Journal of Hazardous Materials B126 (2005) 54–62

Journal of Hazardous Materials

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Degradation of 17β-estradiol and bisphenol A in aqueous medium by using ozone and ozone/UV techniques

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Received 23 August 2004; received in revised form 11 May 2005; accepted 11 May 2005

Abstract

Decomposition and complete degradation of two endocrine disrupters, namely 17β-estradiol (E_2) and bisphenol A (BPA) in aqueous medium by using ozone (O_3) only and O_3/UV advanced oxidation techniques (AOT) has been studied. The efficiency of the O_3 systems used were determined based on the initial conversion and complete degradation of the substrates. Within the limits of the O_3 dosages used, coupling of UV decreased the O_3 consumption by 22.5% in converting the same amount of E_2. Also the time to convert the same amount of E_2 was considerably decreased. It was observed that there is no significant difference in O_3 amount consumed for complete conversion of BPA by O_3 and O_3/UV systems. However, when O_3 dosage decreased the amount of BPA conversion exhibits significant differences between two processes. The intermediate products formed during the oxidation of E_2 were determined to be formed by oxidation of aromatic side of E_2 with $O_3/^{\bullet}OH$ radical.

Keywords: 17β-Estradiol; Bisphenol A; Ozone; UV; Degradation; Endocrine disrupters

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1. Introduction

An endocrine disrupter (or in other terms endocrine modulator) is defined as an exogeneous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and/or behavior [1]. Chemicals which vary widely in their structures and which have numerous different uses have been identified as endocrine disrupters. They include certain types of pesticides (e.g. dicofol, DDE, methoxychlor, toxaphene), plastics and other industry related materials (bisphenol A (BPA), alkylphenols, butyl and dibutylphthalates, hydroxy-polychlorinated biphenyls, etc.) and natural compounds that include human hormones and their breakdown products such as estrogen and the estrogen sterols, 17β-estradiol (E_2) and the synthetic hormone 17α-ethinyl estradiol.

It has been argued that endocrine disrupters may be responsible for decline in sperm counts, abnormalities in the male reproductive tract, slow development in infants and increases in the rate of testicular and breast cancer. Possible links to earlier puberty in females, a shift in the ratio of male to female births, prostate cancer and enlargement, non-Hodgkins lymphoma have also been discussed [2]. The anomalies in reproductive and other systems of juvenile alligators [3], fish intersexuality [4] and synergistic activation of estrogen receptor via the combination of some environmental chemicals [5] are some of the reported observations which had increased the concerns on these type of environmental chemicals. Halling-Sørensen et al. [6] and Daughton and Ternes [7] reviewed the relevant literature in detail explaining the potential risks due to the presence of pharmaceuticals in various environmental matrixes. On the other hand, a group of scientists reported that the extremely low concentrations of these chemicals in environmental matrices do not pose a

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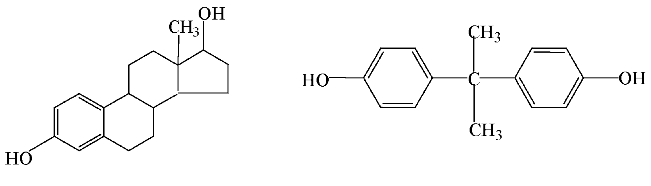
doi:10.1016/j.jhazmat.2005.05.045



17β-estradiol

Bisphenol A

Fig. 1. Structural formulas of E_2 and BPA.

threat on both wildlife and on human health ([8] and the relevant references therein). Because the situation is not clear yet these chemicals in the environmental matrixes are being monitored intensively [9–11].

Besides the works on removal or mineralization of these chemicals have been carried out using various advanced oxidation techniques (AOT) are effective in decomposing refractory organic chemicals [12–14]. In this study, O_3 oxidation was chosen as the main chemical treatment to decompose 17β-estradiol (E_2) and bisphenol A in aqueous medium (Fig. 1). E_2 is the principal intracellular human estrogen and is substantially more active than its metabolites, estrone and estriol. E_2 may enter the aquatic environment from contraceptive pill residues, hormone replacement therapy residues and human excretion [9]. E_2 resists degradation in the course of typical sewage treatment operation [9] and be released into surface waters [15–17]. When the sludges from wastewater treatment plants, which contain these chemicals, are used in agricultural fields they can be transported into surface and/or ground waters [18].

BPA is a monomer of various polymeric materials. In addition to being used as monomers for the production of polycarbonates, epoxide phenol resins, etc., it is also being utilized as an antioxidant in numerous types of plastics [19]. Recent studies have shown that BPA can leach out of the plastic lining of cans used for foods, polycarbonate baby bottles, tableware, white dental fillings and sealents [20]. Epoxy resins used for the renovation of water pipes are based on BPA diglycidyl ether or a mixture of BPA and diglycidyl ether. Residues of this compound in water appear to be due to incomplete polymerization [21]. BPA was also frequently encountered in waters [22]. When BPA was subjected to metabolic activity it bounded to DNA [23].

O_3 reacts with organic compounds through a direct pathway by molecular ozone and a radical pathway by means of hydroxyl radicals. Under acidic conditions and in presence of radical scavengers which inhibit the chain reaction which accelerates the decomposition of O_3, the direct ozonation pathway dominates but under basic conditions or in presence of solutes which promote the radical-type chain reaction which accelerates the transformation of ozone into $^\bullet OH$ radicals the latter, i.e. hydroxyl radical reactions dominate [24,25]. When the medium is basic, O_3 decomposes to generate hydroxyl radical, which is non-selective and highly reactive oxidant for destruction of toxic organic compounds in wastewater.

Ozone decomposition proceeds with chain reactions including initiation, propagation and termination steps [25,26]:

- Initiation step:

  Decomposition reaction of ozone is initiated by OH^- ions in the solution yielding $^\bullet OH$ radicals.

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^\bullet \quad k_1 = 70\,M^{-1}\,s^{-1} \tag{1}$$

- $HO_2^\bullet$ radical is in acid–base equilibrium:

$$HO_2^\bullet = O_2^{\bullet -} + H^+ \quad pK_a = 4.8 \tag{2}$$

- Propagation step:

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \quad k_2 = 1.6 \times 10^9\,M^{-1}\,s^{-1} \tag{3}$$

$$HO_3^\bullet = O_3^{\bullet -} + H^+ \quad pK_a = 6.2 \tag{4}$$

$$HO_3^\bullet \rightarrow {}^\bullet OH + O_2 \quad k_3 = 1.4 \times 10^5\,s^{-1} \tag{5}$$

$$O_3 + {}^\bullet OH \rightarrow HO_4^\bullet \quad k_5 = 2.0 \times 10^9\,M^{-1}\,s^{-1} \tag{6}$$

$$HO_4^\bullet \rightarrow HO_2^\bullet + O_2 \quad k_6 = 2.8 \times 10^4\,s^{-1} \tag{7}$$

- Termination step:

  This step includes any recombination of $^\bullet OH$, $HO_2^\bullet$ and O_2

The combination of ultraviolet (UV) radiation with O_3 may be a more effective advanced oxidation technique than using O_3 alone for certain target materials due to the formation of additional H_2O_2 and $^\bullet OH$ radical generation via photolysis [27].

$$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 + O_2 \tag{8}$$

$$H_2O_2 \xrightarrow{h\nu} 2^\bullet OH \tag{9}$$

However, the photolysis of H_2O_2 to produce two $^\bullet OH$ radicals is rather slow because molar extinction coefficient of hydrogen peroxide is much lower ($19.6\,M^{-1}\,cm^{-1}$) than that of ozone ($3300\,M^{-1}\,cm^{-1}$) at 254 nm [28]. A fraction of hydrogen peroxide is dissociated into HO_2^- ($pK_a = 11.8$) by following reaction [29]:

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{10}$$

This reacts with further ozone by producing $O_3^{\bullet -}$ radicals,

$$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^{\bullet -} \tag{11}$$

and it therefore acts as a further chain carrier [25].

The decomposition of endocrine disruptors E_2 and BPA in aqueous medium by O_3 and O_3/UV oxidation has not been investigated previously. Therefore, in this study E_2 and BPA were treated with both O_3 and O_3/UV in aqueous medium at 0.40 mM initial concentration. The depletion of the initial substrates throughout the treatments were monitored and the efficiency of conversions and complete degradations in two different systems were compared.