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*Article*

# Elementary Steps in Steady State Kinetic Model Approximation for the Homo-Heterogeneous Photocatalysis of Carbamazepine

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**Abstract:** Elucidating physicochemical processes in the degradation of pollutants may optimize their removal from water sources. This work presents a set of elementary steps in the photocatalytic degradation of carbamazepine (CBZ), assuming a steady state approximation in an Advanced Oxidation Process (AOP) combining short-wave ultraviolet radiation (UVC), homogeneous reagent ($H_2O_2$) and heterogeneous ($TiO_2$) catalyst. Elementary steps include excitation of both reagent/catalysts by UVC photons, adsorption of CBZ on the excited $TiO_2$, or its oxidation by hydroxyl radicals. Assuming the steady state approximation on the intermediate products (excited $TiO_2$, CBZ- excited $TiO_2$ complex, and hydroxyl radicals), leads to rate laws for degradation of CBZ, in which UVC radiation, $TiO_2$, and $H_2O_2$ are pseudo first order at all concentrations or intensities, whereas CBZ is shifts from pseudo first order at low concentrations to pseudo-zero order at high concentrations. Several experiments to test the mechanism were conducted, in which varying CBZ, $H_2O_2$, and $TiO_2$ concentrations, and UVC radiation intensities. Measured results indeed fit the suggested mechanism for the first three, but irradiation intensity appears to shift from pseudo-second to pseudo-first order with increased intensities. A corrected elementary step was adapted to fit the results.

**Keywords:** carbamazepine; advanced oxidation process; pseudo-order; rate law; half life time; elementary steps; steady-state approximation

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## 1. Introduction

Pharmaceuticals and personal care products (PPCPs) constitute a large and diverse group of organic compounds, including drugs, chemicals for medical diagnosis, sunscreens, cosmetics, soaps, and more [1] that reach the environment and water sources from hospital and factory effluents, aquaculture facilities, animal excreta, and human excreta from sanitation system and from sewers. Additional PPCPs sources are disposal of expired drugs in landfills, poor storage of drugs in manufacturing plants, and fertilizers based on animal excreta [2].

One of the most common pollutants belonging to this group is carbamazepine (CBZ). CBZ is approved by the US Food and Drug Administration (FDA) as a treatment for manic depression (bipolar disorder), trigeminal neuralgia and epilepsy [3]. Since it is only partially removed by conventional wastewater treatment processes, it was suggested as a marker of anthropogenic activity in water sources [4]. Its global consumption increased from 742 to 1214 tons per year between the years 1995-2015 [5] and it was reported various at concentrations of up to 647 ng/L in surface water, 30 ng/ L in drinking water and up to 610 ng/L in groundwater [6]. Although no significant health hazard were found upon exposure to carbamazepine residues in drinking water, however research performed in animals report possible health damage: for example, a study on its' influence on sperm production in young and adult rats reported that CBZ given before sexual development causes side effects on rat testes, resulting in more severe damage in the adult stage [7]. Another study found increased damage to the DNA of rare Chinese minnows (*Gobiocypris rarus*) with the increase in the

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concentrations of CBZ, together with a significant increase in the concentration of 8-OHdG free radicals and an accelerated process of apoptosis in the liver [8].

Over the years, various methods for removing CBZ from water sources have been tested. Reverse osmosis (RO) and nano filtration (NF) membranes were found effective, but result in the accumulation of CBZ in the filtered brine, requiring complementary treatment [9]. Membrane bio-reactor (MBR) in combination with activated carbon as an adsorbent substrate [10], or adsorption on the surface of clay minerals/organoclays [11], have also been shown to be effective, however the polluted matrix requires additional treatment to achieve CBZ complete removal.

Several studies adopted various Advanced Oxidation Processes (AOP) that have been proven to be effective in the degradation and mineralization of CBZ. Such processes are based on a variety of techniques aiming the production of oxidating agents as free radicals and other forms with a high oxidation potential, mineralizing resilient pollutants.

Several AOP processes found to be effective in the removal of CBZ. For example, the use of ozone ($O_3$), yielded efficient CBZ degradation, but large remains of degradation byproducts were found [12]. Photo-Fenton reaction, which combines $H_2O_2$ and $Fe^{2+}$ has been shown effectiveness – but only in acidic conditions (pH=2.8-5.3), requiring additional treatment and pH adaptation [13]. Several additional AOP treatments effective in CBZ degradation including various combinations of UV radiation, $H_2O_2$ and/or heterogeneous catalysts such as $TiO_2$ and ZnO [12], or specifically engineered catalysts based on $Fe_3O_4/SiO_2/TiO_2$ [14] were described- but in most cases exposure times were 1 h or more. In experiments conducted in our research group (Azerrad & Shahar, 2023, unpublished results) a catalyst based on $Fe_3O_4/SiO_2/TiO_2/Ag$ exhibit efficient CBZ photo-degradation in a few minutes. The most widespread heterogeneous photocatalyst applied in AOP processes is catalytic grade $TiO_2$, since it is available commercially, cheap, non-toxic and chemically stable. Although in some cases results depended on the specific manufacturer [15], its catalytic efficiency has been proven in the degradation of CBZ [6,16]. Homogeneous photo-reaction using $H_2O_2$ also has been proven efficient in CBZ degradation [17]. Hetero-homogenenous photocatalysis combining $TiO_2$ and $H_2O_2$, has been shown to be effective in the degradation of a variety of various organic pollutants in water sources [18,19], including CBZ [11].

Several mechanisms were proposed for the various stages of AOP processes. Absorption of UV radiation by $H_2O_2$, breaks bonds between the oxygen atoms and hydroxyl radicals ($HO\bullet$) are formed, which are known as strong oxidizing agent [20]. Hydrogen peroxide molecules absorb radiation in the range of 185-300 nm, where the highest hydroxyl radicals formation yield is achieved at wavelengths of 200-280 nm [21]. In the UV/$TiO_2$ process, the photons absorbed by the catalyst cause excitation and an electron jump to a higher energy level, which creates a "hole" that acts as an oxidizer agent by attracting electrons. Such combination of excited electron-hole pairs can be applied to degrade specific chemicals [22]. Several scenarios may arise: 1. The excited electron may return and fill the hole. 2. The electron-hole pair may oxidize a water molecule, resulting in the formation of a hydroxyl radical and a proton, which lowers the pH in the suspension. 3. The $TiO_2$ excited molecule may collide with a hydroxyl ion turning it into a hydroxyl radical. 4. The excited electron may attack an oxygen molecule and turn it into a superoxide [23]. Due to the relatively broad energy gap of $TiO_2$ (3.2-4.0 eV) such processes are limited to ultraviolet radiation [24] which is not common in solar radiation [25].

To further elucidate the CBZ photodegradation process, this study presents a series of elementary steps, combined with the steady-state approximation "based on the assumption that intermediates in the reaction mechanism are consumed as quickly as generated", thus their concentration remain constant during the process [26]. Such approach was adopted in several studies as degradation of caffeine [27], the atmospheric degradation of $N_2O_5$ [28] or the Lindemann-Hinshelwood process [29,30]. Although it is in some cases critized for over-simplification [31,32], it still “remains a powerful tool for the simplification of reaction structures” in the elucidation of kinetic processes.

The proposed mechanism may elucidate the physicochemical processes that occur throughout the CBZ degradation process and allow planning and implementation of specific and effective

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treatments for its degradation, depending on its concentration in the treated water source. A wide set of experiments was conducted, aiming to obtain circumstantial evidence of the proposed elementary steps.

## 2. Materials and Methods

### 2.1. Materials

CBZ ($C_{15}H_{12}N_2O$), catalyst-grade industrial high quality $TiO_2$ (Hombikat®) and a 30% (9.79 M) concentrated $H_2O_2$ solution were obtained from Merck/Sigma–Aldrich (Merck KGaA, Darmstadt, Germany). All materials were used without further treatment.

### 2.2. Kinetic analysis

As mentioned in the introduction, this study suggests a series of elementary steps in the process of the degradation of CBZ when irradiated with UVC light in the precense of a combination of homogeneous ($H_2O_2$) and heterogeneous ($TiO_2$) catalysts. The complete process can be described as

$$\text{CBZ} + \text{UVC} + TiO_2 + H_2O_2 \rightarrow TiO_2 + \text{Various degradation products} \tag{1}$$

<u>Step 1 (rate constant $k_1$)-</u> $TiO_2$ (denoted as *T)* may undergo excitation after absorbing photons (denoted as UVC) of the appropriate wavelength yielding an excited titanium dioxide particle (denoted as $T^*$)

$$T + UVC \rightarrow T^* \tag{2}$$

which may release its energy and relax by undergoing internal conversion yielding unexcited $TiO_2$ (rate constant $k_{-1}$)

$$T^* \rightarrow \ \ T \tag{3}$$

<u>Step 2 (rate constant $k_2$)-</u> UVC radiation may break down the $H_2O_2$ yielding hydroxyl radicals-

$$H_2O_2 + UVC \rightarrow 2HO^\bullet \tag{4}$$

which may also occur in the opposite direction to obtain $H_2O_2$ (rate constant $K_{-2}$)

$$2HO^\bullet \rightarrow H_2O_2 \tag{5}$$

<u>Step 3 (rate constant $k_3$)-</u> the pollutant may adsorb on the surface of the excited heterogeneous catalysts yielding an excited complex (denoted as $ZT^*$)

$$T^* + Z \rightarrow ZT^* \tag{6}$$

<u>Step 4 (rate constant $k_4$) -</u> the excited complex may relax by internal conversion to obtain a non-excited complex

$$ZT^* \rightarrow ZT \rightarrow Z + T \tag{7}$$

<u>Step 5 (rate constant $k_5$)-</u> the excited $TiO_2$-CBZ complex may degrade the pollutant to a product (denoted as $P_1$), releasing the catalyst particle

$$ZT^* \rightarrow P_1 + T \tag{8}$$

On the other, there is a another elementary steps performed by the homogeneous catalyst:

<u>Step 6 (rate constant $k_6$)-</u> Step 2 forms hydroxyl radicals, that may oxidize the pollutant to obtain another degradation products (denoted $P_2$)

$$HO^\bullet + Z \ \rightarrow P_2 \tag{9}$$

The whole set of elementary step includes three intermediate products: excited $TiO_2$ ($T^*$), excited $TiO_2$-CBZ complex ($ZT^*$) and hydroxyl radicals ($HO^\bullet$). Assuming all the elementary steps occur according to a collision mechanism that states the rate of a reaction is directly proportional to the concentration of the reactants (and accordingly, the order of each component is equal to its stoichiometric coefficient), and assuming that the intermediate products are in a steady state (thus, their concentration do not change), we can denote the rate of change of the intermediate products with time:

$$\frac{d[T^*]}{dt} = k_1[T][UVC] - k_{-1}[T^*] - k_3[T^*][Z] = 0 \tag{10a}$$

$$\frac{d[ZT^*]}{dt} = k_3[T^*][Z] - k_4[ZT^*] - k_5[ZT^*] = 0 \tag{10b}$$

$$\frac{d[HO^\bullet]}{dt} = 2k_2[H_2O_2][UVC] - 2k_{-2}[HO^\bullet] - k_6[HO^\bullet][Z] = 0 \tag{10c}$$

and isolating the concentration of the excited $TiO_2$ (T*), the excited complex (ZT*) and the hydroxyl radicals (HO•) yields:

$$[T^*] = \frac{k_1[T][UVC]}{k_{-1}+k_3[Z]} \tag{11a}$$

$$[ZT^*] = \frac{k_3[T^*][Z]}{k_4+k_5} \tag{11b}$$

$$[HO^\bullet] = \frac{2k_2[H_2O_2][UVC]}{2\,k_{-2}+k_6[Z]} \tag{11c}$$

But by introducing 11a into 11b, the concentration of the excited complex at steady state became

$$[ZT^*] = \frac{k_3[Z]}{k_4+k_5}\,\frac{k_1[T][UVC]}{k_{-1}+k_3[Z]} \tag{11d}$$

At this stage the rate of formation of the CBZ degradation products may be evaluated. The products degraded by $TiO_2$:

$$\frac{d[P_1]}{dt} = k_5[ZT^*] = \frac{k_5k_3[Z]}{k_4+k_5}\,\frac{k_1[T][UVC]}{k_{-1}+k_3[Z]} = K'\,\frac{k_1[T][UVC]}{k_{-1}+k_3[Z]}[Z] \tag{12}$$

where for the sake of simplicity $K' = \frac{k_5k_3}{k_4+k_5}$

and the rate of formation of the products degraded by the hydroxyl radicals can be described by

$$\frac{d[P_2]}{dt} = k_6[HO^\bullet][Z] = k_6\,\frac{2k_2[H_2O_2][UVC]}{2\,k_{-2}+k_6[Z]}[Z] \tag{13}$$

From equation 12 it can be seen that CBZ degradation by heterogeneous photocatalysis is pseudo-first order on $TiO_2$ (T) and UVC radiation, whereas equation 13 indicates that CBZ degradation by homogeneous photocatalysis is from pseudo-first order on $H_2O_2$ and UVC radiation. However, CBZ influence is more complex: For example, in Eq.12 if $k_3[Z] \ll k_{-1}$, the process will be pseudo-first order on CBZ. On the other hand, if $k_3[Z] \gg k_{-1}$, the concentration of CBZ in nominator and denominator will cancel, and the process will become pseudo zero order, meaning CBZ degradation those conditions does not depend on its concentration. A similar effect can be observed in Eq.13: Low concentrations of CBZ leading to $k_6[Z] \ll 2k_{-2}$ will lead to a pseudo-first order state on the CBZ, while large concentrations ($k_6[Z] \gg 2k_{-2}$) will yield a pseudo -zero order on CBZ. Between those two extreme values, the CBZ pseudo-order will depend on its concentration in the specific process, but range between zero and one.

### *2.3. Description of the experiments*

Experiments were performed as follows: CBZ solutions were put into a 100 mL quartz beaker (refractive Index n = 1.5048), which does not absorb radiation at wavelengths in the UV-visible range (100-800 nm). The beaker was inserted Rayonet RMR-600 mini photochemical chamber reactor (Southern New England Ultraviolet Company, Branford, CT, USA) with an optical path length of 5.3 cm. The chamber was equipped with eight RMR 2537A lamps (254 nm wavelength), each lamp emitting approx. 8 W of enery according to the manufacturer, with an irradiance flux of 1.9 mW cm$^{-2}$ at 254 nm, as measured in previous studies [27] at the center of the chamber. The solution was constantly mixed with an external impeller driven by an overhead stirrer motor (VELP Scientifica, Usmate Velate, Italy) rotating at 100 rpm. Measurements were carried out using a Black Comet SR spectrometer (StellarNet Inc., Tampa, FL) with a dip 20 mm probe (DP400-UVVis-SR) with Deuterium and Halogen bulbs which together emit light in the entire UV-Vis spectrum.

In order to find circumstantial evidence for the existence of the elementary steps, 16 experiments were conducted, divided into four different sets, where each set included changes in the concentration of one of the participants, while the other participants in the process remained at a fixed concentration. In the first set, the CBZ concentration ranges from 1-20 mg L$^{-1}$ (4.23-84.6 μM), in the second set, the $TiO_2$ concentration ranges from 0.02-0.5 mg L$^{-1}$, in the third set, the $H_2O_2$ concentration ranges from 0.5-5 mg L$^{-1}$ (14.7-147 μM) and in the fourth set radiation intensity ranges from 901-3605 W m$^{-2}$ (2-8 UVC lamps).

Analysis of the data was performed following the procedure extensively reported in previous studies [33], and the main equations are presented in Appendix 1. Measurements were recorded for approximately 30 min at a 0.5 min interval. From the large amount of data (about 60 data points) in each experiment, a "bootstrap" [34,35] procedure was performed by choosing 5 sets of 10 values for each experiment. Calculations of the best-fit pseudo-order (n), the half-life and the rate constant (k) by minimizing the overall root mean square error (RMSE), defined as the "square root of the mean of the squared differences between corresponding elements of the forecasts and observations" [36]. Kinetic parameters were also calculated fixing pseudo-order to zero, one and two. Comparing the measured results to the calculated values for the fixed pseudo-orders delivers an indication of the fit to the proposed mechanism.

## 3. Results and discussion

### 3.1. Influence of CBZ concentration on the photocatalytic degradation

CBZ degradation at concentrations ranging between 1-20 mg L$^{-1}$ (4.23-84.64 μM), with 5 mg L$^{-1}$ (147 μM) $H_2O_2$, 0.5 mg L$^{-1}$ $TiO_2$, and UVC at a radiation intensity of 3605 W m$^{-2}$ are shown in Figure 1. The purpose of the experiments is to determine if the behavior is similar to the one described in the mechanism in section 2, in which it appears that low pollutant concentration may behave according to pseudo-first order whereas high CBZ concentrations will exhibit behavior approaching to pseudo-zero order on CBZ. Fig 1a shows CBZ concentration related to its initial value ($C/C_0$).

A good fit to a linear representation of ($C/C_0$) as a function of time

$$C/C_0 = 1 - kt \tag{14}$$

will indicate fit to a zero-order process, whereas good fit to a linear presentation of the natural logarithm of ($C/C_0$) as a function of time (as shown in Figure 1b)

$$ln[\,C/C_0] = -kt \tag{15}$$

will indicate fit to a first -order process. In both cases, the slope (k) will represent the kinetic coefficient [37,38]. Table 1 summarizes, half-life times, root mean square errors (RMSE) and coefficient of determination ($R^2$) assuming 0th or 1st pseudo-order process, and includes also the optimal pseudo-order value as evaluated empirically by minimizing the RMSE [33]. It is interesting to notice that $R^2$ for the 1st order process at high CBZ concentrations is higher than for the optimized process, however lower RMSE should be preferred to determine fit to a model, considering $R^2$ "does not measure how one variable explains another" [39].

**Table 1.** Pseudo-orders, half-life times, root mean square errors (RMSE) and coefficient of determination ($R^2$) for experiments with several CBZ concentrations, 0.5 mg $L^{-1}$ $TiO_2$, 5 mg $L^{-1}$ (147 µM) of $H_2O_2$ and a UVC radiation intensity of 3605 W $m^{-2}$ (corresponding to 8 UVC bulbs). .

| **CBZ concentration (mg $L^{-1}$)** | **Pseudo-order** $n_a$ | **Half life** $t_{1/2}$ **(min)** | **RMSE** | $R^2$ |
|---|---|---|---|---|
| 1 | 0 | 2.77±17.8% | 0.346 | 0.683 |
| 5 | 0 | 5.09±4.26% | 0.328 | 0.765 |
| 15 | 0 | 6.05±7.41% | 0.142 | 0.925 |
| 20 | 0 | 7.37±4.68% | 0.046 | 0.977 |
| 1 | 1 | 1.08±12.02% | 0.077 | 0.921 |
| 5 | 1 | 2.22±3.64% | 0.037 | 0.995 |
| 15 | 1 | 3.96±1.31% | 0.035 | 0.999 |
| 20 | 1 | 6.27±1.31% | 0.028 | 0.999 |
| 1 | 1.11±4.90% | 0.95±6.05% | 0.072 | 0.955 |
| 5 | 0.83±2.04% | 2.33±1.10% | 0.030 | 0.996 |
| 15 | 0.76±3.25% | 4.18±1.28% | 0.021 | 0.998 |
| 20 | 0.61±8.71% | 6.55±1.15% | 0.018 | 0.998 |

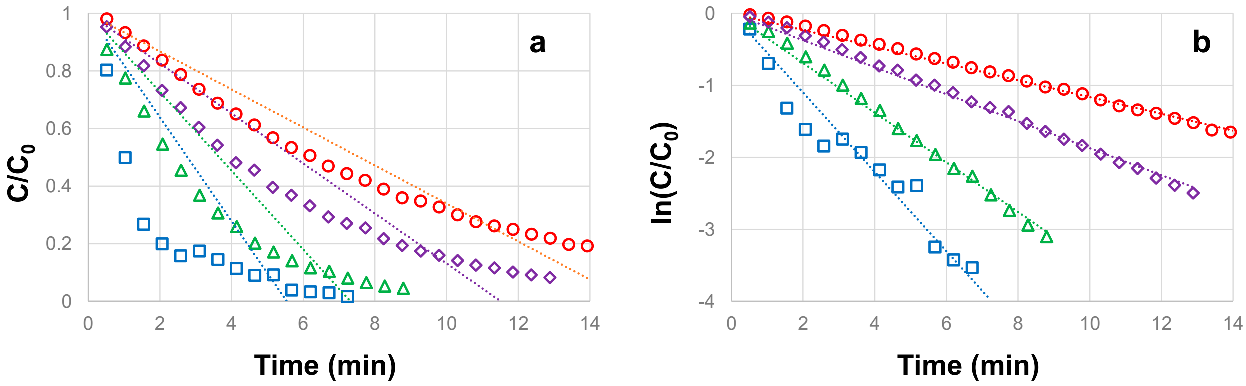

**Figure 1.** Degradation of 1 (squares), 5 (triangles), 15 (rhombus) and 20 (circles) mg $L^{-1}$ CBZ with 0.5 mg $L^{-1}$ $TiO_2$, 5 mg $L^{-1}$ of $H_2O_2$ and 8 UVC lamps. Panel (a) and panel (b) show the concentration related to its initial value ($C/C_0$), and its natural logarithm, respectively. Lines indicate linear regression for each set.

As can be expected, increase of the pollutant concentration for the same catalytic conditions, yields higher half life times indicating slower degradation. For all CBZ concentrations there is a very good fit between measurements and the pseudo-first order model, whereas pseudo-zero does not fit at all at low concentrations but exhibits a reasonable fit at the 15 and 20 mg $L^{-1}$ CBZ. It should be emphasized that even at large CBZ concentration, the process fits better the pseudo-first order than pseudo-zero order, but the optimal pseudo-order (see Table 1) decreases from 1.11 to 0.61 with the increase in CBZ concentration. Thus, results show a trend that corresponds to the scenario described in the mechanism, in which low CBZ concentrations will influence kinetics directly (1st pseudo-order), whereas larger CBZ concentrations will not (0th pseudo-order). To further confirm the effect additional experiments at even larger CBZ concentrations might be required.

### *3.2. Influence of $H_2O_2$ concentration on the photocatalytic degradation of CBZ*

CBZ degradation at 1mg $L^{-1}$ (4.23 µM), was tested with hydrogen peroxide concentrations ranging from 0.5-5 mg $L^{-1}$ (14.7-147 µM), combined with 0.5 mg $L^{-1}$ $TiO_2$, and UVC at a radiation intensity of 3605 W $m^{-2}$. This set of experiments intended to determine if the influence of $H_2O_2$ as homogeneous catalyst fits a pseudo 1st order process for all concentrations, as described in the mechanism presented in section 2.

According to the relationships between the linearity of graphs and the integrated rate laws [38] Fig 2a shows that all $H_2O_2$ concentrations do not fit a 0th pseudo-order kinetics. The conclusion is confirmed by the relatively large RMSE (>0.19) and low $R^2$ (<0.83) values shown in Table 2. On the other hand, a considerable better fit is observed for the 1st pseudo-order model (Figure 2b, Table 2) with relatively low RMSE (<0.090) and larger $R^2$ (>0.9). Confirmation to that can be observed from the optimized pseudo-orders in Table 2: for all four cases values range between 0.93-1.11, thus- close to 1st pseudo-order kinetics. Considering the kinetic model presented hereby predicts that $H_2O_2$ will influence on the kinetics with direct relation with its concentration (e.g. 1st pseudo-order kinetics) at all levels, results show a trend that corresponds to the scenario described in the mechanism.

Another conclusion from the experiment is that although increasing $H_2O_2$ concentrations by one order of magnitude reduces the half life time (from app. 2.5 to 1 min), the influence is not clearly significant in the measurements: Figure 2a confirms that differences in concentrations with time are not very significant. Experiments at larger CBZ concentrations might be required to strengthen the model hypothesis.

**Table 2.** Pseudo-orders, half-life times, root mean square errors (RMSE) and coefficient of determination ($R^2$) for degradation of 1 mg $L^{-1}$ CBZ with 0.5 mg $L^{-1}$ $TiO_2$, UVC radiation intensity of 3605 W $m^{-2}$ (corresponding to 8 UVC bulbs), and $H_2O_2$ ranging between 0.5-5 mg $L^{-1}$ (14.7-147 µM). .

| **$H_2O_2$ concentration (mg $L^{-1}$)** | **Pseudo-order $n_a$** | **Half life $t_{1/2}$ (min)** | **RMSE** | **$R^2$** |
|---|---|---|---|---|
| 0.5 | 0 | 4.99±6.44% | 0.194 | 0.823 |
| 1 | 0 | 4.29±10.4% | 0.248 | 0.707 |
| 2 | 0 | 2.98±5.32% | 0.249 | 0.618 |
| 5 | 0 | 2.77±17.8% | 0.346 | 0.683 |
| 0.5 | 1 | 2.44±1.33% | 0.028 | 0.991 |
| 1 | 1 | 1.82±3.33% | 0.048 | 0.980 |
| 2 | 1 | 1.31±7.37% | 0.087 | 0.905 |
| 5 | 1 | 1.08±12.02% | 0.077 | 0.921 |
| 0.5 | 0.95±2.57% | 2.48±2.48% | 0.027 | 0.992 |
| 1 | 0.93±4.49% | 1.86±1.37% | 0.047 | 0.979 |
| 2 | 1.05±6.78% | 1.25±6.28% | 0.086 | 0.902 |
| 5 | 1.11±4.90% | 0.95±6.05% | 0.072 | 0.955 |

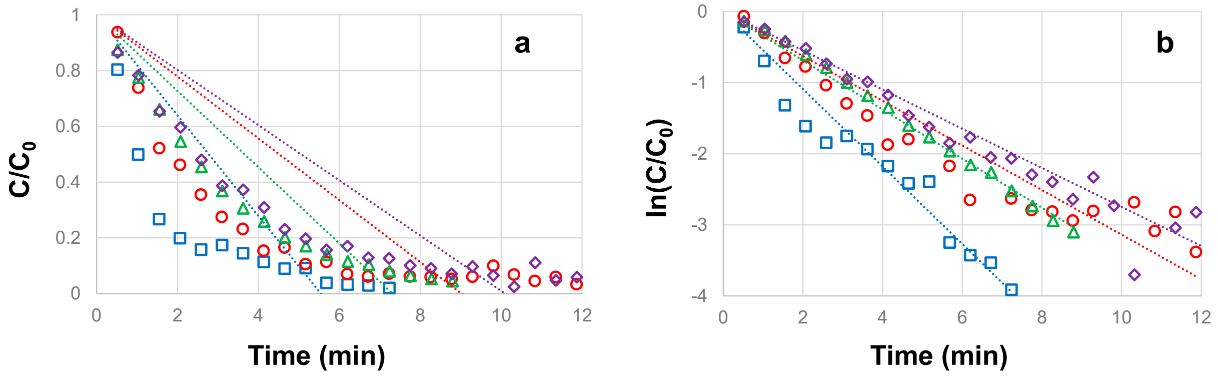

**Figure 2.** Degradation of 1 mg $L^{-1}$ CBZ with 0.5 mg $L^{-1}$ $TiO_2$, 8 UVC lamps and 0.5 (rhombus), 1 (circles), 2 (triangles) or 5 mg $L^{-1}$ (squares) of $H_2O_2$. Panel (a) and panel (b) show the concentration related to its initial value ($C/C_0$), and its natural logarithm, respectively. Lines indicate linear regression for each set.

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### 3.3. Influence of $TiO_2$ concentration on the photocatalytic degradation of CBZ

CBZ degradation at a concentration of 1 mg $L^{-`1}$ (4.23 µM), was tested with $TiO_2$ concentrations ranging from 0.02-0.5 mg $L^{-1}$, combined with $H_2O2$ concentration of 5 mg $L^{-1}$ (147 µM), and UVC at a radiation intensity of 3605 W $m^{-2}$. This set of experiments intended to determine if the influence of $TiO_2$ as heterogeneous catalyst fits a pseudo 1st order process for all concentrations, as described in the mechanism presented in section 2.

Figure 3a shows that all the $TiO_2$ tested in the experiments do not fit a 0th pseudo-order kinetics, whereas Figure 3b indicate a better fit to a 1st pseudo-order process, although far from being as good as in the CBZ experiment. Such statement is reinforced by results Table 3, that present relatively large RMSE (>0.26) and low $R^2$ (<0.7) values for 0th pseudo-order, with considerably better (although far from being optimal) fit for 1st pseudo-order kinetics (RMSE<0.096, $R^2$>0.89) and optimized pseudo-orders between 0.81-1.11. Considering the kinetic model presented hereby predicts that CBZ degradation will be of 1st pseudo-order kinetics on $TiO_2$ at all levels, results tend to present a trend that corresponds to the scenario described in the mechanism. However, it should be noticed from Figure 3a, that all heterogeneous catalyst concentrations yield very similar results- thus- there is no significant influence on the process, and all concentrations yield a half life time of approximately 1 min. We assume that this can be ascribed to the relatively large influence that the homogeneous reactant has at the concentration tested (5 mg $L^{-1}$ of $H_2O_2$). Experiments at lower $H_2O_2$ concentrations might be required to strengthen the model hypothesis on the influence of $TiO_2$.

**Table 3.** Pseudo-orders, half-life times, root mean square errors (RMSE) and coefficient of determination ($R^2$) for degradation of 1 mg $L^{-1}$ CBZ with 5 mg $L^{-1}$ (147 µM) $H_2O_2$, UVC radiation intensity of 3605 W $m^{-2}$ (corresponding to 8 UVC bulbs), and $TiO_2$ ranging between 0.02-0.5 mg $L^{-1}$. .

| $TiO_2$ concentration (mg $L^{-1}$) | Pseudo-order $n_a$ | Half life $t_{1/2}$ (min) | RMSE | $R^2$ |
|---|---|---|---|---|
| 0.02 | 0 | 2.19±16.3% | 0.302 | 0.518 |
| 0.05 | 0 | 2.47±7.39% | 0.293 | 0.578 |
| 0.2 | 0 | 2.84±13.84% | 0.262 | 0.663 |
| 0.5 | 0 | 2.77±17.8% | 0.346 | 0.683 |
| 0.02 | 1 | 0.83±5.29% | 0.096 | 0.889 |
| 0.05 | 1 | 0.90±4.48% | 0.073 | 0.933 |
| 0.2 | 1 | 1.06±4.55% | 0.086 | 0.902 |
| 0.5 | 1 | 1.08±12.02% | 0.077 | 0.921 |
| 0.02 | 0.81±15.6% | 0.88±4.22% | 0.093 | 0.890 |
| 0.05 | 0.88±11.8% | 0.91±5.70% | 0.070 | 0.936 |
| 0.2 | 1.07±8.56% | 1.02±7.34% | 0.085 | 0.907 |
| 0.5 | 1.11±4.90% | 0.95±6.05% | 0.072 | 0.955 |

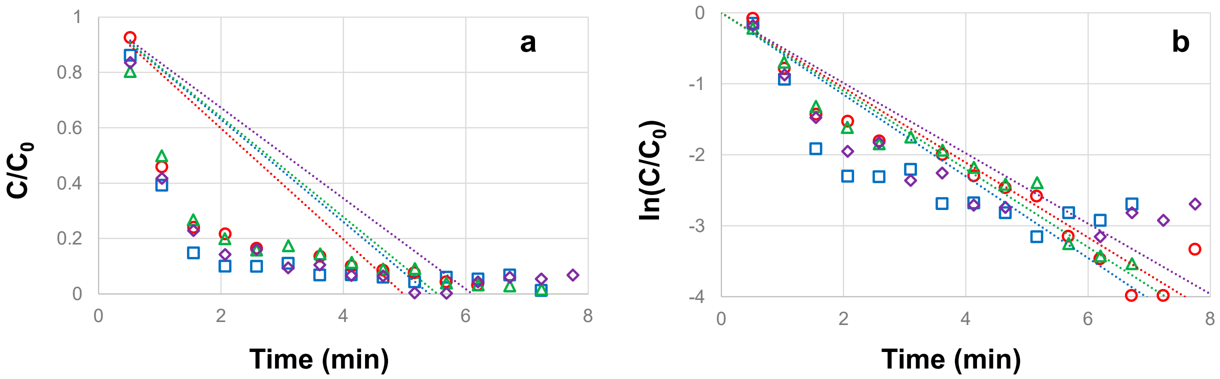

**Figure 3.** Degradation of 1 mg $L^{-1}$ CBZ with 5 mg $L^{-1}$ $H_2O_2$, 8 UVC lamps and 0.02 (squares), 0.05 (rhombus), 0.2 (circles) or 0.5 mg $L^{-1}$ (triangles) of $TiO_2$. Panel (a) and panel (b) show the concentration related to its initial value ($C/C_0$), and its natural logarithm, respectively. Lines indicate linear regression for each set.

### *3.4. Influence of UVC irradiation intensity on the photocatalytic degradation of CBZ*

CBZ degradation at a concentration of 1mg $L^{`1}$ (4.23 μM), was tested with hydrogen peroxide concentration of 5 mg $L^{-1}$ (147 μM), combined with 0.5 mg $L^{`1}$ $TiO_2$, and UVC at radiation intensities ranging from of 901-3605 W $m^{-2}$ (2-8 lamps). This set of experiments intended to determine if the influence of UVC intensity fits a pseudo 1st order process for all concentrations, as described in the mechanism presented in section 2.

**Table 4.** Pseudo-orders, half-life times, root mean square errors (RMSE) and coefficient of determination ($R^2$) for degradation of 1 mg $L^{-1}$ CBZ with 5 mg $L^{-1}$ (147 μM) $H_2O_2$, 0.5 mg $L^{-1}$ $TiO_2$, and UVC irradiation intensity ranging between 901- 3605 W $m^{-2}$ (corresponding to 2-8 UVC lamps).

| UVC irradiation intensity (W $m^{-2}$) | Pseudo-order $n_a$ | Half life $t_{1/2}$ (min) | RMSE | $R^2$ |
|---|---|---|---|---|
| 901 (2 lamps) | 0 | 9.68±2.52% | 0.202 | 0.747 |
| 1803 (4 lamps) | 0 | 5.12±3.36% | 0.254 | 0.689 |
| 2704 (6 lamps) | 0 | 3.42±3.95% | 0.286 | 0.684 |
| 3605 (8 lamps) | 0 | 2.77±17.8% | 0.346 | 0.671 |
| 901 (2 lamps) | 1 | 5.02±5.63% | 0.096 | 0.938 |
| 1803 (4 lamps) | 1 | 1.78±6.06% | 0.068 | 0.947 |
| 2704 (6 lamps) | 1 | 1.18±4.03% | 0.051 | 0.966 |
| 3605 (8 lamps) | 1 | 0.98±17.8% | 0.083 | 0.968 |
| 901 (2 lamps) | 2 | 3.43±1.22% | 0.044 | 0.985 |
| 1803 (4 lamps) | 2 | 1.25±5.26% | 0.075 | 0.979 |
| 2704 (6 lamps) | 2 | 0.89±5.83% | 0.098 | 0.982 |
| 3605 (8 lamps) | 2 | 0.71±1.82% | 0.103 | 0.980 |
| 901 (2 lamps) | 1.92±3.41% | 3.46±4.97% | 0.041 | 0.955 |
| 1803 (4 lamps) | 1.41±2.65% | 1.50±3.53% | 0.057 | 0.950 |
| 2704 (6 lamps) | 1.03±2.86% | 1.16±2.93% | 0.050 | 0.967 |
| 3605 (8 lamps) | 1.11±4.90% | 0.95±6.05% | 0.072 | 0.955 |

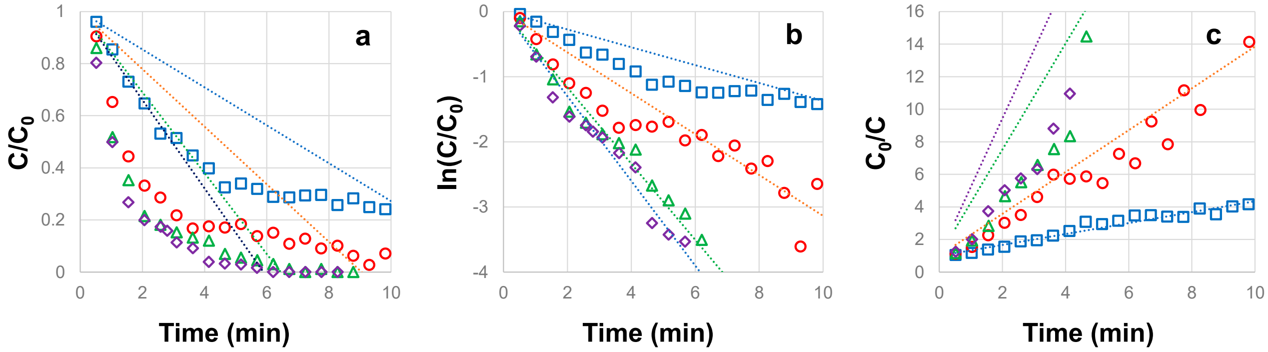

**Figure 4.** Degradation of 1 mg L$^{-1}$ CBZ with 5 mg L$^{-1}$ $H_2O_2$, 0.5 mg L$^{-1}$ $TiO_2$ and 2 (squares), 4 (circles), 6 (triangles) or 8 (rhombus) UVC lamps. Panels (a), (b) and (c) show the concentration related to its initial value ($C/C_0$), its natural logarithm ($\ln(C/C_0)$), and its reciprocal ($C_0/C$), respectively. Lines indicate linear regression for each set.

According to the relationships between the linearity of graphs and the integrated rate laws [38] Fig 4a shows that irradiation intensities do not fit a 0th pseudo-order kinetics, as confirmed by values in Table 4 (RMSE>0.200 and $R^2$ <0.75). A considerable better fit is observed for the 1st pseudo-order model (Figure 4b, Table 4, RMSE<0.100 and $R^2$>0.94). However, evaluation of optimized pseudo-orders (Table 4): indicates that at large irradiation intensities (6 and 8 lamps) the process is indeed close to 1st pseudo-order, but at lower intensities (4 lamps) pseudo-order increases to 1.4, and at 2 lamps it increases close to 2nd pseudo-order. Such behavior is confirmed by Figure 4c, that shows the reciprocal of $C/C_0$. Such representation yields a linear behavior for 2nd order processes according to:

$$\frac{1}{[C/C_0]} = C_0/C = kt + 1 \tag{16}$$

[37,38]. Such behavior does not fit the model presented in Section 2, that predicts irradiation intensity should follow a 1st pseudo-order kinetics at any intensity. Thus, we consider in the following subsection an improved mechanism that fits the results were at low intensities the process is 2nd pseudo-order, moving to a 1st pseudo-order at high irradiation intensities.

### *3.5. Corrected kinetic analysis*

To adapt to the results in the previous section, that indicate that CBZ degradation at low irradiation intensities is a 2nd pseudo-order process we suggest the following changes to the mechanism presented in section 2.2:

Step 5 (rate constant $k_5$)- assume that the excited $TiO_2$-CBZ complex may degrade the pollutant to a product (denoted as $P_1$) only upon absorbing an additional photon. This will change Eq. 8 to:

$$ZT^* + \text{UVC} \rightarrow P_1 + T \tag{8*}$$

Accordingly, Eq.10b that focuses on the rate of change of the intermediate excited $TiO_2$-CBZ complex (ZT*) at steady state will change to:

$$\frac{d[ZT^*]}{dt} = k_3[T^*][Z] - k_4[ZT^*] - k_5[UVC][ZT^*] = 0 \tag{10b*}$$

Leading to changes in the isolated term for ZT* (Eq. 11b):

$$[ZT^*] = \frac{k_3[T^*][Z]}{k_4 + k_5[UVC]} \tag{11b}$$

and after introducing the concentration of the excited heterogeneous catalyst at steady state (Eq. 11a) will change to:

$$[ZT^*] = \frac{k_3[Z]}{k_4 + k_5[UVC]} \frac{k_1[T][UVC]}{k_{-1} + k_3[Z]} \tag{11d}$$

changing the rate of the formation of the product $P_1$ (Eq. 12 based on the elementary step established in Eq.8*):

$$\frac{d[P_1]}{dt} = k_5[ZT^*][UVC] = \frac{k_5 k_3[Z]}{k_4 + k_5[UVC]} \frac{k_1[T][UVC]^2}{k_{-1} + k_3[Z]} \qquad (12^*)$$

At relatively low pollutant concentrations ($k_3[Z] \ll k_{-1}$ ) the process presented in Eq.12* will indeed behave according to the measured results. At relatively low irradiation intensities, $k_5[UVC] \ll k_4$, yielding:

$$\frac{d[P_1]}{dt} = \frac{k_5 k_3[Z]}{k_4} \frac{k_1[T][UVC]^2}{k_{-1}} \qquad (17)$$

Thus, pseudo 2nd order on [UVC]. On the other hand, at relative high irradiation intensities, when $k_5[UVC] \gg k_4$, Eq.12* becomes:

$$\frac{d[P_1]}{dt} \approx \frac{k_5 k_3[Z]}{k_5[UVC]} \frac{k_1[T][UVC]^2}{k_{-1}} = \frac{k_5 k_3[Z]}{k_5} \frac{k_1[T]}{k_{-1}} \; [UVC] \qquad (18)$$

which is obviously pseudo 1st order on [UVC]. Thus, the corrected mechanism based on the requirement for an additional photon to be absorbed by the $TiO_2$-CBZ excited complex, fits to the results presented in section 3.4.

The equations above are based on the assumption that the concentration of the pollutant is relatively low, and the process behaves at pseudo 1st order on CBZ, as it is indeed the case for the conditions in this study. However, influence of the irradiation will apparently remain the same at large CBZ, when ($k_3[Z] \gg k_{-1}$ ). In such case equations (17) & (18) will change to:

$$\frac{d[P_1]}{dt} = \frac{k_5 k_3[Z]}{k_4} \frac{k_1[T][UVC]^2}{k_{-1}+k_3[Z]} \approx \frac{k_5}{k_4} k_1[T][UVC]^2 \qquad (17b)$$

$$\frac{d[P_1]}{dt} \approx \frac{k_5 k_3[Z]}{k_5[UVC]} \frac{k_1[T][UVC]^2}{k_{-1} + k_3[Z]} = k_1[UVC][T] \qquad (18b)$$

Thus, the process will transform to pseudo 0th order on CBZ.

## 5. Conclusions

This study presents a set of elementary steps aiming to elucidate the heterogeneous-homogeneous photocatalysis of carbamazepine. It is based on the formation of three intermediate products (excited heterogeneous catalyst, excited heterogeneous catalyst/pollutant complex, and hydroxyl radicals). According to the preliminary mechanism the different components should influence as follows:

- Carbamazepine should be pseudo 1st order or pseudo 0th order at low or at high concentrations, respectively.
- The homogeneous catalysts ($H_2O_2$) should be pseudo 1st order at all concentrations.
- The heterogeneous catalysts ($TiO_2$) should be pseudo 1st order at all concentrations.
- The UVC irradiation intensity should be pseudo 1st order at all concentrations.

A set of experiments was performed, and indeed points [1]-[3] appear to behave according to the proposed model. As for point 4, since results indicate a different behavior, a slight change in the model was introduced to meet the measured results that indicated that UVC irradiation intensity is pseudo 2nd or pseudo 1st order at low or high intensities, respectively. Additional experiments at other components conditions may be performed to further strengthen or correct and improve the proposed model, for example- point [1] should be tested at higher CBZ concentrations, and point [3] might require testing at lower hydrogen peroxide concentrations.

Assuming the model describes accurately the process, it can be useful to design more efficient AOP devices. For example, since high pseudo-order processes are less effective in achieving complete removal at low pollutant concentrations [33], then maybe low irradiation intensities should not be used to avoid pseudo 2nd order processes.

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## Appendix A: Pseudo-order of a process

This appendix presents the core equations on which the procedure to find the kinetic parameters of the process is based [33]. The change in the concentration of reactant *A* when all other reactants are in non-limited amounts, and/or kept constant, can be described by a simplified rate law [40]:

$$v = \frac{d[A]}{dt} = -k_a[\mathrm{A}]^{n_a} \tag{A1}$$

where $v$ is the reaction rate, $k_a$ is the apparent rate coefficient, and $n_a$ is the apparent or "pseudo" reaction order [30,41], where the term "*apparent*" or "*pseudo*" is used to emphasize that all other parameters were kept constant [42]. Integration of Equation (A1) (as long as $n_a \neq 1$), yields:

$$[A]_{(t)} = \left(\frac{1}{\frac{1}{[A_0]^{n_a-1}}+(n_a-1)k_a t}\right)^{\frac{1}{n_a-1}} \tag{A2}$$

whereas for pseudo-*first* order ($n_a$=1):

$$\frac{d[A]}{A} = -k_a dt \rightarrow [A]_{(t)} = [A]_0 e^{-k_a t} \tag{A2*}$$

To compare different processes the reaction "half-life time" ($t_{1/2}$), can be calculated by solving Eq.(A2) and (A2*) for the case were $[A]_{(t)}=0.5$, yielding:

$$\text{for } n_a \neq 1\text{:} \quad t_{1/2} = \frac{2^{n_a-1}-1}{(n_a-1)k_a[A_0]^{n_a-1}} \tag{A3}$$

$$\text{for } n_a=1\text{:} \quad t_{1/2,n=1} = \frac{\ln(2)}{k_a} \tag{A3*}$$

As can be seen from Eq.(A3), half-life times (except for $n_a$=1) strongly depends on the initial concentration. Thus, when comparing processes, this should be taken in consideration.

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