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Fast degradation of estrogen hormones in environmental matrices by photo-Fenton oxidation under simulated solar radiation

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ABSTRACT

The efficiency of homogeneous Fenton oxidation induced by simulated solar radiation to remove 17α-ethynylestradiol (EE2), a synthetic estrogen hormone, from secondary treated effluents was investigated. Solar radiation was simulated with a 150 W xenon lamp and experiments were conducted varying initial effluent pH (3–8), EE2 concentration (70–315 μg/L), H_2O_2 concentration (1.5–86 mg/L) and Fe^{2+} concentration (1–5 mg/L). Changes in estrogen concentration were followed by high performance liquid chromatography. EE2 was readily oxidizable at acidic conditions (pH = 3) with complete conversion typically occurring in 5–10 min of irradiation at, e.g. 5 mg/L Fe^{2+}, 4.3–15 mg/L H_2O_2 and 200 μg/L EE2 concentration. The process involves two distinct kinetic regimes, a fast one during the very first minutes followed by a far slower one. The contribution of dark Fenton reactions to degradation was found to be considerable, particularly at higher concentrations of Fenton's reagents; nonetheless, the beneficial role of simulated solar irradiation was noticeable at lower concentrations and even in the absence of hydrogen peroxide, as well as for the mineralization of the effluent organic matter. Two natural hormones, namely estrone and 17β-estradiol were also tested and their reactivity values were nearly equal to EE2. The implications for tertiary wastewater treatment (removal of pathogens and estrogenicity) are also discussed.

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1. Introduction

Endocrine disrupting compounds (EDCs) constitute an important class of emerging environmental contaminants, which pose an increasing threat to aquatic organisms, as well as to human health. EDCs are divided in four main categories, namely natural estrogens, synthetic estrogens, phyto-estrogens and various industrial chemicals (i.e. pesticides, persistent organochlorines, organohalogens, alkyl phenols, heavy metals) [1]. EDCs have the ability to interact with the endocrine system of the organisms, thus leading to a variety of developmental and reproductive disorders, as well as feminizing effects [1,2]. Of the various categories, natural and synthetic estrogens exhibit much stronger estrogenic activity than phyto- and xeno-estrogens [1].

EDCs are only partially removed in conventional wastewater treatment plants (WWTPs) mainly through a combination of biodegradation processes and sorption onto microbial flocs, although the relative contribution of each pathway is not fully understood [1,3]. Servos et al. [4] reported the presence of two naturally occurring hormones, namely estrone (E1) and 17β-estradiol (E2) in eighteen Canadian WWTPs; the latter was removed by 75–98% in the treated effluent, while the former up to 98% although in several plants its concentration in the effluent was higher than in the influent. Interestingly, estrogenicity was reduced by only 47% on average as assessed by the in vitro yeast estrogen screening (YES) bioassay. In another monitoring campaign [5], E1 and E2 were identified in seven British WWTPs effluents, while three of them also contained 17α-ethynylestradiol (EE2), a synthetic estrogen used in the oral contraceptive pill. In a follow-up work [6], the estrogenic effect on fish was assessed in vivo and it was concluded that environmentally relevant concentrations of natural estrogens were sufficient to account for the levels of vitellogenin synthesis observed in fish. Similar monitoring campaigns reported the presence of E1, E2 and EE2 in several WWTPs worldwide (i.e. Germany, Canada and Brazil [7], Italy [8], and Japan [9], amongst others). These studies [1,2,4–9] and many more converge to the fact that WWTPs discharges contain residual estrogens at the ng/L level that constitute the main contributors to the effluent's estrogenic

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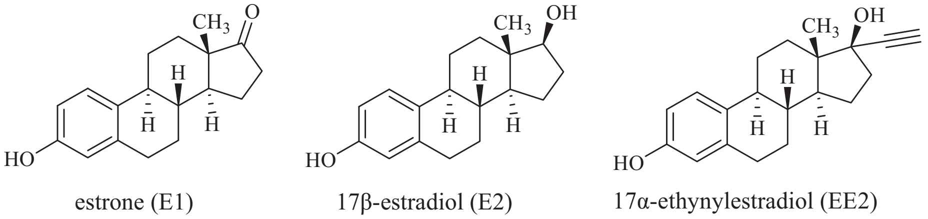

Scheme 1. Chemical formulae of estrogen hormones used in this study.

activity; in this respect, additional treatment may be needed to remove EDCs from the effluent.

In recent years, advanced oxidation processes (AOPs) have gained particular attention for the degradation of emerging micropollutants like EDCs and pharmaceuticals and personal care products in various aqueous matrices [10]. Several recent studies have confirmed the ability of processes like electrochemical oxidation [11], ultrasound irradiation [12], ozonation [13], TiO_2 photocatalysis [14–16] and H_2O_2-promoted photolysis [17,18] to degrade estrogens like E1, E2 and EE2.

In recent years, the Fenton process has been extensively employed for the oxidation of many classes of organic compounds due to its high efficiency to generate hydroxyl radicals, as a result of the decomposition in acidic medium of H_2O_2 by ferrous ions (reaction (1)). This is an attractive oxidation system due to the fact that iron is an abundant and non-toxic element (e.g. 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 [19]) and hydrogen peroxide is easy to handle and environmentally safe. Furthermore, ultraviolet/visible light raises the efficiency of the process by photoreducing Fe^{3+} to Fe^{2+}, producing additional hydroxyl radicals and leading to the regeneration of the catalyst (reaction (2)) [20]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \quad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^+ \quad (2)$$

The decomposition of estrogens by homogeneous photo-Fenton reactions has only merely been studied in the literature. Feng et al. [21] who studied the degradation of E1 in distilled water under UV-A irradiation reported 100% and 57% conversion after 160 min of reaction at 2.5 and 10 mg/L E1 concentration, respectively at $pH_o = 3$, 0.6 mg/L Fe^{3+} and 28.3 mg/L H_2O_2. They also found out that E1 was marginally less oxidizable than E2 and EE2.

Zhao and Hu [22] and Zhao et al. [23] prepared iron oxide-coated resins for the heterogeneous Fenton oxidation of E2 under UV-A irradiation in distilled water. They reported 86% and 100% conversion after 480 min of reaction at $pH_o = 6.5–7.5$, 272 μg/L E2, 330 mg/L H_2O_2 and 5 g/L α-FeOOH [22] or β-FeOOH [23], respectively. E2 conversion remained unchanged when the experiment was repeated in drinking water with α-FeOOH, while several degradation by-products were identified [24]; moreover, the degradation rate could be described by the L–H kinetic model [25].

The aim of this work was to study the degradation of three estrogens, namely E1, E2 and EE2 (with emphasis on the latter) by means of homogeneous photo-Fenton reactions. Besides the lack of adequate literature on the subject, the novelty of the work is associated with (i) the use of environmentally relevant matrices (i.e. secondary treated effluents spiked with estrogens at the μg/L level rather than model solutions at the mg/L level) and the investigation of their interactions, (ii) the application of simulated solar radiation to assess the feasibility of renewable energy to induce this kind of reactions, and (iii) process evaluation for tertiary treatment (i.e. disinfection and removal of overall estrogenicity).

2. Materials and methods

2.1. Materials

Estrone (E1), 17β-estradiol (E2) and 17α-ethynylestradiol (EE2) were purchased from Sigma–Aldrich and used as received. Their chemical structures are shown in Scheme 1, while main physicochemical properties in Table 1. Unless otherwise stated, secondary treated wastewater samples were collected from the outlet (i.e. post-chlorination) of the municipal WWTP of Chania, W. Crete, Greece. The chemical oxygen demand (COD) and dissolved organic carbon (DOC) content was 27 and 8.4 mg/L, respectively, while the effluent's inherent pH was about 8 and its conductivity was 810 μS/cm. Moreover, they contained 172 mg/L chlorides, 194 mg/L bicarbonates, 54 mg/L sulfates, 37 mg/L nitrates and 37 mg/L nitrites. The samples were also checked by ICP/MS for the presence of iron, whose concentration (as total iron) did not exceed 40 μg/L. In some cases, experiments were conducted with samples taken before chlorination to evaluate process performance in terms of simultaneous estrogens removal and disinfection. They contained 220 mg/L chlorides, 188 mg/L bicarbonates, 60 mg/L sulfates, 26 mg/L nitrates and 57 mg/L nitrites, as well as 10^3 CFU/mL of *Escherichia coli*.

Stock estrogen solutions were prepared at 1 mg/L concentration and the appropriate volume was spiked to wastewater to obtain the desired estrogen concentration which, in most cases, was 200 μg/L; this corresponds to about 160 μg/L of DOC, i.e. just 2% of the

Table 1
Properties of estrogen hormones used in this study.

Compound	Estrone (E1)	17β-Estradiol (E2)	17α-Ethynylestradiol (EE2)
IUPAC name	1,3,5(10)-Estratrien-3-ol-17-one	1,3,5-Estratriene-3,17β-diol	17α-Ethynyl-1,3,5(10)-estratriene-3,17β-diol
CAS number	53-16-7	50-28-2	57-63-6
Molecular formula	$C_{18}H_{22}O_2$	$C_{18}H_{24}O_2$	$C_{20}H_{24}O_2$
Molar mass (g/mol)	270.37	272.38	296.40
Appearance	White crystalline powder	White crystalline powder	White crystalline powder
Melting point (°C)	258–260	176–180	182–183
Solubility in water (mg/L)[a]	1.3 ± 0.08	1.51 ± 0.04	9.2 ± 0.09

[a] Data taken from Ref. [26].

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