Article

Evaluation of kinetic pseudo-order in the photocatalytic degradation of ofloxacin

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Abstract: Ofloxacin is a highly efficient and widely used antibiotic drug. It is classified as a refractory pollutant due to its poor biodegradability. Consequently, it is commonly found in water sources, requiring efficient methods for its removal. Advanced Oxidation Processes (AOPs) offer efficient alternatives since those yield complete degradation not achieved in adsorption or membrane processes. Previous studies suggest ofloxacin degradation follows a pseudo-first or -second order processes, whereas for full removal of refractory pollutants – lower pseudo-orders are required. Monitoring the actual "pseudo-order" degradation kinetics of ofloxacin is needed to evaluate any proposed AOP process. This study presents a simple procedure to evaluate pseudo-orders of AOPs. Photolysis of 20 μM ofloxacin solutions follow pseudo-zero order kinetics, with half-life times ($t_{1/2}$) of approx. 60 min. TiO_2 heterogenous catalyst show to have no influence at low concentration (0.2 mg L^{-1}) but a significant reduction of half-life time ($t_{1/2}$ = 20 min) and increase in pseudo-order (0.8) is measured at 2.0 mg L^{-1}. Similar results are obtained with homogenous catalysis by 2.0 mg L^{-1} H_2O_2. The combination of H_2O_2 and TiO_2 catalysts shows additional reduction in half-time life with increase in the pseudo-order to 1.2. The conclusions are (1) heterogenous and homogenous photocatalysis can effectively degrade ofloxacin, (2) combined photocatalysis yields higher pseudo-order, being less prone to achieve full removal, (3) analysis of specific pseudo-orders in AOPs of refractory pollutants helps to further elucidate the efficiency of the processes.

Keywords: ofloxacin, rate-law, pseudo-order, half-life time, homogeneous catalysis, heterogeneous catalysis, photodegradation

1. Introduction

1.1. *Advanced oxidation processes for the removal of ofloxacin*

Ofloxacin (OFL) is a third-generation fluoroquinolone antibiotic that due to its broad-spectrum antibacterial properties is extensively used to prevent or treat human and animal bacterial infection [1]. Since it is refractory to biodegradation [2], it is found at significant concentrations in surface water and wastewater treatment plants (up to 1.8 μg L^{-1}), and 20 fold time higher concentrations in hospital effluents [3], thus requires specific and effective methods to remove it from the environment. While existing methods like adsorption, membrane separation and flocculation mostly separate the pollutant from the water, Advanced Oxidation Processes (AOPs) - if performed effectively- may offer an environmentally oriented alternative for the removal of refractory pollutants from water [4], yielding the complete decomposition of the organic pollutant [5]. Due to its high efficiency, low cost, practicality, and environmental friendliness [6] AOPs in general and photocatalysis in particular are widely studied and reviewed.

The removal of refractory antibiotics from water has been extensible studied in the recent years, reflecting the increasing concern from its accumulation in the environment, and the influences related to that [7,8]. Several studies on AOP processes for the removal of fluoroquinolone antibiotics in general and OFL in particular were reported. This includes direct photochemistry (photolysis)[9] and the influence of natural colloids on it [1], photocatalytic degradation combining UV/TiO_2 and UV/TiO_2/H_2O_2 [3], use of photo-assisted microbial fuel cells with LiNbO3/CF photocatalytic cathodes [10], UV combined with hydrogen peroxide or persulfate [11,12], heterogenous persulfate catalysis with Mn doped CuO particles [13] or MnCeOx composites [4], Fenton based processes combining $MnFe_2O_4$ magnetic particles [2], ozonation and peroxone processes [1], and other combinations yielding formation of a broad range of highly reacting species and oxidating agents [14,15]

In the process of describing the degradation achieved by such AOPs, usually "rate laws" describing the relationship between the concentrations of reactants and the rate of a specific reaction, are developed. In most cases such laws helps to elucidate the full kinetic process, and in some cases- even the mechanism [16]. A full and comprehensive rate law should include the concentrations of all the reactants in a process, each of them its relevant "order". The "kinetic order" is defined as "the power dependence of the rate on the concentration of each reactant" [17]. For example, Batakliev et al. [18] present a series of proposed mechanisms for the decomposition of ozone, considering all possible participants including light, free electrons, molecular and atomic oxygen, and even "third particles" (additional chemicals or compounds). Similar mechanisms were presented for AOPs in general, in some cases developed to full rate laws [19], and in others only as a series of elementary steps [20]. Such kind of studies were also presented for AOPs of OFL [12,21], even though in most cases the specific influence of the concentration of the pollutant on the rate of degradation was not fully elaborated.

1.2. Rate laws and pseudo-orders

Full and comprehensive rate laws, that include the kinetic orders of all participants, are usually complicated to determine and require the identification and quantification of all the reactants in the process, including partial by-products. On the other hand, in the catalyzed degradation of refractory pollutants like ofloxacin, when all the reactants except ofloxacin, are in non-limited amounts, and/or kept constant, a simplified rate law can be defined as [22]:

$$v = \frac{d[A]}{dt} = -k_a [\mathrm{A}]^{n_a} \tag{1}$$

where v is the reaction rate, k_a is the apparent rate coefficient, A is the concentration of the pollutant in case, and n_a is the apparent or "pseudo" reaction order [23,24]. The term "*apparent*" or "*pseudo*" is used to acknowledge the fact that all other influencing parameters (catalyst/degradation agent, by-products, temperature, light, etc.) were kept constant [25], and are indirectly included in k_a. To allow comparison between parameters in different reaction mechanisms, the dimensionless "relative concentration at time t" is defined as $[A]_{(t)} = C_t/C_0$ (the ratio of actual to initial concentration).; thus $A_0 = 1$. This is convenient since it yields apparent kinetic coefficients that always have dimensions of time^{-1}, regardless of the order of the process [26].

Equation (1) can be integrated if $n_a \neq 1$, and the concentration at time t can be calculated if the kinetic rate coefficient k_a and the pseudo-order n_a are known, using

$$[A]_{(t)} = \left(\frac{1}{\frac{1}{[A_0]^{n_a - 1}} + (n_a - 1) k_a t} \right)^{\frac{1}{n_a - 1}} \tag{2}$$

For the specific case of pseudo-*first* order (n_a=1), the integration yields:

$$\frac{d[A]}{A} = -k_a dt \;\rightarrow [A]_{(t)} = [A]_0 e^{-k_a t} \tag{3}$$

Since it is impossible to numerically compare kinetic rate coefficients for different pseudo-order processes, it is common to compare the reaction "half-life time" ($t_{1/2}$), defined by the time which take to the concentration of a reactant to reach half of its initial value [24] . Half-life times can be evaluated by solving mathematically Eq.(2) and (3) to the case were $[A]_{(t)}$=0.5, yielding for $n_a \neq 1$

$$t_{1/2} = \frac{2^{n_a-1}-1}{(n_a-1)k_a[A_0]^{n_a-1}} \tag{4}$$

And for n_a=1:

$$t_{1/2,n=1} = \frac{\ln(2)}{k_a} \tag{5}$$

It is important to emphasize that for all orders except pseudo-first order (n_a=1), half-life times strongly depends on the initial concentration. Thus, for the purpose of a refractory pollutant, the rate law is crucial for the determination of the efficiency of the process. In most studies presenting degradation of OFL, the order is found empirically by fitting the relative concentration (C_t/C_0) at several times of measurement to a pseudo first or even pseudo second order process [1,4,5,9,12,13,27]. In all those cases the fit is based on 5-10 experimental data points. However, it should be emphasized that high pseudo-orders yield higher degradation rates ($\frac{d[A]}{dt}$) and lower half-life times at large concentrations, but at very low pollutant concentrations – lower orders yield better performance. For example, consider different suggested degradation processes yielding the same half-life times at an initial pollutant concentration of 1 μM: If the process is pseudo-first order, half-life time will remain constant, independent from the initial concentration (see Eq.3). However, this is will not be the case for a "pseudo second order" or a "pseudo-zero order" (see Eq.2). If the initial concentration increases to 10 μM, the half-life time of the pseudo second order will decrease by a factor of 10. But refractory pollutants are in most cases at very low concentration and if the initial concentration is, for example 0.01 μM, the half-life time will increase 100 times, yielding almost no efficient pollutant removal. On the other hand, for the "pseudo zero order" process, reaction rate will remain unchanged (Eq.1), and half-life times at the low concentration mentioned will be reduced 100 fold (Eq.4),thus at lower concentrations such low order processes would be beneficial [28].

One of the objectives of this study is to report on the photocatalytic degradation of OFL by combining UV/TiO_2, UV/ H_2O_2 and UV/TiO_2/H_2O_2, and in this sense, it is similar to previous studies [3], although our work was performed at considerably lower catalysts concentrations. However, the main purpose is to present a relatively simple procedure that allows to better evaluate the pseudo-order of degradation processes in general, and by that- might provide a proper relatively objective comparison of the efficiency of refractory pollutants removal using AOP processes

2. Results and Discussion

2.1. Optimization procedure

The optimization procedure to find the pseudo-order that exhibits the best fit to each of the treatments was performed as follows: From the large amount of data (120-250 data points) in each experiment, a "bootstrap" [29,30] procedure was performed by choosing 5 sets of 20 values for each experiment. The values of the kinetic rate coefficients (k_a) and pseudo-orders (n_a) were drawn out for each experimental dataset by evaluating $[A]_{(t)}$ using Eq. (2) and fitting the optimal parameters using the "Solver" tool in *Excel*® software. The fitting procedure was set to minimize 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" [31]. Half-life times were calculated using Eq.(3). To evaluate the sensitivity of the fit, a similar procedure was performed fixing pseudo-orders to 0, 0.5, 1 and 2, and finding the optimal k_a (and accordingly, $t_{1/2}$) for each fixed pseudo-order. As can be understood, RMSE for those evaluations- based only on optimization of k_a but without optimizing n_a- were considerably higher than in the cases when optimizations were evaluated based on both k_a and n_a. Optimization results are shown in Table 1 It should be noted that since the ranges of values for C_t/C_0 are 0-1, RMSE values for the best fit are indeed very low (<0.0001). This conclusion can also be deduced from the fact that measured and best-fit lines in Figs. 1-5 are in complete match.

2.2. AOP degradation experiments of ofloxacin

2.2.1. Photolysis

The photodegradation of 20 µM (7.23 mg L^{-1}) OFL with no catalysts (photolysis experiment) is shown in Figure 1. Red squares show the experimental measured results, whereas lines are evaluated as described in section 2.1. Note that red dashed line describing the best fit is directly above measured results, making it very difficult to distinguish between them.

Table 1. Pseudo-orders, half-life times and root mean square errors for all the experiments. The first row in each treatment (in *italics*) represents the best fit, with errors calculated by bootstrap procedure

Treatment	**Pseudo-order** n_a	**Half life** $t_{1/2}$ **(min)**	**RMSE** **($x10^3$)**
OFL/UV (photolysis)	*0.283±9.63%*	*59.2±0.30%*	*0.0071±15.2%*
	0	59.3	0.102
	0.5	59.4	0.054
	1	60.6	0.445
	2	65.8	1.907
OFL/TiO_2 0.2 mg L^{-1}/UV	*0.261±14.2%*	*57.1±0.31%*	*0.0067±28.7%*
	0	56.9	0.060
	0.5	57.8	0.052
	1	59.5	0.334
	2	65.5	1.411
OFL/H_2O_2 2 mg L^{-1}/UV	*0.701±6.98%*	*20.7±0.88%*	*0.0786±44.9%*
	0	23.3	2.643
	0.5	21.3	0.289
	1	20.1	0.376
	2	19.1	3.673
OFL/TiO_2 2 mg L^{-1}/UV	*0.830±3.42%*	*19.8±1.38%*	*0.0618±29.7%*
	0	30.0	13.630
	0.5	22.3	1.189
	1	18.8	0.345
	2	14.7	7.701
OFL/H_2O_2 2 mg L^{-1}/ TiO_2 2 mg L^{-1}/UV	*1.205±1.17%*	*16.3±0.71%*	*0.0082±52.7%*
	0	29.0	23.22
	0.5	20.6	4.756
	1	17.4	0.324
	2	13.5	2.946

As shown in Table 1, the best fit is at a pseudo-order of ~0.3, whereas pseudo-orders of 0 and 0.5 exhibit also a close fit, with low RMSE values. Optimal fit half-life time (Eq. (3) yield approximately 59 min. The sensitivity of this parameter to the pseudo-order is not very significant for all the range of pseudo-orders 0-1, as seen in the inset in Fig.1, that presents a magnification of the data close to $t_{1/2}$. When compared with the measured data, high pseudo-orders (1,2) deliver underestimate at high relative concentration but overestimate the remaining OFL at low relative concentrations.

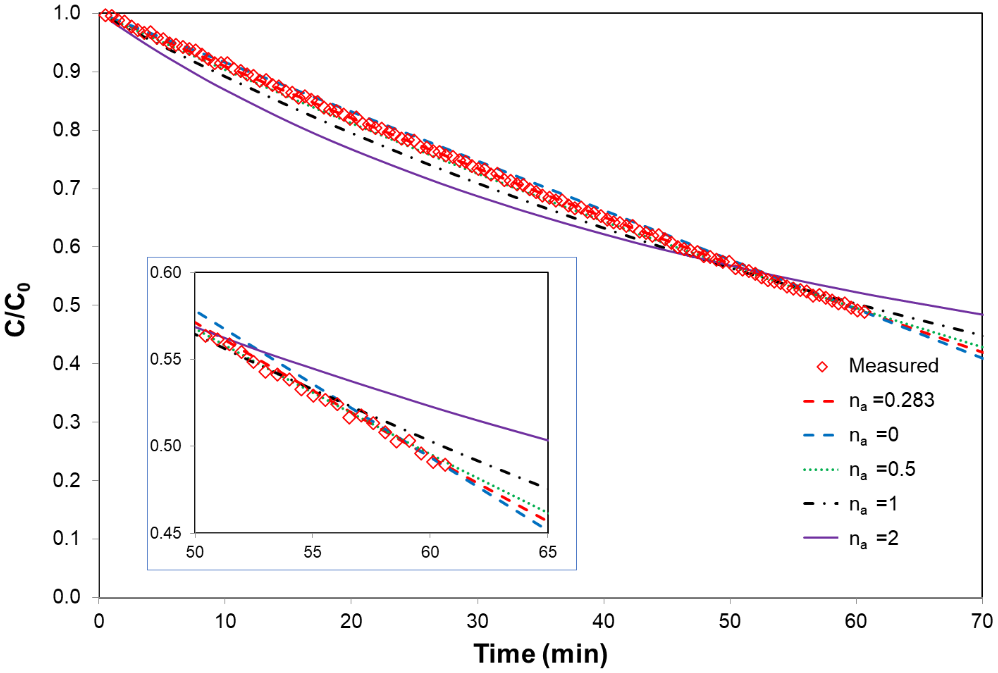

Figure 1. Photolysis of 20 µM ofloxacin. Red squares represent measured values, whereas lines represent different calculated amounts using Eq.2-3 and optimized kinetic coefficient parameters (see Table 1). Inset emphasizes fits and differences close to t=59.2 min.

2.2.2. Heterogenous photocatalysis with low concentration of TiO_2

Degussa P-25® TiO_2 (or an analogue material by other manufacturers) is the most popular photocatalyst for the photodegradation of organic refractory pollutants [27]. In most heterogenous photocatalysis based AOP processes, concentration of the catalyst is from tens to thousands mg L^{-1} [32]. Figure 2 shows the photodegradation results of a 20 µM OFL solution, under UV irradiation, in the presence of a very low concentration (0.2 mg L^{-1}). of a high quality catalytic TiO_2 serving as a heterogeneous catalyst. Low concentration as the ones used in this experiment has been found to be relatively effective in the photocatalytic degradation of bisphenol-S [28]. However, in OFL such low concentration does not exhibit any improvement when compared with photolysis without any catalysts. Half-life times and pseudo-orders results to be almost the same for both treatments.

2.2.3. Homogenous photocatalysis with H_2O_2

Figure 3 shows photodegradation results of a 20 µM OFL solution, under UV irradiation, with 2 mg L^{-1} = 58.8 µM H_2O_2 as homogenous catalyst. The H_2O_2 concentration in this experiment is considered to be significantly lower than the commonly used in most previous studies [1–3,13,21]. A recent study reported that a similar low dose of H_2O_2 successfully reduced the half-life time of BPS degradation to about half of the photolysis value [28] while with caffeine (which is completely stable under photolysis) the half-time life was reduced below 15 minutes [33]. In the case of OFL, the half-life time reduces from almost 1 h to ~21 min. On the other hand, the pseudo-order increases from 0.3 to about 0.7. Pseudo-orders n_a=0.5 and n_a=1 exhibit similar behavior to the best fit close to $t_{1/2}$ (see inset in Fig. 3). Low pseudo-orders (0, 0.5) underestimate the remaining concentration at large irradiation times (and low remaining relative concentrations), whereas higher pseudo-order (1,2) overestimates it.

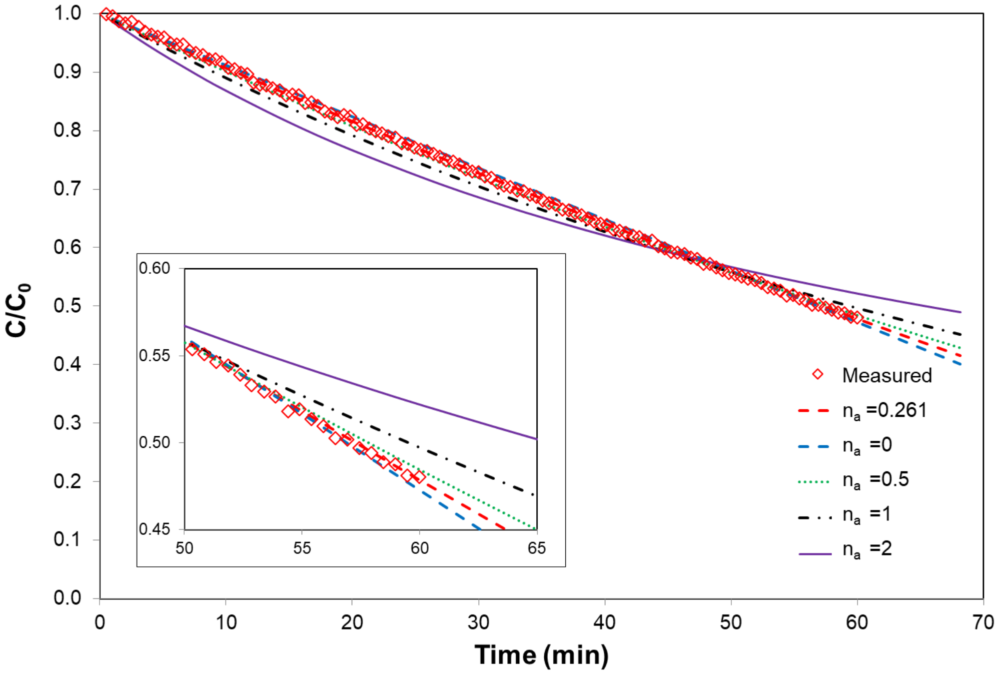

Figure 2. Photocatalytic degradation of 20 µM ofloxacin in the presence of 0.2 mg L^{-1} TiO_2. Red squares represent measured values, whereas lines represent different calculated amounts using Eq.2-3 and optimized kinetic coefficient parameters (see Table 1). Inset emphasizes fits and differences close to $t_{1/2}$=57.1 min.

2.2.4. Heterogenous photocatalysis with high concentration of TiO_2

Low concentrations of TiO_2 (as mentioned in 2.2.2) were ineffective, and the results were very similar to those obtained with no catalyst additive. Degradation of 20 µM OFL solution, under UV irradiation, with 2 mg L^{-1} high quality catalytic TiO_2, is shown in Figure 4. As summarized in Table 1, the $t_{1/2}$ is similar to the homogenous catalysis with 2 mg L^{-1} H_2O_2, and the pseudo-order is slightly higher (0.83 instead of 0.70). Indeed, the inset in Fig. 4 shows that near to $t_{1/2}$, the behavior of n_a=1 is almost identical to the best fit.

Having a positive effect with higher catalysts' concentrations is not obvious: In a previous study on photodegradation of BPS, heterogeneous catalysis was tested at 20 and 0.2 mg L^{-1} catalysts concentration. While increase in the efficacy was reported with increased concentration of TiO_2, two synthetic montmorillonite clay based catalysts exhibited improved efficiency at the low concentration, with lower $t_{1/2}$ and n_{app} [28]. Such behavior was ascribed to light dispersion by the colloids in suspension [34]. It should be mentioned that such clay-based catalysts were also preliminary tested for the photodegradation of OFL but were found completely ineffective (results not shown). It can be deduced that photodegradation processes, as any other water treatment method, are very specific, and an efficient catalyst for one pollutant might be completely ineffective for other.

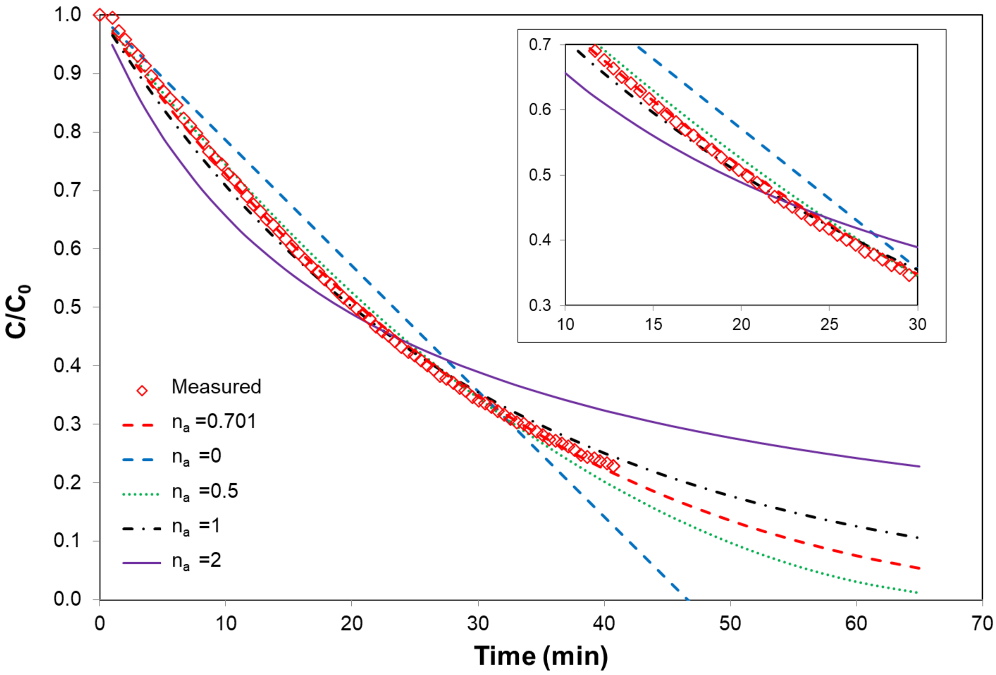

Figure 3. Photocatalytic degradation of 20 µM ofloxacin in the presence of 2 mg L^{-1} H_2O_2. Red squares represent measured values, whereas lines represent different calculated amounts using Eq.2-3 and optimized kinetic coefficient parameters (see Table 1). Inset emphasizes fits and differences close to $t_{1/2}$=20.7 min.

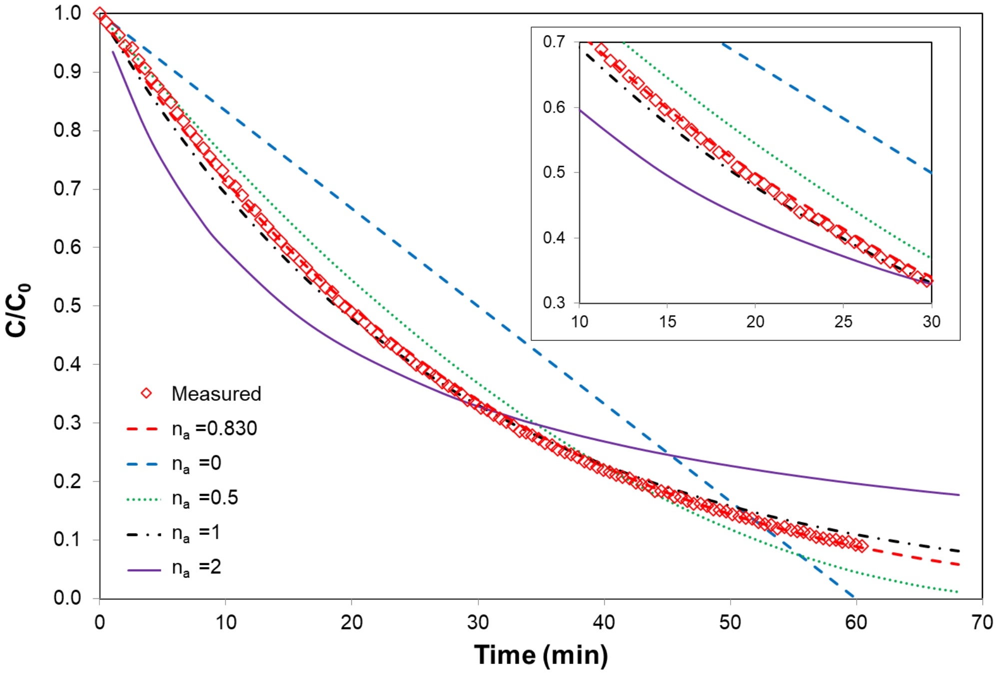

Figure 4. Photocatalytic degradation of 20 µM ofloxacin in the presence of 2 mg L^{-1} TiO_2. Red squares represent measured values, whereas lines represent different calculated amounts using Eq.2-3 and optimized kinetic coefficient parameters (see Table 1). Inset emphasizes fits and differences close to $t_{1/2}$=19.8 min.

2.2.4. Combined heterogeneous/homogenous photocatalysis with TiO_2 and H_2O_2

Considering previous studies report that "simultaneous application of different AOPs promotes the rates of organics oxidation" [15], Figure 5 shows the photodegradation of a 20 μM OFL solution, under UV irradiation, with the addition of 2 mg L^{-1} of both H_2O_2 and TiO_2. Combining both catalysts changes the path of the process and yields a considerably higher value of pseudo-order (~1.2 instead of 0.7-0.8) with a decrease in the half-life time (from ~20 to 16 min). Detailed observation of the results leads to the conclusion that if the purpose is full removal of OFL, the combination of H_2O_2 and TiO_2 is as the matter of fact less effective than when the catalysts are added separately. For example, if we compare Figs. 3, 4 and 5, we can see that at t≈65 min the measured concentration in the combined H_2O_2 and TiO_2 process is approximately 11% of the initial concentration, whereas in Fig.4 when there is only TiO_2, remaining OFL is only about 7.5%, and with H_2O_2 alone (Fig.3) only 5.4%. This happens even though $t_{1/2}$ for the combined process is 16.3 min compared to 19.8 or 20.7 min for TiO_2 or H_2O_2 alone, respectively. This simple example emphasizes that the conception at first sight that higher pseudo-orders should be preferred is erroneous, and for effective complete removal the benefits of lower pseudo-orders are significant.

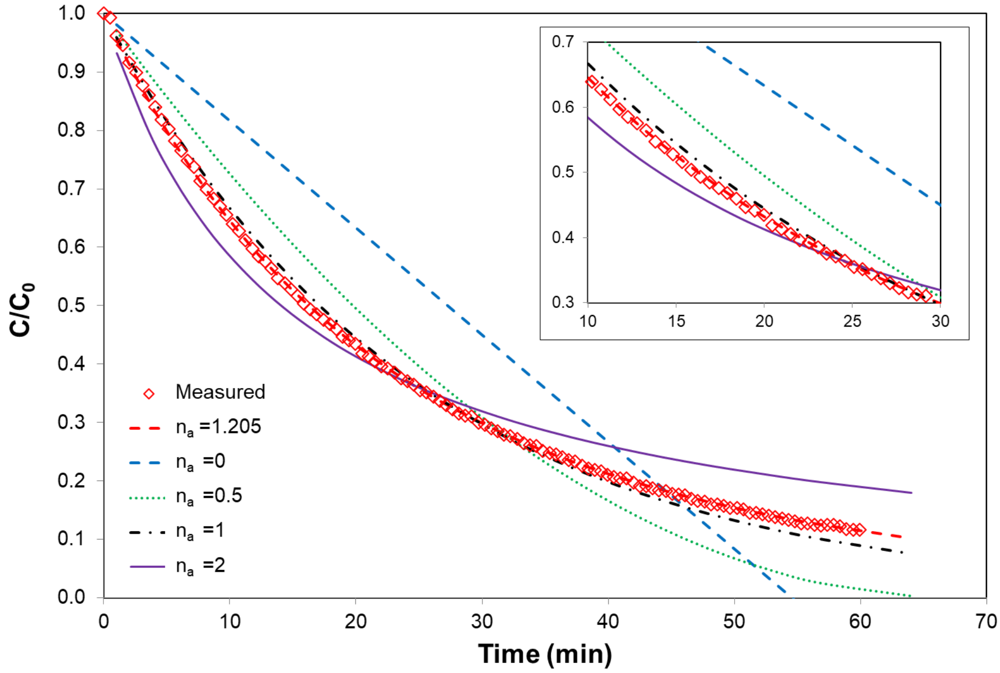

Figure 5. Photocatalytic degradation of 20 μM ofloxacin in the presence of 2 mg L^{-1} H_2O_2 and TiO_2. Red squares represent measured values, whereas lines represent different calculated amounts using Eq.2-3 and optimized kinetic coefficient parameters (see Table 1). Inset emphasizes fits and differences close to $t_{1/2}$=16.3 min.

3. Materials and Methods

3.1. Optimization procedure

Ofloxacin ($C_{18}H_{20}FN_3O_4$), 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. All the experiments were performed at ambient conditions (23 ± 1ºC).

3.2. Methods

The degradation of ofloxacin in all experiments was measured in batch experiments in a 100-mL UV-C-transparent quartz glass (refractive Index n = 1.5048), 5.3-cm diameter beaker placed in a Rayonet RMR-600 mini photochemical chamber reactor (Southern New

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England Ultraviolet Company, Branford, CT, USA), as described in previous studies [22,28,33]. The photoreactor was equipped with eight RMR 2537A lamps (254 nm wavelength), each lamp emitting an average irradiance flux of 19 W m^{-2} at 254 nm, equivalent to an overall intensity of 152 W m^{-2}, as measured in the center of the chamber using a Black Comet SR spectrometer with an F400 UV–VIS–SR-calibrated fiber optic probe equipped with a CR2 cosine light receptor (StellarNet Inc., Tampa, Florida, USA). The same spectrometer was used to measure the spectrum of the solutions during experiments using a 20 mm pathlength DP400 dip probe cuvette placed inside the beaker. The solutions were constantly mixed with an external stirrer (VELP Scientifica, Usmate Velate, Italy) rotating at 100 rpm. Spectra were measured using the SpectraWiz software (StellarNet Inc., Tampa, Florida, USA) every 10–20 s for 50–70 min. Data was transformed to comma separated values (CSV) files, and absorption at the maximum absorption band of OFL (288 nm, ε_{288}=24240 $M^{-1}cm^{-1}$) was downloaded after subtracting a baseline value at 450 nm. Preliminary chromatography measurements using an HPLC system confirm that quantification using this method at those concentrations is reliable. To allow comparisons between parameters in different reaction mechanisms, the "relative dimensionless concentration at time t" $[A]_{(t)}$ was evaluated [35] as Ct/C0 = OD_t/OD_0 (the ratio of actual to initial concentration, or actual to initial light absorbance); thus $A_0 = 1$. Such procedure led to >120–250 data points for each experiment. Analysis of the data was performed as described in subsection 2.1. The experiments performed were as follows:

1. Photolysis (UV lamps, no catalysts) of a solution of 20 mM OFL
2. Heterogeneous photocatalysis of a solution of 20 mM OFL with 0.2 mg L^{-1} TiO_2
3. Homogenous photocatalysis of a solution of 20 mM OFL with 2 mg L^{-1} H_2O_2
4. Heterogeneous photocatalysis of a solution of 20 mM OFL with 2 mg L^{-1} TiO_2
5. Combined hetero-homogeneous photocatalysis of a solution of 20 mM OFL with 2 mg L^{-1} TiO_2 and 2 mg L^{-1} H_2O_2

4. Summary and Conclusions

- This study presents a relatively simple method for the determination of the pseudo-order of an AOP process based on a series of measured data points, using "Solver" tool in Excel® software. A simple worksheet for the evaluation of pseudo-orders and half-life times when concentrations at different times along the degradation process are known - was added to this manuscript and is available as "supplementary material".
- The procedure mentioned above was used to analyze photocatalyzed degradation of the refractory antibiotic ofloxacin, while emphasizing the importance of determining the specific pseudo-order of the process in the advanced oxidation photocatalysis of refractory pollutants. Efficient photo-catalyzed degradation of 20 µM OFL in minutes, by either homogeneous or heterogeneous catalysis was observed. Combining both hetero- and homogeneous catalysis lowers $t_{1/2}$ at the initial concentration tested, but due to increase in the pseudo-order, hinders complete removal.
- AOP procedures for the removal of OFL were widely studied. Most studies used a range of OFL concentration similar to this study, but considerably larger amounts of catalyst (either homogenous or heterogenous). It is very difficult to compare between studies, since all processes strongly depend on the concentration of the pollutant, the specific AOP used, the intensity of the energy (light, wavelength, sonication energy, etc.) and concentration of other solutes in the water or effluent, since those may promote or inhibit the degradation [12,22].
- The general assumption in most reported studies that AOPs are pseudo-first or pseudo-second order process, should be further examined. In this study, for example, all processes were neither pseudo-first nor -second order. Furthermore, it should be considered that at low concentrations a low pseudo-order can achieve completely removal, whereas a high pseudo-order process will lower pollutants

concentration faster at the beginning but leave remains of pollutant in the treated water.

- Anachronistic linearizations performed in the past to determine the kinetic coefficients, are no longer required, and might be avoided even by using relatively simple and available worksheet software packages, as presented in this study- or using relatively simple computer codes.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Worksheet W1: An example of kinetic parameters determination using "Solver" by Excel®

Author Contributions: Conceptualization, G.R; methodology, G.R and A.L.Z.; software, A.L.Z..; validation, G.R and A.L.Z.; formal analysis, G.R.; investigation, G.R and A.L.Z.; resources, G.R and A.L.Z.; data curation, G.R and A.L.Z.; writing—original draft preparation, G.R.; writing—review and editing, G.R and A.L.Z.; visualization, G.R.; supervision, G.R.; project administration, G.R.; funding acquisition, G.R. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All raw data is available from the authors.

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