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## *Abstract:*

Pharmaceuticals are considered among the group of emerging contaminants. Paracetamol is a moderate painkiller, which has been detected in ground and surface water. Photodegradation of paracetamol at a wavelength of radiation of 254 nm with TiO<sub>2</sub> nanotubes was studied by UV-spectroscopy, HPLC and measurement of the potential zeta in dependence of the solution pH. The efficiency of the photodegradation of paracetamol (20 mg L<sup>-1</sup>) was 99% after 100 min exposure. Application of the Langmuir-Hinshelwood equation allowed the evaluation of the rate constant. Non-organic by-products were detected under the conditions of the chromatographic analysis. The photoreaction was faster at pH 6.5, a value at which adsorption was favored, leading to higher efficiency.

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Article

# Photocatalytic Treatment of Paracetamol Using TiO<sub>2</sub> Nanotubes: Effect of pH

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**Abstract:** Pharmaceuticals are considered among the group of emerging contaminants. Paracetamol is a moderate painkiller, which has been detected in ground and surface water. Photodegradation of paracetamol at a wavelength of radiation of 254 nm with TiO<sub>2</sub> nanotubes was studied by UV-spectroscopy, HPLC and measurement of the potential zeta in dependence of the solution pH. The efficiency of the photodegradation of paracetamol (20 mg L<sup>-1</sup>) was 99% after 100 min exposure. Application of the Langmuir-Hinshelwood equation allowed the evaluation of the rate constant. Non-organic by-products were detected under the conditions of the chromatographic analysis. The photoreaction was faster at pH 6.5, a value at which adsorption was favored, leading to higher efficiency.

**Keywords:** photocatalysis; TiO<sub>2</sub> nanotubes; emerging contaminants; paracetamol; pH

## 1. Introduction

The rapid development of modern industry and society occurs hand in hand with the increasing generation of residual liquids that contain highly toxic compounds with limited biodegradability. The high usage of chemical products such as dyes, pesticides and pharmaceuticals, which have recently been called “emerging contaminants”, causes a growing problem because of their concentration and accumulation in the environment, particularly in aqueous effluents [1–3]. A type of water contaminants that is becoming more common are pharmaceuticals. They are mainly attributed to hospital and therapeutic waste, personal care products, and the pharmaceutical industry [4,5]. The presence of these products in drinking water is a public health problem because little is known about the potentially long-term toxic health effects that are associated with the ingestion of mixtures of these compounds in drinking water, even at very low concentrations [6–8].

Innovative treatments, such as Advanced Oxidation Processes (AOPs), are effective in drastically reducing the concentrations of pharmaceutical compounds in effluents. Generally, these processes are based on physicochemical methods that cause internal changes in the chemical structures of the contaminants to make them inert and/or decrease their toxicity. The concept of AOPs was initially established by Halling et al. [9], who defined them as processes that involve the generation and use of potential transitory species, especially the hydroxyl radical (HO•) because it is able to attack almost all organic compounds and can react up to 10<sup>12</sup> times faster than other oxidants because of its very high oxidation potential of 2.80 eV.

Laboratory-scale reports and studies of treatment plants have found that paracetamol has no or very little biodegradability [10,11]. However, when it is subjected to a tertiary treatment, such as chlorination, it produces highly toxic reaction by-products, such as *1,4-benzoquinone* and *N-acetyl-p-benzoquinone imine* [12,13]. Thus, there is a need to investigate highly efficient processes, such as AOPs, that have been recently used to degrade paracetamol, including ozonation, electrocatalysis, photolysis, electrolysis, sonolysis, photo-Fenton oxidation [14–18], and also heterogeneous photocatalysis using nanomaterials of titanium oxide (TiO<sub>2</sub>) as photocatalysts [19,20].

It is particularly important to develop highly effective alternative methodologies that are harmless to the environment, such as heterogeneous photocatalysis, which employs nanocatalysts that are usually composed of TiO<sub>2</sub> because of its low toxicity, low cost and high performance [21,22]. The photocatalytic activity of nanocatalysts is governed by many properties, including its specific surface area, pore volume and distribution, crystal structure, phase composition, particle size and morphology [9,23,24]. In particular, the nanotubes that are synthesized by hydrothermal processes have high surface-weight ratios of up to 120 m<sup>2</sup> per gram [2,25–30].

Many factors affect the reactions that have been proposed for the photodegradation of paracetamol in effluents, such as the catalyst and contaminant concentrations, the excitation wavelength of the catalyst, the oxygenation and the pH [31,32]. The latter has not been thoroughly investigated, which implies that the direct impact of pH on the reaction efficiency is still uncertain. This investigation evaluates the relationship between the pH of paracetamol suspensions and the efficiency of the photocatalytic degradation using ultraviolet radiation with a wavelength of 254 nm in presence of nanostructured TiO<sub>2</sub> catalysts with a nanotubular morphology.

## 2. Materials and Methods

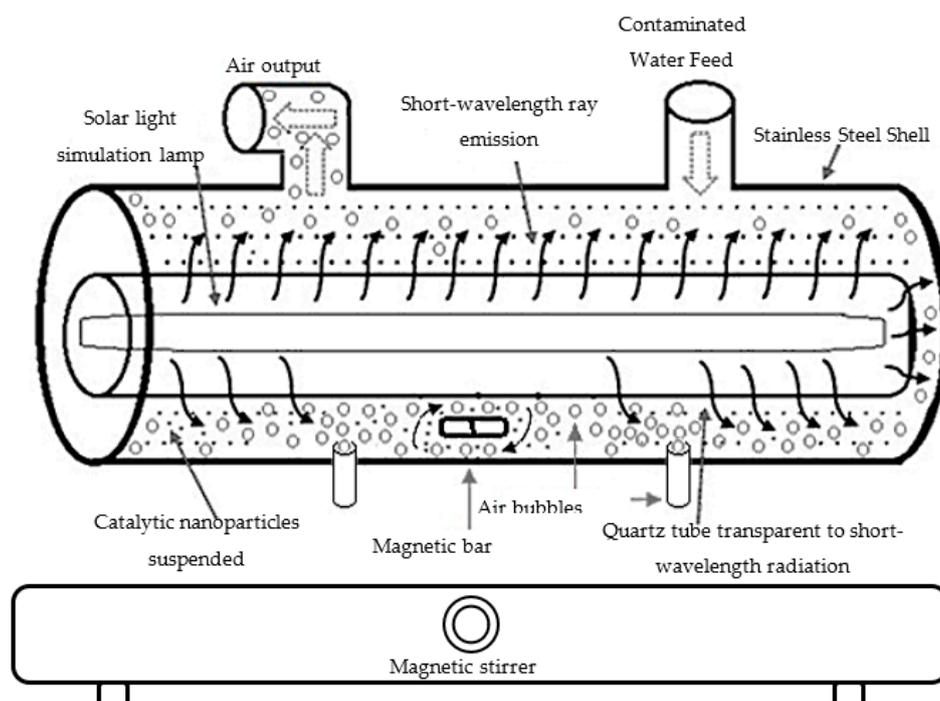
**Reagents:** All the chemical reagents used were analytical-grade. Paracetamol (C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>), 99% purity, and titanium dioxide (P25), 99.5% were purchased from Aldrich. 99.1% Sodium hydroxide (NaOH) and 37% hydrochloric acid (HCl), from sigma Aldrich, were used. HPLC grade water was obtained using a Millipore Milli-Q system (Millipore Sigma Corporation, MA, USA).

**Synthesis of TiO<sub>2</sub> nanotubes:** The TiO<sub>2</sub> nanotubes were produced using a chemical process similar to that described by López et al. [30], TiO<sub>2</sub> powder (P25) with a crystal structure of 80% anatase and 20% rutile and an average particle size of 25 nm was used as a precursor for the synthesis of the nanotubes. To perform the synthesis, 0.3 g of TiO<sub>2</sub> powder was added to 30 mL of 10 M aqueous NaOH solution, and the suspension was vigorously agitated for 2 h at room temperature (30 °C). To perform the hydrothermal treatment, the mixture was transferred to an autoclave, and the temperature was increased to 110 °C for 72 h. The solid precipitate was separated by centrifugation at 10,000 rpm and re-suspended in 200 mL of a 0.1 M HCl solution with constant agitation for 3 h and then centrifuged again. The precipitated samples were washed with distilled water twice until the pH of the solution reached 6.6, which is approximately the pH value of the distilled water that was used. The washed samples were dried in a vacuum oven at 80 °C for 24 h.

**Preparation of paracetamol samples:** An aqueous paracetamol stock solution (volume of 1.5 L) with a concentration of 20 mg L<sup>-1</sup> was prepared. The solution was kept under constant magnetic agitation for 120 min on a stirring plate (LabTech model LMS-1003-Gemini BV Lab, Apeldoorn, The Netherlands) until complete solubilization of paracetamol. Six 250 mL aliquots were taken from the stock solution. The pH of each solution was modified using NaOH and HCl solutions to reach the desired pH values of 2.5, 4.5, 6.5, 8.5 and 10.5. To each aliquot 250 mL of the paracetamol solution, 100 mg of the TiO<sub>2</sub> nanotubes were added, and the suspension was then agitated for 30 min until it was completely dispersed.

**Monitoring of the photodegradation of paracetamol by UV-Vis spectrophotometry:** Batch cylindrical stainless steel photoreactor was used to perform the degradation of the samples. The photoreactor used a high-pressure Hg candle lamp as the energy source, which provided UV light with a wavelength of 254 nm and an intensity of 25 W cm<sup>-2</sup>. The temperature was kept

constant at 25 °C by means of a cooling system and was measured during each sampling during the 3 h of irradiation. The lamp was encapsulated in a quartz tube that was submerged in the center of the reactor along with the aqueous solution (Figure 1). The solution that surrounded the reaction system underwent constant agitation at air pressure and room temperature. The reaction kinetics inside the reactor was monitored by taking 1 mL samples every 10 min and analyzing them with a UV-Vis spectrometer (Hach model DR 5000-Loveland, CO, USA) within the range of 200 to 400 nm with 0.5 nm steps. The final paracetamol concentration  $C_f$  was determined with the aid of a calibration curve ( $m = 55.737$ ,  $R^2 = 0.9995$ ).



**Figure 1.** Experimental setup of the heterogeneous photocatalysis reactor.

Detection of photodegradation by-products by HPLC: The most efficient paracetamol photodegradation reaction was identified using a high-pressure liquid chromatograph (Agilent 1200- Santa Clara, CA, USA) with a C18 reversed-phase column. The chromatographic conditions were similar to those reported by López et al. [33,34]. However, they were optimized for paracetamol and its by-products by using a mobile phase of methanol and acetic acid in 1% water with a v/v ratio of 40/60. The equipment was operated at 25 °C with a flowrate of 1.5 mL min<sup>-1</sup>. A diode array detector (DAD) was used with a principal wavelength of 254 nm, and intervals of 15 nm were used for the detection.

Measurement of the zeta potential: To measure the zeta potential of the TiO<sub>2</sub> nanotubes, an aqueous sample of paracetamol was prepared at a concentration of 0.5 mg L<sup>-1</sup>. Adjustment of the pH was performed with 0.01 M HCl and 0.01 M NaOH solutions using a particle charge titration analyzer Stabino from Microtrac.

Data treatment: Generally, the photochemical oxidation reactions of organic compounds have a first-order kinetics behavior [35]. This is the case for the photocatalytic degradation of paracetamol [36]. The Langmuir-Hinshelwood model (Equation (1)) was applied because in heterogeneous catalysis processes, this model considers the decomposition at the catalyst surface to be the determining step. So, the first-order reaction rate is assumed to be the product of the kinetic constant that is associated with the decomposition and the adsorbate concentration [37,38].

$$r = \frac{dC}{dt} = -\frac{kKC}{1 + KC} \quad (1)$$

where  $k$  is the rate constant, which depends on the light intensity,  $K$  is the adsorption constant of the nanocatalyst, and  $C$  is the concentration of paracetamol. For low adsorption magnitudes and concentrations, ( $KC < 1$ ). So, Equation (1) reduces to the first-order kinetics according to Equation (2).

$$\frac{dC}{dt} = -kKC \quad (2)$$

Separating variables and integrating between the initial conditions  $t = 0$  and  $C = C_0$  at time  $t$  and if  $Kk = k'$ , where  $k'$  is the rate constant for the photocatalytic degradation

$$\ln\left(\frac{C_0}{C}\right) = kKt = k't \quad (3)$$

When plotting Equation (3), the slope is the value of the reaction rate constant  $k'$  and has units of  $\text{min}^{-1}$ . The half-life ( $t_{1/2}$ ), which is an important parameter of photocatalytic degradation because it is the time that is required to reduce the paracetamol concentration by half (i.e.,  $C = C_{0/2}$  in Equation (3)), is given by:

$$t_{1/2} = \frac{\ln 2}{k'} \quad (4)$$

The efficiency of the photocatalytic degradation of the paracetamol was quantified using Equation (5).

$$\text{Efficiency of paracetamol photodegradation (\%)} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (5)$$

where ( $C_f$ ) and ( $C_0$ ) are the paracetamol concentrations in the initial and final solutions, respectively.

### 3. Results and Discussion

#### 3.1. Photodegradation of Paracetamol

Figure 2 shows the absorption spectrum of the paracetamol in the stock solution. The maximum absorption intensity was observed at a wavelength of approximately 243 nm. This change in absorbance at the wavelength of  $\lambda_{\text{max}}$  is consistent with the maximum absorption band of paracetamol observed found in previous studies [39]. The absorbance at this wavelength was used to monitor the changes in concentration and to determine the photodegradation reaction rate constant  $k'$  from the experimental data.

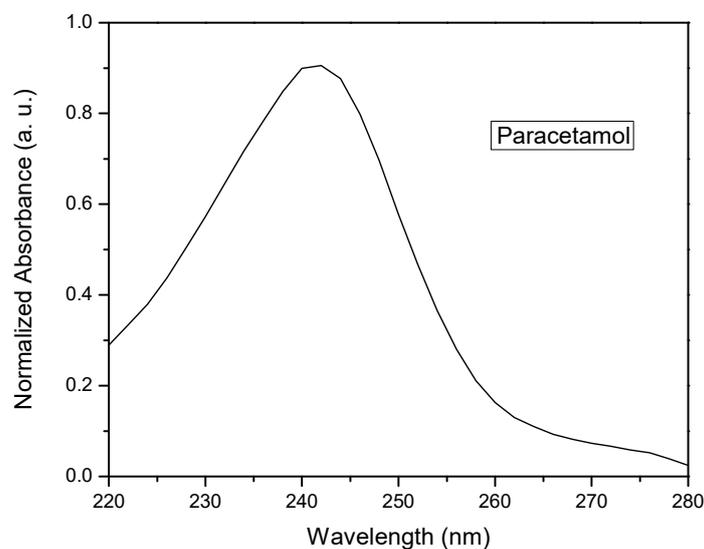
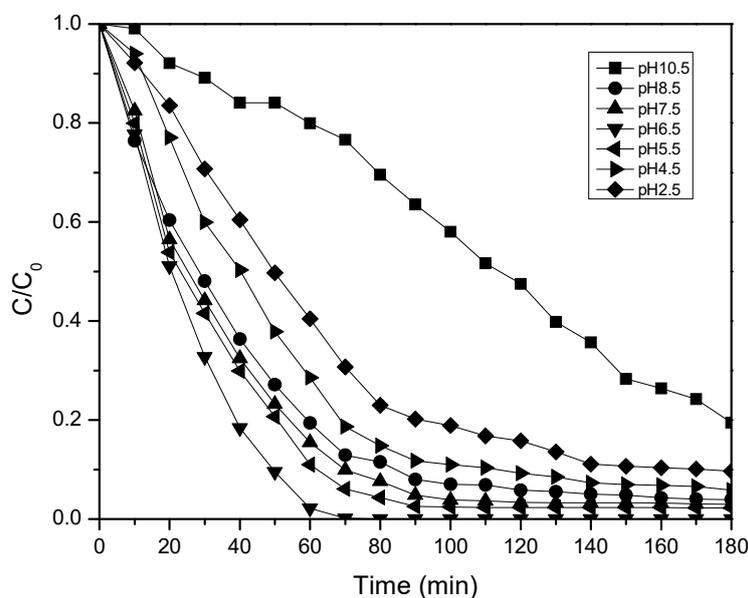


Figure 2. UV-vis absorption spectrum of normalized paracetamol.

Figure 3 shows the normalized decrease of the paracetamol concentration with the reaction time at different pH values. At acidic pH values between 2.5 and 4.5, the reaction rate constants are low because the  $\bullet\text{OH}$  in the reagent medium interacts weakly with the paracetamol molecules because of the possible recombination of free  $\text{H}^+$  protons and hydronium ions ( $\text{H}_3\text{O}^+$ ) with the  $\bullet\text{OH}$  that is generated in the photocatalytic process to form water molecules.



**Figure 3.** Photocatalytic activity of  $\text{TiO}_2$  nanotubes in paracetamol solution at different pHs as function of irradiation time.

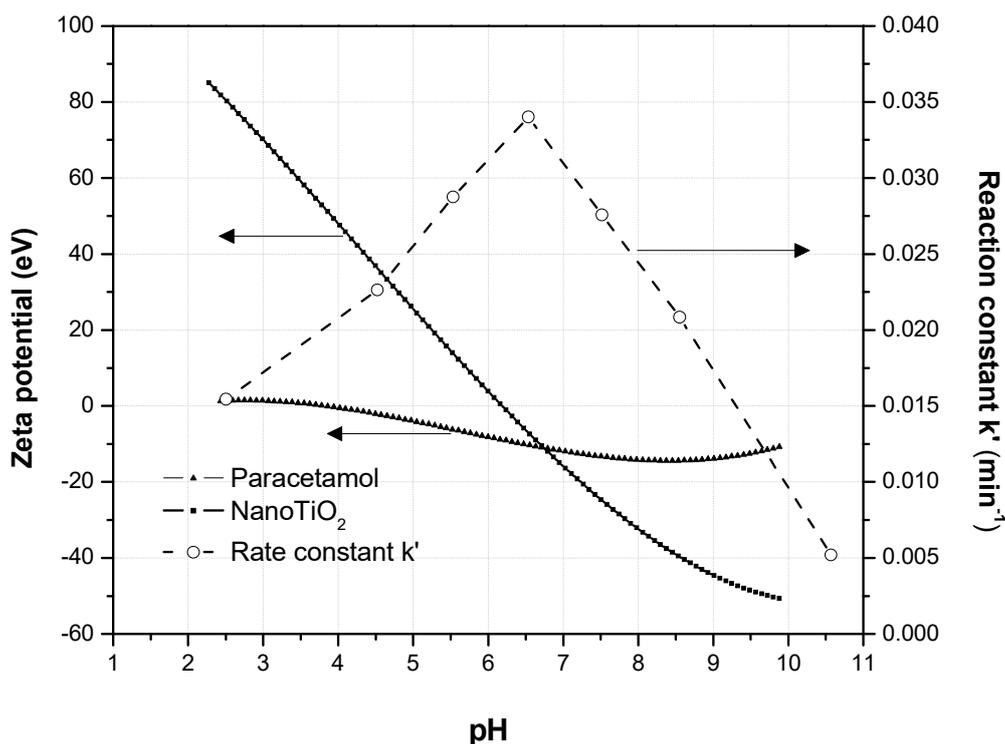
Table 1 shows that at a pH values of 6.5, the magnitudes of the reaction rate constant are higher, and correspondingly of the photodegradation efficiency. This can be attributed to the greater formation of hydroxyl radicals because at high pH values, more  $\bullet\text{OH}$  groups are available at the nanocatalyst surface, and they can easily oxidize [40].

**Table 1.** Values of the photodegradation parameters calculated from Equations (3)–(5).

pH	$K'$ ( $\text{min}^{-1}$ )	$R^2$	$t_{1/2}$ (min)	Efficiency after 180 min (%)
2.5	0.016	0.9571	88.6	46
4.5	0.023	0.9305	60.1	67
5.5	0.029	0.9039	47.8	83
6.5	0.034	0.9641	27.4	99
7.5	0.027	0.9375	51.3	71
8.5	0.024	0.8422	49.9	68
10.5	0.008	0.8958	136.8	32

The graph of the zeta potential (Figure 4) shows the variation of the zeta potential of paracetamol and the catalyst, with the pH of the medium. The curves intersect at pH 6.5; a value at which the paracetamol molecule is not ionized and the surface charge of  $\text{TiO}_2$  is close to zero [41].

Specific interactions of the polar groups and the aromatic moiety of paracetamol with  $\text{TiO}_2$  lead to good adsorption, whereas the free generated and available  $\bullet\text{OH}$  species have more interactions with the paracetamol molecules to degrade them. This explains why the reaction rate constant is higher at pH 6.5 (hollow points in Figure 4). The behavior of the rate constant depicted in Figure 4 also corresponds to the maximum value of the zeta potential. Also, the smaller the charge difference (intersect in Figure 4) between the substrate and the catalyst, the higher  $k$ .



**Figure 4.** Graph of the zeta potential of the substrate and the photocatalyst with the variation of pH.

This result is consistent with the Langmuir-Hinshelwood kinetic model because it suggests that the adsorption-desorption equilibrium between the surface of the semiconductor and the fluid phase is indispensable for initiating the photodegradation of any substrate. Once this equilibrium is established, the photodegradation of the molecule starts through a mechanism that involves radicals. This adsorption-desorption equilibrium is produced precisely when the value of the zeta potential of paracetamol and the nanocatalyst are similar.

At the pH values of 8.5 to 10.5, the photodegradation rate decreases (Figure 4) because 10% paracetamol exists as anion already at pH 8.5 and 92% at pH 10.5 at higher pH values ( $\text{pH} > \text{pKa}$ ). Thus, the increase in the pH gradually increases the electrostatic repulsion between the surface of the nanocatalyst and paracetamol, this considerably reduces the adsorption of paracetamol. Consequently, the reaction rate constant for the photodegradation of paracetamol is expected to decrease gradually at pH values higher than 8.5 [42].

### 3.2. Paracetamol Photodegradation at pH 6.5

To explore the intermediate products that result from the photodegradation of paracetamol, HPLC was used to analyze the treated solution after 100 min of sample treatment at pH 6.5. Only one peak is observed at a retention time of 0.43 min, both for the initial paracetamol sample and after of the photodegradation (Figure 5). This indicates that in our study, the molecule degrades into small molecules or non-detectable compounds under these measurement conditions.

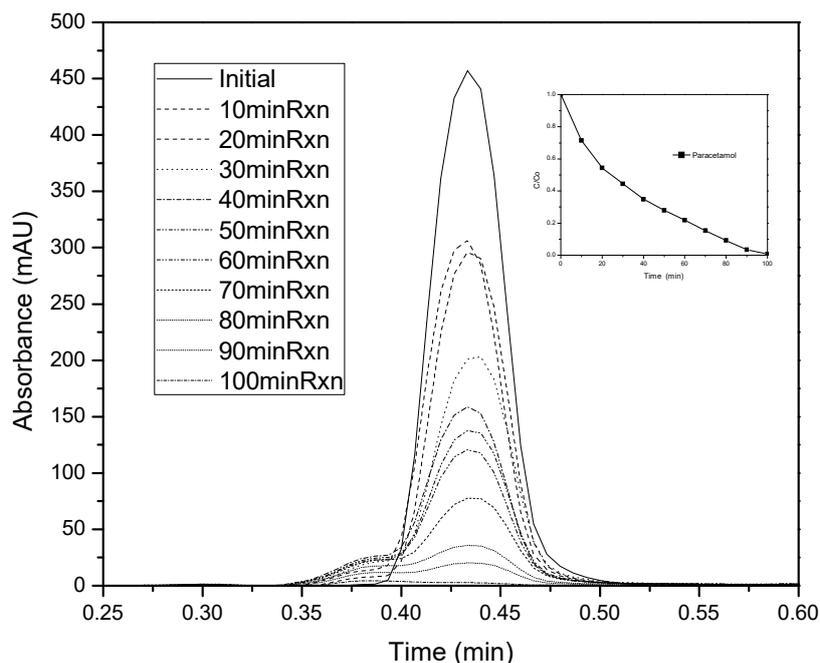


Figure 5. Paracetamol photodegradation kinetics with HPLC data for the samples at pH 6.5.

#### 4. Conclusions

Paracetamol photodegradation in an aqueous solution using radiation with a wavelength of 254 nm is feasible. The best results were obtained at a pH of 6.5 and resulted in 99% photodegradation of paracetamol by catalytic oxidation under the studied conditions. The photodegradation of paracetamol can be performed at concentrations lower than  $20 \text{ mg L}^{-1}$  with relatively short exposure times (100 min) by using  $\text{TiO}_2$  nanotubes. No traces of the metabolites were detected. With measurement of the zeta potential it was demonstrated that the most rapid photoreaction takes place at the pH, at which adsorption is favored. The pH of the photocatalytic process may influence the efficiency of the photodegradation.

**Author Contributions:** Designed the experiments, performed the experiments, analyzed and interpreted the data, wrote the paper, S.A.L.-M.; writing—review and editing, analyzed and interpreted the data, wrote the paper, G.M.; conceived and designed the experiments, contributed reagents, materials, analysis tools or data, M.Á.L.Z.; writing, methodology, formal analysis of the investigation, A.A.-S.; writing, methodology, formal analysis of the investigation and writing—review and editing, F.M.-M.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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