

DECOMPOSITION OF EDCs BY SOLAR LIGHT DRIVEN PHOTOCATALYSIS

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ABSTRACT

The oxidative degradation of a 17 α -ethinylestradiol (EE2) a synthetic estrogen used in the oral contraceptive pill was investigated by means of solar light photocatalysis in the presence of TiO₂. Several commercial TiO₂ catalysts (Kronos vlp7001, Kronos vlp7100, Kronos vlp7001, Millenium PC50, Millenium PC100, Millenium PC105, Millenium PC500, Tronox AK-1, Hombikat UV100, Aldrich, Degussa P25) were screened and Degussa P-25 exhibited considerable higher activity in terms of EE2 degradation and TOC reduction. It was found that EE2 degradation was 98% after 45 min treatment time, while mineralization was substantially slower and after 240 min was about 95%. EE2 reduction appears to follow a first order kinetic expression concerning its concentration and the reaction rate constant was computed 75 $\times 10^{-3}$ min⁻¹. EE2 degradation was faster than mineralization, thus implying the formation of oxidation products that were more resistant to photocatalytic oxidation than the parent compound.

KEYWORDS: EDC, photocatalysis, solar light, 17 α -ethinylestradiol, Titanium dioxide.

INTRODUCTION

An important class of emerging environmental contaminants is endocrine disrupting compounds (EDCs) (Auriol et al., 2006). EDCs posse increasing threat to human health, aquatic organisms and micro-organisms, livestock, and wildlife. It has been found that EDCs mimic or interfere with the action of animal endogenous hormones by acting as estrogen antagonists, binding to the estrogen receptor, altering the synthesis and metabolism of natural hormones, modifying hormone receptor levels or eliminating a normal biological response (Yang et al., 2007). The exposure of the organisms to EDCs may lead to a variety of effects in the field of developmental and reproductive disorders, including feminizing effects, while the increasing incidence of cancer and the hypothesis of a decreasing reproductive fitness of men are thought to be attributed to EDCs (Yang et al., 2007). In light of their frightening effects, efficient removal of EDCs from the aqueous environment has received increasing attention in recent years. Various advanced oxidation processes (AOPs) have been successfully employed for the degradation of EDCs in water and wastewaters (Belgiorno et al., 2007; Darlymple et al., 2007; Esplugas et al., 2007) with special emphasis given on TiO₂ photocatalysis (Coleman et al., 2005; Rosenfeldt et al., 2004).

17 α -ethinylestradiol (EE2), a synthetic estrogen used in the oral contraceptive pill, as well as natural estrogens such as 17- β -estradiol (E2), were detected in concentrations ranging from ng/L to μ g/L in sewage effluents, surface water, river water, bed sediments, and in

activated and digested sludge (Weber et al., 2005). In fish, as in all other vertebrates, estrogens play an important role in many reproductive and developmental processes, including sexual differentiation. The annual production of EE2 is estimated to be a couple of hundreds kilograms per year in Europe (Fent et al., 2006). In vivo tests have demonstrated that EE2 is approximately 11-27 times more potent in terms of estrogen activity than the natural female sex hormone E2 (Huber et al., 2004) leading to suggestions that EE2 may be the most important endocrine disruptor.

Photocatalysis is a chemical oxidation process in which a semiconductor immersed in water and irradiated with photons possessing energy equal to or greater than its band gap energy results in the formation of free hydroxyl HO[•] radicals. Although several semiconductors exist, TiO₂ is the most widely used catalyst, mainly because of its photo-stability, non-toxicity, low cost and water insolubility under most environmental conditions. However, conventional TiO₂ materials absorb radiation below 400 nm because of its relatively high band gap energy. In addition, only 3%-5% of the solar light reaching the surface of the Earth is in the UV range. In order to be able to effectively utilize solar light as the light source, the doping of TiO₂ is currently attracting considerable interest as a promising route to extend its absorption band to the visible region (Esplugas et al., 2007). Doping TiO₂ with non-metallic elements (Wang et al., 2000) has been proved to be more effective than doping with transition metals, which suffers from a thermal instability, an increase of carrier trapping, or the requirement of an expensive ion-implantation facility necessary for their preparation. Compared to nitrogen doping (Zhang et al., 2007), carbon doped TiO₂ has not received considerable attention.

The aim of the present work was to study the visible light driven photocatalytic degradation of EE2 in aqueous solutions using several TiO₂ samples. Various commercially available pure un-doped TiO₂ samples as well as carbon doped TiO₂ were screened for their efficiency to degrade and completely mineralize aqueous solutions of EE2.

METHODS

Materials

EE2 (its structure is shown in Figure 1 and its properties are summarized in Table 1) used in this study was purchased from Aldrich (purity>98%). Eleven commercially available titanium dioxide TiO₂ samples were employed in this study. Three of them, namely Kronos vlp-7001, Kronos vlp -7100, Kronos vlp-7101 kindly provided by Kronos International, Inc, were carbon doped TiO₂. On the other hand, the remaining eight catalysts, namely Millennium PC50, Millennium PC100 , Millennium PC105, Millennium PC500 (kindly supplied by Millennium Inorganic Chemicals), Tronox A-K-1 (supplied by Kerr McGee chemicals), Hombikat UV100 (supplied by Sachtleben Chemie), Aldrich (supplied by Sigma-Aldrich) and Degussa Aeroxide P 25 (supplied by Degussa AG) were pure un-doped TiO₂ samples. The catalysts were used as received and their physical properties, as given by the manufacturers, are summarized in Table 2. Deionized water used for solution preparation was prepared on a water purification system (EASYpureRF) supplied by Barnstead/Thermolyne (USA).

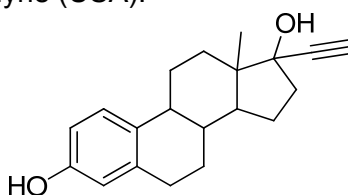


Figure 1. Molecular structure of EE2

Table 1. Properties of EE2

IUPAC Name	(17alpha)-estra-1,3,5(10)-triene-3,17-diol
CAS number	[57-91-0]
Molecular Formula	C ₁₈ H ₂₄ O ₂
Molar mass	272.38 g/mol
Appearance	White crystalline powder
Density	1.20 g/cm ³ , solid
Melting point	173-179 °C
Solubility in water	9.2 ppm (at 21.5°C)*

*Shareef et Al ,2006

Photocatalytic degradation experiments

The experimental procedure for the photocatalytic degradation of EE2 under simulated solar irradiation was as follows: 500 mL of a 1 mg/L EE2 solution in ultrapure water was added in a pyrex cylindrical vessel and the appropriate amount of catalyst was added giving the desired catalyst loading. The resulting suspension was magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption of EE2 onto the catalyst surface. After that period, the reaction vessel was placed under a metallic frame on which 9 Philips 36W/630 lamps and 1 Philips BLB TL-D 36W lamp were mounted, and the lamps were turned on, while the reaction mixture was continuously stirred. In all cases, experiments were performed at ambient pH and left uncontrolled during the reaction.

Table 2. Characteristics of TiO₂ samples used in the present study A: Anatase, R: Rut

Catalyst	Doping	Crystal Form	Crystallite Particle Size (nm)	BET surface area (m ² /g)
Kronos vlp7001	Carbon	A > 87.5 %	15	> 225
Kronos vlp7100	Carbon	A > 95 %	15	> 80
Kronos vlp7101	Carbon	A > 92.5 %	15	> 125
Millenium PC50	-	A >97%	20-30	>54
Millenium PC100	-	A>99%	15-25	80-100
Millenium PC105	-	A>95%	20	80-100
Millenium PC500	-	A 82-86%	5-10	287
Tronox AK-1	-	A>95%	20	90
Hombikat UV100	-	A>99%	5	>250
Aldrich	-	A >99%	25	200-220
Degussa P25	-	A 75%, R 25%	21	50

Analytical measurements

Samples periodically drawn from the reaction vessel were centrifuged at 13,000 rpm to remove catalyst particles and were analyzed with respect to their EE2 concentration and total organic carbon (TOC) content. TOC was measured using a Shimadzu 5050A TOC analyzer. EE2 concentration was monitored by HPLC on an Agilent 1100 system equipped with a fluorescence detection HP 1046. The excitation wavelength was 280 nm and the emission wavelength was 305 nm. Separation was achieved on a Supelco C-18

column (150 mm ×4.6 mm ×5 μm). The flow rate was 0.5 mL/min and the mobile phase was a mixture of ultrapure water and acetonitrile with a linear gradient starting from 50/50 and resulting to 25/75 after 15 min. Under these experimental conditions, the retention time of EE2 was 7.1 minutes.

RESULTS AND DISCUSSION

In an initial set of photocatalytic experiments, eleven commercially available TiO₂ samples were tested for their efficiency to decompose EE2 in aqueous solutions as well as to completely mineralize the organic content of the solutions under simulated solar irradiation. Three catalysts, namely, Kronos vlp 7001, vlp 7100 and vlp 7101, were carbon doped TiO₂, while the remaining eight catalysts namely, Millennium PC 50, PC 100, PC 105 and PC 500, Hombikat UV 100, Aldrich TiO₂, Tronox A-K-1 and Degussa P 25 were pure un-doped TiO₂. The initial concentration of EE2 was 1 mg/L, while catalyst loading was 500 mg/L. The degree of mineralization of the EE2 solutions after 240 min of photocatalytic treatment is shown in figure 2, while figure 3 shows the TOC temporal decrease for the four more active catalysts. As can be seen, Degussa P-25 and Hombikat UV 100 were more active than the other TiO₂ samples. For example, after 240 min of treatment time EE2 mineralization was 76%, 64%, 79%, 92% and 95% for Aldrich TiO₂, Kronos vlp-7100, Millenium PC 50, Hombikat UV 100 and Degussa P 25 respectively at a common catalyst loading of 0.5 g/L. Therefore, all subsequent photocatalytic experiments were performed using Degussa P-25 TiO₂ and Hombikat UV 100 as a photocatalyst.

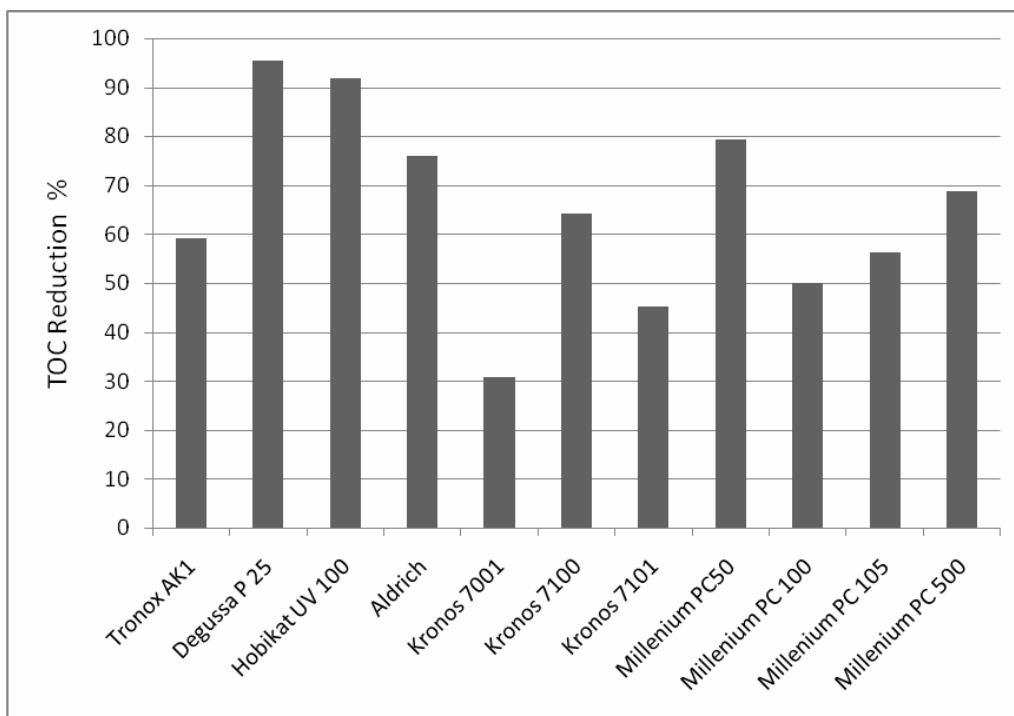


Figure 2. TOC reduction after 240 min photocatalytic treatment of aqueous solutions of EE2 at 1 mg/L initial concentration, and at catalyst loading of 500 mg/L

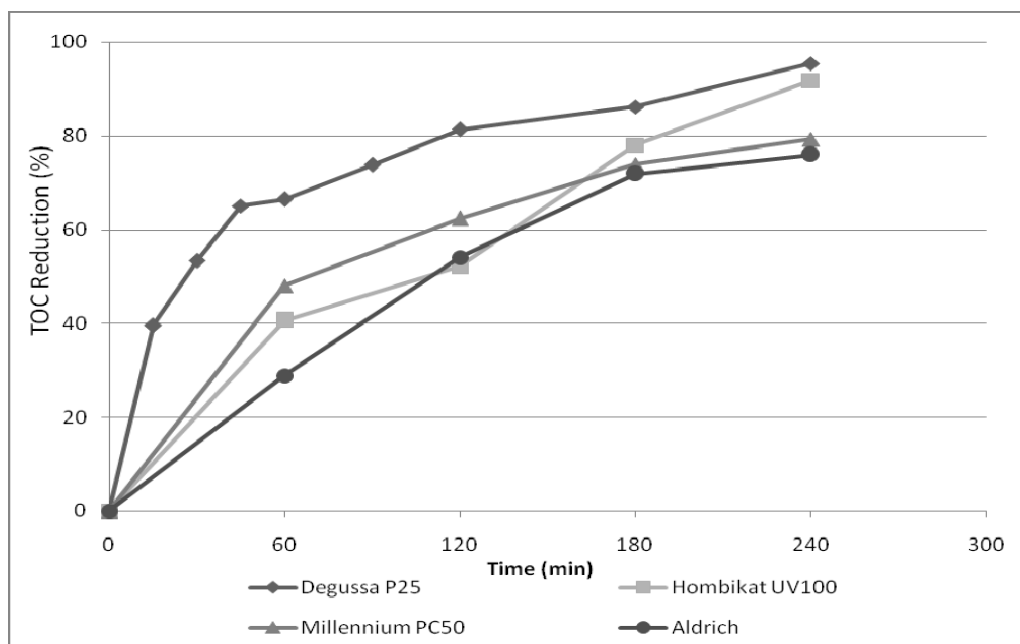


Figure 3. TOC reduction after 240 min photocatalytic treatment of aqueous solutions of EE2 at 1 mg/L initial concentration, and at catalyst loading of 500 mg/L for the four more active catalysts

EE2 Degradation

In further experiments, the degradation of EE2 was studied and the results are summarized in Figure 4. As can be seen for 500 mg/L of catalyst loading, after 120 min of treatment time EE2 degradation was 100% and 65.5% for Degussa P-25 and Hombikat UV 100 respectively, while the corresponding values for EE2 mineralization were 81%, and 52% (figure 3). As can be seen, EE2 degradation is faster than EE2 mineralization, thus implying the formation of oxidation products that are more resistant to photocatalytic oxidation than the parent compound. Complete EE2 degradation could be achieved with both catalysts although Degussa P 25 decomposes EE2 almost completely within 45 minutes of reaction whereas Hombikat requires almost 240 minutes achieving similar extent in conversion. It could be assumed that this is attributed to a slow electron/hole recombination rate of Degussa P-25 (Velegraki et al., 2008). In the case of Degussa P 25 TiO_2 , EE2 reduction appears to follow a first order kinetic expression concerning its concentration reduction. By plotting $-\ln C/C_0$ versus time the experimental data points fit a straight line relatively well and the computed kinetic constant was $75 \times 10^{-3} \text{ min}^{-1}$ and the correlation coefficient of the linear fitting was 0.987.

CONCLUSIONS

The conclusions drawn from this study can be summarized as follows:

TiO_2 -mediated photocatalysis under simulated solar irradiation was capable of degrading EE2 in aqueous solutions. Of several commercially available TiO_2 samples tested, Degussa P-25 was found to be considerably more effective in terms of EE2 degradation and TOC removal. The extent of degradation depends on the operating conditions employed.

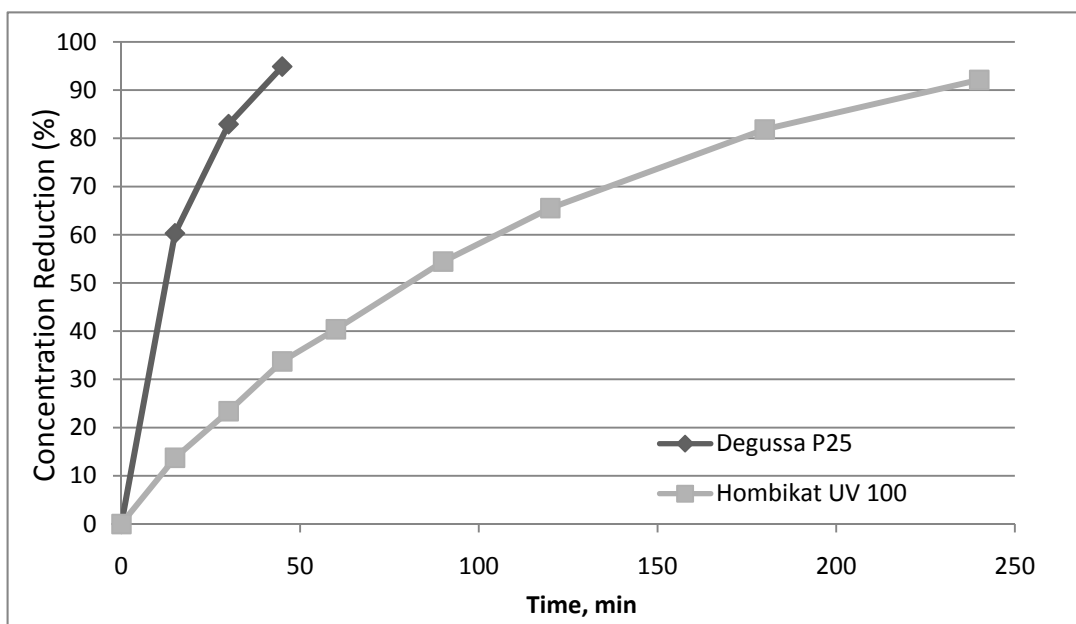


Figure 4. Degradation of EE2, initial concentration 1 mg/l , catalyst loading 0.5 g/L

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REFERENCES

- Belgiorno V., Rizzo L., Fatta D., Della Rocca C., Lofrano G., Nikolaou A., Naddeo V. and Meric S., (2007). Review on endocrine disrupting-emerging compounds in urban wastewater: occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse, *Desalination* 215 166–176.
- Coleman H.M., Abdullah M.I., Eggins B.R., Palmer F.L., (2005). Photocatalytic degradation of 17 β -oestradiol, oestril and 17 α -ethinyloestradiol in water monitored using fluorescence spectroscopy ,*Applied Catalysis B: Environmental* 55 23–30
- Darlymple O.K., Yeh D.H., Trotz M.A., (2007). Removing pharmaceuticals and endocrine disrupting compounds from wastewater by photocatalysis, *Journal of Chemical Technology and Biotechnology*, 82, 21-134.
- Esplugas S., Bila D.M., Krause L.G.T. and Dezotti M., (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents, *Journal of Hazardous Materials* 149 631–64
- Fent K., Weston A.A. and Caminada D., (2006). Ecotoxicology of human pharmaceuticals *Aquatic Toxicology* 76 122–159
- Huber M., Ternes T.A. and Gunten U.V., 2004). Removal of Estrogenic Activity and Formation of Oxidation Products during Ozonation of 17 β -Ethinylestradiol, *Environ. Sci. Technol.*, 38 (19), 5177-5186
- Parsons S., (2004). *Advanced Oxidation Processes for Water and Wastewater Treatment*, IWA Publishing, Cornwall, UK..
- Rosenfeldt E.J. and Linden K.G., (2004), Degradation of Endocrine Disrupting Chemicals Bisphenol A, Ethinyl Estradiol, and Estradiol during UV Photolysis and Advanced Oxidation Processes" *Environmental Science & Technology* 38, 5476-5483
- Shareef A., Angove.M.J, Wells.J.D. and Johnson.B.B., (2006). Aqueous Solubilities of Estrone, 17 α -Estradiol, 17 β -Ethinylestradiol and Bisphenol A. *J. Chem. Eng. Data*, 51, 879-881

- Velegaki T., Mantzavinos D., (2008). Conversion of benzoic acid during TiO₂-mediated photocatalytic degradation in water. *Chemical Engineering Journal*; 140
- Wang X., Meng S., Zhang X., Wang H., Zhong W. and Du Q., (2007). Multi-type carbon doping of TiO₂ photocatalyst, *Chemical Physics Letters* 444 ,292–296
- Weber S., Leuschner P. Kämpfer P. Dott W. and Hollender J., (2005). Degradation of estradiol and ethinyl estradiol by activated sludge and by a defined mixed culture *Appl Microbiol Biotechnol* 67: 106–112
- Yang M., Park M.S., Lee H.S., (2007). Endocrine Disrupting Chemicals: Human Exposure and Health Risks, *J. Environ. Sci. Health Pt. C-Environ. Carcinog. Ecotoxicol. Rev.*, 24 183 – 224.
- Zhang J., Wang Y., Jin Z., Wu Z. and Zhang Z., (2008). Visible-light photocatalytic behavior of two different N-doped TiO₂, *Applied Surface Science* 254 4462–4466