



## Photodegradation behaviour of estriol: An insight on natural aquatic organic matter influence



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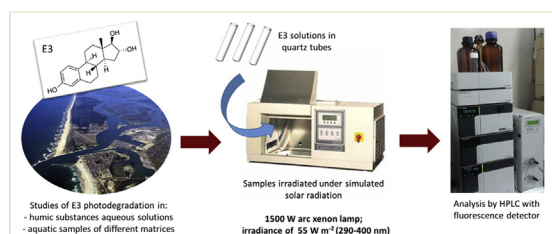
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### HIGHLIGHTS

- Direct photodegradation of E3 occurred at  $k_{meas} = 0.0138 \text{ h}^{-1}$  ( $t_{1/2} = 50 \text{ h}$ ).
- Humic acids (HA), fulvic acids (FA) and XAD-4 favored E3 photodegradation.
- $t_{1/2}$  (E3) in HA, FA and XAD-4 was 10.4, 5.6, 4.9 h, respectively.
- In environmental aquatic matrices  $t_{1/2}$  (E3) varied between 1.6 and 9.5 h.
- Estuarine water matrix contributed to 97% of the overall E3 photodegradation.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Estriol (E3) is one of the steroidal estrogens ubiquitously found in the aquatic environment, photodegradation being an important pathway for the elimination of such endocrine disrupting compounds. However, it is important to understand how environmentally important components present in aquatic matrices, such as organic matter, may affect their photodegradation. The main objective of this work was to investigate the photodegradation of E3 in water, under simulated solar radiation, as well as the effect of humic substances (HS - humic acids (HA), fulvic acids (FA) and XAD-4 fraction) in E3 photodegradation. Moreover, the photodegradation behaviour of E3 when present in different environmental aquatic matrices (fresh, estuarine and waste water samples) was also assessed.

Results showed a completely different E3 degradation rate depending on the aquatic matrix. In ultrapure water the half-life obtained was about 50 h, while in presence of HS it varied between 5 and 10 h. Then, half-life times between 1.6 and 9.5 h were determined in environmental samples, in which it was observed that the matrix composition contributed up to 97% for the overall E3 photodegradation. Therefore, E3 photodegradation in the considered aquatic matrices was mostly caused by photosensitizing reactions (indirect photodegradation).

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## 1. Introduction

Steroid hormones include glucocorticoids, androgens, estrogens and progestogens, which are generally synthesized from cholesterol (Yoshimoto et al., 2004). Estrogens are important in menstrual and reproductive cycles. The predominant female natural hormones are estrone (E1), 17 $\beta$ -estradiol (E2) and estriol (E3; Fig. 1), while 17 $\alpha$ -ethinylestradiol (EE2) is a synthetic estrogen, mainly used in contraceptive pills. These compounds belong to the so-called endocrine disrupting compounds (EDCs) group, representing a potential threat to both human health and aquatic life (Silva et al., 2012). Their negative effect on the endocrine system of humans and animals is due to their ability to mimic and/or antagonize the effect of endogenous hormones and to disrupt the synthesis and metabolism of the same hormones (Matozzo et al., 2008; Mendes, 2002).

Estrogens present in domestic sewage and livestock waste water are directly discharged into receiving waters or as the effluents of sewage treatment plants (STPs), therefore reaching the aquatic environment (Janex-Habibi et al., 2009; Zuo et al., 2006a, 2006b, 2013). Natural and synthetic estrogens have been detected in influents and effluents of STPs and also in surface waters in concentrations generally in the  $\mu\text{g}\text{-ng L}^{-1}$  range (Baronti et al., 2000; Chen et al., 2013; Lima et al., 2013, 2014; Zuo et al., 2006a, 2006b; Zuo et al., 2013). When released into the environment, estrogens are exposed to solar radiation, including both the UVA and UVB wave band of the solar spectrum, with the wavelengths in the range of 320–400 nm and 280–320 nm, respectively. For this reason, the investigation of estrogens behaviour under UV radiation is extremely important. Photodegradation in aquatic environment may occur via two principal processes: direct and indirect photolysis. In the direct photolysis, light is absorbed directly by the chemical itself, leading to bond cleavage (Liu and Liu, 2004). Indirect photolysis consists of light absorption by photosensitizers, which generate photoreactants, such as OH radicals ( $\cdot\text{OH}$ ) or singlet oxygen ( $^1\text{O}_2$ ) (Zuo, 2003). The most important photosensitizers are natural dissolved organic matter (DOM), nitrate and nitrite (Lin and Reinhard, 2005; Wang et al., 2015; Zuo and Deng, 1998; Zuo and Jones, 1997; Zuo et al., 2006a, 2006b, 2013). During the last decade, studies on the photodegradation of estrogens have focused mainly on E1, E2 and EE2 (Silva et al., 2016a,b) while comparatively few works have been published on the photodegradation of E3 (Chen et al., 2013). This estrogen is produced during pregnancy in significant amounts (placenta is the predominant site of E3 synthesis) and its formation is also possible through oxidation of E2 (Lai et al., 2000). In aqueous solution, E3 may undergo both direct and indirect photodegradation under the presence of natural photoreactive constituents, such as humic acids (HA) (Chen et al., 2013). The effect of HA and the other fractions of humic

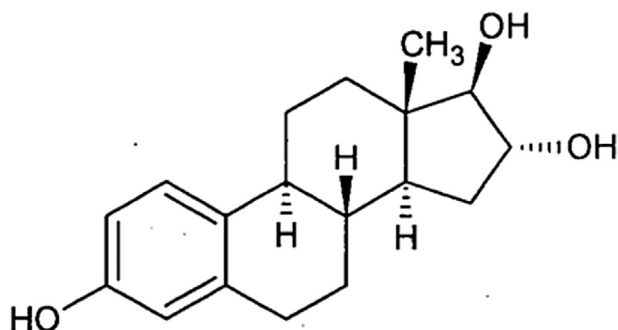


Fig. 1. E3 chemical structure.

substances (HS), namely fulvic acids (FA) and XAD-4, on the photodegradation of E1, E2 and EE2 has been proved to be different (Silva et al., 2016a,b). However, in the case of E3 photodegradation, a better knowledge about the influence of natural aquatic organic matter is needed. A novelty of this work is the evaluation, for the very first time, of the effect of the XAD-4 fraction on the photo-transformation of E3. Therefore, the aim of this work was to study the kinetics of E3 degradation under simulated solar irradiation, the effect of three HS fractions (HA, FA and XAD-4 fraction) in the photodegradation and also the E3 photodegradation behaviour in environmental aquatic matrices from different origins (estuarine water, freshwater and waste water samples).

## 2. Material and methods

### 2.1. Chemicals

E3 (>99%) was purchased from Sigma-Aldrich. Ultrapure water used in the preparation of solutions was obtained from a Milli-Q Millipore system (Milli-Q plus 185). Acetonitrile (HPLC grade) used for HPLC analysis, was obtained from VWR, Prolabo.

### 2.2. Chromatographic analysis of E3

A stock solution of  $100 \text{ mg L}^{-1}$  was prepared in acetonitrile due to the low solubility of E3 in water and stored at  $4 \text{ }^\circ\text{C}$ . The E3 calibration curve was obtained using standard solutions with concentrations from 1 to  $100 \text{ }\mu\text{g L}^{-1}$  through dilution of the stock solution with ultrapure water.

A Shimadzu High-Performance Liquid Chromatograph Prominence system equipped with a fluorescence detector (HPLC-FLD) was used. This device consisted of a degasser DGU-20A5, a pump LC-20AD and a column oven CTO-10ASVP. An ACE<sup>®</sup> C18-PFP column ( $5 \text{ }\mu\text{m}$ ,  $150 \text{ mm} \times 4.6 \text{ mm}$ ) connected to an ACE<sup>®</sup> 5 C18  $4.6 \text{ mm i.d.}$  guard column was used for the separation and the mobile phase consisted in an ultrapure water:acetonitrile mixture (40:60, v/v), at a flow rate of  $0.8 \text{ mL min}^{-1}$  with an injection volume of  $20 \text{ }\mu\text{L}$ . Before use as mobile phase, water and acetonitrile were filtered through a  $0.2 \text{ }\mu\text{m}$  polyamide membrane filters (Whatman). Detection was performed using a Shimadzu Prominence RF-20A XS fluorescence detector at an excitation wavelength of 280 nm and an emission wavelength of 310 nm. Both the cell and column temperatures were maintained at  $25 \text{ }^\circ\text{C}$ .

### 2.3. Photodegradation experiments

#### 2.3.1. Irradiation

All irradiation experiments were performed using a Solarbox 1500 (Co.fo.me.gra, Italy). The device contained an arc xenon lamp (1500 W) and outdoor UV filters that limited the transmission of light with wavelengths shorter than 290 nm. The irradiance of the lamp was kept constant throughout all the experiments and was set to  $55 \text{ W m}^{-2}$  (290–400 nm). Also, in order to keep a constant temperature, the device was refrigerated by an air cooled system. To monitor the irradiance level and temperature, a multimeter (Co.fo.me.gra, Italy), that was equipped with a UV 290–400 nm large band sensor and a black standard temperature sensor, was used. Furthermore, to guarantee the uniformity of the irradiation inside the chamber a parabolic reflection system was used.

E3 photodegradation studies were performed using quartz tubes ( $1.8 \text{ cm}$  internal diameter and  $20 \text{ cm}$  height). To hold the quartz tubes suspended inside the irradiation chamber, a home-made metallic holder was used. For each set of experiments, 4 tubes were introduced into the Solarbox: three of them were exposed to radiation and the other one was covered with

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