



## Photodegradation of 17 $\beta$ -estradiol in aquatic solution under solar irradiation: Kinetics and influencing water parameters

Rajib Roy Chowdhury, Paul A. Charpentier, Madhumita B. Ray\*

Department of Chemical and Biochemical Engineering, University of Western Ontario, Thompson Engineering Building, London, Ontario N6A 5B9, Canada

### ARTICLE INFO

#### Article history:

Received 10 September 2010  
Received in revised form 14 January 2011  
Accepted 27 January 2011  
Available online 2 February 2011

#### Keywords:

17 $\beta$ -Estradiol  
EDCs  
Photodegradation  
Hydroxyl radicals  
Solar simulator

### ABSTRACT

Photodegradation of the natural steroid 17 $\beta$ -estradiol (E2), an endocrine disrupting hormone which is commonly released into aquatic environments, was investigated under simulated sunlight (290–700 nm) using a solar simulator in the presence of several natural water constituents including  $\text{NO}_3^-$ ,  $\text{Fe}^{3+}$ ,  $\text{HCO}_3^-$ , humic acid and turbidity. The E2 degradation followed pseudo-first-order kinetics, with the rate constant decreasing slightly with increasing initial constituent concentration while increasing with the square root of solar intensity in the region of 25–100  $\text{mW cm}^{-2}$ . The rate of mineralization based on the total organic carbon (TOC) reduction was always lower than E2 degradation, although the TOC of the solution decreased steadily with irradiation time. In the presence of  $\text{NO}_3^-$ ,  $\text{Fe}^{3+}$ , and humic acid, the photodegradation rate increased significantly, attributed to photosensitization by the reactive species, while  $\text{HCO}_3^-$  slowed down the degradation rate because of  $\text{OH}^\bullet$  scavenging. Turbidity also reduced the photodegradation of E2 by decreasing light transmittance due to attenuation. The solution pH also had a considerable effect on the rate with maximum degradation occurring around a neutral pH of 7.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

The ubiquitous presence of emerging contaminants (ECs) in aquatic environments is becoming a major worldwide concern. Among the ECs, special importance is given to endocrine disrupting compounds (EDCs), as they can interfere with the normal function of hormones by interacting with the endocrine system presenting a potential threat to both aquatic life and human health [1,2]. In addition to industrial chemicals such as bisphenol-A, DDT, atrazine, methoxychlor, chlordecone, alkylphenols, PCBs and phthalic esters, several natural steroid estrogens including estrone (E1), 17 $\beta$ -estradiol (E2), estriol (E3) and mestranol (MeEE2) and synthetic pharmaceuticals such as diethylstilbestrol (DES), ibuprofen, norfloxacin and 17 $\alpha$ -ethynylestradiol (EE2) were found to be the most potent of the EDCs [1–4].

Among the EDCs, natural estrogens are thought to be the most likely to cause estrogenic effects on aquatic life due to their very potent estrogenic activities, even at very low concentrations. Of the natural estrogens, 17 $\beta$ -estradiol is the most potent natural estrogen among those including estrone and estriol [4]. Estrogenic steroids are detected in both the influent and effluent of sewage treatment plants in different countries at various concentrations [2]. These steroid hormones make their way into the aquatic envi-

ronment through sewage discharge and animal waste disposal due to both human and animal excretions. These steroids have also been detected at elevated levels in soil, ground water as well as surface water adjacent to agricultural fields fertilized with animal manure [5].

Although the concentrations of the steroid hormones in natural aquatic environments are in the low ng/L range (10–1830 ng/L), it is very important to understand the fate of these EDCs in aquatic environments. Understanding their degradation rates helps to determine their environmental impact and potential threat to aquatic life due to their extremely high biological potency and procreation toxicity [6,7]. The degradation time of these organic pollutants in the environment may vary from a few hours to months depending on various environmental parameters [8]. Among the various environmental degradation processes (abiotic/biotic), photodegradation from solar irradiation is one of the most important factors for determining the ultimate fate of the persistent pollutants in aquatic environments [9].

Solar phototransformation or degradation of organics in aquatic environments may occur by either direct or indirect photolysis. Direct photolysis is the result of light absorbance by the pollutants causing their molecular degradation. As all steroid estrogens have considerable sunlight absorbance in the ultraviolet and blue spectral region (290–360 nm) [10], it is believed that direct photolysis plays a crucial role for the photodegradation of steroid estrogens in aquatic environments [11]. For indirect photolysis,  $\text{NO}_3^-$ ,  $\text{Fe}^{3+}$  and humic substances play crucial roles, which are ubiquitous in

\* Corresponding author. Tel.: +1 519 661 2111x81273; fax: +1 519 661 3498.  
E-mail address: [mray@eng.uwo.ca](mailto:mray@eng.uwo.ca) (M.B. Ray).

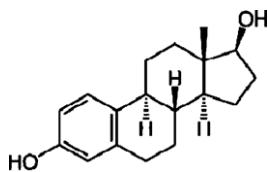


Fig. 1. Structure of 17 $\beta$ -estradiol (E2).

surface water and absorb solar radiation to reach an excited state, subsequently generating free radicals comprised of reactive oxygen species (ROS) (e.g., hydroxyl radicals (OH $\cdot$ ), peroxy radicals (ROO $\cdot$ ), and singlet oxygen ( $^1\text{O}_2$ )) and other non-ROS transients [12]. Among these reactive photochemically generated species in surface waters, OH $\cdot$  plays a very important role in the phototransformation of organic pollutants because of its very high oxidizing potential. In addition, reaction between most organics and OH $\cdot$  occurs with rate constants that are essentially diffusion controlled [13]. The major sources of OH $\cdot$  in natural water have been identified as NO $_3^-$ , Fe $^{3+}$ , and humic substance, while HCO $_3^-$  plays a negative role due to its scavenging effect on OH $\cdot$  in surface water [14]. Another important water parameter is turbidity, as it controls light attenuation in the water.

Steroid hormones are known to degrade rapidly in the presence of high intensity UV-C (254 nm), and many degradation studies of these hormones are available in the literature using advanced oxidation processes (AOP) such as semiconductor photocatalysis, UV/H $_2\text{O}_2$ , UV/O $_3$ , and O $_3$ /H $_2\text{O}_2$  [15–17]. Although photodegradation of steroid hormones has been studied in engineered systems, comprehensive studies documenting their fate in the presence of sunlight are still limited. Earlier, we reported the solar degradation of estrone (E1) in water [11], however, environmental photodegradation of 17 $\beta$ -estradiol (E2), the most potent of natural estrogens has not yet been fully investigated. A recent study conducted by Leech et al. showed the effect of natural organic matter on the solar degradation of E2 [18]. The objective of this comprehensive study is to determine the kinetics of the photodegradation of steroid E2 (see Fig. 1) in simulated aquatic environments due to direct solar irradiation (i.e. UV-B, UV-A, and visible radiation, 290–700 nm) using a solar simulator with controlled doses of sunlight under various environmental conditions including solar intensity, initial concentration of E2, pH, natural photosensitizers (dissolved uncharacterized organic matter or the humic substances, Fe $^{3+}$  and NO $_3^-$ ), and other water constituents such as HCO $_3^-$  and turbidity. The extent of mineralization of E2 under various conditions was also evaluated. In addition, wherever possible, a comparative analysis of the photodegradation of E1 and E2 is provided.

## 2. Experimental

### 2.1. Chemicals

E2 (MW: C $_{18}$ H $_{24}$ O $_2$ , CAS registry number: 50-28-2) was obtained from Sigma–Aldrich (Oakville, Ontario, Canada) and used without further purification. Acetonitrile (AcN) for HPLC analysis was of HPLC grade and purchased from Fisher Scientific (Ottawa, Ontario, Canada). Humic acid (Technical grade, CAS registry number: 1415-93-6) was also obtained from Sigma–Aldrich (Oakville, Ontario, Canada). AMCO clear turbidity standard, 1000 NTU was purchased from Fisher Scientific (Ottawa, Ontario, Canada). All other reagents used for solutions were reagent grade and used without further purification. Laboratory grade water (LGW, 18 M $\Omega$ ) was prepared from an in-house Millipore purification system (Billerica, MA).

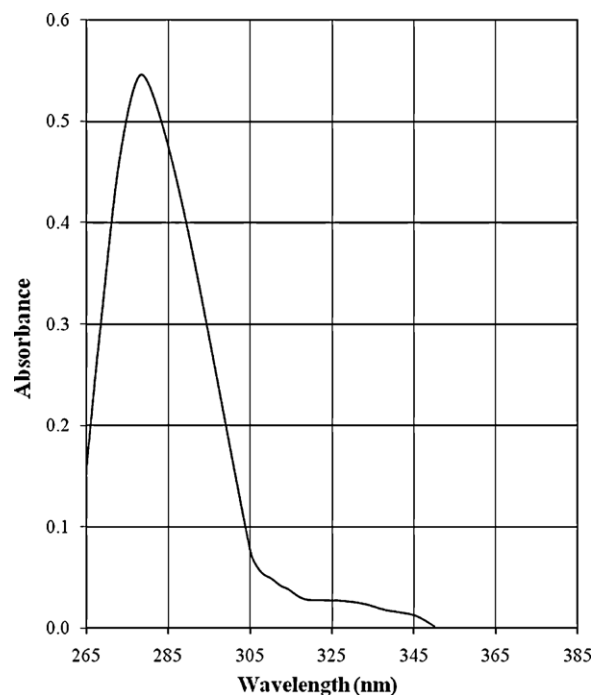


Fig. 2. Absorption spectrum of E2 over 265–385 nm at pH 6.5.

### 2.2. Standard and sample preparation

Stock solutions ( $5 \pm 0.05$  mg/L) of E2 (solubility: 13 mg/L at 20  $^{\circ}\text{C}$ ) were prepared by dissolving an appropriate amount of E2 in purified water in a volumetric flask by stirring for 2 h to ensure complete dissolution. The working water samples were prepared by adding the stock solution to purified water to obtain the desired initial concentration. The stock and working solutions were wrapped with aluminum foil and stored at 4  $^{\circ}\text{C}$  to prevent any degradation. The natural pH of Milli-Q water is 6.5, which is also the pH of the E2 solution. All experiments were conducted at pH 6.5 except for evaluating the effect of pH and HCO $_3^-$  on the degradation of E2, where NaOH or HCl were used to adjust the pH.

### 2.3. Photodegradation experiments

Photodegradation experiments were carried out using a solar simulator (Model: SS1KW, Sciencetech, ON, Canada) with a 1000 W xenon arc lamp. An air mass filter (AM filter) AM1.5G was installed in the radiation beam to produce simulated 1 SUN irradiance of 100 mW cm $^{-2}$  at full power that matches the global solar spectrum (Class A standards as per JIS-C-8912 and ASTM 927-05) at sea level and zenith angle 37 $^{\circ}$  (Fig. S1 in Supporting information). The light absorption spectra of E2 were measured and shown in Fig. 2. In spite of  $\lambda_{\text{max}} = 278$  nm, E2 exhibits a slight absorption in the 300–350 nm wavelength region, which can induce photolysis of E2. Hence, photon flux from the solar simulator was calculated in the 300–400 nm range, being  $5.3 \times 10^{-5}$  Einstein m $^{-2}$  s $^{-1}$  at 1 SUN irradiation.

An open water-jacketed vertical glass vessel (length: 11 cm  $\times$  diameter: 9 cm) was used as the solar photo-reactor, which was placed on a magnetic stirrer during all experiments, under aerated conditions at 350 rpm and a temperature of  $22 \pm 2$   $^{\circ}\text{C}$ . The aqueous solution was irradiated directly from the top using a vertical solar beam of 8 in. (20.3 cm) diameter from the solar simulator. In all experiments, the total irradiated solution volume was 300 mL. The irradiation intensity was measured at the top surface of the experimental solution by a Broadband Thermopile Detector (Model: UP19K-15W, Sciencetech, ON, Canada), which

Download English Version:

<https://daneshyari.com/en/article/28801>

Download Persian Version:

<https://daneshyari.com/article/28801>

[Daneshyari.com](https://daneshyari.com)