



Photocatalytic degradation of estradiol under simulated solar light and assessment of estrogenic activity



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ABSTRACT

The ability of nanostructured titanium materials developed in the FP7/EU collaborative Clean Water project to photocatalytically degrade pollutants was tested, using 17 β -estradiol (E2) as the model compound. The photocatalytic degradation of E2 was carried out under simulated solar light (both the UV part (280–400 nm) and full spectrum (200 nm–30 μ m)). The efficiency of the process was assessed using several indicators including the conversion yield, the mineralization yield, the formation of by-products and their endocrine disrupting effects. The newly synthesized catalysts significantly degraded E2 and their efficiency was found to depend on the irradiation wavelength range. Some of the intermediates formed during the photocatalytic treatment with ECT-1023t and Evonik P25 were identified and their estrogenic effect was evaluated *in vivo* using the ChgH-GFP transgenic medaka line. This analysis confirmed that in the structure of the identified by-products, the phenol group is not destroyed and that the estrogenic effect is still present in the corresponding solution. The persistence of the estrogenic effect after the photocatalytic treatment is hypothesized to be due to the presence of the phenol group in the by-products.

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1. Introduction

Numerous studies reveal the presence of micropollutants in surface and ground water which can interfere with the endocrine system of humans and animals [1–4]. These endocrine disrupting compounds (EDCs) have been shown to cause a number of reproductive and sexual abnormalities in wildlife as well as a decline in sperm count. They are also suspected of being involved in numerous types of cancer in human beings [5–7].

EDCs, of natural and/or anthropogenic sources have been shown to disrupt the estrogen axis. 17 β -Estradiol (E2) is the most potent natural estrogen [8], presenting an estrogenic effect even at low concentrations (ng/L level) [5,9]. Around 90% of E2 excreted in

human and live-stock urine is endogenously produced but an additional <10% results from pharmaceuticals used in hormone replacement therapy.

The European commission has established water policies in order to ensure a sufficiently good water quality and environmental protection throughout the EU. The main objective of the Water Framework Directive of 2000 is to achieve a healthy state of water by 2015. In Brussels, in January 31st 2012, the Commission proposed the addition of 15 chemicals to the list of 33 pollutants that are monitored and controlled in EU surface waters. Because of its adverse effects, 17 β -estradiol is found in the proposed list of additional priority substances.

Conventional waste water treatments are not able to completely remove this compound. Therefore, it is released into the environment *via* the effluent of conventional waste water treatments plants [10,11]. Thus, in order to achieve the requirements stated in the Water Framework Directive, there is a need for sustainable

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treatment technologies capable of removing estradiol from surface water.

Advanced oxidation processes (AOPs) and technologies (AOTs) have proved to be a promising alternative for the remediation of organic pollutants. The most popular AOPs studied are heterogeneous photocatalysis with semiconductors, ozonation and the photo-Fenton process [12,13]. Heterogeneous photocatalysis and the photo-Fenton process are of special interest since sunlight can be used as the irradiation source [14]. Among the catalysts used in heterogeneous photocatalysis, TiO₂ has been gaining attention due to its strong photoinduced oxidation power [15].

Most photocatalytic treatments applied to remove E2 have used UV light [16–19], but this is costly and potentially dangerous for human health. On the contrary, the use of solar light as an irradiation source is more appropriate since it is freely available and environmentally friendly.

Nowadays, the research for extremely active TiO₂ catalysts under near UV–vis irradiation is a hot topic. The strategies aiming at exploiting solar light efficiently focus on titanium nanostructured materials with high photocatalytic activity as well as doping of TiO₂ with transition metals or with non-metallic elements [20].

In this context, the collaborative project Clean Water (FP7 Grant Agreement number 227017) aimed to synthesize innovative nanostructured photocatalysts with photocatalytic activity within the UV–vis range of solar light [21–23]. The catalysts manufactured within this project were tested with high success for the degradation of several micropollutants [21–25].

Results are presented here for the photocatalytic degradation of E2 under different experimental conditions: UV spectrum (280–400 nm) or the full UV–vis spectrum simulating solar light (200 nm–30 μm).

Special attention was paid to the reaction intermediates as a function of the type of catalyst as well as to the estrogenic effect of the intermediates.

In a number of studies dealing with the photocatalytic degradation of E2, the evaluation of the estrogenic effect of the treated solution was performed using the Yeast Estrogen Screen [16,19]. This test is carried out *in vitro* and can detect estrogen receptor agonists and antagonists. However, estrogen axis disrupting compounds do not only act as directly on the estrogen receptor, they can also inhibit enzymatic catalysis reactions, the transport of hormones in the blood or the production of hormone. In this case, only *in vivo* analysis can identify the full spectrum of possible mechanisms of disruption caused by these compounds in a whole organism. Thus, to identify a broad range of endocrine disrupting compounds, it is more rigorous to carry out *in vivo* estrogenic tests which enable the detection of several mechanisms of endocrine disruption.

In the present study, the estrogenic effect of E2 intermediates was assessed using a ChgH-GFP transgenic medaka line, enabling the detection of multiple types of estrogen axis disruption (estrogen agonists and antagonists, inhibitors and activators of enzymatic catalysis reactions, aromatizable androgens).

2. Materials and methods

2.1. Materials

Estradiol was purchased from Sigma Aldrich. Titanium dioxide (AEROXIDE® TiO₂ P25, $S_{BET} = 50 \text{ m}^2/\text{g}$) was obtained from Evonik Degussa GmbH (Frankfurt, Germany) and used as reference. Analytical reagents were obtained from Merck. Three catalysts in powder form were received from project partners: sol–gel synthesized, sieved (where aggregates were selected before

thermal treatment and calcined at 1023 K) nanocrystalline TiO₂ (ECT-1023t, $S_{BET} = 18.3 \text{ m}^2/\text{g}$) [21]; nitrogen-modified TiO₂ (N-TiO₂, $S_{BET} = 141 \text{ m}^2/\text{g}$); and reduced graphene oxide-TiO₂ composite (GO-TiO₂, $S_{BET} = 110 \text{ m}^2/\text{g}$). GO-TiO₂ (graphene oxide content of 4.0 wt.%) were prepared by liquid phase deposition followed by post-thermal reduction at 200 °C [22], whereas N-TiO₂ was synthesized as the hydrolysis condensation product of tetrabutyl titanate reaction with urea [23].

2.2. Photocatalytic experiments

Photocatalytic experiments were carried out in a cylindrical reactor irradiated from above with a solar simulator (Newport, USA), equipped with a 450 W Xenon arc lamp. A quartz cover was placed on the top of the glass reactor to minimize water loss due to evaporation. An AM1.5 filter was placed at the beam output to obtain a solar-like spectrum and, by using dichroic mirrors, a correct working wavelength range was selected. To conduct experiments, two wavelength ranges were chosen: 280–400 nm and 200 nm–30 μm. The volume of the reactor was 1 L. Catalyst load (P25, ECT-1023t, N-TiO₂ and GO-TiO₂) was 20 mg/L and the initial E2 concentration was 1 mg/L in ultra pure water (measured pH between 6 and 7). The solution of E2 and catalyst was allowed to equilibrate for at least 2 h before beginning each experiment. No significant adsorption phenomenon was observed. During irradiation, the solution was shaken and continuously bubbled with atmospheric oxygen. Aliquots were taken at various time intervals to determine the E2 residual concentration, the dissolved organic carbon concentration and the endocrine disruption effect. Prior to analysis, the solution was filtered through glass micro filters (GF/B, $D = 1 \mu\text{m}$, Whatman).

2.3. Analytical methods

The analysis of E2 was performed by HPLC (Model 600E, Waters) using a Nova Pack C18 reverse phase column (150 mm × 3.9 mm, I.D. 4 μm, Waters). A mobile phase isocratic elution program was applied with two solvents; Milli-Q water and acetonitrile ($V_{\text{water}}/V_{\text{acetonitrile}} = 55/45$) at a flow rate of 1 mL/min. The detection was performed with a UV detector (Model 486, Waters) at 197 nm. Dissolved Organic Carbon (DOC) was monitored with a Shimadzu 5000 TOC analyzer. The detection and quantification limits were 12 μg/L and 40 μg/L for the HPLC/UV and 16 μg/L and 32 μg/L for the TOC analyzer.

For the identification of estradiol intermediates, samples taken during the photocatalytic experiments were analyzed in infusion by tandem mass spectrometry (MS/MS) (Thermo Fischer) with an electrospray ionization (ESI) source, a triple quadrupole analyzer and a photomultiplier electron detector (TSQ Quantum Discovery). Mass spectra were obtained as an average of 50 scans, each requiring 0.02 s. ESI source conditions were as follows: negative mode, heated capillary temperature 350 °C; sheath gas (N₂) 40 psi, auxiliary gas (N₂) 15 psi, spray voltage 3500 V, tube lens offset voltage 100 V.

2.4. Evaluation of estrogenic effect

The estrogenic test was performed by WatchFrog using a ChgH-GFP transgenic medaka line. The ChgH-GFP transgenic medaka line harbors the coding sequence of the green fluorescence protein (GFP) gene driven by the regulatory sequence of the estrogen responsive choriogenin H (ChgH) gene. In the WatchFrog test, the estrogenic activity is indicated by the fluorescence of transgenic medaka eleutheroembryos when they are exposed to estrogenic compounds.

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