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Comparative study of reactions of endocrine disruptors bisphenol A and diethylstilbestrol in electrochemical treatment and chlorination

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ABSTRACT

Transformations of diethylstilbestrol (DES) and bisphenol A (BPA) in conventional chlorination and electrochemically (EC) treated solutions were examined using spectrophotometry and chromatographic analyses. EC treatment was carried out using an undivided EC cell with a PbO_2 anode and a stainless steel cathode. EC-treatment and conventional chlorination caused DES and BPA to undergo a rapid degradation accompanied by the generation of low molecular weight chlorinated organic species indicative of the breakdown of DES and BPA. The identified compounds were predominated by chloroacetic acids (HAAs), but approximately 80% of the total organic halogen (TOX) was comprised by unidentified species. For EC treatment, the HAA yields were lower and HAAs were predominated by monochloroacetic acid (MCAA), while in the case of conventional chlorination, trichloroacetic acid (TCAA) was predominant and MCAA was virtually absent. The changes in the HAA speciation and yields were concluded to be caused by the EC-driven reductive dehalogenation which, however, did not affect the unidentified fraction of TOX. This indicated that the unidentified part of TOX was comprised by aromatic chlorinated forms of BPA and DES. Their resistance to degradation in EC reactors indicates that these compounds may be stable in conditions typical for drinking water treatment and distribution.

1. Introduction

Occurrence, effects and fate of organic species of anthropogenic origin that have been associated with disruption of the endocrine function have become increasingly important for the scientific and engineering communities and for regulating agencies (Snyder et al., 2003; Sumpter and Johnson, 2005; Westerhoff et al., 2005). Among compounds associated with endocrine disruption, bisphenol A (BPA) and diethylstilbestrol (DES) occupy a prominent place (Boyd et al., 2003; Stackelberg et al., 2004; Killops and Killops, 2005). The molecular structures of these compounds are shown in Fig. 1. DES is a potent endocrine disruptor that has been banned since 1971. Although it had been widely used for more than three decades prior to its ban, little has been learned about the degradation of DES in the environment or engineered systems. On the other hand, endocrine disruption caused by BPA is much more subtle than that caused by DES but the use of BPA is extremely widespread, and 800 million kg of BPA are produced annually in the United States alone (Zoeller et al., 2005). BPA has been found in virtually all compartments of the environment, including drinking water supplies. A recent study by Stackelberg et al. (2004) has shown that at least in some cases, BPA concentrations in finished water from a

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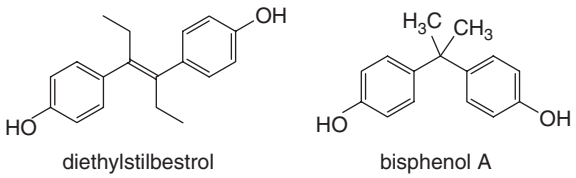

Fig. 1 – Molecular structures of diethylstilbestrol and bisphenol A.

drinking water treatment plant that chlorinates its water can be the same as in the plant influents, indicating that BPA can survive drinking water treatment.

The wide occurrence of BPA and a number of other endocrine disruptors necessitates gaining a better understanding of their reactivities in the environment and ways to remove them. Adsorption, oxidation by chlorine, chlorine dioxide and ozone (Westerhoff et al., 2005; Gallard et al., 2004; Lee et al., 2003; Lenz et al., 2004; Moriyama et al., 2004; Pinkston and Sedlak, 2004; Hu et al., 2002; Lee et al., 2004) have been shown to degrade many endocrine disruptors and pharmaceuticals. Free chlorine reportedly causes a relatively rapid degradation of BPA followed by the formation of its chlorinated congeners (Gallard et al., 2004; Hu et al., 2002; Lee et al., 2004). The reactivity of these products has not been explored in much detail but they have been linked to increased estrogenic activity of chlorinated solutions of BPA and DES (Lenz et al., 2004; Hu et al., 2002).

Alternative technologies such as photodegradation (Zhou et al., 2004) or electrochemical (EC) treatment have also been shown to perform well in the removal of BPA and DES. In EC methods, these species can either be oxidized directly with metal or carbon-based anodes (Andreescu et al., 2003; Ngundi et al., 2003; Kuramitz et al., 2004), or they can be degraded indirectly by powerful oxidants such as O_3 and OH that are EC-produced with transition metal oxides or boron-doped diamond electrodes (Boscoletto et al., 1994; Tanaka et al., 2002; Gozmen et al., 2003; Korshin et al., 2005). The direct EC oxidation of BPA, DES and other species that contain phenolic groups proceeds via the formation of phenoxy radicals that initiate their surface polymerization. Because the polymerized forms of BPA and similar compounds are insoluble, EC-driven surface oxidation followed by polymerization can be used to remove these species (Andreescu et al., 2003; Kuramitz et al., 2004). In contrast with the direct EC oxidation of BPA and DES, their indirect EC degradation with oxide-based electrodes is accompanied by a rapid breakdown of the target without its polymerization or formation of stable oxidized forms (Tanaka et al., 2002).

Chlorine species can also be generated upon EC treatment of most natural waters (Korshin et al., 2004). This is caused by the EC oxidation of naturally present chloride ion with most metallic or oxide-based electrodes. Because the interactions of chlorine with BPA and DES in EC reactors can differ from those in conventional chlorination and also because products of BPA and DES chlorination can also be EC-active, it is relevant to compare their degradation in conventional chlorination and EC treatment. Virtually no information concerning differences between these two types of treatment is currently available. The goal of this paper is to provide it.

2. Materials and methods

High-purity water (18.2 MΩ-cm resistivity, residual dissolved organic carbon < 0.1 mg/L) obtained with a Milli-Q Plus system was used to prepare all solutions. BPA and DES were purchased from Aldrich. For EC experiments, these compounds were dissolved in 0.01 M NaCl background electrolyte. Concentrations of the analytes were determined by measurements of concentrations of dissolved organic carbon and also of the UV absorbance at characteristic wavelengths (275 and 245 nm for BPA and DES, respectively).

Chlorination was carried out in the presence of 0.03 M phosphate buffer at pH 7.0 using headspace-free Teflon bags. Stock solution for chlorination studies was prepared by dilution of a sodium hypochlorite solution (5% available chlorine) with Milli–Q water. The solution was standardized by the DPD colorimetric method after the instrument was calibrated with potassium permanganate in accord with Standard Methods (1995). Reaction time was varied from 5 min to 24 h. Excess of free chlorine in the samples was quenched by sodium sulfite. Analyses for individual DBP species were carried out in accord with EPA Methods 551.1 and 552.2. Major identified DPB species quantified in this study included chloroform, mono-, di and trichloroacetic acids (MCAA, DCAA and TCAA, respectively). Conditions of all of analyses for individual DBPs and total organic halogen (TOX) were identical to those described in more detail in (Korshin et al., 1997; Korshin et al., 2002).

EC treatment was carried out using an undivided flow-through EC cell (ElectroCell AB, Sweden) similar to that described in more detail by Johnson et al. (2000). Cobalt-promoted PbO_2 (Co–PbO_2) and stainless steel were used as the anode and cathode, respectively. The synthesis and properties of Co–PbO_2 were described by Velichenko et al. (2002). The surface area of the electrodes was 10 cm^2 and the inter-electrode distance was 0.5 cm. The range of current densities was from 0 to 50 mA/cm^2. The flow rate was set at 25 mL/min, which corresponded at a 12 s hydraulic residence time in the cell. Concentrations of DBP species and TOX in EC treated solutions were determined as described in the preceding paragraph. Concentrations of dissolved organic carbon (DOC) were measured using a Model 1010 OI Analytical carbon analyzer. Absorbance spectra were acquired using a Perkin–Elmer Lambda-18 spectrophotometer.

3. Results and discussion

Reactions of DES and BPA with chlorine were accompanied by pronounced changes of their absorbance spectra. For DES, the initial absorbance spectrum was characterized by an intense band at wavelengths < 305 nm. Its maximum was located at 242 nm; there was also a less intense shoulder in the range of wavelength 260–290 nm (Fig. 2). The first feature appears to correspond to the electronic transitions associated with the double C = C bond in DES molecules while the shoulder in the