First, an amount of sediment samples was mixed with a volume of distilled water. Then, a pH 2 solution of HCl was used to adjust the pH of the suspension system. Immersion stirring was continued for 24 h. The system was washed by distilled water until the pH of the suspension system was 4.0. The samples were then filtered, air-dried, and ground to pass 60–80 mesh sieves. This treatment could remove the carbonate of sediment and the percentage of organic carbon content of sediment on dried weight basis was accordingly increased.
- C. *H₂O₂-treatment*. The sediment from (B) was added to 6 ml of 30% H_2O_2 and 3 ml of 0.02 mol/L HNO_3 solution with final pH 2.0, and the mixture was heated to $85 \pm 2^\circ\text{C}$ for 2 h with occasional agitation. A second 3 ml aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added, and the sample was again heated to $85 \pm 2^\circ\text{C}$ for 4 h with intermittent stirring. Finally, the samples were washed in distilled water, filtered, dried, and ground to pass 60–80 mesh sieves. This treatment aimed to remove most of the sediment organic carbon. By means of H_2O_2 oxidation, about 90% of the organic carbon in the sediment could be removed (Xu and Li, 2008).

The mineralogical constituents of the sediments were analyzed by Model D/max-rb X-ray diffraction instrument (Rigaku, Japan), pore width and BET surface area of the sediments were measured by Model ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics Instrument Co., USA), and the organic carbon contents of the sediments were determined by PE2400 Series II CHNS/O (USA). Analytical results are listed in Table 1.

2.4. Experimental methods

To determine the sorption equilibration time, 0.8 g of sediment, 8.0 ml of E1 standard solution, and 42 ml of seawater (NSW, DSW1 or DSW2) or 38 ml of natural seawater and 4.0 ml of different surfactant solutions, were added to a series of 150 ml glass-stoppered flasks to obtain a whole suspension volume of 50 ml. After the pH of suspension was adjusted to 8.00 ± 0.03 , samples were shaken at $25 \pm 0.5^\circ\text{C}$ at a speed of 200 ± 3 r/min in a Model SHZ-82A constant-temperature air-bath shaker (Changzhou Guohua Appliance Co., China) at different time intervals as indicated in Fig. 1. Solid and aqueous phases were separated by a Model SC-3610 centrifuge (USTC Chuangxin Co., China) at a speed of 5000 rpm for 5 min. Then the supernatant solution was analyzed by fluorescence absorption at excitation wavelength 284 nm and emission wavelength 314 nm using a Model F-4500 spectrophotometer (Hitachi High-Technologies Co., Japan). The precision of the analytical method was generally better than 4% in a concentration range of 0.05–1.0 $\mu\text{mol/L}$ E1. The limit of detection for E1 in this study was 0.01 $\mu\text{mol/L}$. The quantity of E1 adsorbed to sediments was calculated from the initial and final concentrations of the solution.

Sorption isotherm experiments were carried out by a method similar to the above. The major difference was that the volumes of E1 standard solution added were variable. After equilibration, the suspension was separated, filtered, and then analyzed by fluorescence absorption. A blank sorption experiment with no added sediment testified that photolysis and microbial degradation of E1 could be ignored.

3. Results and discussion

3.1. Sorption kinetics

The sorption kinetics of E1 on marine sediments was firstly investigated, and the changing trend of C_s with time is illustrated in Fig. 1. Our result showed that sorption equilibration time of E1 on No. 2 H_2O -treatment sediment in different mediums was about 22 h at 25°C , while it was approximately 4 h, whichever surfactant (CTAB, Tween 80 and SDBS) was added. Firstly, about 77.3% and 80.5% of sorption equilibration amount was rapidly sorbed within 1 h in different mediums and with addition of surfactant, respectively. Secondly, sorption equilibration amount of E1 gradually increased within 21 h and 3 h in different mediums and with addition of surfactant, respectively. Thirdly, no further sorption could be observed after the sorption reached to equilibrium. The phenomenon could be explained by the fact that E1 was sorbed onto the external sediment surface in the initial rapid sorption phase, while it was diffused into the intra-aggregate micro pores and interlayer materials in the slower adsorption phase (Emmerik et al., 2003). The sorption equilibrium time of E1 accelerated about 81.8% with surfactant relative to no addition of surfactant. It is proved that the surfactant plays an important role in the sorption of E1. Two-step processes can explain the acceleration: firstly, surfactant is sorbed on the sediment more quickly, and then the hydrophobic material is directly partitioned between surfactant and water, instead of being gradually sorbed on the sediment surface (Hernández-Soriano et al., 2009). In addition, Fig. 1 indicates that sorption capacity of E1 varied with mediums in the sequence of $\text{NSW} > \text{DSW1} > \text{DSW2}$, and varied with surfactants in the sequence of $\text{CTAB} > \text{Tween 80} > \text{SDBS}$. This phenomenon favorably proves that changing salinity of the medium and addition of surfactant may influence the sorption behaviour of E1, as discussed below. In order to assure the sufficient sorption of E1 onto sediment in different mediums and with different surfactants, 22 h and 5 h was chosen in the experiment, respectively.

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