

Photodegradation of 17 β -estradiol in water by UV-vis/Fe(III)/H₂O₂ system

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Abstract

Photodegradation of 17 β -estradiol (E2) in aqueous solutions by UV-vis/Fe(III)/H₂O₂ system, namely Photo-Fenton system, was preliminarily investigated under a 250 W metal halide lamp ($\lambda \geq 313$ nm). The influences of initial pH value, initial concentration of H₂O₂ and E2 on photodegradation efficiency of E2 were discussed and the amount of CO₂ produced by the photodegradation reaction was measured. The results indicate that E2 could be decomposed efficiently in UV-vis/Fe(III)/H₂O₂ system. Under the condition of 10.0 $\mu\text{mol L}^{-1}$ Fe(III), 1000 $\mu\text{mol L}^{-1}$ H₂O₂ and pH 3.0, the degradation efficiency of 18.4 $\mu\text{mol L}^{-1}$ E2 reach 75.2% after the irradiation of 160 min. Over the range of pH 3.0–6.0, the higher acidity, the higher the degradation efficiency of E2 and initial reaction rate are. The degradation efficiency of E2 increases with increasing of initial concentration of H₂O₂ and with decreasing of initial concentration of E2. The E2 mineralization efficiency increases with reaction time but the mineralization efficiency was lower. When the initial concentration of Fe(III) and H₂O₂ were 10.0 and 1000 $\mu\text{mol L}^{-1}$, respectively, the mineralization efficiency of 18.4 $\mu\text{mol L}^{-1}$ E2 solution with pH 3.0 was only 21.6% after 160 min irradiation. It is suggested that the mineralization occurred probably only at aromatic ring.

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1. Introduction

It has been reported that estrogenic compounds can damage human and animal health. These compounds may interact with the organisms' endocrine system and disturb or inhibit the natural hormone action [1]. 17 β -Estradiol (E2), one of the natural estrogens, has been reported to be an important endocrine disruptor (ED) due to the very potent estrogenic activity even at very low concentration [2]. The literatures indicated level of E2 in natural water and sewage effluents was in pg L⁻¹ to ng L⁻¹ and the concentration of E2 in sewage effluents was higher than in natural water [3–5].

There are few studies focusing on the treatment of estrogens. Ohko et al. [6] reported the degradation of E2 in water by TiO₂ photocatalysis and 1 $\mu\text{mol L}^{-1}$ E2 was totally min-

eralized to CO₂ in 1 g L⁻¹ TiO₂ suspension under UV irradiation for 3 h. Coleman et al. [7] reported 0.05–3 $\mu\text{mol L}^{-1}$ E2 were 98% destroyed in 3.5 h by photocatalysis over the immobilized TiO₂ and the pseudo-first order rate constant was 0.0157 min⁻¹. The study of Liu et al. [8] indicated that E2 could be degraded in some extent under UV lamp ($\lambda = 254$ nm), but the degradation could not occur under high-pressure mercury lamp. Tanizaki et al. [9] reported the catalytic photodegradation of 13 EDs, including E1, E2 and EE2, using TiO₂ photo-semiconductor thin films under UV light. E2 could be decomposed 90% with TiO₂ after 30 min of irradiation and the decomposition rate is 0.015 min⁻¹.

Photo-assisted Fe³⁺/H₂O₂ (also called Photo-Fenton) processes as a kind of advanced oxidation processes (AOP) is getting more and more popular during these years, due to its high efficiency in degrading a wide variety of organic pollutants in water. It combines hydrogen peroxide, catalytic amounts of Fe(III) and UV-vis light to produce OH radicals.

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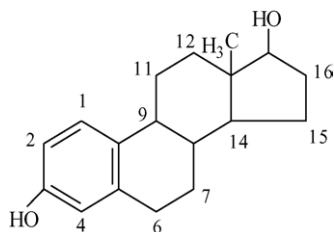


Fig. 1. Molecular structure of E2.

The main feature of this system is iron cycling between +2 and +3 oxidation states with OH production being only limited by H_2O_2 availability [10]. Previous reports published indicated that Fe(III)/ H_2O_2 have shown photon absorption up to 550 nm [12,13]. Hence, the reaction can be carried out efficiently with longer wavelengths. Photo-Fenton processes are a potential cost-reduced AOP that can be run under solar irradiation [11].

Previous research has shown effective in degrading various organic compounds in water using the photo-assisted Fenton reaction [14–16]. But the treatments of estrogen by the means of Photo-Fenton have not been reported. In the present work, the photodegradation of 17 β -estradiol (molecular structure shown in Fig. 1) by Photo-Fenton system, which used a metal halide lamp as light resource, was studied. The effects of pH value, initial concentration of E2 and H_2O_2 were discussed. CO_2 produced by degradation reaction was measured to evaluate the mineralization degree. This work provides basic data for photochemical treatment of 17 β -estradiol.

2. Experimental

2.1. Materials

17 β -Estradiol (E2) provided by Sigma (USA) was analytical-grade and used without further treatment. Acetonitrile was analytical-grade and provided by Wuhan Pharmaceutical Plant (China), which was used as cosolvent of E2. Concentration of E2 stock solution was $367 \mu\text{mol L}^{-1}$. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2O_2 (30%), HCl, NaOH, $\text{Ba}(\text{OH})_2$ were also analytical-grade and di-distilled water was used throughout.

2.2. Experimental apparatus

The photocatalytic reactor was a 50 mL color-comparison-tube. The solution was irradiated through the wall of color-comparison-tube using a 250 W metal halide lamp ($\lambda \geq 313 \text{ nm}$, Chenguang Illumination Instrument Co., Jinzhou, China). The light intensity was $1.7 \times 10^5 \text{ lx}$, which was detected using TES1332 digital Lux meter (Taiwan). pH measurements were performed by DELTA-320-S pH-meter (METTLER).

The concentration of E2 was detected by HPLC (Shimadzu LC-6A pump, SUPELCO 561C-18 column ($15 \text{ cm} \times 4.6 \text{ mm}$, $5 \mu\text{m}$) equipped with an UV detector ($\lambda = 280 \text{ nm}$, Waters 481, USA).

2.3. Procedures

2.3.1. Photoreaction procedures

Different concentrations of E2, Fe(III) and H_2O_2 were mixed and the pH value of solution was adjusted with HCl or NaOH to the desired values. The mixed solution was filled into 50 mL color-comparison-tubes and was irradiated under a 250 W metal halide lamp. At different time intervals, the E2 concentration of the solution in the tube was detected.

2.3.2. CO_2 measurement procedures

Carbon dioxide produced upon irradiation was determined as BaCO_3 . CO_2 was removed from solution by a nitrogen flow (N_2 scrubbed from CO_2 by passing through a concentrated $\text{Ba}(\text{OH})_2$ solution) and trapped in two consecutive $\text{Ba}(\text{OH})_2$ solutions. The solutions were collected, BaCO_3 was allowed to precipitate and the excess of $\text{Ba}(\text{OH})_2$ was titrated with $0.02011 \text{ mol L}^{-1}$ HCl solution with phenolphthalein as indicator. A blank experiment without E2 was performed under the same conditions.

Each experiment was conducted in triplicate with errors less than 5%. The average value was employed as the experimental data.

2.4. Analyses

The E2 concentration was detected by HPLC. The mobile phase was acetonitrile–water mixture (50/50, v/v) at a flow rate of 1.0 mL min^{-1} . The injection volume was $20 \mu\text{L}$. The retention time of E2 was 4.62 min. The calibration equations of E2 over the concentration range of $0\text{--}36.7 \mu\text{mol L}^{-1}$ was peak area = $2695C + 115$ ($r = 0.9996$).

To estimate the degradation rates, the first-order kinetics equation $\ln C/C_0 = -kt$ was used to fit the experiment data of the changes of E2 concentration versus reaction time and the initial rates (V_0) of the reaction at different conditions were obtained according to the equation $V_0 = kC_0$. In all experiments of this work, the correlation coefficient ranged from 0.9921 to 0.9993, $n = 9$ ($n = 9$, $\alpha = 0.001$, critical correlation coefficient $r_c = 0.8982$).

3. Results and discussion

3.1. Photodegradation of E2 in the control experiment

The control experiment of E2 degradation was conducted and the result are shown in Fig. 2.

UV-vis/Fe(III)/ H_2O_2 is an advanced oxidation process generating $\bullet\text{OH}$ radical as principal active species, the

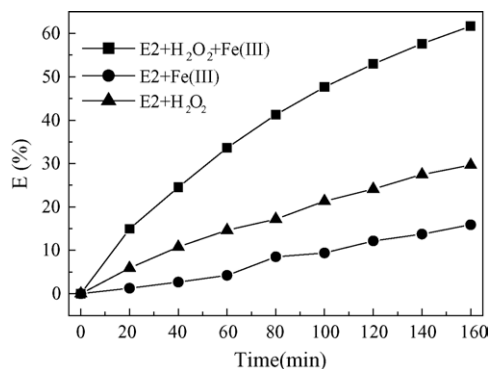


Fig. 2. Degradation efficiency E (%) vs. reaction time in the control experiment of E2 photodegradation. $[E2]_0 = 36.7 \mu\text{mol L}^{-1}$, $[\text{Fe(III)}]_0 = 10.0 \mu\text{mol L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 1000 \mu\text{mol L}^{-1}$, pH 3.0.

oxidation ability of which depends on the concentration of $\bullet\text{OH}$ radical. In fact, the reactions occurred in this system are very complex. Generally, it is suggested that there are three pathways to produce $\bullet\text{OH}$ radical: (1) direct photolysis of H_2O_2 . Degradation efficiency of E2 is only 29.6% at 160 min when only H_2O_2 present in E2 solution under the condition shown in Fig. 2, (2) direct photolysis of various of Fe(III)–hydroxyl complexes (e.g. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3$, $\text{Fe}_2(\text{OH})_2^{4+}$). Among these species, $\text{Fe}(\text{OH})^{2+}$ is the most potent photoactive species [17]. Hence, when only Fe(III) was added into E2 solution, degradation efficiency of E2 was 15.9% at 160 min and (3) the reaction between Fe(II) and H_2O_2 according to conventional Fenton reaction. When H_2O_2 and Fe(III) were mixed together in E2 solution, $\bullet\text{OH}$ radical could be generated by above three ways. Simultaneously, the redox circle of Fe(III)/Fe(II) greatly accelerated E2 photodegradation. After 160 min irradiation, the degradation efficiency of E2 was 61.7%, which is more than the total amount of only with H_2O_2 and only with Fe(III). This result is consistent with the degradation of other organic compounds by Fenton system in previous reports [18]. Evidently, E2 could be decomposed efficiently by UV–vis/Fe(III)/ H_2O_2 system.

3.2. Effects of pH values, initial H_2O_2 concentration and initial E2 concentration

The pH effects on E2 photodegradation were estimated over the pH range of 3.0–8.0. Table 1 shows the result. The degradation efficiency of E2 and initial rate of the reaction increased with increasing acidity of solution. When the pH value decreased from 6.0 to 3.0, the degradation efficiency of E2 increased from 26.3 to 61.7%. The initial reaction rate at pH 3.0 ($0.230 \mu\text{mol L}^{-1} \text{min}^{-1}$) is three times that of at pH 6.0 ($0.077 \mu\text{mol L}^{-1} \text{min}^{-1}$). All this illuminated that the acidity of solution has a significant effect on E2 photodegradation reaction.

The species distribution of Fe(III)–hydroxyl complex, which is responsible for the concentration of $\bullet\text{OH}$ radical, was dependent on pH value. At pH 3.0, more $\bullet\text{OH}$ was produced because that among the multiplicate species of Fe(III)–OH complexes the distribution coefficient of $\text{Fe}(\text{OH})^{2+}$ was highest and the photoactivity was strongest. On the other hand, it was calculated theoretically that when pH value increased to 3.7, $10.0 \mu\text{mol L}^{-1}$ Fe(III) would flocculate as the specie of $\text{Fe}(\text{OH})_3$. This indicated that the valid concentration of Fe(III) in solution would be reduced. Just because of above, the lower the pH value, the higher the photodegradation efficiency and the initial rate were.

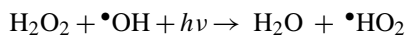
Under the condition of pH 3.0, $36.7 \mu\text{mol L}^{-1}$ E2 and $10.0 \mu\text{mol L}^{-1}$ Fe(III), the effects of H_2O_2 concentration on degradation of E2 were investigated (the theoretically required concentration of H_2O_2 is $1689 \mu\text{mol L}^{-1}$ for total mineralization of $36.7 \mu\text{mol L}^{-1}$ E2). The result are shown in Table 1. It is well shown that with increasing of the initial H_2O_2 concentration, the photodegradation efficiency of E2 and initial rate increased over the range of 200–2000 $\mu\text{mol L}^{-1}$ of H_2O_2 concentration. But the improvement was not prominent. When the initial concentration of H_2O_2 increased from 200 to 2000 $\mu\text{mol L}^{-1}$, the degradation efficiency of E2 only increased from 48.5 to 69.0%. The initial rate of 2000 $\mu\text{mol L}^{-1}$ H_2O_2 was only 1.8 times that of 200 $\mu\text{mol L}^{-1}$ H_2O_2 . From Table 1, it was also shown that the curve became relative planar when the concentration of H_2O_2 increased from 1000 to 2000 $\mu\text{mol L}^{-1}$,

Table 1
pH effect on E2 photodegradation efficiency and initial reaction rate

Initial E2 concentration ($\mu\text{mol L}^{-1}$)	Initial pH value	Initial H_2O_2 concentration ($\mu\text{mol L}^{-1}$)	Photodegradation efficiency (%)	Initial reaction rate ($\mu\text{mol L}^{-1} \text{min}^{-1}$)
36.7	3.0	1000	61.7	0.230
36.7	4.0	1000	47.9	0.155
36.7	5.0	1000	34.5	0.103
36.7	6.0	1000	27.3	0.077
36.7	3.0	200	48.5	0.152
36.7	3.0	500	53.7	0.179
36.7	3.0	1000	61.7	0.230
36.7	3.0	2000	69.0	0.270
18.4	3.0	1000	75.2	0.157
73.4	3.0	1000	47.3	0.311

$[\text{Fe(III)}]_0 = 10.0 \mu\text{mol L}^{-1}$.

which indicated with the continuous increase in the concentration of H_2O_2 , the photodegradation rate of E2 began to decrease. This could be explained by the equation below [19]



The excess of H_2O_2 could scavenge $\bullet\text{OH}$. Therefore, during the treatment of E2, it is important to control the amount of H_2O_2 required to minimize the cost of the treatment process.

To investigate the effects of E2 initial concentration on photodegradation efficiency and initial photodegradation rate, the experiments were conducted at different E2 initial concentration of 18.4, 36.7 and $73.4 \mu\text{mol L}^{-1}$. The result shown in Table 1 indicated that the higher initial E2 concentration, the lower E2 degradation efficiency was. When the initial concentration of E2 increased from 18.4 to $73.4 \mu\text{mol L}^{-1}$, the degradation efficiency of E2 decreased from 75.2 to 47.3%. The initial rate of E2 photodegradation increased with increasing of the concentrations of E2, the initial rate of $73.4 \mu\text{mol L}^{-1}$ E2 was twice that of $18.4 \mu\text{mol L}^{-1}$ E2 ($0.311/0.157 \mu\text{mol L}^{-1} \text{min}^{-1}$).

3.3. Mineralization of E2 in UV-vis/Fe(III)/ H_2O_2 system

To investigate the mineralization degree of E2 in UV-vis/Fe(III)/ H_2O_2 system, the experiments of E2 photodegradation were conducted at E2 initial concentration of $18.4 \mu\text{mol L}^{-1}$. The amount of CO_2 produced by the photodegradation reaction was measured. Productivity of CO_2 was regarded as mineralization efficiency. The result are shown in Fig. 3.

It was shown that the mineralization efficiency of E2 increased with increasing reaction time. But the mineralization efficiency was only 21.6% at 160 min. The great difference between degradation efficiency and mineralization efficiency also implied that the products of E2 oxidation mostly stayed at intermediate products stage under the present experimental conditions.

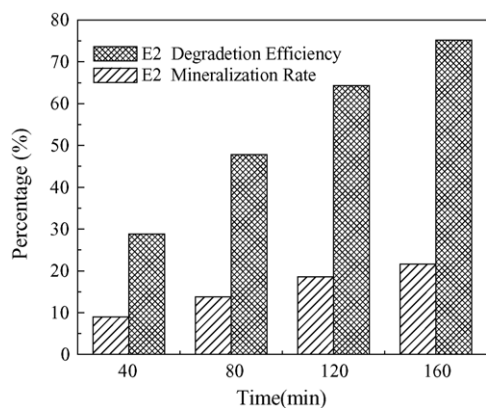


Fig. 3. Mineralization rate of E2. $[\text{Fe(III)}]_0 = 10.0 \mu\text{mol L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 1000 \mu\text{mol L}^{-1}$, $[\text{E2}]_0 = 18.4 \mu\text{mol L}^{-1}$, pH 3.0.

Ohko [6] investigated the degradation of E2 in water by TiO_2 photocatalysis. 10ϵ - 17β -Dihydroxyl-1,4-estradien-3-one and testosterone-like species were elucidated as intermediate products by GC/MS analysis. The mechanisms of E2 degradation by TiO_2 photocatalysis were discussed not only experimentally but also theoretically by calculating the frontier electron densities of the E2 molecule. On the basis of the results obtained, it was concluded that the phenol moiety of the E2 molecule, one of the essential function groups to interact with the estrogen receptor, should be the starting point of the photocatalytic oxidation of E2.

The mechanism of Photo-Fenton, generating $\bullet\text{OH}$ radical to oxidize organic compounds, is also similar to that of TiO_2 photocatalysis. Consequently, it can be deduced that the degradation of E2 in UV-vis/Fe(III)/ H_2O_2 system is initiated from aromatic ring, then the intermediates undergo further oxidation, benzene ring cleavage and decarboxylation, up to mineralization ultimately. In this experiment, lower mineralization efficiency implied that only aromatic ring of E2 was mineralized, while other alicyclic rings were not destroyed. It is difficult to oxidize the section of alicyclic ring due to the stability of alicyclic rings.

4. Conclusion

E2 could be decomposed efficiently by UV-vis/Fe(III)/ H_2O_2 system. During 160 min of irradiation, the photodegradation efficiency of $18.4 \mu\text{mol L}^{-1}$ E2 could reach 75.2% at pH 3.0 when initial concentration of Fe(III) and H_2O_2 are 10.0 and $1000 \mu\text{mol L}^{-1}$, respectively. The degradation efficiency of E2 increased with the decreasing of pH initial value over the range of 3.0–6.0, with the increasing of H_2O_2 initial concentration and with the decreasing of E2 initial concentration. The photodegradation of E2 was pseudo-first order reaction. The degradation rate increased with initial concentration of H_2O_2 . The E2 mineralization efficiency increased with reaction time, but the value was lower. It was suggested that the mineralization probably occurred mainly at aromatic ring.

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