

Photocatalytic Degradation of 17 α -Ethinylestradiol in Aqueous Solution

Degradación Fotocatalítica de Ethinylestradiol en solución acuosa

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Abstract

In the present investigation work, the degradation of 17 α -ethinylestradiol (EE2) in aqueous solution was studied. The main objective of this work is the degradation of EE2 through the process of heterogeneous photocatalysis using TiO₂ as a catalyst. The objective was the determination of the reaction parameters of the drug such as the photochemical effect, the adsorption rate of the catalyst and the initial concentration of the contaminant. The degradation was evaluated by the appropriate techniques of UV-vis and TOC spectroscopy. Like other works, the mineralization of this compound is reported, however, the % of EE2 mineralization can be determined in a solution that uses a photocatalytic process.

Degradation, Photocatalysis and 17 α -ethinylestradiol

Resumen

En el presente trabajo de investigación se estudió la degradación de 17 α -etinilestradiol en solución acuosa. Como objetivo principal del presente trabajo es la degradación del EE2 mediante el proceso de fotocatalisis heterogénea utilizando TiO₂ como catalizador. Los objetivos particulares fueron la determinación de los parámetros de reacción del medicamento como lo son el efecto fotoquímico, índice de adsorción del catalizador y la concentración inicial del contaminante. Se evaluó la degradación mediante las técnicas adecuadas de espectroscopía UV-vis y TOC. Al igual que otros trabajos se reporta la mineralización de este compuesto, sin embargo, se logro determinar el % de mineralización del EE2 en solución acuosa utilizando un proceso fotocatalítico.

Degradación, Fotocatalisis y 17 α -etinilestradiol

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Introduction

A micro-contaminant is any compound present in soil and wastewater at concentrations expressed in $\mu\text{g/L}$ and ng/L , which are persistent and resistant to conventional treatments and considered harmful to the environment. Among the micro-contaminants are pesticides, petroleum products and medicines [1-3].

Medicines have certain physicochemical characteristics and some of them are resistant to hydrolysis, to natural degradation and are considered highly disturbing for flora and fauna, also affecting abiotic factors by the alteration of pH, salinity, dissolved oxygen, etc. [4-6]. The inadequate final disposal of expired medicines causes the arrival to effluents, dissolved in wastewater, agricultural and veterinary use, being very difficult to eradicate [7-10].

Among the medicines that are commonly found in effluents, hormonal treatments are an alarming source, they are commonly used to alter the menstrual cycle and the impediment of conception, examples of such medications are EE2 (Figure 1) which is a synthetic estrogen compound that are used in contraceptive methods [11-18]. This compound is part of the so-called endocrine disruptors, which have the effect of simulating or altering the hormonal processes. These compounds cause a stress to the environment. Exposure to small amounts over prolonged periods can alter the development of fish tissues, are toxic to some species of algae, fish and invertebrates [19]. They can produce sexual inversion, reduction of the masculine sex and of the production of eggs, affecting the trophic chains and in some birds the thinning of the shell of eggs [20-24].

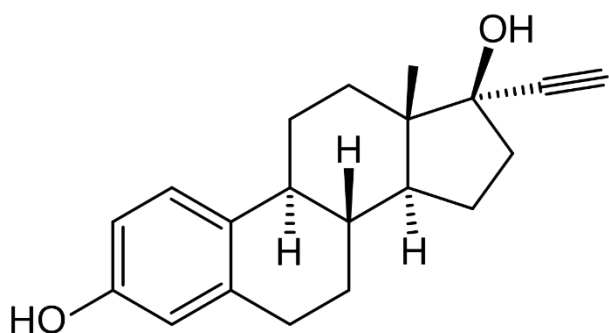


Figure 1 Chemical structure of 17 α -ethinylestradiol. Chemical formula: $\text{C}_{20}\text{H}_{24}\text{O}_2$. And the molecular weight: 296.178 g/mol

Reports indicate the presence of concentrations between 1 and 5 ng/L of EE2 in different regions of the world, in surface waters and sediments have been detected in concentrations ranging between 1 and 100 ng/L [25-29]. Currently, it has been shown that EE2 has strong ecotoxic effects on the environment, in addition to interacting with other compounds, the byproducts generated can be harmful to wildlife, as well as the alteration of fish spawning cycles [29-31].

In recent years, advanced oxidation processes are an alternative to eliminate micro-contaminants. This set of techniques are physicochemical processes with the ability to produce structural changes in the chemistry of pollutants, because they involve the formation of powerful transient species such as hydroxyl radical, which allow the destruction of a large variety of organic compounds resistant to natural degradation. The hydroxyl radicals (OH) are highly oxidizing for organic matter and can be generated by photochemical processes either sunlight or radiant light, or by other forms of energy that do not involve radiant light [32-35].

Heterogeneous photocatalysis has been widely studied in the decontamination of wastewater and has proven its effectiveness for the degradation of medicines [33-36].

The photocatalyst TiO_2 presents physicochemical properties [37], which demonstrate a high efficiency for the elimination of a wide variety of contaminants including dyes, pesticides and medicaments [35,38,39,40-42].

Experimental

Chemical

The 17 α -Ethinylestradiol (EE2) used for the photodegradation experiments is a white powder purchased from Sigma-Aldrich grade ReagentPlus ($\geq 98\%$) with a solubility of 19 mg/L . For the photocatalytic experiments, commercial titanium dioxide TiO_2 Evonik-Degussa P25 with a composition of 80% anatase and 20% rutile was used. Also, distilled water and ethanol were used to prepare the EE2 solutions. For the analysis of total organic carbon, potassium biphthalate was used $\text{C}_8\text{H}_5\text{O}_4\text{K}$, sodium bicarbonate NaHCO_3 y sodium carbonate Na_2CO_3 TOC grade as reference standards.

Photoreactor

The photodegradation experiments were carried out in a self-made system by the research group. Which consists of an annular cylinder of stainless steel with mirror finish, which supports 4 lamps of UV light brand Purikor of 16 watts. In the center of the system, a glass container is placed that functions as a batch reactor. The reactor is equipped with an oxygen supply and a magnetic stirrer to keep the reaction solution homogenized.

Photochemical Degradation Test

A photochemical degradation test was performed to monitor the effect of UV radiation on the contraceptive molecule under the established reaction conditions. The solution was maintained in constant magnetic stirring with a bubbling of oxygen saturated with a flow of 100 mL/minutes, at room temperature. Oxygen acted as an electron acceptor species throughout the experiment.

Adsorption Test

For this test, a load of 0.5 g of TiO₂ in a volume of 250 mL was used to evaluate the effect caused by a porous material such as TiO₂ in suspension in a solution of EE2 as a function of the change in the concentration of EE2 with respect to time. For this, the catalyst charge was added to the solution and kept under constant magnetic agitation for a period of 240 minutes in dark conditions. At every time care must be taken that the catalyst is not exposed to sources of light, for example, when weighing. It was also taken care that the solution was not exposed now of taking the samples or filtering them.

Photocatalytic Degradation Test

Solutions were tested with concentrations of EE2 at 5, 10 and 15 ppm, in each experiment the compound was previously diluted in 2 mL of ethanol using a 250 mL aqueous solution volume. A load of 0.5 g of TiO₂ exposed to UV irradiation is used in the reaction system for a period of 300 minutes, in which aliquots of 5 mL were taken, in addition to taking a pre-experiment sample without catalyst and in the times: 0, 15, 30, 45, 60, 90, 120, 180, 240 and 300 minutes, respectively.

The solution was kept homogenized by constant stirring, in addition saturated oxygen was supplied to the solution with a flow of 100 mL/minutes.

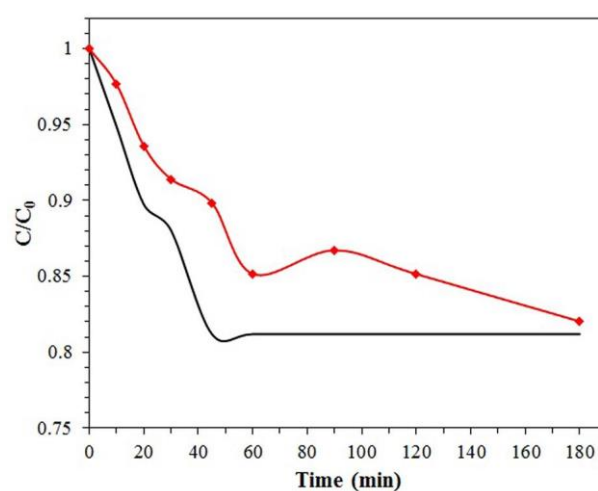
Analytical Methods

The progress monitoring of the reaction was performed by UV-vis spectroscopy using a JENWAY 7305 spectrophotometer; TOC analysis was also performed with a SHIMADZU TOC-5000A total organic carbon analyzer. Before analyzing each sample, it was centrifuged and filtered through Millipore GV membranes (0.22 µm pore diameter) to eliminate any traces of catalyst.

Results and Discussion

Photochemical Effect

The results of the photochemical effect indicate that the relative concentration of EE2 decreases 18% in 180 minutes of reaction, this does not represent a significant change, therefore, the contaminant shows resistance to photodegradation. The EE2 is a refractory compound which prevents the removal with light, therefore, it is necessary to use some advanced oxidation process [43-48].



Graphic 1 Degradation profile of the photochemical effect as a function of the relative concentration at a concentration and index adsorption of the TiO₂ catalyst

Index Adsorption

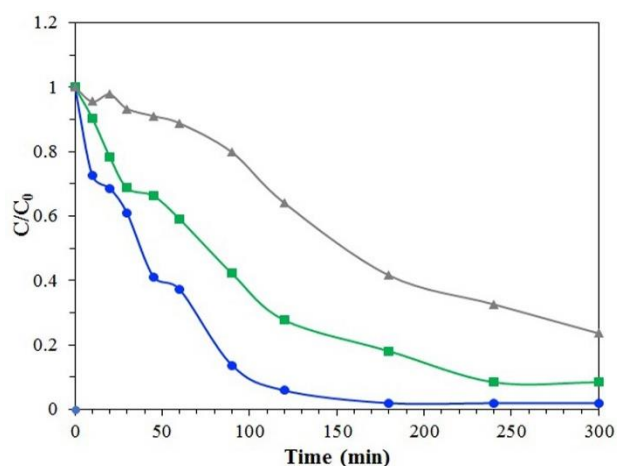
The relative concentration profile of the adsorption experiment in dark conditions is presented in Graphic 1.

The results of the adsorption test show a slight decrease in which it adsorbs approximately 19% during the first 45 minutes and subsequently reaches a state of equilibrium under these experimental conditions. This period of adsorption coincides with that reported by [49] in which it indicates 30 minutes and 10% adsorption with TiO_2 using lower concentrations of EE2 and amount of catalyst.

Photocatalytic Degradation with TiO_2

Relative concentration profiles by UV-vis spectroscopy indicate that the EE2 molecule degrades relatively easily in the first 300 minutes of reaction by the OH radicals generated in the photocatalytic process. Figure 3 shows that in the experiment of 5 ppm of EE2 there was a degradation of 99% in the 180 minutes. Meanwhile for the solution of 10 ppm of EE2 a degradation of 91.56% is shown in 240 minutes. The highest concentration of 15 ppm of EE2 reaches a degradation percentage of 76.40% at the end of the 300-minute experiment. These results could surpass that reported by [50] that reached a maximum percentage of 29% degradation for a concentration of 5 ppm of EE2. Other studies report higher percentages of photocatalytic degradation of EE2 using concentrations lower than those of this study [49].

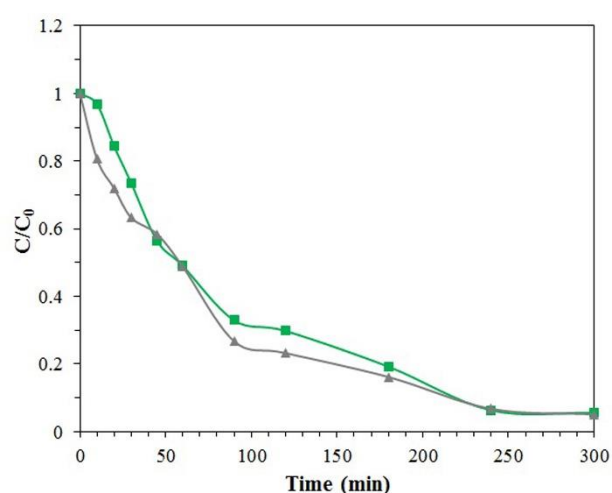
The heterogeneous photocatalysis applied for the degradation of EE2 with TiO_2 turns out to be mostly efficient in comparison with other photocatalysts and the adsorption and electrochemical processes [51-54].



Graphic 2 Photocatalytic degradation of EE2 at different concentrations monitored by UV-vis spectroscopy ($V=250$ ml, $\text{TiO}_2=0.5$ g)

Total Organic Carbon (TOC)

The total organic carbon analysis was performed on the concentration experiments of 10 and 15 ppm of EE2 to monitor the degree of mineralization of the micro-contaminant. Graphic 3 shows a comparative graph showing that the mineralization profiles follow a similar behavior reaching 94% on average. In addition, the degree of mineralization of a known concentration of 15 ppm of EE2 is shown, which at the end of the reaction shows 95.52% total organic carbon values.



Graphic 3 Initial concentration effect on the photocatalytic mineralization of EE2 ($V = 250$ mL, $\text{TiO}_2 = 0.5$ g, analyzed by TOC)

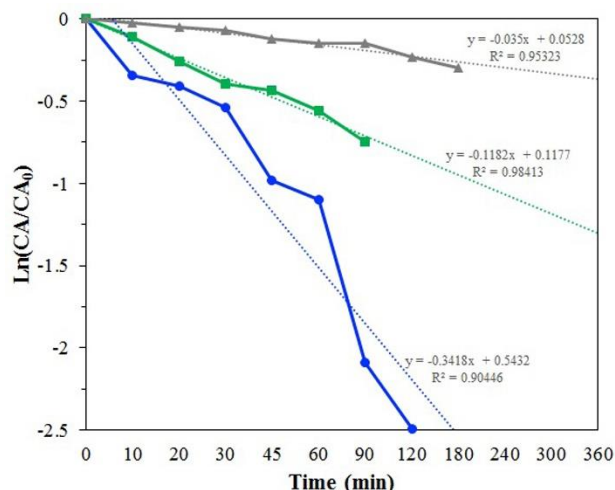
Chemical Kinetic

The results of the kinetic analysis of the reaction samples are shown in Graphic 4, indicating that the photocatalytic degradation of EE2 is adjusted to a first-order kinetic model, like other reports in the literature on this molecule [49, 55- 58]. Since the photocatalytic degradation reactions of organic compounds with aromatic character generates a series of organic products through a series-parallel mechanism [59]. The initial velocity of the photocatalytic degradation reaction of EE2 was determined, for which the velocity constant of a first-order reaction was evaluated using the initial concentration values of EE2 at times not greater than 180 minutes. Table 1 shows the kinetic parameters calculated as a function of the initial concentration of EE2.

It is observed that the reaction rate constant decreases as the initial concentration of the contaminant increases and the rate of degradation of EE2 is inversely proportional to the initial concentration of the original reagent.

Initial concentration (ppm)	Initial concentration (mMol)	Apparent reaction constant kapar (min ⁻¹)	R ²	Reaction rate (-r) (mMol/min)
5	0.0168	0.3418	0.9045	0.0057
10	0.0337	0.1182	0.9841	0.0039
15	0.0500	0.0350	0.9532	0.0017

Table 1 Initial reaction rate as a function of the initial concentration in the photocatalytic degradation of EE2



Graphic 4 Photocatalytic degradation kinetic model of EE2. $C_0 = 5$ ppm (blue line), $C_0 = 10$ ppm (green line), $C_0 = 15$ ppm (gray line). [$V = 250$ mL, $TiO_2 = 0.5$ g, analysis of samples by UV-vis spectroscopy]

Material Balance

By means of a material balance it is possible to determine the fraction of EE2 transformed to intermediate organic products in the photocatalytic degradation of the hormone. With the experimental results, the relative concentrations of EE2 are calculated with equations 1 and 2, respectively.

The fraction of EE2 mineralized to CO_2 is determined with equation 3, and the fraction of EE2 transformed to intermediate organic products is calculated with equation 4.

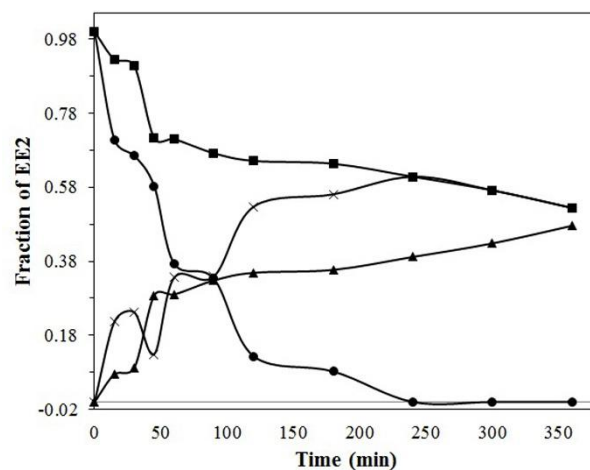
$$aC_m = \frac{C_m}{C_{m0}} \quad (1)$$

$$aTOC = \frac{TOC}{TOC_0} \quad (2)$$

$$fCO_2 = 1 - aTOC \quad (3)$$

$$fOIP = aCOT - aC_m \quad (4)$$

The intermediate organic products formation and consumption for the reactions of 5 ppm EE2 initial concentration is presented in Graphic 5. It is clearly seen that the fraction of intermediate organic products increases gradually as a function of time. After 120 minutes, the $OH\cdot$ radicals initially generated by the TiO_2 begin to attack the products of the reaction mixture, which decrease slightly and turn out to be persistent to the radical attack, because the profile remains almost constant until the end of the reaction. The products of the photocatalytic degradation of EE2 are widely reported by [49, 54]. In both articles, they propose that within the reaction mechanism the by-products generated conserve the original structure of EE2, therefore, it is necessary to increase the reaction time, to achieve total oxidation and environmentally harmless final products [60].



Graphic 5 Material balance for the photocatalytic degradation of EE2 in aqueous solution. ($V = 250$ mL, $C_0 = 5$ ppm, $TiO_2 = 0.5$ g). ● = 17 α -ethinylestradiol; ▲ = Carbon Dioxide; × = Organic Intermediates; ■ = Total Organic Carbon

Conclusions

17 α -ethinylestradiol (EE2) is not efficiently degraded by a photochemical process with UV light, the simple effect of radiation is not enough to eliminate this micropollutant in aqueous solution. The solution of EE2 with commercial TiO₂ Evonik-Degussa-P25 achieved its degree of saturation in 45 minutes, in this period the catalyst stops adsorbing the synthetic hormone and reaches its equilibrium point. The EE2 photocatalytic process in the presence of UV light, TiO₂ in a batch of photogravure was achieved with relative ease, a few minutes in reaction EE2 molecule is degraded by the action of the generated OH \cdot radicals. The mixture of by-products generated at low levels are persistent to the oxidation and require long reaction times to convert them into CO₂ and H₂O. The photocatalytic degradation of EE2 is adjusted to a first-order kinetic equation.

Recommendations

The recommendations are that these and many others micropollutants of pharmaceutical origin continue analyzed due to their adverse impact on the environment since it affects the biota and fauna as well as the entire trophic chain. Another recommendation for future works is to thoroughly analyze the intermediate products for a specific characterization, in the same way an analysis of ecotoxicity to see how harmful the metabolites of EE2 are, unlike the molecule initial.

Nomenclature

aC_m = Relative concentration of EE2

aTOC = Relative concentration of TOC

C_m = EE2 Concentration

C_{m0} = Initial concentration of EE2

EE2 = 17 α -Ethinylestradiol

fCO₂ = Fraction of mineralized EE2

fOIP = Fraction of organic intermediates products

K_{apar} = Kinetic reaction apparent rate constant

-r = Photocatalytic degradation reaction rate

TOC = Total organic carbon

TOC₀ = Initial total organic carbon

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