



Short communication

**UV-light induced photodegradation of
17 α -ethynylestradiol in aqueous solutions**Bin Liu^{a,b}, Feng Wu^a, Nan-sheng Deng^{a,*}^a Department of Environmental Science, Wuhan University, Wuhan 430072, PR China^b Department of Environmental and Chemical Engineering, Huangshi Polytechnic College, Huangshi 435003, PR China

Received 30 April 2002; received in revised form 30 April 2002; accepted 5 October 2002

Abstract

The photodegradation of 17 α -ethynylestradiol (EE2) in aqueous solutions induced by UV-light was preliminarily studied in this paper by means of fluorescence, UV and infrared spectra. The result suggested that EE2 in aqueous solutions underwent photodegradation under irradiation with UV disinfection lamp ($\lambda = 254$ nm, 30 W), but the photodegradation was not observed under high pressure mercury lamp ($\lambda \geq 365$ nm, 250 W). The photodegradation of 1.6–20.0 mg/l EE2 in aqueous solutions at a given initial pH value of 6.8 was pseudo-first order reaction. Increasing the initial concentration of EE2 lowered the photodegradation rate. The photodegradation rate of EE2 reached the lowest value at pH about 5.0, higher pH values of 6.0–8.0 benefited the photodegradation. Ferric ions can promote the photodegradation of EE2 in aqueous solutions at pH value of 2.0–5.0. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: 17 α -Ethinylestradiol (EE2); Photodegradation; UV-light; Fluorescence spectra

1. Introduction

Many exogenous chemicals, both natural and synthetic, have been identified to be potential of interfering with the endocrine activity of the natural hormones both in the animals and human, which is called endocrine disrupting chemicals (EDCs) or endocrine disruptors (EDs) [1,2]. Besides industrial chemicals such as DDT, bisphenol A, methoxychlor, chlordecone, alkylphenols, PCBs and phthalic esters, some natural estrogens such as estradiol (E2) and estrone (E1), and synthetic pharmaceuticals such as diethylstilbestrol (DES) and 17 α -ethynylestradiol (EE2, molecule structure in Fig. 1) are found to be the most potent

* Corresponding author. Tel.: +86-27-87682682; fax: +86-27-87882661.

E-mail address: nsdeng@whu.edu.cn (N.-s. Deng).

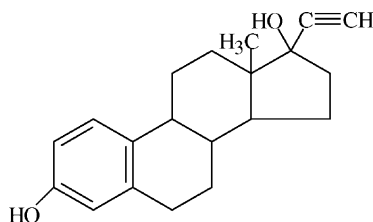


Fig. 1. Molecule structure of EE2.

endocrine disruptors [3]. There are few published articles focusing the degradation of estrogens in the environment or lab [4–6]. These estrogens are difficult to be totally removed from wastewaters by the traditional primary and secondary treatment. New methods are needed for treating them in wastewaters prior to their release into the environment.

Photochemical methods are of great potential of treating persistent organic pollutants (POPs) in environment. Coleman et al. [7] reported $\mu\text{mol/l}$ concentrations of aqueous 17β -estradiol were 98% destroyed in 3.5 h by photocatalysis over the immobilized TiO_2 . To exam the pharmaceutical antioxidation, Segmuller et al. [8] investigated photodegradation of EE2 in acetonitrile solution at a high concentration of 4.3 g/l. However, photochemical method applied in treating EE2 in water has not been reported.

The objectives of this work were to preliminarily exam the UV-light induced photolysis and degradation of EE2 in aqueous solutions at high concentrations, including reaction kinetics and factors affecting the photodegradation. Through fluorescence, UV and infrared spectra analysis for the photodegradation process and products, it could give us a better understanding on the photochemical behavior of EE2. This work is also essential for exploring the feasibility of photochemical treating EE2.

2. Material and methods

2.1. Material and reagents

17α -Ethinylestradiol (Sigma, USA) were used in this study. Ferric chloride was used as the source of ferric ion. HCl and NaOH were used to adjust the pH of the EE2 solutions. Ethanol was used as co-solvent for EE2 in aqueous solutions. All reagents were analytical grade and double distilled water was used throughout.

2.2. Procedure

The working solutions of EE2 were prepared by dilution of the 100 mg/l stock solution with water and adjusted to the desired pH values. The solutions were respectively irradiated by a high pressure mercury lamp (125 W, $\lambda \geq 365$ nm, Shanghai lamp Co. Ltd., PRC) and an UV disinfection lamp (30 W, $\lambda_{\text{max}} = 254$ nm, Shanghai lamp Co. Ltd., PRC). Irradiation was performed in the quartz tubes about 8 cm long and 1.5 cm diameter with

2 mm thickness of tubes wall. At different time intervals, the concentrations of EE2 were detected with fluorescence spectrophotometer.

2.3. Analysis

The concentrations of EE2 solutions were determined with fluorescence spectrophotometer F-4500 (Hitachi, Japan). The wavelength of the maximum excitation peak and the emission peak of EE2 are at 288 nm at 307 nm, respectively. The linear range for this fluorescence method is 1.0–23 mg/l, the detection limit 0.6 mg/l and the R.S.D. below 2%.

The UV spectra of EE2 solutions were recorded with a Shimadzu UV-1601 spectrophotometer. IR absorbance spectrum was measured by an AVATAR-360 FTIR spectrometer (Nicolet, USA), using KBr pellets. To conduct IR spectra analysis of the photodegradation products, the samples in the solutions were concentrated after radiation to a very small volume with a K-D concentrator under nitrogen gas at 80 °C, and then dried with an infrared lamp at a temperature less than 100 °C.

3. Results and discussion

3.1. Effect of light sources on the photodegradation of EE2

Apparent decrease of the concentration of EE2 in aqueous solutions was observed during irradiation with UV disinfection lamp, which implied that photodegradation of EE2 occurred. However, no change was observed with high pressure mercury lamp radiation. Concentration profiles of EE2 solutions during irradiation with both light sources were shown in Fig. 2. Other radiation experiments were under UV-light.

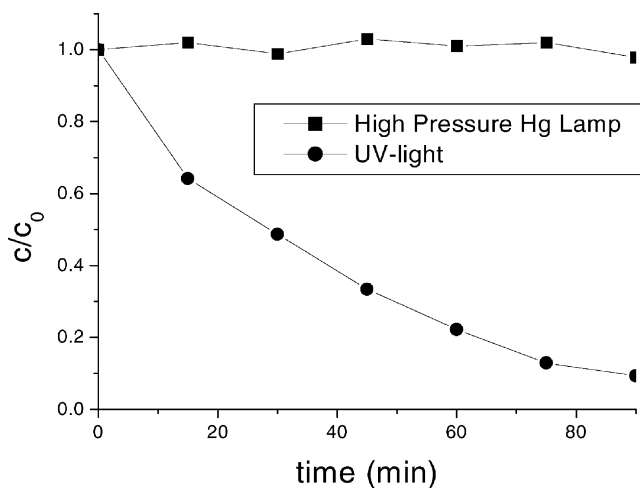


Fig. 2. Concentration profiles of EE2 solutions irradiated with UV disinfection lamp and high pressure Hg lamp.

To preliminarily inspect the mechanism of photodegradation of EE2 in aqueous solution, UV spectra of EE2 solutions were recorded. The main conjugated structure of EE2 is hydroxyl substituted benzene ring, which has light absorption in the UV region with the absorbance peak at 288 nm. The UV absorption of EE2 solutions decreased after irradiation. The second-derivative spectra showed that EE2 in aqueous solution has several absorbance peaks at 226.5, 235.7 and 291.6 nm, respectively. These peaks are assigned to the substituted benzene ring. All peaks in the second derivative spectra decreased after radiation and no new peak occurred, which indicated that the substituted benzene ring was destroyed and broken. Since EE2 nearly absorb no light at wavelength above 350 nm, high pressure Hg lamp ($\lambda \geq 365$ nm) cannot induce the photodegradation of EE2.

Infrared spectra of EE2 and its photodegradation products showed that EE2 had benzene ring absorbance peaks at about 1582 and 1499 cm^{-1} , while these peaks decreased obviously and even disappeared after photolysis. Moreover, the peaks at about 1712 cm^{-1} , assigned as carbonyl group, occurred in the IR spectra of the products after radiation. This result indicates that the photodegradation of EE2 causes the breakage and oxidation of benzene rings to produce compounds containing carbonyl groups.

3.2. UV-light photodegradation kinetics of EE2

To exam the photodegradation kinetics and the effect of initial concentration of EE2, experiments were repeated at pH 6.8 containing 1.6, 4.8, 8.0, 10.0, 16.0 and 20.0 mg/l EE2, respectively. Pseudo-zero order model and pseudo-first order model were applied to investigate the kinetics of photodegradation. The results listed in Table 1 indicate that the UV-light photodegradation kinetics of EE2 in aqueous solutions is in accordance with pseudo-first order law. Over the concentration range inspected in this work, the photodegradation rate constant k decreases with raising the initial concentrations of EE2.

3.3. Effect of the initial pH values on the photodegradation of EE2

To study the effect of the initial pH values of the solutions on the photodegradation of EE2 under the UV-light, pH values in the range of 2.0–8.0 were chosen to conduct

Table 1
Photodegradation kinetics analysis

Initial concentration C_0 (mg/l)	$-r_0$	$-r_1$	Kinetics equation
1.6	0.8797	0.9978	$\ln C/C_0 = -0.03032t$
4.8	0.9455	0.9871	$\ln C/C_0 = -0.02432t$
8.0	0.9290	0.9885	$\ln C/C_0 = -0.02001t$
10.0	0.9283	0.9807	$\ln C/C_0 = -0.01561t$
16.0	0.9105	0.9539	$\ln C/C_0 = -0.01125t$
20.0	0.8985	0.9628	$\ln C/C_0 = -0.00864t$

The number of samples is 7, the critical correlation coefficient $r_c = 0.9507$ ($\alpha = 0.001$). r_0 and r_1 represent correlation coefficients calculated under pseudo-zero order law and pseudo-first order law, respectively; t represents reaction time in unit of minute.

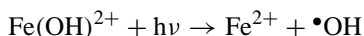
Table 2
Effect of ferric iron on photodegradation of EE2 in aqueous solutions at different initial pH values

	Photodegradation rate constant k (min^{-1})			
	pH 2.0	pH 3.0	pH 4.0	pH 5.0
Without Fe^{3+} (k)	0.01355	0.01295	0.01269	0.01251
With Fe^{3+} (k')	0.01548	0.01583	0.01562	0.01496
Enhancement ($k'-k$)/ k (%)	14.3	22.2	23.1	19.6

photodegradation experiments for 10 mg/1 EE2 solutions. There was a general decrease in the rate with increasing pH up to pH 5.0, at which point there was a sharp rise to pH 7.0 followed by a slow rise to pH 8.0. At present, it is difficult to explain clearly the pH dependence in our experiment. We think EE2, like phenol, was ionized to the phenoxide ion at higher pH values, which might be easily photodegraded.

3.4. Effect of iron ion on photodegradation of EE2

Ferric ion in acidic aqueous solutions can photolyze under UV-light irradiation to produce hydroxyl radicals, which is an extremely strong nonselective oxidant for almost all organic compounds [9,10]:



The hydroxyl radical may react with EE2, so degradation could be enhanced. To approve this idea and determine the effect of ferric ion on the photodegradation of EE2 in aqueous solution, 30 $\mu\text{mol/l}$ Fe^{3+} was added into 10 mg/1 of EE2 solutions at four acidic pH values of 2.0, 3.0, 4.0 and 5.0, respectively. Higher pH values more than five will easily cause precipitation of ferric hydroxide. Table 2 shows the photodegradation was enhanced significantly, especially at pH 3.0 and 4.0. The pH behavior of the kinetics is similar to that for other organic compounds in the UV/ Fe^{3+} system, with rate maximum at pH 3.0.

4. Conclusions

17 α -Ethinylestradiol is readily destroyed by UV-light ($\lambda = 254$ nm) radiation. The UV photodegradation reaction kinetics of EE2 fits the pseudo-first-order law. High pressure Hg lamp with radiation wavelength above 365 nm cannot initiate photodegradation of EE2. The initial pH dependence shows rate maximum at pH 8.0 and minimum at pH 5.0. Ferric ions can promote the photodegradation of EE2 in aqueous solutions at pH value of 2.0–5.0. Further work is required to elucidate the degradation pathway of EE2 and to determine whether or not the intermediate breakdown products have estrogenic activity. As an alternative treatment method for EE2 in wastewater, more researches in this area need to be carried out.

Acknowledgements

This work was financed by the Natural Science Foundation of PR China (No. 20177017) and Wuhan Municipal Environmental Protection Bureau. We thank Mr. Dong Xu and Zhe Zhang for their contributions to this work.

References

- [1] T. Colborn, C. Clement, *Chemically Induced Alterations in Sexual Development: the Wildlife/Human Connection*, Princeton Scientific Publishing Company Inc., Princeton, 1992.
- [2] EAWAG und BUWAL, *Stoffe mit endokriner Wirkung in der Umwelt*, BUWAL, Bern, Schriftenreihe Umwelt Nr. 308, 1999.
- [3] C. Desbrow, E.J. Routledge, G.C. Brighty, J.P. Sumpter, M. Waldock, *Environ. Sci. Technol.* 32 (1998) 1549.
- [4] T. Tanaka, K. Yamada, T. Tonosaki, T. Konishi, H. Goto, M. Taniguchi, *Water Sci. Technol.* 42 (2000) 89.
- [5] J.S. Vader, C.G. Van Ginkel, F.M.G.M. Sperling, J. De Jong, W. De Boer, J.S. De Graaf, M. Van der Most, P.G.W. Stokman, *Chemosphere* 41 (2000) 1239.
- [6] S.A. Snyder, D. Villeneuve, D. Verbrugge, J.P. Giesy, *Environ. Sci. Technol.* 33 (1999) 2814.
- [7] H.M. Coleman, B.R. Eggins, J.A. Byrne, F.L. Palmer, E. King, *Appl. Catal. B Environ.* 24 (2000) 1.
- [8] B.E. Segmuller, B.L. Armstrong, R. Dunphy, A.R. Oyler, *J. Pharm. Biomed. Anal.* 23 (2000) 927.
- [9] N. Deng, T. Fang, S. Tian, *Chemosphere* 33 (1996) 547.
- [10] F. Wu, N. Deng, H. Hua, *Chemosphere* 41 (2000) 1233.