



# UV and simulated solar photodegradation of 17 $\alpha$ -ethynylestradiol in secondary-treated wastewater by hydrogen peroxide or iron addition



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## ABSTRACT

The extensive use of estrogens and their release, through various pathways, into the environment, constitutes an emerging environmental problem that poses serious threats onto public health. In this work the efficiency of UVC/H<sub>2</sub>O<sub>2</sub> and solar/Fe<sup>2+</sup> treatment to degrade 17 $\alpha$ -ethynylestradiol (EE2) in environmentally relevant concentrations of 100  $\mu$ g/L in secondary-treated wastewater matrices was investigated. Also, photolytic treatment was performed under different irradiation sources, namely UVC, UVA and simulated solar light. The effect of H<sub>2</sub>O<sub>2</sub> (0–20 mg/L) and Fe<sup>2+</sup> (0–15 mg/L) concentration was investigated and, at optimal operating parameters, EE2 removal was 100% after 15 min of UVC/H<sub>2</sub>O<sub>2</sub> treatment, while EE2 removal reached 86% after 60 min of solar/Fe<sup>2+</sup> treatment. In addition, the effect of water matrix and pH was studied. Total organic carbon (TOC) and yeast estrogen screening (YES) measurements showed the formation of stable intermediate products during EE2 treatment and an attempt to elucidate the reaction pathways and mechanisms through the identification of transformation products (TPs) by means of UPLC–MS/MS was made. Several TPs, including quinone methide and 1,2-quinone derivatives, were identified and competing pathways were suggested, in which hydroxylation, alkylation, dealkylation, demethylation and dehydroxylation, amongst others were described as major transformation mechanisms.

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## 1. Introduction

Endocrine disrupting compounds (EDCs) is an emerging environmental issue that poses serious threats to human beings. EDCs have the ability to interact with the endocrine system of organisms and either mimic or inhibit the action of animal endogenous hormones, thus leading to a variety of developmental and reproductive disorders, as well as feminizing effects [1]. Estrogens include natural, synthetic, and phyto-estrogens and are well-known EDCs. Of them, synthetic estrogens, such as 17 $\alpha$ -ethynylestradiol (EE2), which is the basic component of the

contraceptive pill, are generally more stable than natural estrogens in aqueous environment and have greater estrogenic potency (approx. 11–27 times) than the natural estrone (E1) and estradiol (E2) [2]. Recent in vivo studies showed that EE2 even in the order of  $\mu$ g/L was able to affect continuously exposed rats, by decreasing their bodyweight, accelerating vaginal opening, and altering estrous cycles in young animals [3]. Also, chronic exposure to environmentally relevant concentrations of EE2 could cause liver and gill lesions in zebrafish [4], depress gonadal growth in males mummichogs [5], and could affect the pituitary transcriptome in female salmon in previtellogenic stages of ovarian growth, altering the expression of hundreds of genes involved [6].

EE2 can enter into aqueous environments (i.e. surface and ground water bodies) through several pathways, such as wastewater treatment plants (WWTPs), septic systems, and after use in agriculture [7]. Besides, EE2 is resistant to biological oxidation and escapes intact from conventional WWTPs, thus accumulating

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in the environment [8]. Several studies have reported the occurrence of EE2 in WWTP effluents worldwide (in the range of ng/L), while even more studies have detected EE2 at surface and drinking water raising serious concerns for public health [7,8]. All these findings indicate that current treatment processes at WWTPs are inadequate to completely remove EE2. Hence, additional or alternative processes should be applied to support existing WWTP and increase their efficiency.

Due to the effectiveness of UV light for disinfecting drinking water, many water treatment plants are installing UV based systems. Such UV systems may also be effective for treatment of chemical contaminants, although their ability to destruct them completely is still under investigation. Nasuhoglu et al. [9] reported that EE2 can be degraded by about 90% and 50% in pure water and in industrial wastewater matrices, respectively, after 30 min of UVC treatment. Other studies also showed that UVC has the potential to effectively destruct EE2 in the order of mg/L by UVC [10–12], UVC/TiO<sub>2</sub> [11], UVC/H<sub>2</sub>O<sub>2</sub> [12,13] or UV/Fe<sup>3+</sup> [10] systems. However, more work has to be done to further optimize UV process and assess its efficiency to treat environmentally relevant EE2 concentrations in real wastewater matrices.

Another effective, low-cost and robust alternative that can be used as an additional or as a tertiary treatment in existing WWTPs, is the use of solar-driven photocatalytic processes. These seem to be the most suitable treatment technology for using natural sunlight; an abundant and free source of energy [14]. The role of iron in environmental chemistry was first reported in the 1990s and since then, several studies on the photo-assisted Fe<sup>2+</sup>, mainly in the form of the Fenton reagent (i.e. Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>), for water treatment applications were published [14]. Iron can play a dominant catalytic role in organics degradation under natural environmental conditions. Also, iron is an abundant and non-toxic element and it can be found at concentrations between 0.5 and 50 mg/L in natural fresh waters, while it does not present a hazard to human health at levels up to 2 mg/L in drinking water [15]. The decomposition of EE2 by photo-Fenton process under simulated solar irradiation has been studied by Frontistis et al. [15] who found that solar photo-Fenton (5 mg/L Fe<sup>2+</sup>/8.6 mg/L H<sub>2</sub>O<sub>2</sub>) treatment could completely remove 70 µg/L EE2 from wastewater matrix after only 6 min of treatment. Moreover, estrogens degradation by UV/Fe<sup>3+</sup> [10] treatment system was studied and showed that the addition of iron can significantly enhance photolytic processes.

The aim of this work is to investigate the degradation of EE2 by UVC and solar irradiation. Environmentally relevant EE2 concentrations at the µg/L level are used, while emphasis is given on EE2 degradation in secondary-treated WWTP effluents. Additional materials, such as H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> to support the photolytic process are used and operating parameters, including pH, EE2 initial concentration, concentration of peroxide or iron, water matrix and treatment time are investigated. In addition, transformation products are identified and potential EE2 degradation pathways are proposed. It should be noted that up to now, a limited number of studies exist with regard to the transformation products of EE2 [16–20] and that the photocatalytic degradation of EE2 proves to be a quite complex process due to the stable structure of the molecule even against such powerful oxidation processes.

## 2. Materials and methods

For this work, 17 $\alpha$ -ethynylestradiol (EE2) (>98%, Fluka), H<sub>2</sub>O<sub>2</sub> (35% w/w, Merck) and humic acid (Sigma-Aldrich, CAS number: 57-63-6) were purchased and used as received. EE2 (chemical formula: C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>) is a white to creamy white, odourless crystalline powder with a molecular mass of 296.40 g/mol and its chemical structure is shown in Fig. 1. Its solubility in water is 9.20  $\pm$  0.09 mg/L

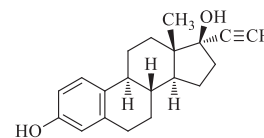


Fig. 1. Chemical structure of EE2.

at 25.0  $\pm$  0.5 °C [21] and its octanol-water partitioning coefficient ( $K_{ow}$ ) is 3.67 [22]. To add, EE2 in distilled water has a maximum absorbance in UV–vis electromagnetic spectrum at 221 nm [16].

Fe<sup>2+</sup> is added in the aqueous solutions in the form of FeSO<sub>4</sub>·7H<sub>2</sub>O ( $\geq$ 99%, Sigma-Aldrich). The wastewater (WW) matrix is collected from the outlet of the secondary treatment of the municipal WWTP of Chania, Greece. The effluent's TOC content is 7.8 mg/L, its inherent pH is about 8 and its conductivity is 820 µS/cm. Ultrapure water (UPW) at pH = 6.1 is taken from a water purification system (EASYPureRF–Barnstead/Thermolyne, USA). Commercially available bottled water is used as the drinking water matrix for this study.

In each photocatalytic run, 300 mL of the water matrix spiked with the appropriate amount of EE2 and other chemical substances if required, are fed in the photochemical reactor. Magnetic stirring is always provided and temperature is kept constant at 25  $\pm$  2 °C, while the reactor is open to the atmosphere. In those cases when hydrogen peroxide was used, residual H<sub>2</sub>O<sub>2</sub> was scavenged, in withdrawn samples, adding the appropriate amount of Na<sub>2</sub>SO<sub>3</sub> ( $\geq$ 98%, Sigma-Aldrich).

UVA and UVC experiments are conducted in an immersion well, batch type, laboratory scale photoreactor, purchased from Ace Glass (Vineland, NJ, USA) which is described in detail elsewhere [23]. UVA irradiation is provided by a 9W lamp (Radium Ralutec, 9W/78, 350–400 nm). UVC irradiation is provided by an 11 W low pressure mercury lamp (Phillips, TUV PL-S). The photon fluxes of the UV lamps are determined actinometrically using the potassium ferrioxalate method and they are estimated at 4.69  $\times$  10<sup>-6</sup> E/s and 7.15  $\times$  10<sup>-6</sup> E/s for the UVA and UVC lamp, respectively. Simulated solar irradiation is emitted by a Newport 96000-150 W solar simulator system. Light source is placed on top of a double-walled cylindrical pyrex cell containing the aqueous reactant mixture. The photon flux of the solar lamp was measured using 2-nitrobenzaldehyde (purchased from Sigma-Aldrich) as the chemical actinometer [24] and it was found to be 17.4  $\times$  10<sup>-8</sup> E/s.

Changes in EE2 concentration are followed by an HPLC (Alliance 2690, Waters) system where separation is achieved on a Luna C-18(2) column (5 µm, 250 mm  $\times$  4.6 mm) and a security guard column (4 mm  $\times$  3 mm), both purchased from Phenomenex. Detection is achieved through a fluorescence detector (Waters 474) and method details are described in detail elsewhere [15]. Analyses of transformation products (TPs) of EE2 photodegradation were performed by ultra performance liquid chromatography coupled with tandem mass spectrometry on an ACQUITY TQD UPLC–MS/MS system (Waters) by a method described in detail elsewhere [16]. Sample extraction was performed by solid phase extraction (SPE) using cartridges built of hydrophilic and a lipophilic monomer (Oasis-HLB; 50 mg/3 mL), and purchased from Waters (Milford, MA, USA). The sample (10 mL) is filtered through a syringe-filter (22 µm pores) prior to the SPE. TOC is measured on a Shimadzu 5050A TOC analyzer. EE2 absorbance spectrum is measured on a Shimadzu UV–Vis 1240 spectrophotometer. Residual H<sub>2</sub>O<sub>2</sub> concentration was monitored using Merck peroxide test strips in the range 0–25 mg/L. Finally, the *in vitro* yeast estrogen screen (YES) bioassay was employed to assess estrogenic activity of the effluent before, and after treatment [15].

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