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E-mail: ambi.agua@gmail.com

Degradation of 17α-ethinylestradiol in water by heterogeneous photocatalysis

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Wilton Silva Lopes[1*]; Maria Graziela Cristo de Oliveira Azevedo[1]; Valderi Duarte Leite[1]; José Tavares Sousa[1]; Josué Silva Buriti[2]

[1]Universidade Estadual da Paraíba (UEPB), Campina Grande, PB, Brasil
Departamento de Engenharia Sanitária e Ambiental
[2]Universidade Federal de Campina Grande (UFCG),Campina Grande, PB, Brasil
Departamento de Engenharia dos Materiais
[*]Corresponding author: e-mail: wiltonuepb@gmail.com,
grazielaspb@yahoo.com.br, valderileite@uol.com.br, jtdes@uol.com.br,
josueburiti@gmail.com

ABSTRACT

We investigated the degradation of 17α-ethynylestradiol in an aqueous solution using a batch heterogeneous photocatalytic (HPC) reactor with ultraviolet (UV) light and TiO_2 catalyst. In order to determine appropriate operating conditions, a 2^3 factorial experiment was conducted with initial an substrate concentration of 15 or 30 mg L^{-1}, TiO_2 concentration of 0.02 or 0.05%, pH of 5.0 or 9.0 and total reaction time 240 min. Degradation profiles and kinetic parameters were determined with an initial substrate concentration of 15 or 30 mg L^{-1}, 0.02% TiO_2 and pH 7.0.With17α-ethynylestradiol at 15 mg L^{-1}, degradation efficiency was 100% after 120 min independent of TiO_2 concentration and pH. However, less than 50% of the substrate was degraded when the initial concentration was 30 mg L^{-1} (0.05% TiO_2 and pH 5.0). Initial substrate concentration was a limiting factor for HPC, although the reaction was also strongly influenced by TiO_2 concentration and the interaction between initial substrate concentration and TiO_2 concentration. All degradations followed first-order kinetics. With 17α-ethynylestradiol at 15 mg L^{-1}, the half-life time ($t_{½}$) was 64.16 min and the rate constant was 0.108 min^{-1}, while at 30 mg L^{-1}, substrate degradation proceeded in two stages, the $t_{½}$ values of which were 44.71 and 433.12 min.

Keywords: endocrine disrupters, reaction kinetic, water treatment.

Degradação de 17α-etinilestradiol em água por fotocatálise heterogênea

RESUMO

O objetivo desse trabalho foi investigar a degradação de 17α-etinilestradiol em solução aquosa usando um reator fotocatalítico heterogêneo em batelada com radiação ultravioleta e TiO_2 como catalisador. Com a finalidade de obter as condições ideais, um planejamento fatorial 2^3 foi realizado com concentração inicial de 15 e 30 mg L^{-1}, concentração de TiO_2 de 0.02 e 0.05%, variou-se o pH em 5.0 e 9.0 e tempo total de reação de 240 min. O perfil da degradação e parâmetros cinéticos foram determinados com concentração inicial de 15 e 30 mg L^{-1}, 0.02% de TiO_2 e pH 7.0. Com concentração inicial de 15 mg L^{-1} de 17α-etinilestradiol a eficiência de degradação foi 100% após 120 min independente da concentração de TiO_2 e pH. Contudo menos que 50% do substrato foi degradado quando a concentração inicial utilizada era de 30 mg L^{-1} (0.05% TiO_2 e pH 5.0). A concentração inicial do substrato foi um fator limitante para a fotocatálise heterogênea. A reação também foi fortemente influenciada pela concentração de TiO_2. Todas as degradações seguiram cinética de primeira ordem. Para concentração de 17α-etinilestradiol de 15 mg L^{-1}, o tempo de meia vida ($t_{½}$) foi 64.16 min e a constante cinética foi 0.108 min^{-1}, enquanto para a concentração de 30 mg L^{-1}, a degradação do poluente aconteceu em dois estágios, com valor de $t_{½}$ de 44.71 e 433.12 min.

Palavras-chave: disruptores endócrinos, reação cinética, tratamento de água.

1. INTRODUCTION

Pharmaceuticals, persistent organic pollutants (POP) and endocrine disrupters (ED) are frequently found in effluents and surface water and on various solid matrices such as soils and sediments. The synthetic oestrogen 17α-ethynylestradiol ($C_{20}H_{24}O_2$), which is used as an oral contraceptive and in treating the symptoms of menopause and the prevention of abortion (Ghiselli and Jardim, 2007), is one of the major contributors to ED activity in the effluent from water treatment plants (Johnson and Sumpter, 2001). Although the Brazilian Ministry of Health has established standards for drinking water (Brasil, 2011), the majority of ED drugs are not listed in the resolution and, therefore, water treatment plants do not test for them. However several published articles have shown that such compounds are not removed completely by the conventional processes employed in water and sewage treatment plants (Bila and Dezotti, 2007; Pereira et al., 2011).

Advanced oxidation processes (AOP) are based on the generation of reactive hydroxyl radicals ($OH^{\bullet}$) with strong oxidant power ($E^o = 2.8$ V) that are capable of mineralizing POP to non-toxic CO_2 and H_2O. AOP offer operational simplicity and high efficiency in the oxidation of a vast array of substances (Taffarel et al., 2011), and can be applied as alternative procedures or in combination with conventional methods (Konstantinou and Albanis, 2003; Ferreira and Daniel, 2004). Among the various AOP strategies that have been described, heterogeneous photocatalysis (HPC), induced by radiation and performed with the help of a semiconductor, has received considerable attention because of its high efficiency in removing organic pollutants from drinking water and effluents.

In this context, the aims of the present study were (i) to investigate the degradation of 17α-ethynylestradiol in a batch HPC reactor under ultraviolet (UV) light and with TiO_2 as catalyst, and (ii) to verify the influence of the initial concentration of substrate on the kinetics of the reaction.

2. MATERIALS AND METHODS

Solvents and reagents. The water used in the experiments was supplied by the Estação Experimental de Tratamento Biológico de Esgotos Sanitários (EXTRABES, Campina Grande, PB, Brazil). The 17α-ethynylestradiol (CAS 57-63-6; 98% purity; Sigma-Aldrich, St. Louis, MO, USA) was first dissolved in methanol (Index-No 603-001-00-X; purity > 99,9%; Merck, Darmstadt, German), then a stock solution containing 100 mg L^{-1} was prepared in water under constant agitation and stored in a refrigerator at 4^oC. Working solutions were obtained by diluting an aliquot of the stock solution with an appropriate volume of water and adjusting the pH with 1M HCl or 1M NaOH as required. TiO_2 (98.5% purity; 0.5% loss on drying; Labsynth, Diadema, SP, Brazil) was used as catalyst.

Photocatalytic reactor. The reactor consisted of a wooden chamber (1 m long x 0.60 m wide x 0.65 m high) equipped with eight UV lamps (254 nm wave length; 15 W) and an orbital shaker (Orbital TE 141, Tecnal) with capacity for 12 x 100 mL Erlenmeyer flasks. The distance between the surface of the solutions and the lamps was 0.25 m, and the total light intensity was 7.46 mW cm^{-2}.

Experiment I - Operating conditions. In order to establish appropriate operating conditions for the degradation of 17α-ethynylestradiol, assays were conducted according to a 2^3 factorial design using the conditions shown in Table 1. Each assay was conducted in triplicate to give a total of 24 assays. Flasks containing the assay solutions (100 mL) were placed inside the HPC reactor, the catalyst was added in the absence of UV light, and the reaction mixtures were agitated for a few minutes. The UV lamps were then switched on and the residence time set to 240 min. In order to determine the percentage of substrate degraded, samples of the reaction suspensions were removed at 0 min (T_0) and 240 min (T_{240}), centrifuged for 15 min at 3600 rpm (Baby^R I centrifuge, model 206, FANEM São Paulo Brazil), and the supernatants analyzed according to the method of Teixeira and Teixeira (2006). Statistical analyses of the data were performed with the aid of Minitab 14 software in order to detect the individual and paired effects of the reaction parameters: differences were considered statistically significant at $p = 0.05$.

Table 1. Parameters and levels of the 2^3 factorial experiment.

Treatment	Codified			Numerical		
	X1	X2	X3	X1	X2	X3
T1	-	-	+	5.0	0.02	30
T2	+	-	+	9.0	0.02	30
T3	-	+	+	5.0	0.05	30
T4	+	+	+	9.0	0.05	30
T5	-	-	-	5.0	0.02	15
T6	+	-	-	9.0	0.02	15
T7	-	+	-	5.0	0.05	15
T8	+	+	-	9.0	0.05	15

X_1=pH; X_2=Percentage of catalyst TiO_2 (%); X_3=Initial concentration of substrate (mg L^{-1}).

Experiment II – Degradation time and kinetics. Based on the results obtained in Experiment I, the profile and kinetics of the degradation of 17α-ethynylestradiol were examined by conducting assays under the following conditions: initial concentration of substrate, 15 or 30 mg L^{-1}; concentration ofTiO_2, 0.02%; pH of reaction mixture, 7.0. HPC was conducted as described above and sampling of the reaction suspensions was performed every 10 min from T_0 to T_{30}, then every 15 min to T_{90} and then every 30 min to T_{240}. In each case, the concentration of substrate remaining in the sample was determined as described above. The degradation rate constant was calculated according to the first-order rate (Equation 1).

$$\ln C_t/C_0 = kt_{1/2} \quad \text{......(1)}$$

in which

C_0 and C_t are the concentrations of substrate (mg L^{-1}) at T_0 and T_{240}, respectively, k is the rate constant (min^{-1}) and

$t_{1/2}$ is the reaction half-life (min).

3. RESULTS AND DISCUSSION

Experiment I – Influence of reaction parameters. Table 2 shows the amount of 17α-ethynylestradiol (mg L^{-1}) removed from the reaction mixtures and the percentage degradation following the 240 min reaction. Degradation of the substrate was achieved under all operating conditions, and the mean efficiency was 81%. It was not determined whether by-products were formed or if the estrogenic activity of the reaction mixture was reduced. The most efficient degradation (100%) was obtained under operating conditions T5 to T8, while the least appropriate condition was T3, under which a degradation efficiency of less than 50% was obtained. It is noteworthy that 100% degradation was attained whenever the initial concentration of 17α-ethynylestradiol was 15 mg L^{-1}, independent of the amount of catalyst present or the pH of the reaction mixture. When the initial substrate concentration was increased to 30 mg L^{-1}, the degradation efficiency diminished considerably. This effect may be attributed to the substrate absorbing more radiation than the catalyst, as previously suggested by Kashif and Ouyang (2009) following studies involving the photo-degradation of phenol in the presence of UV light and TiO_2.

Table2. Degradation of 17α-ethynylestradiol following 240 min of heterogeneous photocatalysis.

Treatment	pH	TiO_2 (%)	C_i^a (mg L^{-1})	C_f^b (mg L^{-1})	Substrate Removed (mg L^{-1})	Substrate Degraded (%)
T_1	5.0	0.02	30	8.66	21.33	71.13
T_2	9.0	0.02	30	7.40	22.60	75.30
T_3	5.0	0.05	30	15.12	14.90	49.60
T_4	9.0	0.05	30	14.30	15.71	52.35
T_5	5.0	0.02	15	0	15.00	100
T_6	9.0	0.02	15	0	15.00	100
T_7	5.0	0.05	15	0	15.00	100
T_8	9.0	0.05	15	0	15.00	100

[a] initial concentration of substrate; [b] final concentration of substrate.

Experiment I – Statistical analysis. The Pareto diagram presented in Figure 1 shows the individual and paired effects of the reaction parameters on the degradation of 17α-ethynylestradiol. The bars represent the magnitude of the effects, while the transversal line corresponds to the *p* value of 2.12 and reveals the effects that were statistically significant at an alpha level of 0.05.

The most important parameters for HPC degradation were, in decreasing order, C (initial concentration of 17α-ethynylestradiol) > B (TiO_2 concentration) > BC (interaction between the initial concentration of substrate and the concentration of TiO_2). According to Dallago et al. (2009), pH is very important during the adsorptive phase, which is the rate-limiting step in the degradation process, since particles of TiO_2 may agglomerate in acidic solution and consequently reduce the surface area for adsorption of substrate and absorption of photons.

However, while pH may negatively influence the adsorptive phase of HPC, neither this factor alone, nor its interaction with other parameters, exerted a significant effect on the degradation of 17α-ethynylestradiol.These findings contrast with the results of Gálvez et al.

(2001), which revealed a strong influence of pH on photo-catalysis. These authors state that pH not only modifies the surface properties of the catalyst and the chemical form of the substrate, but also promotes the flocculation of the catalyst. In the present study, 17α-ethynylestradiol at an initial concentration of 15 mg $L^{-1}$was degraded efficiently at both pH 5 and pH 9.

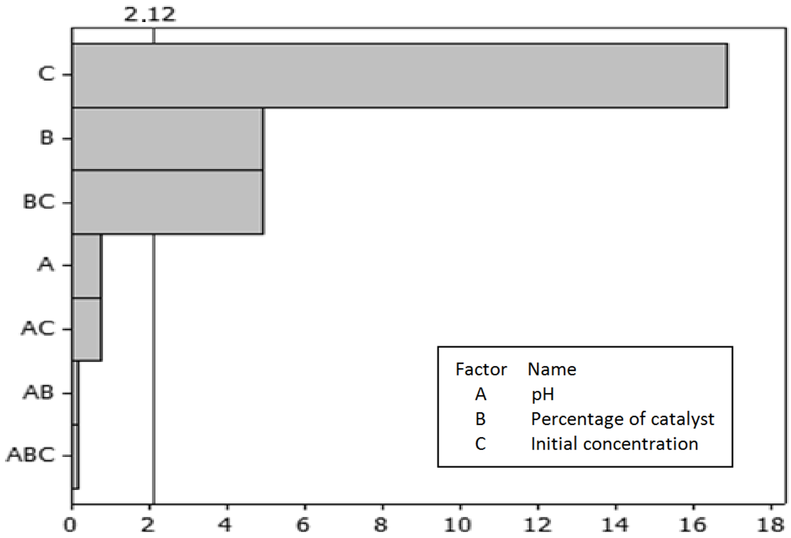

Figure 1. Pareto diagram showing the magnitude of the effects of the reaction parameters (**A**, pH; **B**, TiO_2 concentration; **C**, initial concentration of 17α-ethynylestradiol) on the degradation of17α-ethynylestradiol (p = 0,05).

However, at the higher substrate concentration, pH exerted a stronger influence when the TiO_2 concentration was high (0.05%); hence it was not possible to draw any conclusions regarding the influence of pH on the photo-degradation of 17α-ethynylestradiol. Similarly, Liu et al. (2003) could not evaluate the influence of pH in their experiments involving the degradation of 17α-ethynylestradiol in aqueous solutions.

The results presented herein demonstrate that the interaction between TiO_2 concentration and the initial concentration of substrate exerts a strong effect on degradation efficiency, being greater at the lower values tested (i.e. 0.2% and 15 mg L^{-1}, respectively). Evidently, a high concentration of catalyst provides a larger number of irradiated particles thereby increasing the rate of generation of free electrons up to a threshold level. Méndez-Arriaga et al. (2008) observed that the turbidity of the reaction mixture in the presence of excess catalyst reduced the infiltration of radiation, while Chiou et al. (2008) reported that excess catalyst diminished light penetration and, consequently, reduced the photo-degradation of phenol. Another possible cause of reduced photo-degradation efficiency in the presence of excess catalyst is the deactivation of active molecules through collision with ground-state molecules (Zhang et al., 2007). Zhang and Zhou (2005) have also stated that UV-induced photo-degradation does not depend on the initial concentration of substrate, suggesting the potential of process applications involving various types of matrices. Moreover, the authors emphasized the value of this method for the degradation of different organic pollutants, possibly involving the use of immobilized catalysts as a way of avoiding their removal at the end of the reaction.

Experiment II–Profile of degradation reaction. Figure 2 shows the progress of 17α-ethynylestradiol degradation as a function of time, and confirms that the efficiency of HPC was much higher (100% degradation in 120 min) when the initial concentration of substrate was 15 mg L^{-1}. At the higher substrate concentration (30 mg L^{-1}), degradation remained incomplete even after 240 min of reaction.

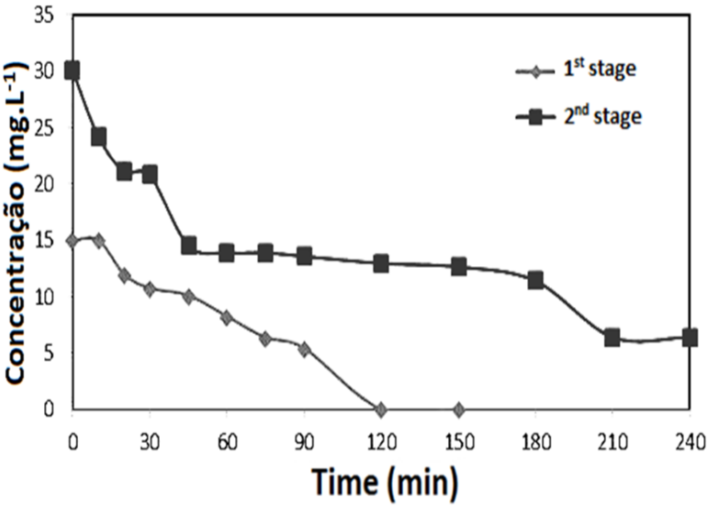

Figure 2. Degradation profiles of 17α-ethynylestradiol at initial concentrations of 15mg L^{-1}(♦) and 30mg L^{-1}(■) in the presence of UV light and 0.02% TiO_2 (pH 7.0).

Experiment II–Kinetics of degradation reaction. The photo-catalytic degradation of organic compounds typically follows first-order kinetics. However, the rate of reaction varies with the complexity of degradation, the amount of substrate adsorbed onto the surface of the catalyst, and the absorption spectra of the substrate. When substrates with high UV absorption coefficients are used in excess, they cover the surface of the catalyst and impede the penetration of radiation. In the present study, when the initial concentration of 17α-ethynylestradiol was15mg L^{-1}, the degradation process was rapid (90 min; Figure 3A): at the higher concentration of substrate; however, photo-catalysis occurred in two distinct stages, the second of which was very much slower (Figure 3B).

The kinetic parameters for the photo-degradation of 17α-ethynylestradiol are presented in Table 3. The reaction followed first-order kinetics regardless of the initial concentration of substrate employed. At an initial concentration of 17α-ethynylestradiol of 15 mg L^{-1}, 50% of the substrate was degraded in approximately 60 min. However, when the initial concentration was 30 mg L^{-1}, two degradation stages were required in order to reduce the level of substrate from 30 to 7.5 mg L^{-1}. The first stage involved a reaction with a $t_{½}$ of less than 45 min, while that of the second stage was 433.12 min. Lau et al. (2005) reported similar results following a study of the photo-degradation of di-*n* butyl phthalate except that, in this case, pH exerted a strong influence on the reaction kinetics. In the present study, the degradations were carried out at the fixed pH of 7.0 and, therefore, it was not possible to draw any conclusions regarding the significance of this parameter on the performance of HPC.

Table 3. Kinetic parameters of the photo-degradation of 17α-ethynylestradiol.

C_i^a(mg L^{-1})	Stage	k^b(min^{-1})	R^{2c}	$t_{½}^d$(min)
15	1	0. 0108	0. 9861	64.16
30	1	0.0155	0. 9716	44.71
30	2	0. 0016	0. 9733	433.12

[a] Initial concentration of substance; [b]rate constant; [c]linear correlation coefficient; [d] half-life time.

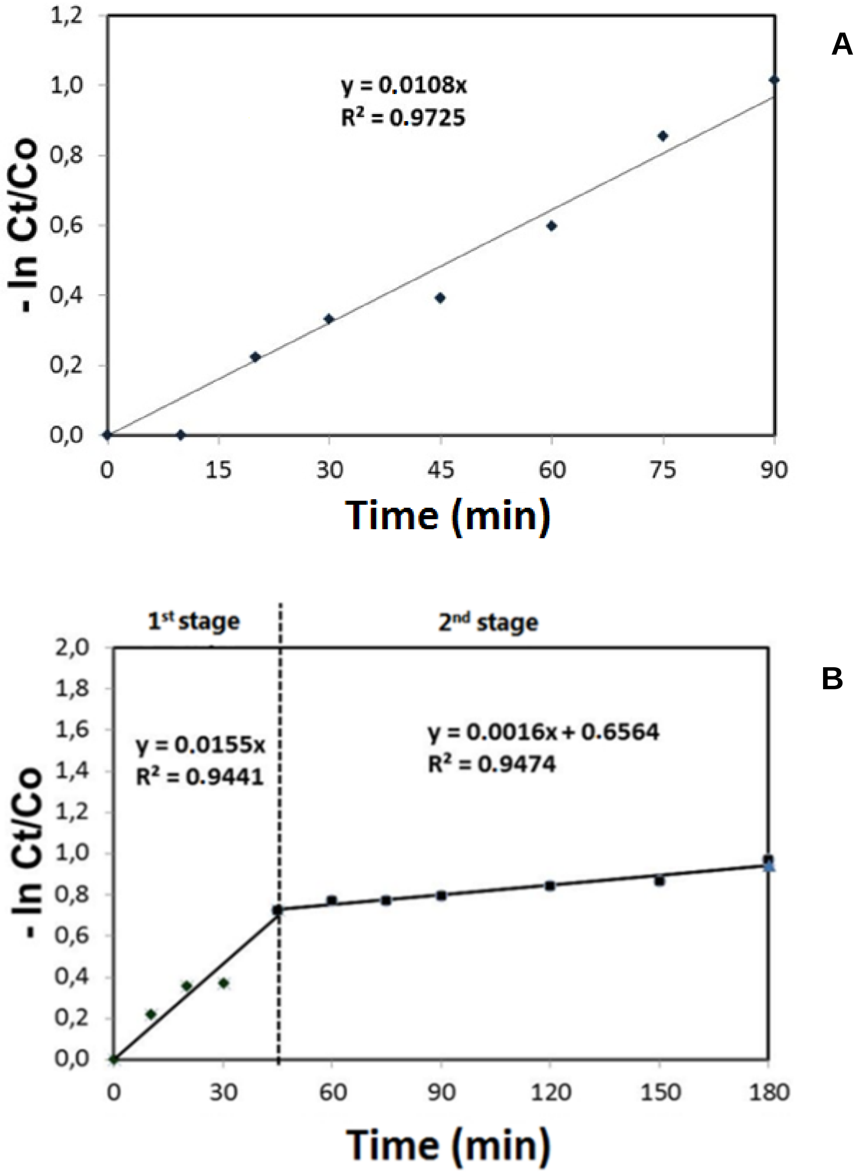

Figure 3. Rates of degradation of 17α-ethynylestradiol at initial concentrations of (**A**) 15mg $L^{-1}$and (**B**) 30mg L^{-1} in the presence of UV light and 0.02% TiO_2 (pH 7.0) (p=0,05).

4. CONCLUSIONS

Experiment I showed that degradation of 17α-ethynylestradiol using a HPC system was very efficient (mean value 81%). When the initial concentration of 17α-ethynylestradiol was 15 mg L^{-1}, the degradation efficiency was 100% after 120 min of reaction, independent of the TiO_2 concentration and pH, while the efficiency was less than 50% when the substrate was present at 30 mg L^{-1} (0.05% TiO_2 and pH 5.0). Experiment II confirmed that the initial concentration of substance was a limiting factor for the HPC process, although the reaction was also strongly influenced by TiO_2 concentration and by the interaction between the initial concentration of substance and TiO_2 concentration. When the initial concentration of 17α-ethynylestradiol was 15 mg L^{-1}, the $t_{½}$ of the reaction was 64.16 min. However, when the initial concentration of substrate was 30 mg L^{-1}, the degradation process developed in two stages, the $t_{½}$ values of which were 44.71 and 433.12 min.

5. ACKNOWLEDGEMENTS

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