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Interaction of bisphenol A with dissolved organic matter in extractive and adsorptive removal processes

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ABSTRACT

The fate of endocrine disrupting chemicals (EDCs) in natural and engineered systems is complicated due to their interactions with various water constituents. This study investigated the interaction of bisphenol A (BPA) with dissolved organic matter (DOM) and colloids present in surface water and secondary effluent as well as its adsorptive removal by powdered activated carbons. The solid phase micro-extraction (SPME) method followed by thermal desorption and gas chromatography–mass spectrometry (GC–MS) was utilized for determining the distribution of BPA molecules in water. The BPA removal by SPME decreased with the increased DOM content, where the formation of BPA–DOM complexes in an aqueous matrix was responsible for the reduced extraction of BPA. Colloidal particles in water samples sorbed BPA leading to the marked reduction of liquid phase BPA. BPA–DOM complexes had a negative impact on the adsorptive removal of BPA by powered activated carbons. The complex formation was characterized based on Fourier transform infrared (FTIR) and ultraviolet–visible (UV–Vis) spectroscopy, along with the calculation of molecular interactions between BPA and functional groups in DOM. It was found that the hydrogen bonding between DOM and BPA would be preferred over aromatic interactions. A pseudo-equilibrium molecular coordination model for the complexation between a BPA molecule and a hydroxyl group of the DOM was developed, which enabled estimation of the maximum sorption site and complex formation constant as well as prediction of organic complexes at various DOM levels.

1. Introduction

Endocrine disrupting chemicals (EDCs) have received significant attention with respect to their fate and removal in water and wastewater treatment (Mendes, 2002; Auriol et al., 2006; Kim et al., 2007; Chang et al., 2009). The physicochemical behavior of EDCs in an aqueous phase, such as partition coefficient and transformation, is affected by various environmental factors, such as pH, salt, microorganisms, dissolved organic matter (DOM), and colloids (DePaolis and Kukkonen, 1997; Bowman et al., 2002; Zhan et al., 2006; Durjava et al., 2007; Ge et al., 2008; Xu and Li, 2008; Neale et al., 2009).

DOM, which is a complex mixture of organic components from low molecular weight acids to high molecular weight proteins, carbohydrates, and natural organic matter (NOM), plays an important role in water chemistry and treatment (Kang et al., 2002; Georgi et al., 2007; Cornelissen et al., 2008; ter Laak et al., 2009). It may serve as a microreactor being involved in the physicochemical reactions of trace organics (e.g., EDCs) in natural water, such as the bonding of dissolved hydrophobic molecules into the DOM (Hassett, 2006). This phenomenon can decrease their ability to be captured by particles, taken up by organisms, or transported into the atmosphere. NOM may change the fate and transport of organic chemicals in aqueous solutions, such as phenol and fluoranthene (Poerschmann et al., 1997). It was also noticed that NOM in the water matrix led to an improvement of 5–31% in estrone rejection by nanofiltration membranes depending on NOM properties (Jin et al., 2007). Hydrophobic NOM, which can be adsorbed onto the membrane, improved the partitioning of estrone to the membrane. Such a phenomenon was also observed with porous membranes (Schafer et al., 2002). It was reported that a significant acceleration with UV photodegradation of 17β-estradiol occurred in the presence of NOM in water, primarily due to the radicals produced by NOM (Leech et al., 2009). The removal of EDCs may be also affected by the presence of colloids in water (Rogers, 1996; Schafer et al., 2002). However, the effects of water constituents on the fate and removal of the EDCs in the aqueous phase have not been well established yet.

Several reaction mechanisms between DOM and EDCs have been proposed by previous studies, such as hydrogen bonding, aromatic interaction, and molecular inclusion (Kubicki and Apitz, 1999; Hollrigl-Rosta et al., 2003; Yamamoto et al., 2003; Chelli et al., 2007; Trout and Kubicki, 2007). According to previous

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findings (Yamamoto et al., 2003), the formation of hydrogen bonds was possible between DOM and EDC molecules having carboxylic, phenolic, or hydroxyl groups. A strong affinity between tannic acid and EDCs (e.g., steroid estrogens and alkylphenols) was observed, where their phenolic groups seemed to be involved. It was also revealed that the aromatic interactions between selected aromatic hydrocarbons (e.g., benzene, phthalate, pyridine, naphthalene and salicylate) and four different types of NOM (e.g., humic acid, Suwannee River fulvic acid, lignin, soot) took place (Kubicki and Apitz, 1999). They provided several calculated models between the two entities. Similar work was conducted by other researchers (Trout and Kubicki, 2007). The aromatic interaction between benzene and NOM was evaluated through the energy minimization calculation using the Gaussian program, considering van der Waals, hydrophobic, stacking, and electrostatic interactions. The stabilization energy level for these interactions was estimated to be approximately -4 to -84 kJ mol^{-1}, showing the high impact of these interactions (Muller-Dethlefs and Hobza, 2000; Hunter et al., 2001). The inclusion of bisphenol A (BPA), which is one of the most common EDCs found in aquatic environments, into a specific structure of cyclodextrins (CDs) was suggested by other researchers (Chelli et al., 2007). Yet it has not been clearly demonstrated what types of interactions are most responsible for the binding between DOM and BPA and how their interactions affect the removal of BPA.

The purpose of the present study was primarily to investigate the interaction of BPA with DOM as well as colloids in water samples, such as river water and secondary effluent. The effect of BPA–DOM complexes on activated carbon adsorption was evaluated based on mass balances on BPA. The physicochemical interactions between DOM and BPA were characterized based on Fourier transform infrared (FTIR) and UV–Vis spectroscopy while monitoring the wavelength shift at the representative functional groups. The possible molecular interactions between BPA and DOM were computed using the Gaussian electronic structure program and then a pseudo-equilibrium model was developed to quantify the formation of BPA–DOM complexes at various dissolved organic contents.

2. Materials and methods

2.1. Water sources

The two types of typical water samples used in this study were river water and secondary effluent, which were collected from the Nakdong River and the Shincheon municipal wastewater treatment plant (MWTP), Daegu, Korea, respectively. Water samples were shipped to the laboratory and stored in a 4 °C refrigerator before use. The key water characteristics are summarized in Table S1 (Supplementary information).

A 100-mL stirred cell reverse osmosis (RO) filtration unit with a piece of RO membrane (RE-1810-30, Woongjin Chemical, Korea) was used to concentrate the DOM level of each water source by a factor of 2 when needed. The concentrated water sample from the stainless steel RO unit was collected for further sample preparation and the loss of organics during RO was negligible.

2.2. Reagents and solid phase micro-extraction (SPME) fibers

The major chemicals, such as BPA and humic acid, were purchased from Sigma–Aldrich (St. Louis, USA). A stock solution of BPA (log octanol–water partitioning coefficient = 3.32) with a concentration of 100 mg L^{-1} was prepared by dissolving 0.1 g BPA into 5 mL methanol followed by filling up the beaker with Milli-Q (MQ) water up to one liter. Powdered activated carbon (PAC) particles (A-51, Norit, USA), which has meso-sized pores and may be suitable for the sorption of macromolecules, were used for the adsorption tests of DOM and BPA. SPME fiber assortment kits (57324-U) for the extraction of BPA were purchased from Supelco (USA). Detailed information on the SPME fiber used is provided in Table S2.

2.3. Sample preparation and experimental procedures

To remove particulate matter in water samples, they were filtered through a 0.45-μm filter (Millipore, USA) and were defined as particle-free water. 100 mL aqueous solutions containing 1, 10, and 100 ppb BPA were prepared while adding an appropriate amount of the BPA stock solution to filtered Nakdong River water and Shincheon secondary effluent. At least more than two replicate experiments were performed for each individual test. Regarding the specific tests of competition and inhibition between DOM and BPA, water samples were prepared as follows. For the competition test, a SPME fiber was first placed in a water sample containing DOM of ~6 mg L^{-1} as TOC, but without BPA. The fiber was immersed in the sample for 90 min at 800 rpm. Then, the same fiber was moved to a BPA solution containing no DOM and then stayed submerged for another 90 min for BPA sorption. On the other hand, for the inhibition test, a SPME fiber was immersed in a pre-mixed solution of DOM and BPA under the same stirring and exposure conditions. For control runs, a SPME fiber was immersed in an aqueous solution containing BPA alone without DOM under the same conditions.

Colloidal particles collected from the bottom of a carboy containing the Nakdong River water were added to the same river filtered water in order to adjust the water turbidity as needed. Before collecting the sediment, the river water was allowed to settle for more than 24 h. The PAC adsorption tests for BPA were conducted with water samples containing different amounts of DOM (0–6 mg L^{-1} as TOC) with 100 ppb BPA. After adding 100 mg L^{-1} PAC to water samples, they were shaken at 300 rpm and 25 °C for ~16 h. Before the BPA measurements, the samples were filtered through a 0.45-μm Millipore membrane filter to remove the PAC particles.

BPA molecules were classified into several categories depending on their presence either in the liquid phase or solid (colloids or PAC): liquid phase free BPA, liquid phase complexed BPA, solid phase free BPA, and solid phase complexed BPA. Mass balances on BPA were performed for estimating the sorption of BPA onto solid surfaces. The liquid phase free BPA was determined directly extracting BPA from the liquid phase by SPME, while the liquid phase complexed BPA was considered as non-extractable BPA in the presence of DOM but without particles. The BPA sorbed on colloids or PAC particles was estimated from the difference in liquid phase BPA between with and without the solids.

2.4. Computation of BPA–DOM interactions using the Gaussian program

The Gaussian electronic structure program was used to simulate and optimize the possible interactions between different chemical entities with visible three-dimensional molecular structures, and thereby to find some key information on these interactions, such as energy and bond length (Miao et al., 2004; Robiette, 2006; Bachrach et al., 2007; Bachrach, 2008). In this study, the energy minimization of possible structures, which mimic the interaction between BPA and DOM, was carried out using BPA, phenol, and 4-hydroxybenzoic acid as model compounds.

The Gaussian program contains a hierarchy of procedures corresponding to different approximation methods (i.e., different levels of theory). The calculation level of B3LYP/6-31G(d) used in this study is one of the most widely utilized methods, with an absolute