

The role of pH in aqueous photocatalytic oxidation of β -estradiol

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ABSTRACT. Experimental studies of aqueous photocatalytic oxidation (PCO) of β -estradiol in TiO₂ suspensions were undertaken. The dependence of PCO efficiency and adsorption of β -estradiol on pH was studied. It was found that both the adsorption of β -estradiol and the PCO efficiency increased practically linearly with increasing concentration of OH⁻ ions. The predominant role of direct β -estradiol oxidation with positively charged holes was thus indirectly confirmed.

1. INTRODUCTION

Recently, it has been suggested that several types of chemical present in the aquatic environment, even in nanogram concentrations, affect the reproduction of wildlife, livestock and even humans [1]. Owing to their steroid-like structures, it is assumed that these chemicals disrupt normal endocrine functions through interaction with steroid hormone receptors [2]. They are believed to have severe toxicity, high accumulation potential in the body, and persistence in the environment [3]. A growing number of industrial chemicals (phenolics, phthalates, polychlorinated biphenyls and organochlorine pesticides), some natural estrogens, and synthetic pharmaceuticals have been found to be most potent endocrine-disrupting compounds (EDCs). Municipal and industrial wastewaters together with runoff from agricultural production are considered important sources of EDCs in water. Farming plays a further significant role as a source of synthetic estrogens used for hormonal growth promotion [4].

Endocrine-disrupting compounds are difficult to remove totally from wastewaters by traditional primary and secondary treatment [5]. Moreover, the activated sludge process, which is commonly used for treating sewage at wastewater treatment plants (WTPs), is now assumed to act as a chemical reactor producing free estrogens. For example, commonly found estrogenic alkylphenols and steroidal estrogens are the products of incomplete breakdown of their respective parent compounds [6]. As a result EDCs have been detected in discharge water from various sewage WTPs. Domestic effluents have been reported to contain levels of EDCs between 1 and 50 ng L⁻¹, concentrations that are enough to influence the reproduction of male fish [7].

The penetration of EDCs into the water environment has consequently become a subject of worldwide growing concern. An effective water and wastewater treatment method able to eliminate EDCs is thus

needed. Recent interest in the removal of steroidal estrogens has resulted in publications concerning biological treatment [5, 6, 8], membrane separation [9], adsorption [10] and various advanced oxidation processes (AOPs). Although some publications show safe oxidation of steroidal estrogens in nitrification-denitrification stage of wastewater biological treatment at WTPs [8], a certain risk of EDC discharge to the environment remains [6, 11]. Attributable to separation methods, simple redistribution of pollutants does not allow safe and complete elimination of contaminants. In addition, the release of pollutants accumulated at the membrane surface presents a further risk [9]. Advanced oxidation methods are promising in EDC removal, although a certain risk of residual estrogenic activity at ozone doses commonly applied in potable water treatment has been pointed out [12]. Photocatalytic oxidation (PCO) strategies, however, have exhibited effective mineralisation of EDCs without formation of estrogenic intermediates [13–15]. Despite the clear potential of PCO, there is a lack of information concerning the mechanism of EDC elimination. For example, Coleman et al. [13] indicated an alkaline aqueous medium to be preferable in β -estradiol PCO; however, no explanation for such behaviour has been given.

The PCO may proceed via a dual mechanism [16]: (1) adsorption of the pollutant by the surface of the titanium dioxide, which is followed by a direct subtraction of the pollutant's electrons, i.e. oxidation, with positively charged holes; (2) oxidation with hydroxyl radicals at the catalyst surface or in its vicinity. Both reactions may proceed simultaneously, although positively charged holes have an oxidation potential about 1.25 times bigger than a hydroxyl radical [17]. Which mechanism dominates in PCO depends on the chemical and adsorption properties of the pollutant.

β -Estradiol is one of the basic natural estrogens, exhibiting the highest estrogenic activity and persistence in waters [6]. This study examined the dependence of PCO efficiency and adsorption of β -estradiol

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on pH and in particular a possible connection between the PCO performance and the β -estradiol adsorption on the TiO₂ surface.

2. MATERIALS AND METHODS

The aqueous solution of β -estradiol was prepared according to the recommendations of Nakashima [18]. Due to the hydrophobic character of β -estradiol, its solubility in water is low, which makes its dissolution even in microgram amounts difficult. β -Estradiol in the amount of 10,000 μg (Sigma-Aldrich) was dissolved in 100 ml of 99.5%-ethanol (Altia Oy, Finland). Following this, the alcoholic stock solution was gradually diluted in an ultrasonic bath with Milli-Q water to prepare 1 L of initial aqueous solution for complete dissolution of β -estradiol colloids. The initial aqueous solution was constantly stirred at room temperature in a hermetically sealed flask to avoid re-crystallisation of β -estradiol. The chromatographic analysis of the solution showed satisfactory stability of the target pollutant in the flask for at least two weeks. The sample solutions with the required concentrations for the experiments were prepared by dilution of the initial aqueous solution with Milli-Q water under stirring for 30 min. The initial concentration of the sample solutions was 500 $\mu\text{g L}^{-1}$ if not otherwise specified. All experiments were conducted at 25 ± 1 °C. The pH value was adjusted with sulphuric acid or sodium hydroxide.

Titanium dioxide (TiO₂, Degussa P25) under near-UV irradiation (365 nm) was selected as a photocatalyst. Synthetic syringe filters with a pore size 0.45 μm were initially used to separate the catalyst from the solution. However, a partial adsorption of β -estradiol by the filter material was observed. Consequently, centrifugation at 10,000 rpm was used to separate TiO₂ from the samples before the analysis.

The PCO experiments were performed in a 0.25-L capacity thermostatted batch glass reactor, having an inner diameter of 100 mm, equipped with a magnetic stirrer. The agitation intensity was maintained with a standard 25-mm Teflon stirrer at 300 rpm. A 365 nm UV-lamp was positioned horizontally over the reactor; the irradiance was about 1.1 mW/cm², measured by the optical radiometer UVX (UVX, USA) at a distance corresponding to the level of the free surface of the reactor.

The concentrations of TiO₂ in the suspensions for the PCO experiments were carefully selected so that the target compound concentration decreased due to adsorption on the catalyst from an initial 500 to equilibrium 200 $\mu\text{g L}^{-1}$.

The experiments determining the adsorption isotherms were performed in 0.50-L capacity flasks, in which the β -estradiol solution was mixed with TiO₂ at a stirring frequency of 900 rpm for 24 hours. The TiO₂ concentrations in the flasks corresponded to the amounts of TiO₂ established previously for

a measurable, a few hundreds $\mu\text{g L}^{-1}$, decrease in β -estradiol aqueous concentration at different pH. Each flask was handled separately as a single-point sample, i.e. without intermediate sampling, and each experiment was repeated three times. The equilibrium concentration of β -estradiol adsorbed on the surface of the catalyst q , mg g^{-1} TiO₂, was calculated from the mass balance of the sample.

The concentration of β -estradiol was determined by means of HPLC with 150-mm ZORBAX Eclipse XDB-C18 column (Agilent), UV-detector at the wavelength 278 nm, and mobile phase acetonitrile/water 1 : 1 at a flow rate of 1 mL min⁻¹.

3. RESULTS AND DISCUSSION

The experiments showed that β -estradiol readily yields to PCO over UV-irradiated TiO₂. Since the most effective catalyst concentration is between 1 and 3 g L^{-1} [19], a concentration of TiO₂ of 1 g L^{-1} was initially used in the preliminary study. This concentration was also chosen because it was used in previous studies [15] and would make our data comparable. However, under these experimental conditions a sharp decrease in β -estradiol concentration was noticed as a result of the introduction of TiO₂. This could be attributed to the abundant presence of TiO₂ in comparison to the concentration of the target compound: β -estradiol may simply be adsorbed by the catalyst. Further PCO experiments were carried out with carefully selected TiO₂ concentrations, the choice of which was attributed to the adsorption behaviour of β -estradiol.

Adsorption isotherms. The adsorption isotherms were determined at pH 3, 5, 7, 9, and 11. The results are shown in Figure 1. One can see that β -estradiol is much better adsorbed by TiO₂ in an alkaline medium than in neutral and acidic media. In fact, a practically linear logarithmic increase of the surface concentration q versus increase of pH was observed. This corresponds with a linear dependence of β -estradiol adsorption on the concentration of OH⁻ ions in the solution (Figure 2).

The amount of TiO₂ necessary to decrease the initial concentration of β -estradiol from 500 to 200 $\mu\text{g L}^{-1}$ is shown in Figure 3. At pH 11 a mere 10 mg L^{-1} of TiO₂ was sufficient to obtain the pre-set change in concentrations. In acidic media the proper TiO₂ concentration at pH 5 was 1750 mg L^{-1} . At pH 3 no appropriate TiO₂ concentration was found up to 12 g L^{-1} of catalyst, i.e. in strongly acidic media the adsorption is very poor.

PCO experiments. The catalyst amounts obtained for suitable decrease in β -estradiol concentrations due to adsorption were then used in the PCO experiments. Initially, the β -estradiol solution was brought to equilibrium with TiO₂ during 24-h adsorption. After this the resulting suspension was divided between two reactors: the one used for the PCO was called "active" and the other, with no UV light applied, was called "reference".

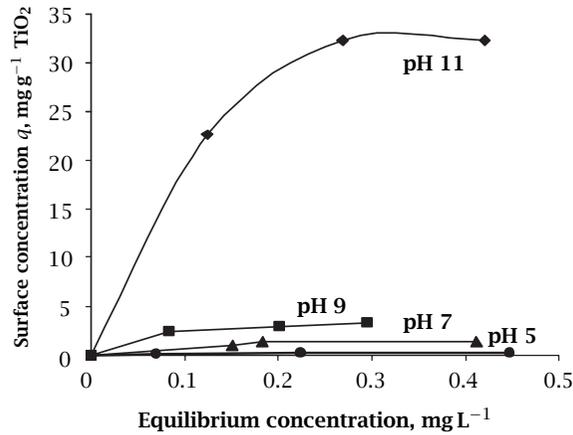


Figure 1. Adsorption isotherms for β -estradiol on TiO_2 catalyst at different pH values at 25 °C. Concentrations of TiO_2 , mg L^{-1} : pH 5-1750, pH 7-320, pH 9-100, pH 11-10.

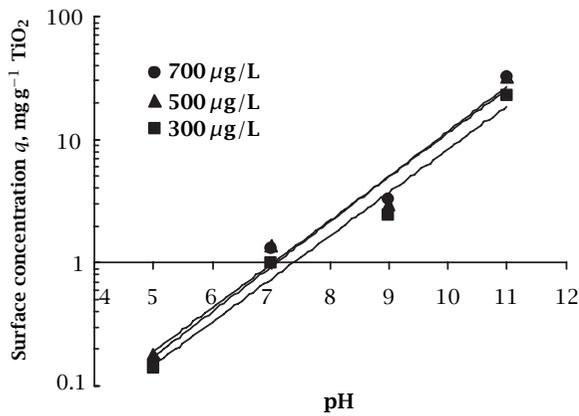


Figure 2. β -Estradiol equilibrium surface concentration on TiO_2 vs. pH at different β -estradiol initial concentrations.

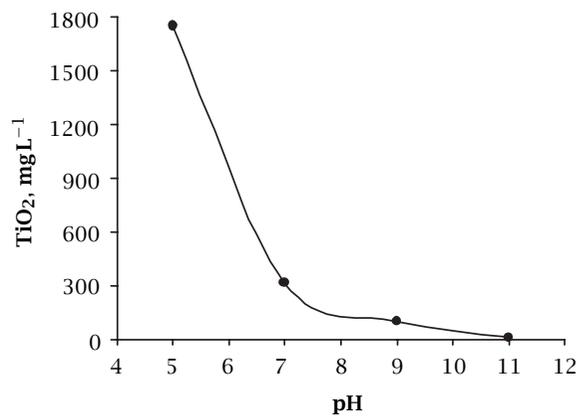


Figure 3. The TiO_2 catalyst concentration sufficient for the adsorption of β -estradiol from initial 500 to equilibrium 200 $\mu\text{g L}^{-1}$ in 24-h experiments vs. pH.

Both reactors were exposed to identical experimental conditions. The samples from the active reactor were compared to the reference samples to avoid complications caused by water evaporation. The results of the PCO experiments can be seen in Figure 4.

The results showed that the PCO of β -estradiol proceeds more slowly in a strongly alkaline medium. This could be explained by the difference in the TiO_2 concentrations used at different pH as they were obtained in the adsorption experiments (Figure 3). To bring the results to a uniform basis for assessment, the performance of PCO was characterized by the process efficiency E . The PCO efficiency relative to the catalyst concentration was calculated as the decrease in the concentration of the target compound divided by the amount of energy reaching the surface of the sample and by the concentration of the catalyst used:

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t \cdot m}$$

E —PCO process efficiency, $\mu\text{g W}^{-1} \text{h}^{-1}/(\text{g L}^{-1}) \text{TiO}_2$; Δc —decrease in the compound concentration, $\mu\text{g L}^{-1}$; V —the volume of treated sample, L; I —irradiation intensity, mW cm^{-2} ; s —solution irradiated surface area, cm^2 ; t —treatment time, h; m —concentration of TiO_2 , g L^{-1} .

The dependence of the PCO efficiency on pH can be seen in Figure 5: at pH 11 PCO proceeds with the highest efficiency. One can see that the efficiency E decreases with treatment time, which can be explained by the decreasing adsorption (Figure 1) and, thus, the reaction rate with the decreasing concentration of β -estradiol. Analysis of the obtained dependence shows a practically linear dependence of the PCO efficiency on OH-ions concentration.

Both the amount of β -estradiol adsorbed on the TiO_2 surface and the PCO efficiency follow a similar pattern: the adsorption and the PCO exhibit simple linear dependence on OH-ion concentration. The slopes

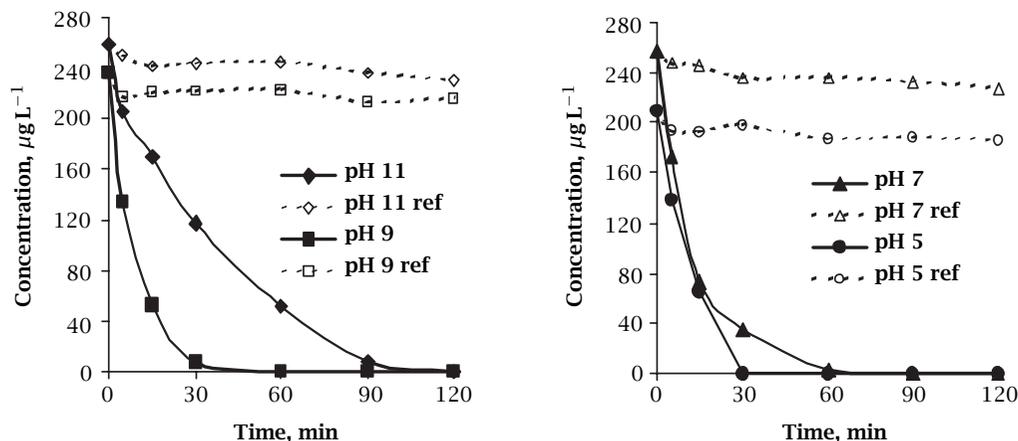


Figure 4. The rate of PCO of β -estradiol. Concentrations of TiO_2 , mg L^{-1} : pH 5-1750, pH 7-320, pH 9-100, pH 11-10.

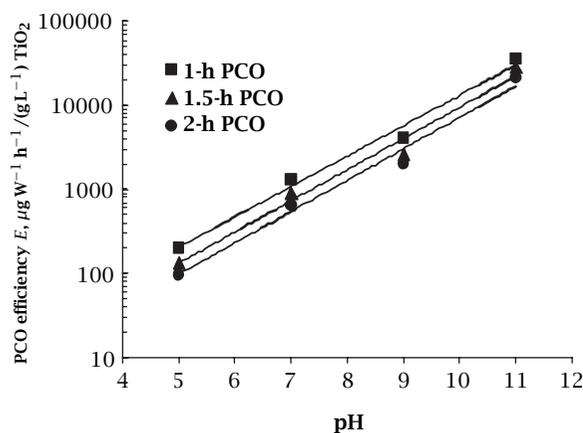


Figure 5. Dependence of PCO efficiency E on pH of β -estradiol solution at different treatment times.

of the logarithmic dependence of the PCO efficiency at different treatment times are only slightly, within 5%, bigger than the ones for adsorption (Figures 2 and 5). Perhaps, this number indicates the extent to which OH-radicals accelerate PCO. This slight difference indicates that OH-radicals may play only a minor role in PCO.

The fact that the β -estradiol molecule is adsorbed well in a strongly alkaline medium may indicate that the adsorption takes place with the molecule attached with its alcoholic group not the phenolic moiety: phenolic compounds exhibit poor adsorption by TiO_2 in alkaline media [20]. However, phenolic compounds yield better to PCO also under alkaline media conditions [21], which indicates a difference in the oxidation mechanisms of β -estradiol and phenolic compounds. This suggests the predominant transformation of the phenolic moiety in PCO shown in [15] results presumably from more complicated processes than a direct oxidation of the phenolic moiety with the positively charged holes.

4. CONCLUSIONS

The results of the research showed that β -estradiol could easily be degraded by PCO over UV-irradiated TiO_2 . The PCO of β -estradiol in TiO_2 suspension proceeds with the highest efficiency in a strongly alkaline medium. This was found to be determined by the adsorption properties of β -estradiol on the TiO_2 surface: the target pollutant was observed to adsorb to a greater extent under alkaline media conditions. Analysis of the experimentally obtained data indicates that OH-radicals may play a minor role in PCO of β -estradiol.

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