

Estrogen Mineralization by a Modular Plug Flow Photocatalytic Reactor

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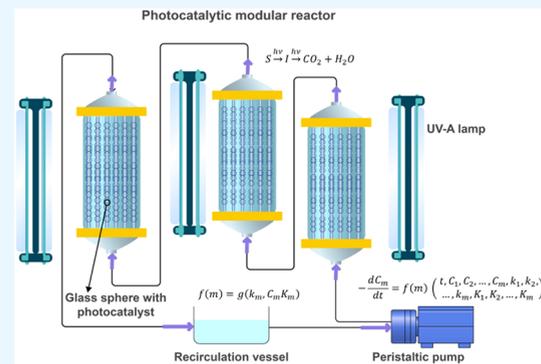
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ABSTRACT: Estrogens are currently on the watch list of contaminants of emerging concern in the aquatic environment due to their strong impact on it. Ethinyl estradiol is one of the estrogens often found in contraceptive pills, and it can easily reach water bodies mainly through insufficiently treated wastewater. Photocatalysis is one of the solutions that ensure the complete mineralization of refractory organic compounds in wastewater treatment. Therefore, this work deals with the nonlinear modeling of the photocatalytic mineralization kinetics of ethyl estradiol in aqueous solutions. A modular photocatalytic reactor operated in a plug flow system under UV-A radiation was used. The TiO_2/ZnO photocatalyst is deposited on an inert glass support arranged inside the reactor in the form of rows of glass balls. This type of photocatalytic reactor ensures the rapid mineralization of both the initial organic substrate and the formed organic intermediates. The obtained results indicated that the nonlinear modeling of the mineralization kinetics of both the initial organic substrate and the formed organic intermediates fit the experimental data well. On the contrary, the classical Langmuir–Hinshelwood kinetic model does not fit the experimental data regarding the mineralization of the organic intermediates formed, most likely due to an underestimation of the adsorption equilibrium constant of the initial organic substrate, which competes with the organic intermediates for the active centers of the photocatalyst.



1. INTRODUCTION

Commission Implementing Decision (EU) 2018/840 introduced three estrogens on the watch list of substances to be monitored at the level of the entire European Union, namely, estrone, estradiol (17β -estradiol), and ethinyl estradiol (17α -ethinyl estradiol) due to the increase in collective concern regarding the negative effects that these estrogens have in the aquatic environment.¹ Estrogens are naturally released into the environment, especially from livestock farms, but the healthcare sector, both human and veterinary, also plays a significant role.² Synthetic estrogens, such as ethinyl estradiol, are often used in contraceptive pills or other treatment regimens in human and veterinary medicine. Although most of the administered estrogens are metabolized, a portion may remain unmetabolized and thus be excreted through urine and feces, reaching wastewater or even directly into natural water bodies.³ Their presence in the aquatic environment can lead to serious problems for aquatic organisms, as they can act as endocrine disruptors under certain circumstances.⁴ The information regarding their removal in conventional wastewater treatment plants indicates that estrogens are not completely removed, and even in some cases, the degree of removal is quite low (around 20%).⁵ Often, to increase the degree of removal of such refractory organic compounds, it is necessary to introduce an advanced treatment step, such as an

advanced oxidation step. Photocatalysis is one of the advanced oxidation processes that has recently received a lot of attention in this field, its application leading to a rapid, complete mineralization of the refractory organic substrate in wastewater.⁶ The study of reaction kinetics is crucial for the design of photocatalytic reactors. Thus, understanding kinetics helps in optimizing reaction conditions, correctly sizing the photocatalytic reactor, evaluating the efficiency of the photocatalyst, as well as making predictions for scaling (the information obtained in the laboratory can be extrapolated for large-scale applications, which are essential for industrial implementation).⁷

There are several studies regarding the photocatalytic degradation of estrogens under various experimental conditions that address reaction kinetics. In many of these studies, linear forms of classical kinetic models are used to determine kinetic parameters, such as zero-order kinetics,^{8,9} first-order

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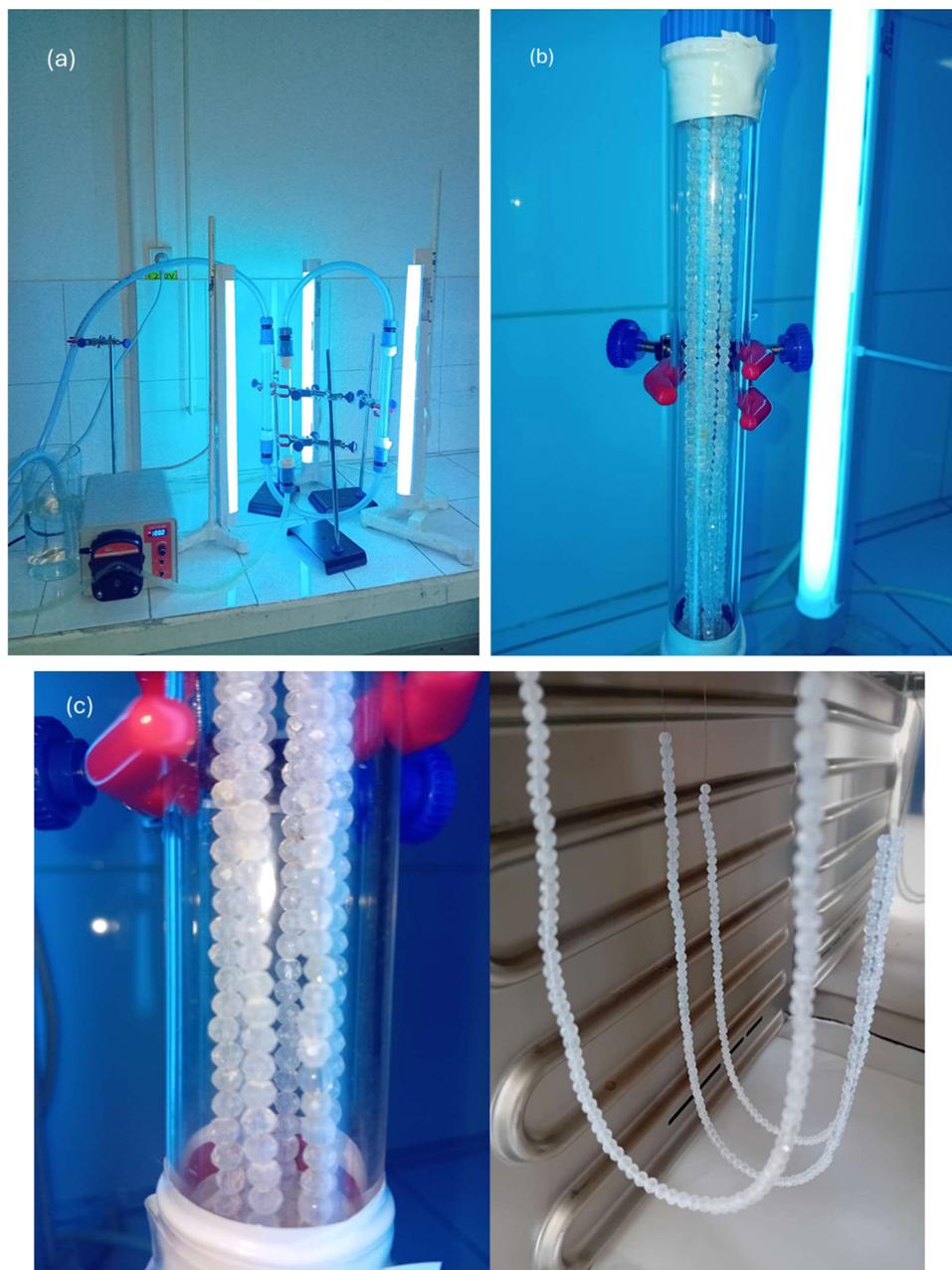


Figure 1. Modular photocatalytic reactor: (a) the actual photocatalysis installation; (b) photocatalytic module; and (c) glass bead strings on which the photocatalyst is deposited.

kinetics,^{10,11} second-order kinetics,^{12,13} or Langmuir–Hinshelwood (L-H) kinetics,^{14,15} or modified L-H kinetics.¹⁶ Even though good results have been obtained, these models have limitations when it comes to describing the kinetics of the entire organic content mineralization from aqueous solutions. In this regard, it is clearly demonstrated that the apparent reaction order varies with the concentration of the organic substrate, showing a transition from a limiting zero-order (close to saturation of the photocatalyst with the adsorbed organic substrate) at high concentrations to a limiting first-order (at the beginning of the photocatalytic degradation of the organic substrate when it is slightly adsorbed on the surface of the photocatalyst), at low concentrations.^{16–18} Additionally, the Langmuir–Hinshelwood model cannot adequately describe the kinetics of organic substrate mineralization except in

the initial rate segment.¹⁹ This is because the Langmuir–Hinshelwood model describes the surface photocatalytic reactions of adsorbed organic substrate based on the conditions of the Langmuir adsorption theory. Thus, the organic substrate follows monolayer adsorption dynamics, which makes the validity of the model dependent on the condition that the photocatalyst surface does not become saturated. This condition is satisfied at the beginning of photocatalytic degradation because, subsequently, there is strong competition between the initial organic substrate and the organic intermediates formed for the active sites of the photocatalyst, which usually implies saturation of its surface with the organic substrate. This can also happen in the case of high concentrations of initial organic substrate.^{20–22} In contrast, very good results have been obtained with the

nonlinear modeling of the entire organic content mineralization kinetics for organic compounds, such as 2,4-dichlorophenol in aqueous solutions,²³ *n*-alkanes in aqueous solutions,²⁴ methane in air and aqueous solutions,²⁵ and perchloroethylene in air.²⁰ Thus, through nonlinear modeling, unique values of the kinetic parameters have been identified that fit the entire kinetic curve of organic substrate mineralization, regardless of its initial concentration. Additionally, many first-order differential kinetic equations can be written as there are organic intermediates identified in the system, and their simultaneous resolution leads to the iterative determination of the kinetic parameters that accurately describe each reaction until the complete mineralization of the entire organic content.

Therefore, the main objective of this work is to describe the kinetics of ethinyl estradiol mineralization through nonlinear modeling, considering the formation of a unique arbitrary intermediate that represents the entire organic content throughout the photocatalytic process. To highlight the advantage of nonlinear modeling in the photocatalytic degradation processes of organic substrates, the results obtained from this approach are compared with those obtained using the classical Langmuir–Hinshelwood kinetic model. It should be noted that this work is strictly focused on the nonlinear modeling of the kinetics of organic substrate mineralization. All other information related to the characteristics and performance of the photocatalyst, the determination of the optimal operating conditions for the photocatalytic reactor, the design of the photocatalytic modules, etc., has been extensively described elsewhere.²⁶

2. MATERIALS AND METHODS

2.1. Materials. Ethinyl estradiol of analytical grade was purchased from Merck KGaA (Darmstadt, Germany). 5-Chloro-2,4-dinitroaniline (analytical grade) was purchased from Cymit Quimica S.L. (Barcelona, Spain), and it was used for colorimetric measurement of ethinyl estradiol. The other reagents required for the colorimetric analysis of ethinyl estradiol, namely, sodium nitrite, 1 N hydrochloric acid solution, 0.1 and 1 N sodium hydroxide solution, and sodium acetate, were purchased from Merck KGaA. Photocatalyst synthesis reagents (all analytical grade), such as titanium(IV) isopropoxide 97%, zinc acetate dihydrate 98%, ethanol absolute 99.9%, and nitric acid 65%, were purchased from Merck KGaA. Hydrogen peroxide 30% used in the photocatalysis tests, sulfuric acid 95–98%, potassium dichromate, and silver nitrate (analytical grade) used in COD (Chemical Oxygen Demand) analysis were also purchased from Merck KGaA.

The photocatalytic reactor consists of three interconnected tubular photocatalytic modules made of quartz. Inside the tubes are positioned six strings of 65 glass balls each on which the photocatalyst is deposited. All materials used in the construction of the photocatalytic reactor were purchased from various local companies.

2.2. Preparation of the Photocatalyst. The synthesis of the photocatalyst was carried out by the sol–gel method, which begins with the preparation of titanium and zinc precursor solutions. The titanium precursor solution was prepared by adding nitric acid (1.3% w/w) dropwise over a solution of titanium(IV) isopropoxide in absolute ethanol at a volumetric ratio of 1:3, under continuous stirring for 2 h at 60 °C. The zinc precursor solution was prepared by dissolving

three grams of zinc acetate in a mixture of absolute ethanol and nitric acid at a volumetric ratio of 1:2, under continuous stirring for 10 min. The two precursor solutions are subsequently mixed under continuous stirring at 60 °C.

2.3. Photocatalyst Deposition on the Inert Support. The strings of glass balls (the balls are strung on stainless steel wire) are immersed in the photocatalyst solution prepared according to the procedure described above for 1 h, after which they are removed from it and transferred to the oven, where they are kept for 24 h at 105 °C. Finally, they are calcined in the furnace for 4 h at 500 °C. The physicochemical characteristics of the obtained photocatalyst are presented elsewhere.²⁶ Thus, the morphostructural characterizations indicated that the TiO₂/ZnO photocatalyst has excellent photocatalytic performance, mainly deriving from the fact that it presents a compact structure with small crystallites as well as a highly reactive specific surface area.

2.4. Photocatalytic Mineralization Experiments. The photocatalytic mineralization experiments were carried out in a modular photocatalytic reactor under UV-A radiation (Figure 1). Following some preliminary experiments, an optimal number of three photocatalytic modules was established so that the dose of the photocatalyst corresponding to these modules ensures the complete mineralization of the organic material in no more than 2 h of irradiation. The photocatalytic modules (Figure 1) consist of interconnected quartz tubes with the dimensions 5 cm (D) × 10 cm (H) through which the aqueous working solution moves from bottom to top with a flow rate of 20 L/h, continuously recirculated in the photocatalytic modules with a peristaltic pump (LBX Pump-60J-001, Labbox Labware, S.L., Barcelona, Spain) through a recirculation vessel. The photocatalyst (TiO₂/ZnO) is deposited on an inert support (according to the procedure described above), which consists of six strings of glass balls positioned inside the quartz tubes on their entire circumference. Each string contains 65 glass balls with a diameter of 4 mm, which are drilled in the center so that they can be strung on a wire made of stainless steel (Figure 1). The average amount of photocatalyst corresponding to a photocatalytic module is 1 g (0.92–1.15 g), and therefore, the dose of photocatalyst can only be changed by increasing or decreasing the number of photocatalytic modules. The UV-A radiation source (Osram L Blue UV-A 18 W/78 G13 lamps, OSRAM GmbH, München, Germany) surrounds the modular photocatalytic reactor so that each module receives an approximately equal amount of radiation, namely, around 2400 μw/cm², which was measured with a Cole-Parmer UV-meter equipped with a mobile probe from General Tools & Instruments (General Tools & Instruments LLC, New York, NY).

The working aqueous solution was brought to pH 3 by acidulation with sulfuric acid, and a quantity of hydrogen peroxide was added so that the ethinyl estradiol/hydrogen peroxide molar ratio was stoichiometric. These conditions have been established in previous studies as optimal for TiO₂-based photocatalysts.²⁷ Under acidic conditions, on the one hand, the surface of the TiO₂-based photocatalyst is positively charged, which increases its adsorption capacity for the species involved in the photocatalytic process, the highest value of which is recorded at a pH of the aqueous solution of 3. On the other hand, increasing the acidity of the system to a pH value of 3 favors the formation reactions of hydroxyl radicals (·OH) due to the direct dependence that exists between the concentration of hydrogen ions (H⁺) and the concentration of hydroxyl

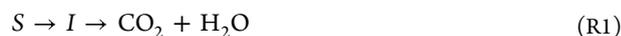
radicals (*OH).²⁸ The total volume of the working solution is 2 L, and the initial concentration of ethinyl estradiol in it was 25, 50, 75, and 100 mg C/L, where mg C/L is mg carbon equivalent per liter of solution. The range of initial concentrations of the organic substrate was chosen so as to avoid as many experimental errors as possible that could occur when working at concentrations that are too low or too high and which could generate results that are outside the linearity range in which the initial velocity method for determining kinetic parameters is valid. Also, a constant increase in the initial organic substrate concentration of 25 mg of C/L in the aqueous solution subjected to photocatalysis was taken into account, which led to the experiments being carried out at only four initial organic substrate concentrations. The reason for expressing the concentration of ethinyl estradiol in equivalent carbon is to have the same unit of measure for both the concentration of the initial organic substrate (ethinyl estradiol) and the concentration of the organic intermediates formed as measured by COD analysis. Therefore, both the concentration of ethinyl estradiol initially expressed in milligrams per liter of solution (mg/L), as well as the concentration of the organic intermediates formed initially expressed in milligrams of equivalent oxygen per liter of solution (mg O₂/L) were transformed into milligrams of carbon per liter of solution (mg C/L). This way of expression greatly helps in the kinetic modeling of the photocatalytic mineralization process.

The variation in the concentration of the organic substrate during the irradiation time was monitored by taking samples at predetermined time intervals. The concentration of ethinyl estradiol was measured by spectrophotometric analysis using the colorimetric method with diazotized 5-chloro-2,4-dinitroaniline.²⁹ In short, this consists of the formation of an azo dye through condensation of diazotized 5-chloro-2,4-dinitroaniline with ethinyl estradiol, and the resulting color is measured at 450 nm by using a UV–vis spectrophotometer UV-1900 from Shimadzu USA Manufacturing, Inc. (Austin, TX). The concentration of organic intermediates was measured by COD analysis according to the APHA 5220 D standard method (closed reflux, colorimetric method)³⁰ by using a Hach LT 200 thermostat and Hach DR 3800 spectrophotometer (Hach, Loveland, CO).

It should be noted that before carrying out the experimental program, the contribution of photolysis and assisted photolysis (with the addition of hydrogen peroxide) to the degradation of the organic substrate was verified, as well as the adsorption capacity of the photocatalyst in relation to the initial organic substrate (ethinyl estradiol). To check the photolysis contribution, the tests were carried out under the working conditions presented above but using a single concentration of the organic substrate, without the addition of hydrogen peroxide, and in the absence of the photocatalyst. Briefly, before the introduction of the photocatalyst into the reactor modules, an aqueous solution of the organic substrate with a concentration of 100 mg C/L at a pH of 3 was recirculated for 2 h in the presence of UV radiation. At the end of 2 h of irradiation, samples were taken for COD analysis. All analyses were performed in triplicate. To verify the contribution of assisted photolysis, a similar procedure was used but with the addition of hydrogen peroxide. On the other hand, dark adsorption experiments (in the absence of both UV radiation and hydrogen peroxide) were performed to evaluate the adsorption capacity of the photocatalyst.

3. RESULTS AND DISCUSSION

3.1. Kinetic Modeling of Photocatalytic Mineralization of Ethinyl Estradiol. The nonlinear modeling of the kinetics of ethinyl estradiol mineralization involves solving a system of three first-order differential eqs 1–3 that describe the following sequence of photocatalytic reactions



where *S* is the concentration of the initial organic substrate, *I* is the concentration of the organic intermediates formed during the degradation of the initial organic substrate, and CO₂ is the concentration of carbon dioxide formed following the mineralization of the entire organic content. It is assumed that the initial organic substrate is not mineralized directly, but first, it is degraded into organic intermediates. The information provided by the literature suggests a photocatalytic degradation mechanism based largely on the reactivity of hydroxyl radicals (*OH), these being identified as the most reactive oxidants present in the photocatalytic system. It seems that this mechanism is imposed due to the predominant formation of hydroxylated intermediates during the photocatalytic process. However, chromatographic analysis of samples taken during the irradiation period indicates a complex mixture of organic intermediates that compete for interaction with the reactive species in the photocatalytic system.^{31,32} Although the degradation of the initial organic substrate involves the formation of several organic intermediates, the kinetic model takes into account the formation of a single organic intermediate, which, after appearing in the system, will mineralize at a rate that depends on the concentration of the initial organic substrate. It is assumed that this organic intermediate represents, from a physicochemical point of view, all of the other organic intermediates that are surely formed in the system^{23–25}

$$-\frac{dC_S}{dt} = \frac{k_1 K_1 C_S}{1 + K_1 C_S + K_2 C_I} \quad (1)$$

$$\frac{dC_I}{dt} = \frac{k_1 K_1 C_S - k_2 K_2 C_I}{1 + K_1 C_S + K_2 C_I} \quad (2)$$

$$\frac{dC_{\text{CO}_2}}{dt} = \frac{k_2 K_2 C_I}{1 + K_1 C_S + K_2 C_I} \quad (3)$$

The parameters *k*₁, *k*₂, *K*₁, and *K*₂ from eqs 1–3 are as follows: *k*₁ is the rate constant of the degradation reaction of the initial organic substrate in the organic intermediate, *k*₂ is the rate constant of the mineralization reaction of the formed organic intermediate, *K*₁ is the adsorption equilibrium constant of the initial organic substrate on the photocatalyst surface, and *K*₂ is the adsorption equilibrium constant of the intermediate formed on the photocatalyst surface.

It should be noted that these equations have the form of the Langmuir–Hinshelwood equation and are written considering that both the initial organic substrate and the single intermediate formed compete for adsorption on the active centers of the photocatalyst, with implications on the variation of their concentration during irradiation. Adopting this consideration leads to the need to solve the three kinetic equations in the three dependent variables *C*_S, *C*_I, and *C*_{CO₂} simultaneously. The solution of the system of three first-order differential equations involves initially estimating the values of the kinetic parameters, followed by optimizing them by

minimizing the error sum $F(k_1, K_1, k_2, K_2) = \sum_{i=1}^n w_i (C_{\text{exp}}^i - C_{\text{calc}}^i)^2$, where C_{exp}^i and C_{calc}^i represent the concentration values of the organic substrate both measured and calculated and $w_i = 1/\sigma^2(C_{\text{exp}}^i)$ represents the weighing factor. To optimize the values of the kinetic parameters, two categories of experiments were used, with each category comprising four sets of data. The optimization process was therefore aimed at finding the best values for the four parameters (k_1 , k_2 , K_1 , and K_2) of the system of kinetic equations to fit all of the eight sets of experimental data as well as possible. The first category of experimental data refers to the disappearance kinetics of the initial organic substrate. In this respect, spectrophotometric measurements of the concentration of ethinyl estradiol during photocatalysis were carried out. The second category of experiments refers to the kinetics of the entire organic content disappearance (of the organic intermediates formed). Thus, measurements of the concentration of organic material during photocatalysis were carried out through a COD (Chemical Oxygen Demand) analysis. In order to have the concentration expressed in the same unit of measure and thus to facilitate solving the system of kinetic equations, it was expressed as equivalent carbon (mg C/L).

To evaluate the effectiveness of the nonlinear model used, the results obtained with it were compared to those obtained with the classical Langmuir–Hinshelwood kinetic model. The mathematical expression of this kinetic model, as well as its linearized form, are presented in eqs 4 and 5, where C_S is the concentration of the organic substrate, k is the rate constant of the degradation reaction of the organic substrate, K is the adsorption equilibrium constant of the organic substrate on the photocatalyst surface, C_0 is the initial concentration of the organic substrate, and r_0 is the initial rate of the reaction³³

$$r_0 = -\frac{dC_S}{dt} = \frac{kKC_S}{1 + KC_S} \quad (4)$$

$$\frac{1}{r_0} = \frac{1}{kKC_0} + \frac{1}{k} \quad (5)$$

The plot $1/r_0$ versus $1/C_0$ leads to a straight line with a slope of $1/kK$ and an intercept of $1/k$. The initial velocities needed to determine the parameters of the kinetic model were calculated based on the same two types of experiments used to optimize parameters in nonlinear modeling, but separately. Therefore, the experimental data related to the kinetics of the disappearance of the initial organic substrate were used to determine parameters k_1 and K_1 , and the experimental data related to the kinetics of the entire organic content disappearance were used to determine parameters k_2 and K_2 . Next, the values of these parameters were used in the nonlinear modeling, and the results obtained were compared with those obtained in the direct nonlinear modeling by optimizing the values of the kinetic parameters.

3.2. Photocatalytic Mineralization of Ethinyl Estradiol. The results obtained regarding the kinetics of the disappearance of the ethinyl estradiol during the irradiation time (Figure 2a) indicate a rapid photocatalytic degradation of the initial organic substrate, registering a slight time difference until the complete disappearance with the increase in its initial concentration. Thus, for the lowest initial substrate concentration, the complete disappearance time is around 10 min, while for the highest concentration, the complete disappearance time is approximately 40 min. It is assumed that the

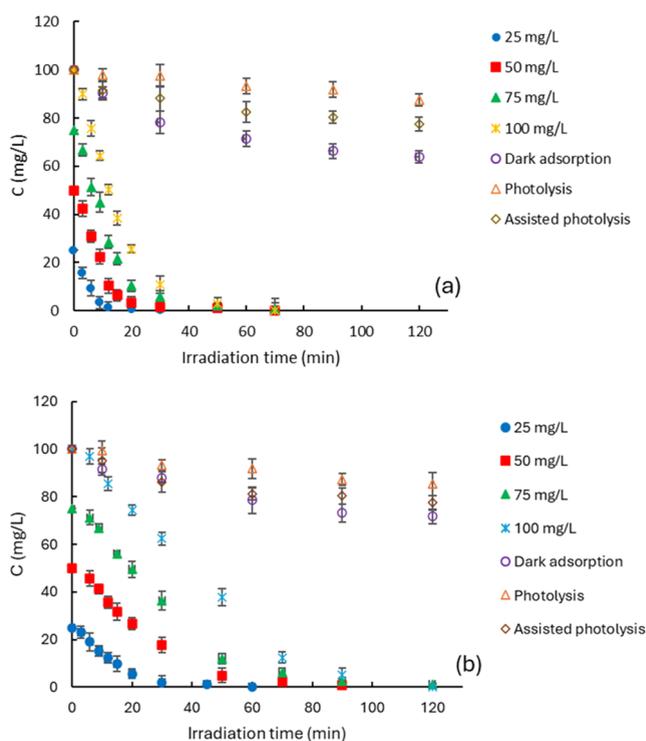


Figure 2. Kinetics of the photocatalytic mineralization, dark adsorption, photolysis, and assisted photolysis of the ethinyl estradiol by using the TiO_2/ZnO photocatalyst: (a) kinetics of disappearance of ethinyl estradiol during the irradiation time. (b) kinetics of disappearance of the entire organic content during the irradiation time. Concentrations for both ethinyl estradiol and entire organic content are expressed as equivalent carbon (mg C/L). The results corresponding to dark adsorption, photolysis, and assisted photolysis are for the initial organic substrate solution of 100 g C/L. Error bars were added to the graphs based on estimates made from triplicate data for each individual sample.

mineralization of the initial organic substrate takes place through the formation of organic intermediates, which, in turn, are degraded gradually until complete mineralization. After the irradiation process begins, the organic substrate consists of undegraded initial organic substrate (ethinyl estradiol) and organic intermediates, expressed as entire organic content. As can be seen in Figure 2b, the entire organic content disappearance kinetics is somehow different from that of the initial organic substrate disappearance (Figure 2a). First of all, the rate of disappearance is lower, the complete mineralization of the entire organic content being recorded in a time interval of approximately 25 to 100 min of irradiation, depending on the concentration of the initial organic substrate. Second, it can be observed (Figure 2b) that in the first minutes of irradiation (first 5–10 min), the decrease in the organic carbon concentration is slow, which denotes the formation of the initial organic substrate degradation intermediates, which could have, in the first phase, a slightly higher resistance to the working conditions in the photocatalytic reactor. This result supports the hypothesis according to which mineralization of the initial organic substrate takes place through degradation intermediates and not through direct mineralization.

It is worth mentioning that the decrease in the mineralization rate of the organic substrate with an increase in its initial concentration is most likely due to the saturation

of the photocatalyst surface in an increasingly shorter time. Also, the increase in the concentration of the organic substrate has the effect of increasing the competition between the initial organic substrate and the organic intermediates formed for the active sites of the photocatalyst, which leads to the slowing of the photocatalytic degradation process. Moreover, in addition to the competition between the initial organic substrate and the organic intermediates formed during the degradation process for adsorption on the active sites of the photocatalyst, there is also competition between the total organic substrate and reactive species such as hydroxyl radicals for adsorption on the same active sites of the photocatalyst. Therefore, the higher the concentration of the organic substrate, the more restricted the access of the reactive species to the photocatalyst surface, and thus, the photocatalytic degradation process is inhibited.

It is also evident that the photocatalyst plays an important role in the mineralization process of the organic substrate, the results obtained in its presence being clearly superior to those obtained in the processes of simple photolysis (degradation efficiency of approximately 12% after two h of irradiation) or assisted photolysis (degradation efficiency of approximately 22% after two h of irradiation). In addition, it presents a relatively good adsorption capacity of the organic substrate, being approximately 24 mg C/g of photocatalyst, corresponding to a contact time of two h when the values seem to stabilize.

For the nonlinear modeling of the photocatalytic mineralization of the organic substrate, the kinetic parameters were initially set to indicative values established based on information found in the literature for ethinyl estradiol subjected to photocatalytic degradation by using TiO₂-based photocatalysts. The starting values of the kinetic parameters are the following (converted units): $k_1 = 1.13$ mg C/(L·min) and $K_2 = 0.31$ L/mg C (values with converted units obtained by linear regression processing of the original data related to the kinetics of disappearance of ethinyl estradiol),³¹ and $k_2 = 2.23$ mg C/(L·min) and $K_2 = 0.12$ L/mg C (values with converted units related to the kinetics of the disappearance of the total organic content).³⁴ Subsequently, these values were optimized by minimizing the error sum based on the experimental results and those calculated using the indicative values. In this respect, the error sum $F(k_1, K_1, k_2, K_2) = \sum_{i=1}^n w_i (C_{\text{exp}}^i - C_{\text{calc}}^i)^2$ was minimized to obtain the best values of the kinetic parameters so that the nonlinear model would fit the experimental data. The optimized values of the kinetic parameters are presented in Table 1. The calculation of the

theoretical concentrations of the organic substrate subjected to the irradiation process was performed by solving a system of three first-order differential equations using the Runge–Kutta method.

The results obtained from the nonlinear modeling of the photocatalytic mineralization of the organic substrate are compared with those obtained using the classical Langmuir–Hinshelwood kinetic model. It is noteworthy that two simulations were conducted using two different sets of experimental data: the first set refers to the kinetics of the disappearance of the initial organic substrate from the aqueous solution subjected to photocatalysis, from which the kinetic parameters k_1 and K_2 were determined; the second set refers to the kinetics of disappearance of the entire organic content (initial organic substrate and organic intermediates formed from the degradation of the initial organic substrate) from the aqueous solution, from which the kinetic parameters k_2 and K_2 were determined. The values of these kinetic parameters are presented in Table 1 and were also used in nonlinear modeling to compare the results obtained to those from the direct nonlinear analysis.

The results obtained from direct nonlinear modeling of the ethinyl estradiol mineralization kinetics are presented in Figure 3. The experimental results regarding the kinetics of the disappearance of ethinyl estradiol, as well as those regarding the kinetics of the disappearance of the entire organic content from the aqueous solution subjected to irradiation, are fitted with the theoretical results obtained from solving the system of three first-order differential equations. As can be seen, the nonlinear kinetic model fits the experimental results well, regardless of the initial concentration of the ethinyl estradiol. The fact that there is a good correlation between the experimental and theoretical results is also highlighted by the RMSE values. Thus, the difference between the experimental results and those obtained with the proposed model is less than 10% regardless of the initial concentration of the organic substrate, as well as the type of organic substrate analyzed (ethinyl estradiol or total organic carbon). The maximum concentration of the formed intermediates is reached when approximately 90% of the initial concentration of the organic substrate is removed from the aqueous solution. This trend holds true regardless of the initial concentration of the organic substrate. This result denotes the fact that the degradation of the initial organic substrate occurs at a higher rate than the rate at which the formed organic intermediates are degraded. This can also be seen from the values of the kinetic parameters, namely, the rate constant corresponding to the photocatalytic degradation of the initial organic substrate is almost twice higher than that corresponding to the degradation of the intermediates formed. In the reaction mixture formed during irradiation, there is competition between the initial organic substrate and the organic intermediates formed for the adsorption centers on the surface of the photocatalyst. The optimized values of the adsorption equilibrium constants indicate that the equilibrium constant corresponding to the adsorption of the initial substrate is three times higher than the one corresponding to the adsorption of the formed intermediates. In general, the k_1K_1 and k_2K_2 couples can be considered as apparent rate constants ($k_{1\text{app}}$ and $k_{2\text{app}}$), and after comparing their values, it appears that the apparent rate constant corresponding to the organic substrate is approximately six times higher than that corresponding to the formed intermediates. Of course, in the aqueous solution subjected to

Table 1. Kinetic Parameters of Photocatalytic Mineralization of the Ethinyl Estradiol

	kinetic parameters			
	nonlinear modeling ^a		Langmuir–Hinshelwood ^b (linear approach)	
k_1 (mg C/(L·min))	5.97	k_1 (mg C/(L·min))	6.94	
k_2 (mg C/(L·min))	3.11	k_2 (mg C/(L·min))	3.46	
K_1 (L/mg C)	0.12	K_1 (L/mg C)	0.05	
K_2 (L/mg C)	0.04	K_2 (L/mg C)	0.06	

^aKinetic parameters are initially set based on preliminary estimates and then optimized by minimizing the error sum. ^bKinetic parameters: determined from the kinetics of disappearance of ethinyl estradiol (k_1, K_1) and from the kinetics of disappearance of the entire organic content during the irradiation time (k_2, K_2).

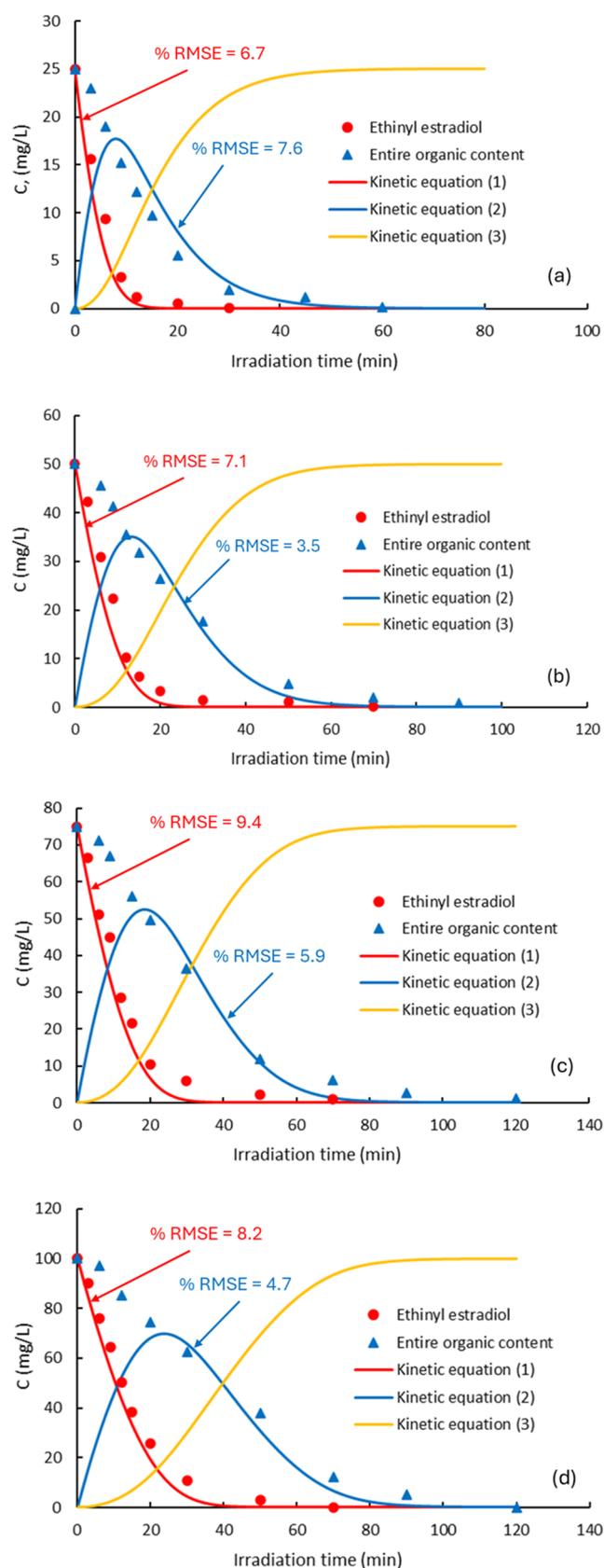


Figure 3. Nonlinear modeling of the kinetics of the photocatalytic mineralization of the ethinyl estradiol by using TiO_2/ZnO photocatalyst: (a) 25, (b) 50, (c) 75, and (d) 100 mg C/L. Concentrations for both ethinyl estradiol and entire organic content are expressed as equivalent carbon (mg C/L). The kinetic parameters were initially set

Figure 3. continued

based on indicative values, after which their values were optimized based on the experimental results by minimizing the error sum. % RMSE is the Root Mean Square Error in percentages, which quantifies the correlation between the experimental and theoretical results obtained with the model.

irradiation, there are several organic intermediates that have different stabilities under the conditions in the photocatalytic reactor. It is certain that, as the obtained results show, in all cases, regardless of the concentration of the initial organic substrate, the maximum concentration of organic intermediates formed, although recorded at different irradiation times, represents approximately 70% of the concentration of the initial organic substrate. This denotes the fact that part of the intermediates formed (approximately 30%) degrade more easily under the working conditions of the photocatalytic reactor.

Regarding the kinetic parameters determined by using the Langmuir–Hinshelwood model, their values are different from those obtained by nonlinear modeling (Table 1), especially regarding the adsorption equilibrium constant (K_2). The Langmuir–Hinshelwood model is based on determining the initial reaction rates from experimental data and their graphic representation using the linearized form of the model to determine its parameters by linear regression, namely, the rate constant (k) and the adsorption equilibrium constant (K). As can be seen in Figure 4a, the inverse values of the initial reaction rates, calculated on the basis of the experimental data regarding the kinetics of the disappearance of the initial organic substrate, fit well on the regression line. On the contrary, the inverse values of the initial reaction rates, calculated from the experimental data regarding the entire organic content disappearance kinetics, do not fit well on the regression line (Figure 4b). This is also supported by the values of the correlation coefficients (R^2) for the two data sets. This result indicates a first sign that this model based on the initial reaction rates cannot describe, as well as the nonlinear modeling of the sequence of photocatalytic reactions that take place in the reactor.

Figure 5 shows the degradation kinetics of the initial organic substrate and the organic intermediates formed, along with the results of their nonlinear modeling using the kinetic parameters determined with the Langmuir–Hinshelwood model. As can be seen, the theoretical kinetic curve corresponding to the kinetics of the disappearance of the initial organic substrate fits the experimental results well, regardless of the concentration of the initial organic substrate. Regarding the theoretical kinetic curve corresponding to the kinetics of the entire organic content disappearance, it does not fit well the experimental results, and moreover, the disagreement between the two sets of data increases as the concentration of the initial organic substrate increases. These results are confirmed by the RMSE values, which, for the disappearance of ethinyl estradiol, are below 10%, and for the disappearance of the entire organic substrate, they are even very high, which denotes a clear contradiction between the two data sets. If for an initial concentration of 25 mg C/L of the ethinyl estradiol (Figure 5a), the model reasonably fits the experimental data, although the maximum concentration of organic intermediates is greatly underestimated, at higher concentrations (50, 75, and 100 mg C/L), the model no longer fits the experimental data (Figure

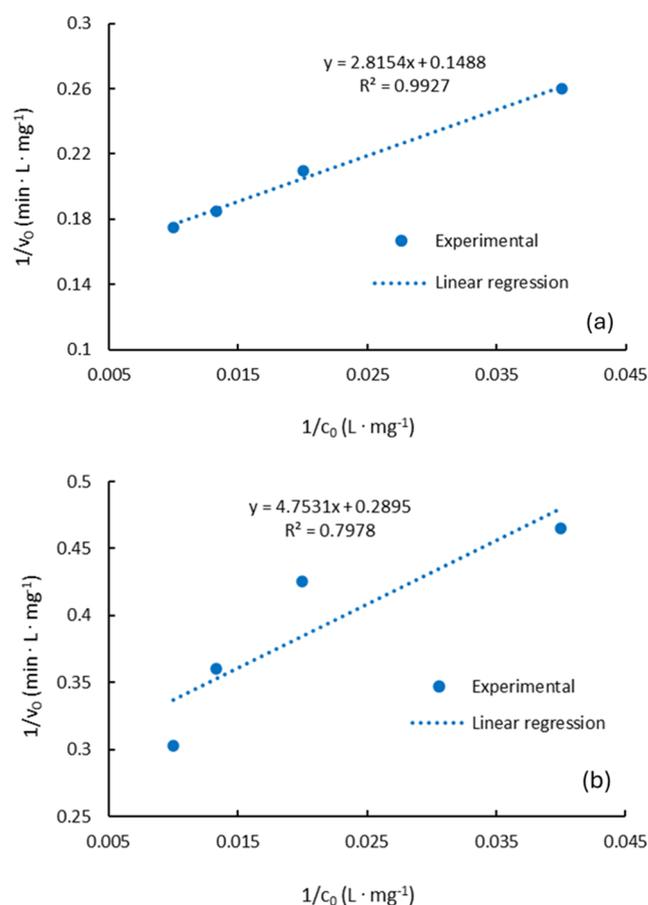


Figure 4. Langmuir–Hinshelwood modeling of the kinetics of the photocatalytic mineralization of the ethinyl estradiol by using the TiO_2/ZnO photocatalyst: (a) kinetics of disappearance of ethinyl estradiol during the irradiation time (the kinetic parameters k_1 and K_1 were determined), (b) kinetics of disappearance of the entire organic content during the irradiation time (the kinetic parameters k_2 and K_2 were determined). Concentrations for both ethinyl estradiol and entire organic content are expressed as equivalent carbon (mg C/L).

5b–d). The comparative study of the values of the kinetic parameters (Figure 6) determined by the two types of models used indicates a considerable difference between them. The influence of this difference on the results regarding the entire organic content disappearance kinetics modeling could be interpreted based on the competition for the adsorption sites in which the organic species from the aqueous solution participate during irradiation.

In this respect, on the one hand, a small value of the adsorption equilibrium constant for the initial organic substrate does not influence too much the kinetics of its disappearance from the system. On the other hand, it gives the possibility, at least theoretically, that the organic intermediates formed with values of the constant of adsorption equilibrium close to it compete equally with the initial organic substrate for adsorption on the available active centers of the photocatalyst. This results in a faster degradation of the organic intermediates and, therefore, a lower maximum concentration of them in the system. It is practically what can be observed in Figure 4, when the modeling was carried out using a value of the adsorption equilibrium constant of the initial organic material more than twice lower than the one optimized in the nonlinear modeling.

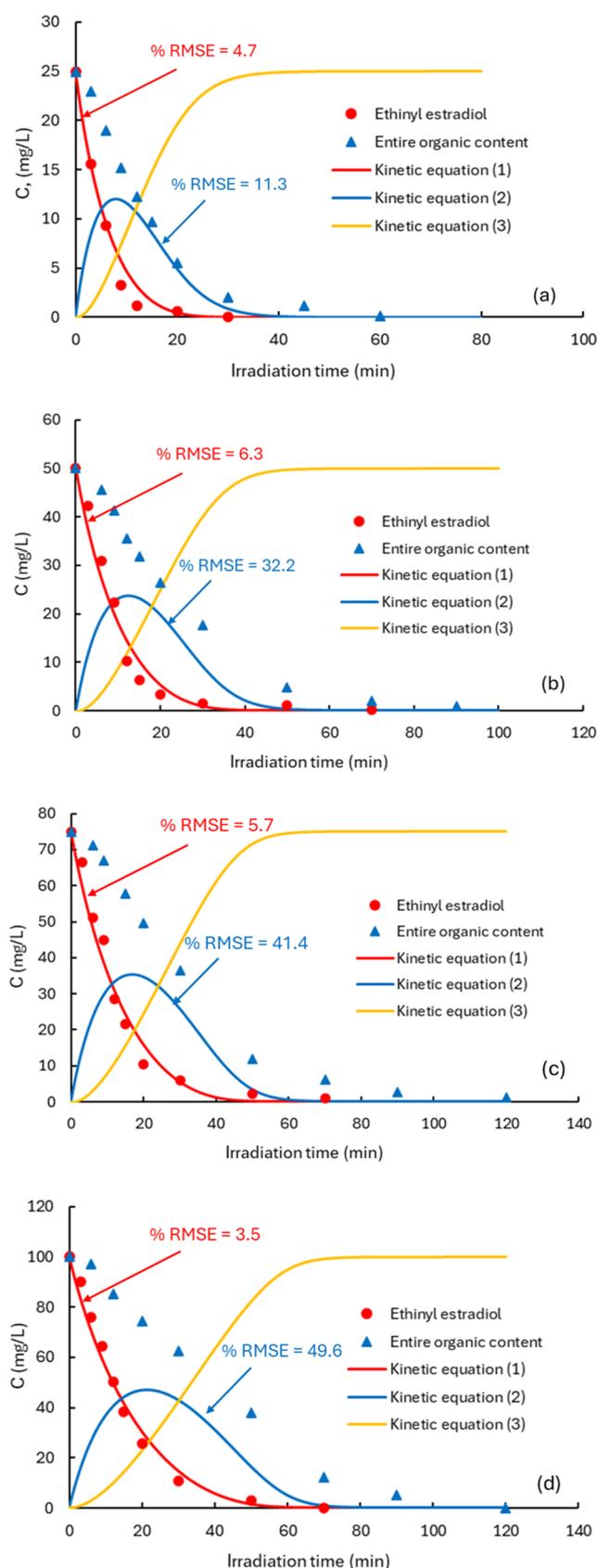


Figure 5. Nonlinear modeling of the kinetics of the photocatalytic mineralization of the ethinyl estradiol by using TiO_2/ZnO photocatalyst: (a) 25, (b) 50, (c) 75, and (d) 100 mg C/L. Concentrations for both ethinyl estradiol and entire organic content are expressed as equivalent carbon (mg C/L). The kinetic parameters were

Figure 5. continued

determined by using a linear form of Langmuir–Hinshelwood equation. The kinetic parameters k_1 and K_1 were determined from the kinetics of the disappearance of ethinyl estradiol during the irradiation time, while the kinetic parameters k_2 and K_2 were determined from the kinetics of the disappearance of the entire organic content during the irradiation time. %RMSE is the Root Mean Square Error in percentages, which quantifies the correlation between the experimental and theoretical results obtained with the model.

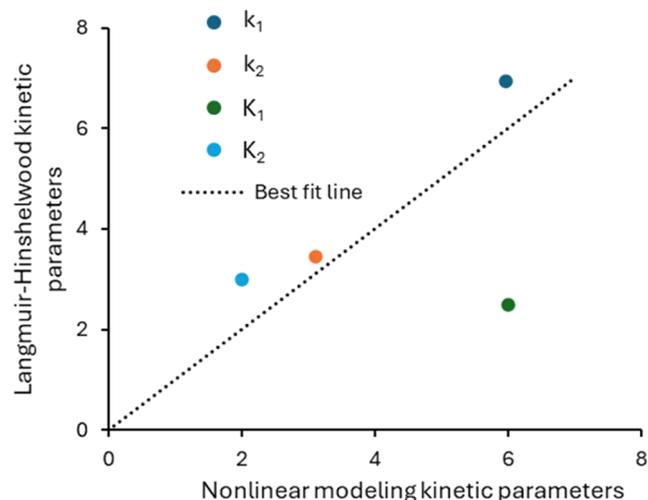


Figure 6. Comparison between the kinetic parameters established by nonlinear modeling and those determined by the Langmuir–Hinshelwood kinetic model.

Comparing the results obtained regarding the mineralization of the entire organic substrate with the two kinetic models clearly indicates the limitations of the Langmuir–Hinshelwood model, which does not take into account the competition for adsorption on the photocatalyst surface of the initial organic substrate and the intermediates formed, and the kinetic parameters are determined by linear regression over the entire irradiation interval (from the beginning of the degradation process of the initial organic substrate until the complete mineralization of the entire organic substrate).

4. CONCLUSIONS

The kinetic study of ethinyl estradiol mineralization revealed the following:

- The kinetics of the disappearance of the initial organic substrate (ethinyl estradiol) indicate a rapid mineralization, regardless of its initial concentration. On the other hand, the rate of disappearance of the entire organic content, which, besides the initial organic substrate, also contains the organic intermediates formed, is lower, indicating higher stability of these intermediates to the working conditions in the photocatalytic reactor.
- Both the mineralization kinetics of the initial organic substrate and of the organic intermediates formed during irradiation are well described mathematically by nonlinear modeling. The optimized kinetic parameters can well fit the entire mineralization curve regardless of the concentration of the initial substrate.
- The results obtained by nonlinear modeling of the mineralization kinetics of the initial organic substrate

and of the formed organic intermediates were compared with those obtained with the classical Langmuir–Hinshelwood kinetic model. It has been proven that the classic Langmuir–Hinshelwood model fits well only the mineralization of the initial organic substrate, it being unable to fit the mineralization kinetics of the organic intermediates formed.

- The comparison of the pairs of kinetic parameters of the two types of kinetic models used highlighted a strong underestimation of the adsorption equilibrium constant for the initial organic substrate in the case of the Langmuir–Hinshelwood model. This fact is most likely responsible for the overestimation of the degradation rate of the formed intermediates, which is in disagreement with the experimental results obtained regarding the kinetics of the entire organic content disappearance from the aqueous solution subjected to photocatalysis.

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Notes

The authors declare no competing financial interest.

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