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Photocatalytic (UV-A/TiO_2) degradation of 17α-ethynylestradiol in environmental matrices: Experimental studies and artificial neural network modeling

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ABSTRACT

The efficiency of heterogeneous photocatalysis to degrade 17α-ethynylestradiol (EE2), a synthetic estrogen hormone, in environmentally relevant samples was investigated. In most cases, UV-A radiation at a photon flux of 2.81×10^{-4} einstein/min was provided by a 9 W lamp and experiments were conducted at various concentrations of Aeroxide P25 TiO_2 (50–1000 mg/L), EE2 concentrations (50–900 μg/L) and water matrices (from ultrapure water to secondary treated wastewater). Some runs were performed at photon fluxes between 6.4×10^{-7} and 3.7×10^{-4} einstein/min to study the effect of intensity on degradation. Changes in estrogen concentration were followed by high performance liquid chromatography. EE2 degradation, which follows first order kinetics, increases with (i) increasing catalyst loading up to a threshold value beyond which it remains unaffected; (ii) increasing photon flux and (iii) decreasing matrix complexity, i.e. the organic and inorganic constituents of wastewater retard degradation. This may be overcome coupling photocatalysis with ultrasound radiation at 80 kHz and 41 W/L power density; the combined sonophotocatalytic process acts synergistically toward EE2 degradation. Several transformation products were identified by means of UPLC–MS/MS and a reaction network for the photocatalytic degradation of EE2 is suggested.

An artificial neural network comprising five input variables (reaction time, TiO_2 and EE2 concentration, organic content and conductivity of the water matrix), thirteen neurons and an output variable (EE2 conversion) was optimized, tested and validated for EE2 degradation. The network, based on tangent sigmoid and linear transfer functions for the hidden and input/output layers, respectively, and the Levenberg–Marquardt back propagation training algorithm, can successfully predict EE2 degradation.

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, which include natural estrogens, synthetic estrogens, phyto-estrogens and various industrial chemicals (i.e. pesticides, persistent organochlorines, organohalogens, alkyl phenols, heavy metals), 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 and suspended solids, although the relative contribution of each pathway is not fully understood [1]. Several monitoring campaigns [3–7] have confirmed the presence of estrogen hormones in WWTP discharges worldwide, including the naturally occurring estrone (E1) and 17β-estradiol (E2), as well as 17α-ethynylestradiol (EE2), a synthetic estrogen used in the oral contraceptive pill. These studies [1–7] and many more converge to the fact that WWTP discharges contain residual estrogens at the ng/L level that constitute the main contributors to the effluent's estrogenic activity; in this respect,

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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 micro-contaminants of emerging concern in various aqueous matrices with photochemical and photocatalytic processes playing a key role [8]. Semiconductor photocatalysis based on TiO_2 has been employed to degrade a mixture of E1 and E2 in model aqueous solutions concerning the effect of operating conditions (i.e. radiation wavelength, pH, catalyst and H_2O_2 concentration) on kinetics [9]. In further studies [10], a synthetic solution of E1, E2, EE2 and estriol was subjected to TiO_2 photocatalysis under UV-C or UV-A radiation in an annular photoreactor to model the radiation field and, subsequently, develop kinetic expressions independent of the reactor geometry and field. EE2 in pure water or in water:methanol mixture was photocatalytically oxidized to identify its major transformation intermediates and suggest possible degradation pathways [11]. The effect of adding ethanol and/or urea in aqueous solutions of E2 and EE2 on the extent of estrogen adsorption onto titania particles and subsequent photodegradation was evaluated in other studies [12]. A pilot system comprising a slurry photocatalytic reactor and a microfiltration membrane was tested to treat a mixture of 32 pharmaceuticals and EDCs (including five estrogen hormones) spiked in drinking water; emphasis was given on the effective removal of target compounds and associated estrogenicity in relation to energy consumption of the UV lamps [13]. Besides TiO_2 photocatalysis [9–13], the use of iron oxide-coated resins for the heterogeneous photo-Fenton oxidation of E2 in distilled water has been reported [14,15].

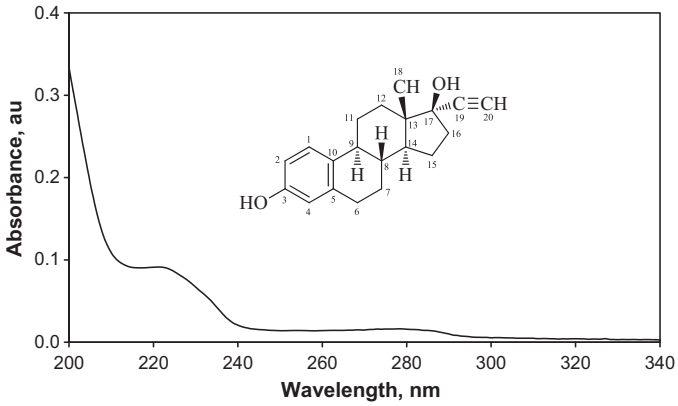
Although the aforementioned studies [9–15] are important describing mostly experimental work in the area, they have exclusively been carried out in model aqueous solutions and/or at conditions that are far from those typically met in environmental samples (e.g. presence of organic solvents, estrogen concentrations at the mg/L level, highly acidic or alkaline conditions, etc.). In this perspective, the aim of our work was to study the UV-A/TiO_2 degradation of EE2 in environmentally relevant samples (i.e. secondary treated effluents spiked with EE2 at the μg/L level) with emphasis on the effect of water matrix, catalyst type and concentration, estrogen concentration, photon flux and ultrasound radiation on degradation kinetics. An attempt was also made to elucidate reaction pathways and mechanisms through the identification of primary transformation products (TPs).

In addition to experimentation, artificial neural networks (ANNs) were employed to simulate the process and define the significance of the various operating variables. ANN are computer-based systems designed to simulate the learning process of neurons in the human brain [16]. In recent years, they have been employed in many areas of science and engineering to model various complex processes including biological and physicochemical water/wastewater treatments [17]. Notably, the number of publications dealing with ANN modeling in heterogeneous photocatalysis is rather limited as pointed out in a recent review article [16].

2. Experimental and analytical

2.1. Materials

The majority of the experiments were performed with 17α-ethynylestradiol ($C_{20}H_{24}O_2$), which was purchased from Sigma–Aldrich (CAS number: 57-63-6) and used as received. Its structural formula and absorbance spectrum are shown in Schematic 1. Some runs were done with other EDCs, namely bisphenol A (BPA) and 17β-estradiol, which were also purchased from Sigma–Aldrich and used as received.



Scheme 1. The structural formula and absorbance spectrum of EE2.

Three commercially available titania samples were tested, namely: (i) Aeroxide P25 (formerly known as Degussa P25, 75:25 anatase:rutile, 50 m^2/g BET area, 21 nm particle size, supplied by Evonik Industries); (ii) Hombikat UV100 (>99% anatase, >250 m^2/g BET area, 5 nm particle size, supplied by Sachtleben Chemie); (iii) Tronox AK1 (100% anatase, 90 m^2/g BET area, 20 nm particle size, supplied by Tronox Inc.).

Stock estrogen solutions were prepared at 1 mg/L concentration and the appropriate volume was spiked to the water matrix to obtain the desired estrogen concentration; four matrices were employed, namely: (i) wastewater (WW) collected from the outlet of the secondary treatment of a municipal WWTP. The matrix was characterized by standard methods [18] as follows: the chemical oxygen demand and dissolved organic carbon (DOC) was 24 and 8.4 mg/L, respectively, while its pH was about 8 and the conductivity 820 μS/cm. Moreover, it contained 172 mg/L chlorides, 194 mg/L bicarbonates, 54 mg/L sulfates, 37 mg/L nitrates and 37 mg/L nitrites; (ii) ultrapure water (UPW) taken from a water purification system (EASYpureRF – Barnstead/Thermolyne, USA) with 5.5 μS/cm conductivity and pH 6.1; (iii) a 50:50 mixture of WW and UPW; (iv) drinking water (DW) at pH 7.9, 308 μS/cm conductivity and 152 mg/L bicarbonates.

2.2. Photocatalytic experiments

Unless otherwise stated, UV-A radiation at 2.81×10^{-4} einstein/min was provided by a 9 W lamp (Radium Ralutec, 9W/78) emitting predominantly at 350–400 nm. The photon flux was determined actinometrically using the potassium ferrioxalate method. Experiments were conducted in an immersion well, batch type, laboratory scale photoreactor, purchased from Ace Glass (Vineland, NJ, USA) and described in detail elsewhere [19]. To study the effect of radiation intensity on degradation, experiments were also performed at various fluxes in the range of 6.4×10^{-7}–3.7×10^{-4} einstein/min; this was done either using a similar lamp of lower (i.e. 7 W) nominal intensity or partially covering the 9 W lamp with aluminum foil.

In a typical run, 0.3 L of the water matrix containing EE2 in the range of 50–900 μg/L were introduced in the reaction vessel made of borosilicate glass and then added titania in the range of 50–1000 mg/L. The suspension was magnetically stirred for 30 min in the dark and then the lamp was turned on, while air was continuously sparged in the reaction mixture under stirring. All experiments were performed at inherent pH which, although it was left uncontrolled during the reaction, remained practically unchanged. The temperature was maintained constant at 25 ± 2 °C with a temperature control unit.