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A Study on the Degradation of Carbamazepine and Ibuprofen by TiO_2 & ZnO Photocatalysis upon UV/Visible-Light Irradiation

Irene Georgaki[1], Eva Vasilaki[1,2], Nikos Katsarakis[1,3*]

[1]Center of Materials Technology and Photonics, School of Applied Technology, Technological Educational Institute of Crete, Heraklion, Greece
[2]Chemistry Department, University of Crete, Heraklion, Greece
[3]Institute of Electronic Structure and Laser, Foundation for Research & Technology-Hellas, Heraklion, Greece
Email: *katsan@iesl.forth.gr

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Abstract

The degradation of carbamazepine (CBZ) and ibuprofen (IBP) in aqueous matrices was investigated by TiO_2 and ZnO photocatalysis initiated by UV-A and visible-light irradiation. Emphasis was given on the effect of operating parameters on the degradation effectiveness, such as catalyst type and loading (50 - 500 mg/L), initial drug concentration (10, 40, 80 mg/L) and wavelength of irradiation (200 - 600 nm). In an effort to understand the photocatalytic pathway for CBZ and IBP removal in terms of primary oxidants, the contribution of HO• was evaluated. With this scope, the radical-mediated process was suppressed by addition of an alcohol scavenger, isopropanol, (*i*-PrOH), described as the best free hydroxyl radical quencher. The photodegradation rate of the pharmaceuticals was monitored by high performance liquid chromatography (HPLC). According to the results, visible-light exposure, at λ_{exc} > 390 nm, takes place as a pure photocatalytic degradation reaction for both compounds. IBP was found to have overall high conversion rates, compared to CBZ. IBP oxidized fast under photocatalytic conditions, regardless the adverse effect of the increase of initial drug concentration, or low catalyst load, irradiation upon visible-light, by either titania or zinc oxide. Finally, addition of isopropanol showed a significant inhibition effect on the CBZ degradation, taken as an evidence of a solution-phase mechanism. In the case though of IBP degradation, the hole mechanism may be prevailing, suggested by the negligible effect upon addition of isopropanol indicating a direct electron transfer between holes (h^+) and surface-bound IBP molecules. A plausible mechanism of IBP and CBZ photocatalysis was proposed

*Corresponding author.

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and described.

Keywords

Photodegradation, Carbamazepine, Ibuprofen, Titania Photocatalysis, Zinc Oxide Photocatalysis, Oxidation Pathway

1. Introduction

None can deny how significant is the continuous development and research on the area of synthesis and production of a variety of drugs of pharmaceutical importance for both mankind and animals. However, within the last few years, both the occurrence and fate of pharmaceutical residues and their metabolites in environmental matrices, have attracted scientific interest. These compounds are classified as emerging pollutants, while their main pathway into the environment is pharmaceutical industries, excretory products of medically treated humans and animals followed by their inefficient removal in wastewater treatment plants [1] [2]. They also enter the environment after inappropriate disposal of unused or expired pharmaceuticals in the sewage system or in the garbage. Pharmaceuticals finally end up in the aquatic receiver of the effluent (river, lake or sea) [3] and have been detected in surface and ground waters, sediments, as well as in tap water [4]-[10].

Non-steroidal anti-inflammatory drugs (NSAIDs) are some of the most frequently detected groups of pharmaceuticals in environmental samples, one of the most widely available drugs in the world. The main common characteristic in the NSAID group is the carboxylic aryl acid moiety that provides their acidic properties. Ibuprofen (IBP) belongs to this family of medicines, which is an analgetic drug mainly used for the treatment of rheumatoid arthritis, myoskeletal injuries and fever. Its presence in effluents of wastewater treatment plants in Greece has been reported: 0.05 μg/L were quantified in the effluent of the plant of Heraklion [11] and respectively, average concentration of 12.5 μg/L in the influent and 1.5 μg/L in the effluent was detected at Ioannina [12]. IBP has been reported to have toxic impact on microbial communities [13] and to cause the suspension of growth of L. Minor plants up to 25% [14].

Carbamazepine (CBZ) is a neutral anticonvulsant pharmaceutical, used primarily in cases of epilepsy and bipolar disorder. It is also used as drug of first choice in situations of trigeminal neuralgia and in the treatment of bipolar disorder [15]. CBZ has been reported to be present in the effluent of the wastewater treatment plant of Heraklion at a concentration of 1.03 μg/L [11], while at the plant of Ioannina, it was quantified at 0.8 μg/L in the inflow and at 0.9 μg/l in the effluent [12]. Toxicity studies have concluded that CBZ is associated with early maturation and reproduction of Daphnia, as well as with chronic toxicity on ceriodaphnids [16].

Even though their concentration in the environment is low (ng/L to μg/L), harmful effects may arise from their continuous input, their synergistic toxicity and additive effects because of their presence as mixtures [17]-[19]. The removal of pharmaceuticals with conventional methods turns out to be inadequate [20]-[22] and therefore it has been proposed that further elimination could be achieved by combination of conventional and advanced treatment methods [23]. Towards this direction, advanced oxidations processes (AOPs) and among them heterogeneous photocatalysis, have shown promising results [4] [15] [20] [24], being capable of achieving a complete oxidation of both organic and inorganic species.

TiO_2 together with ZnO are two semiconductors broadly used in heterogeneous photocatalysis to degrade a broad range of pollutants due to their wide band gap, their spectral overlap with sunlight emission (about 5%), biological and chemical stability, low toxicity and reduced cost [20] [25] [26]. Although over the past several years, semiconductor photocatalysis based on titania induced by UV/Vis illumination has experienced many applications, as a promising technology for water purification, it has not yet been extensively employed for pharmaceuticals degradation [16]. Among the latest studies, Martinez *et al*. [20] were the first that developed a detailed kinetic and mechanistic study of the photocatalysed degradation of aqueous CBZ using titania P-25, ZnO and multi-walled carbon nanotubes-anatase composites, under UV and NUV (Near UV) irradiation. Achilleos *et al*. [16] studied the performance of TiO_2 photocatalysis under solar and UV-A for the degradation of CBZ and IBP. In both works, factors such as initial drug concentration, catalyst loading, pH of the solution, type of matrix (pure water and wastewater) and addition of active species, such as H_2O_2, were among the main parameters un-

der investigation, in an effort to determine the optimal photocatalytic conditions.

Mendez-Arriaga *et al.* [24] applied solar photocatalysis at three different pilot-scale installations for the degradation of IBP in a water matrix. They suggest that, IBP, as a pollutant in water at high concentrations, can be degraded in a biological treatment after pre-oxidation by photocatalysis treatment with TiO_2, based on the biodegradability test of the treated IBP solutions. Alternatively, according to Achilleos, *et al.* [16] photocatalysis could be employed as a post-secondary treatment to remove residual drugs, as well as inactivate waterborne pathogens.

AOPs are based on the oxidation of the target pollutant by reactive species. Upon irradiation, the first step in the heterogeneous TiO_2 photocatalysis is the production of electrons $\left(e_{cb}^{-}\right)$ and holes $\left(h_{vb}^{+}\right)$ in the conduction and valence band, respectively (Equation (1)). The photogenerated holes that escape direct recombination (Equations (4) and (5)) reach the surface of TiO_2 and react with surface adsorbed hydroxyl groups (Equation (2), or with water (Equation (3)) to form trapped holes. A trapped hole ($\equiv Ti^{IV}O\bullet$) is usually described as a surface-bound or adsorbed HO• radical ($HO\bullet_{ads}$) [27]-[29]. The HO• generated at the surface of the semiconductor desorbs from the surface and diffuses into the bulk medium to form free HO• ($HO\bullet_{free}$) [30]. If electron donors (Red_{org}) are present at the TiO_2 surface, electron transfer may occur according to Equations (6), (7) and (8). In aerated systems, oxidative species, such as $O_2\bullet^-$ and H_2O_2 generate from the reduction site (Equations (9) to (12)):

$$\text{electron-hole generation: } TiO_2 + h\nu \rightarrow h_{vb}^{+} + e_{cb}^{-} \tag{1}$$

$$\text{hole trapping: } h_{vb}^{+} + \equiv Ti^{IV}OH \rightarrow \left\{\equiv Ti^{IV}HO\bullet\right\}^{+} \rightarrow \equiv Ti^{IV}O\bullet + H^{+} \tag{2}$$

$$h_{vb}^{+} + H_2O \rightarrow H_2O\bullet^{+} \rightarrow H^{+} + HO\bullet \tag{3}$$

$$\text{electron-hole recombination: } h_{vb}^{+} + e_{cb}^{-} \rightarrow \text{heat} \tag{4}$$

$$e_{cb}^{-} + \equiv Ti^{IV}O\bullet + H^{+} \rightarrow \equiv Ti^{IV}OH \tag{5}$$

$$\text{charge transfer at the oxidation site: } h_{vb}^{+} + Red_{org} \rightarrow Ox_{org} \tag{6}$$

$$Ti^{IV}O\bullet + Red_{org} \rightarrow Ox_{org} \tag{7}$$

$$HO\bullet + Red_{org} \rightarrow Ox_{org} \tag{8}$$

$$\text{charge transfer at the reduction site: } e_{cb}^{-} + O_{2(ads)} \rightarrow O_2\bullet^{-} \tag{9}$$

$$O_2\bullet^{-} + e_{cb}^{-} \left(+2H^{+}\right) \rightarrow H_2O_2 \tag{10}$$

$$O_2\bullet^{-} + H_2O_2 \rightarrow HO\bullet + OH^{-} + O_2 \tag{11}$$

$$H_2O_2 + h\nu \rightarrow 2HO\bullet \tag{12}$$

It is therefore accepted that in heterogeneous photocatalysis two oxidative agents can be considered: the photo-produced holes h^+ (mainly involved in the de-carboxylation reaction ("photo-kolbe") and/or the HO• radicals, free or surface-bound, which are known as strongly active and degrading but non-selective agents. Previous research [31]-[33] has pointed out that the rate-determining step of a photocatalytic reaction may be the formation of the HO• since they react very rapidly with aromatic ring compounds. The HO• radicals (either adsorbed or free) are often assumed to be the major species responsible for the photocatalytic oxidative reactions. However, controversy exists over whether direct hole oxidation plays a major role. Early studies reported that the initial photoreaction process appeared to vary according to the model pollutants and experimental conditions. Carboxylic acids, lacking abstractable hydrogens or C-C unsaturation such as trichloroacetic acid and oxalic acid, seemed to be oxidized primarily by valence band holes via a photo-Kolbe process [34]. At pH 3 the initial step of photocatalytic transformation of 2,4-dichlorophenoxyacetic acid was established to be the direct hole oxidation, whereas below and especially above pH 3 it shifted progressively to a hydroxyl-radical-mediated mechanism [27].

The effect of alcohols [27] [35]-[39], such as MeOH, *i*-PrOH and *t*-BuOH (*tert*-butanol), on the photocatalytic

rate has been used to estimate the oxidation mechanism. In a work on adsorption measurements it was found that, in the presence of an alcohol, negligible influence on the adsorption amount of a dye, named Acid Orange 7 (AO7), was observed. The alcohol due to its low affinity to the catalyst surface is expected to compete mainly for HO• radicals rather than the adsorption catalyst sites [35] [40]. Despite the contributions from a number of research groups, detailed mechanisms of the photocatalytic oxidation processes have not yet been determined and further studies are still essential.

The aim of this work was to study the degradation of two pharmaceuticals, CBZ and IBP, in an aqueous matrix by TiO_2 (P-25) and ZnO photocatalysis, initiated by UV-A and, most importantly, visible-light irradiation. Emphasis was given on the effect of operating parameters on the degradation effectiveness, such as catalyst type and loading, initial drug concentration and wavelength of irradiation. Furthermore, the contribution of HO• to the photooxidation mechanism for the pharmaceutical removal was evaluated. To achieve this goal, we suppressed the HO• radical-mediated process by addition of an alcohol scavenger, isopropanol [*i*-PrOH]. Isopropanol has been described as the best hydroxyl radical quencher due to its high-rate constant reaction with the radical (1.9×109 $L \cdot mol^{-1} \cdot s^{-1}$) [34]. In conclusion, in the present study, a plausible mechanism of IBP and CBZ photocatalysis was proposed and described in details.

2. Materials and Methods

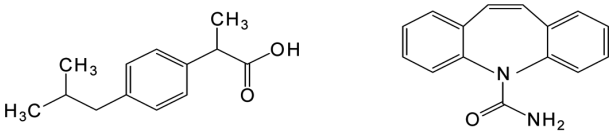
2.1. Chemicals

IBP and CBZ, both of 99% purity, were purchased from Sigma Aldrich and used as received. Their molecular structures are presented in **Scheme 1**, while their main properties are shown in **Table 1**. The catalysts, Aeroxide TiO_2 P-25 (a non porous 75:25 (w/w) mixture of anatase: rutile) and ZnO nanopowder were supplied by Degussa AG and Sigma Aldrich, respectively. According to the manufacturer data, properties of the two catalysts are given in **Table 2**. Milli-Q water was obtained from a Millipore apparatus with a resistivity of 18.2 $mOhm \cdot cm^{-1}$ at 298 K. Acetonitrile was supplied by Panreac, isopropanol by Fischer Scientific and potassium dihydrogen phosphate was obtained by Merck. Experiments were carried out at the natural pH corresponding to aqueous solutions of CBZ and IBP, *i.e.*, pH at ca. 6 and 4 respectively, which did not change significantly during the process. For CBZ, the given isoelectric point reported in literature is ca. 7, while for IBP is 4.9, both compatible with their recorded natural solution pH.

2.2. Photolytic and Photocatalytic Experiments

Aqueous solutions of each pharmaceutical were prepared by addition of the appropriate amount of the drug (10, 40 and 80 mg/L) to 500 mL deionised water. For detection and quantification purposes, the range of concentrations in this study is higher than those typically detected in the environment. In the experiments conducted for the evaluation of the contribution of hydroxyl radicals to the photocatalytic degradation, isopropanol, which is a well known hydroxyl radical scavenger, was added to the solution. An amount of isopropanol (1.62 mL for CBZ and 1.85 mL for IBP) was added at the beginning of the photocatalytic reaction, at a molar concentration 10^3 times higher than the initial concentration of the pharmaceuticals.

For the photocatalytic experiments, a metal oxide semiconductor catalyst, namely TiO_2 or ZnO, was added to the solution and maintained in suspension by magnetic stirring. A series of experiments were run varying catalyst concentration from 50 to 500 mg/L for each pharmaceutical. Each time, the suspension was first stirred in the dark for *ca*. 40 min, to ensure establishment of adsorption/desorption equilibrium. For the initiation of the photocatalytic experiment, light was allowed to irradiate the reactor. In the case of photolysis, no catalyst was added to the solution. The progress of the photochemical and photocatalytic drug removal as a function of time was monitored periodically by withdrawing aliquot from solution/suspension with a help of a pipette. With-



(a) (b)

Scheme 1. Chemical structures of (a) IBP and (b) CBZ.

Table 1. Main properties of the pharmaceuticals used.

Property	Ibuprofen	Carbamazepine
Therapeutic group	NSAIDs	Antiepileptic
Molecular formula	$C_{13}H_{18}O_2$	$C_{15}H_{12}N_2O$
Molecular weight	206.3	236.3
Solubility in water (mg/mL)	0.041 (25˚C)	0.17 (25˚C)
pKa	4.9	7
Type	Anionic	Cationic

Table 2. Main properties of the applied catalysts (manufacturer data).

Property	Titania-P25	Zinc oxide
Energy gap (eV)	3.20	3.37
BET surface (m^2/g)	55 ± 15	20 ± 5
Mean particle size (nm)	21	100
pH_{pzc}	6.8	9 ± 0.3

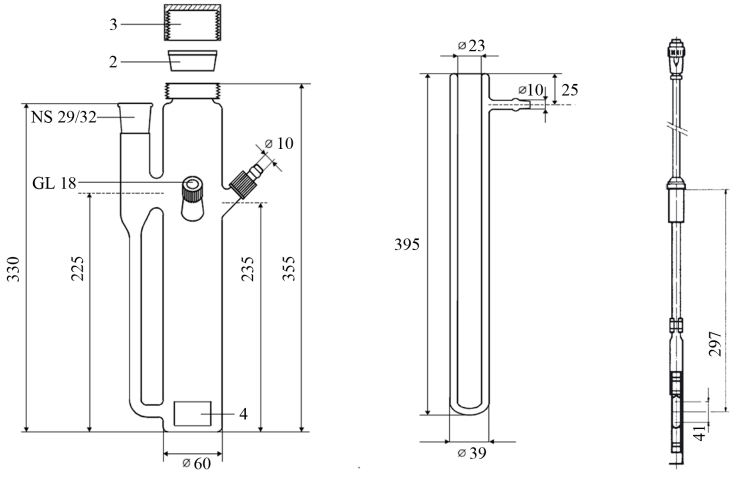
drawn samples as required were filtered with 0.22 mm filters to remove catalyst particles prior to analysis. The first sample was taken at the end of the dark adsorption period, just before light irradiation, in order to determine the concentration of the compound in solution, which was hereafter considered as the initial concentration [C_0].

2.3. Photoreactor and Light Source

The photocatalytic degradation of the two pharmaceuticals was carried out in a specially designed photocatalytic reactor provided by Heraeus (Noblelight GmbH, Hanau-Germany), equipped with a light source (**Scheme 2**). The borosilicate glass reactor of diameter 1 - 1.5 cm and 500 mL capacity were made with ports for sampling and gas/air purge. The irradiation was provided by a medium pressure mercury lamp (TQ 150), keeping a constant power at 150 W, with an emission spectrum of 200 - 600 nm, and λ_{max} at 365 nm. The lamp was mounted axially in the reactor inside a cylindrical, double walled lamp jacket. The UV-A experiments were run using a lamp jacket made of quartz, while the visible-light experiments were conducted with a M380 glass jacket, which filtered out the UV lines at λ_{exc} < 390 nm, limiting the irradiation near to the visible-light spectrum. Light intensity in the reactor was 58 - 60 mW/cm^2 in the UV experiments, while for the visible-light transmission runs it was ~31 mW/cm^2. Photocatalytic experiments were carried out at a constant stirring speed (600 rpm) insured by a magnetic stirrer at the reactor basis, at a constant temperature maintained by water circulating in the double walled lamp jacket.

2.4. Analytical Technique

The photodegradation of the pharmaceuticals was followed by HPLC, where the filtered transparent solution samples were analysed for the detection of IBP & CBZ compounds in solution, using a Hewlett Packard 1100 system, equipped with a G1315A diode array detector (DAD). The analytical column was a Hypersil BDS C8 (250 mm × 4 mm × 5 μm) from Thermo Electron, thermostated at 35˚C. Analytes were separated by gradient elution with ACN (A) and a 25 mM potassium dihydrogen phosphate solution (B) at a flow-rate of 1.2 ml/min. The gradient elution was as follows: 0 min, 15% A; 5 min, 15% A; 15 min, 70% A; 18 min, 15% A. The DAD signal was set at 288 nm for CBZ and 225 nm for IBP and peak areas were used for the quantification of each pharmaceutical. According to a review work by Munoz *et al.* [41], HPLC is a reliable and inexpensive method, for the determination of the most common pharmaceutical compounds, in influent and effluent wastewater and surface water.



Scheme 2. Photoreactor set up by Heraeus Noblelight GmbH, Hanau-Germany.

3. Results and Discussion

3.1. Photocatalytic Degradation of CBZ & IBP

The photochemical and photocatalytic degradation of the two tested drugs, CBZ and IBP in aqueous matrices, was investigated using UV-A and visible-light irradiation sources. The type and catalyst load, together with the initial drug concentration effect were assessed as fundamental operational parameters in heterogeneous photocatalysis.

For CBZ aquatic solution, the pH was 6.0, less than the point of zero charge of the TiO_2 (6.8 for P-25) and ZnO (9 ± 0.3), leaving the surface of the catalysts slightly electropositive. In the case though of aquatic IBP solution, pH recorded to be 4, meaning that the charge-character of the catalyst surface in this solution was strongly electropositive.

Control experiments under otherwise identical conditions showed that no degradation was observed when the experiments were conducted in the dark or in the absence of the semiconductor. Therefore, both UV light and catalyst were indispensable for the pharmaceuticals degradation. From the dark period measurements, the adsorption extent of approximately 10% was observed for CBZ, same as in the case of IBP, indicating that a fraction of nearly 10% of each drug was adsorbed on either TiO_2 or ZnO surface because of the electrostatic attractions. Beginning with the assumption that the Langmuir model is strictly followed, that is the adsorption-desorption process approaches the equilibrium, the surface of the catalyst is homogeneous, the different active adsorption sites on the surface are equivalent, while a single layer of drug molecule is formed onto the surface, the kinetic would be accounted as a pseudo-first order model [3] [20]. The kinetic rate constants k for all experiments are introduced in separate tables (**Tables 3-9**) for each parameter examined, as calculated from the first-order equation:

$$\frac{dC}{dt} = -kC$$

where, C is the drug concentration, k is the rate constant, and t is the reaction time.

By integrating the equality, the following equations were obtained:

$$\frac{\ln C_t}{C_0} = -kt$$

where, C_t is the drug concentration at time t, and C_0 is the initial drug concentration.

The logarithmic plots of the normalized drug concentration with time gave a straight line. The regression coefficient of the linear fitting, R^2 was greater than 0.97 in all cases.

Drug photocatalytic efficiency, indicated by the decrease of initial concentration, in each case was assessed by HPLC measurements at the indicated irradiation times.

3.1.1. Effect of the Initial Drug Concentration

Heterogeneous photocatalysis depends on the initial concentration of the organic substrate [20] [42], having a controlling effect on the photocatalytic performance. There is a critical value that the initial concentration of the organic pollutant must not exceed, because then the rate of its degradation will drastically decrease. As the initial concentration of the pollutant increases, the path length of photons entering the solution decreases, due to retardation in light penetration [32]. Further, as the initial drug load increases, the requirement of catalyst surface needed for the degradation also increases. Since illumination and amount of catalyst are constant, the hydroxyl radicals attacking the CBZ molecule decrease with an increase in drug concentration.

In this work, in order to test the effect of the initial drug load on the photocatalytic rate, two different concentrations of CBZ (10 and 80 mg/L) and IBP (10 and 40 mg/L) were tested, irradiated under UV light in the presence of 100 mg/L catalyst. As pharmaceuticals have only been traced in environmental samples within a concentration range of μg/L, or even less in the case of ibuprofen, assessment of drug photodegradation at higher loadings is impractical and of no actual interest.

As seen in **Figure 1** the percentage removal of CBZ decreased radically with increasing initial solute concentration. It was calculated that 96% of the initial 10 mg/L CBZ is removed after 30 min of irradiation, when 100 mg/L of TiO_2 P-25 is used as a catalyst, while 93% in the case of ZnO. However, when the initial CBZ load increased to 80 mg/L, the UV irradiation time required for same amount drug removal by either catalysts radically increased, to the level of 3 h.

In the case of IBP, the initial 10 mg/L load resulted in an overall fast-rate catalysis, *i.e.*, in ca. 10 min of UV irradiation in the presence of 100 mg/L of TiO_2, almost all drug was removed, with similar findings for ZnO assisted catalysis (**Figure 2**). Interestingly, for this drug, increasing its initial concentration to 40 mg/L a profound drop in the overall rate was not observed, as in this time, keeping the same catalyst load (100 mg/L) it takes only a time-delay of 15 min, for the IBP removal. Rate constants for the tested drug degradation are given in **Table 3**, **Table 4**.

3.1.2. Effect of Catalyst Load

A series of experiments by many different works [16] [20] [24] [31] [32] have shown a strong dependency of catalyst loading on the rate of photodecomposition of organic pollutants. All findings are in good agreement with an optimal load value under which the rate of degradation increases linearly with catalyst load, but above which the rate drops drastically, assuming a constant initial solute concentration. This threshold loading depends on the reactor geometry and operating conditions, as well as the initial substrate concentration [16].

In this work, the concentration of TiO_2 (P-25) and ZnO in the suspension was varied between 50 and 500 mg/L to test the catalyst load effect on the degradation of each pharmaceutical, keeping its initial concentration each time constant (10 mg/L). **Figures 3-6** present the $[CBZ]_0$ and $[IBP]_0$ removal-time profiles of each drug with each catalyst at different loadings. In **Table 5** and **Table 6** the rate constants for the linear fit of the data are provided.

As shown in **Figures 3-6** for the same drug solute concentration (that of 10 ppm of either CBZ or IBP), increasing in each case the amount of catalyst in suspension from 50 to 500 mg/L, of both P-25 & ZnO, the rate of

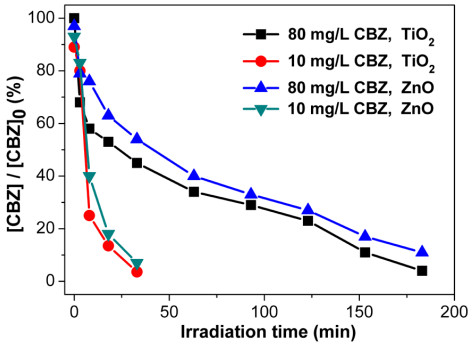


Figure 1. Effect of the $[CBZ]_0$ on the photocatalytic degradation, comparing two different initial concentrations (10 & 80 mg/L) of the drug, under UV irradiation, $[TiO_2] = [ZnO] = 100$ mg/L.

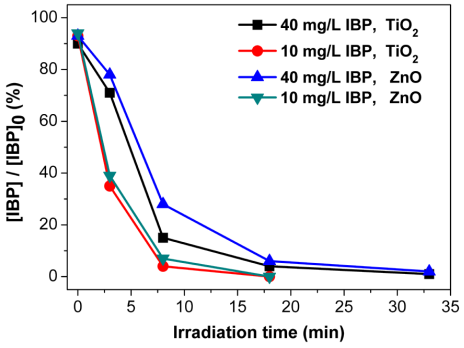


Figure 2. Effect of the $[IBP]_0$ on the photocatalytic degradation, comparing two different initial concentrations (10 & 40 mg/L) of the drug, under UV irradiation, $[TiO_2] = [ZnO] = 100$ mg/L.

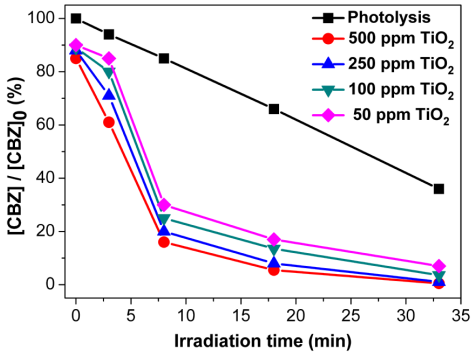


Figure 3. Effect of P-25 TiO_2 loading on CBZ degradation upon UV irradiation: % removal-time profiles at $[CBZ]_0 = 10$ mg/L and various catalyst loadings.

Table 3. Apparent first-order rate constants for aqueous CBZ degradation upon UV-A irradiation at different initial drug concentrations $[TiO_2\text{-P25}] = [ZnO] = 100$ mg/L.

[CBZ] (mg/L)	k_1 (min^{-1}) × 10^{-3} (TiO_2)	k_2 (min^{-1}) × 10^{-3} (ZnO)
10	97	81
80	14	11

Table 4. Apparent first-order rate constants for aqueous IBP degradation upon UV-A irradiation at different initial drug concentrations $[TiO_2\text{-P25}] = [ZnO] = 100$ mg/L.

[IBP] (mg/L)	k_1 (min^{-1}) × 10^{-3} (TiO_2)	k_2 (min^{-1}) × 10^{-3} (ZnO)
10	382	326
40	139	122

the photocatalytic process increases, indicating the importance of available catalyst surface (higher number of active sites) for adsorption-degradation on the surface of the particle, upon UV illumination. However, the rate from 250 to 500 mg/L gradually slows down, pointing that the optimal adsorption of efficient photons has been nearly reached. Higher amount of the catalyst may not be useful both in view of possible aggregation, as well as reduced irradiation field. Above a limit value, the increase in turbidity of the solution reduces the light transmission through the solution. In addition to this, at high solid concentration, there is a loss in surface area available for light-harvesting for the generation of h^+/e^- pairs, occasioned by agglomeration (particle-particle interactions). Finally, part of the originally activated TiO_2 may also be deactivated through collision [20] [43].

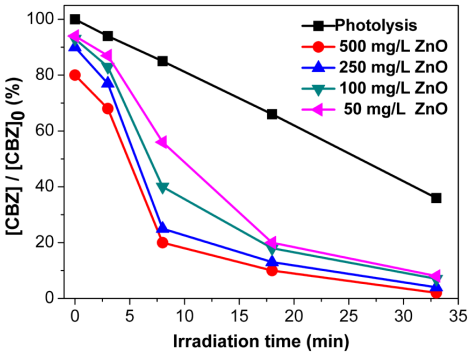


Figure 4. Effect of ZnO loading on CBZ degradation upon UV irradiation: % removal-time profiles at $[CBZ]_0$ = 10 mg/L and various catalyst loadings.

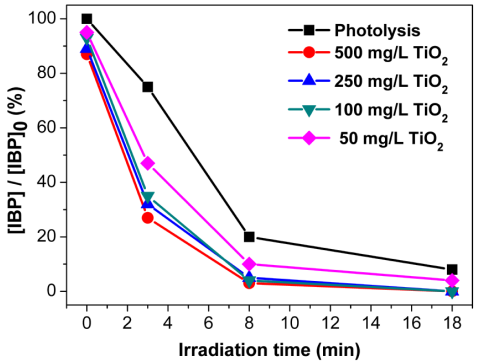


Figure 5. Effect of P-25 TiO_2 loading on IBP degradation upon UV irradiation: % removal-time profiles at $[IBP]_0$ = 10 mg/L and various catalyst loadings.

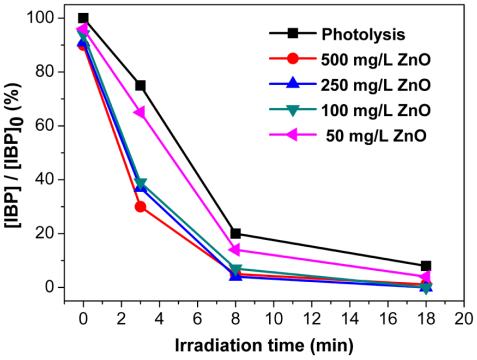


Figure 6. Effect of ZnO loading on IBP degradation upon UV irradiation: % removal-time profiles at $[IBP]_0$ = 10 mg/L and various catalyst loadings.

In the case of IBP photodegradation, the important observation is that the rates for both catalysts are significantly higher for all different catalyst loadings, with a complete conversion of the chemical to take place almost at half time than in the case of CBZ, *i.e.*, within 15 min nearly all of the initial IBP concentration was already removed from solution under UV-A irradiation.

3.1.3. Effect of Catalyst Type

In **Figure 7** and **Figure 8**, the catalyst type effect can be described comparing the two catalysts used in this

Table 5. Apparent first-order rate constants for aqueous CBZ degradation upon UV-A irradiation under different type and catalyst loadings ($[CBZ]_0$ = 10 mg/L).

$[TiO_2]$ (mg/L)	$k_1 \times 10^{-3}$	[ZnO] (mg/L)	$k_2 \times 10^{-3}$
zero (photolysis)	31	zero (photolysis)	31
50	78	50	75
100	97	100	81
250	133	250	94
500	155	500	113

Table 6. Apparent first-order rate constants for aqueous IBP degradation upon UV-A irradiation under different type and catalyst loadings ($[IBP]_0$ =10 mg/L).

$[TiO_2]$ (mg/L)	$k_1 \times 10^{-3}$	[ZnO] (mg/L)	$k_2 \times 10^{-3}$
zero (photolysis)	140	zero (photolysis)	140
50	175	50	181
100	382	100	326
250	390	250	366
500	422	500	390

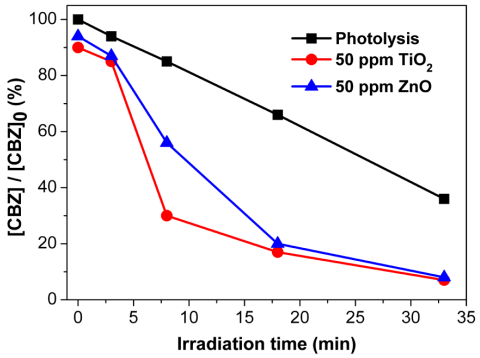


Figure 7. Effect of TiO_2-P25 compared with ZnO on CBZ degradation % removal-time profiles at $[CBZ]_0$ = 10 mg/L and catalyst loading of 50 mg/L.

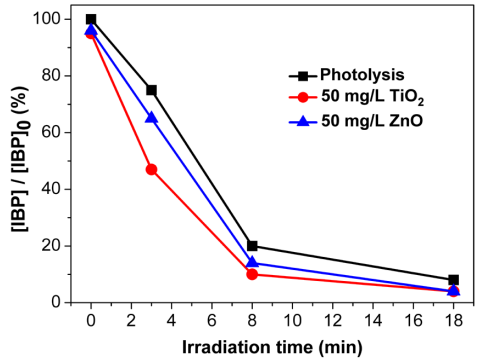


Figure 8. Effect of TiO_2-P25 compared with ZnO on IBP degradation % removal-time profiles at $[IBP]_0$ = 10 mg/L and catalyst loading of 50 mg/L.

study, at the same load, for the degradation of the same initial amount of the tested drugs. Even though a similar trend was overall observed for both P-25 and ZnO loadings, **Figure 7** points out that at a catalyst concentration of 50 mg/L, at the early stages of CBZ degradation, P-25 is significantly more reactive, recording a 70% drug removal in the first 7 min of UV irradiation, versus a 40% drug removal when ZnO is tested. This observation can be attributed to factors, such as: 1) the ca. 0.2 eV difference in gap energies between valence and conduction bands; 2) the expected different adsorption behavior of both semiconductors toward CBZ, due to the different catalyst surface charge, dependent on the solution pH, and the different characteristics of each catalyst (surface area, size, morphology). It must be mentioned that the P-25 type is concerned to be the most reactive among the different TiO_2 phases, which has frequently been used as a benchmark for photocatalysis [44]. Commercial P-25, consists of a mixture of 75% anatase and 25% rutile phase with a surface area of ca. 55 m^2/g^{-1} (of mean diameter, 21 nm) in comparison to the one of 20 m^2/g^{-1} (of mean diameter, 100 nm) of ZnO. This allotropic form of titanium dioxide has an unusual microstructure, within which anatase and rutile particles can interact with a synergetic effect [45]. The increase in charge-separation efficiency, resulting from interfacial electron-transfer at the interface between anatase and rutile, increases its photocatalytic activity [46] [47].

However, after the high initial photocatalytic rate for TiO_2, a steady state follows, with both catalysts reaching after 30 min the same level of CBZ photodegradation (that of 90%).

In the case of IBP photodegradation, as seen in **Figure 8**, kinetics are generally fast for both catalysts, with a same overall trend, but again a slightly better removal efficiency was observed when titania-P25 was used as a catalyst.

3.1.4. Effect of the Irradiation Source: UV-A vs Visible-Light

The effect of the irradiation wavelength on the rate of degradation of CBZ and IBP pharmaceuticals was studied, using UV-A and visible-light irradiation. **Figure 9** & **Figure 10** show the photolysis results obtained for both CBZ and IBP water matrices, while **Table 7**, **Table 8** present the rate constants in each case. In the absence of any photocatalyst, spectral changes are observed from the early stages of UV-A irradiation, recording a 60% removal of the initial CBZ after almost 30 min of irradiation. For IBP, UV-A photolysis presented a much better efficiency, *i.e.*, within 15 min nearly 90% of the initial chemical is already converted. On the other hand, when the irradiation source is visible-light, CBZ degradation is negligible, the same as for IBP.

Figure 9 & **Figure 10** also present the photocatalytic degradation of CBZ and IBP upon UV-A and visible-light irradiation for the two types of catalyst tested. As seen, when catalyst, (100 mg/L), either TiO_2 (P-25) or ZnO is added, over 90% removal of CBZ is achieved in 30 min with rate constants, *k*, computed as 0.097 min^{-1} and 0.081 min^{-1} under UV-A light, in comparison to ca. 80% CBZ conversion under visible-light irradiation, with k equals to 0.057 min^{-1} for TiO_2 and 0.049 min^{-1} for ZnO. For IBP, again catalysis is significantly faster, as within only 8 min over 90% of the drug has already converted, with k equals to 0.382 and 0.326 min^{-1}, for TiO_2 and ZnO respectively, slowing down to 0.199 and 0.144 min^{-1} when irradiation was changed to visible-light.

Having that UV-A assisted photodegradation (photolysis) of CBZ and IBP is significant, especially for the reactive IBP (*k* of 0.140 min^{-1}), it may be assumed that conversion of the chemicals cannot work in a pure photocatalytic regime, meaning that the use of any catalyst works in addition to photolysis, so as to improve the rate

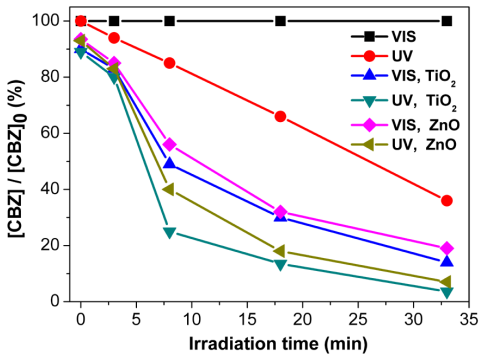


Figure 9. Comparison of CBZ degradation upon irradiation with UV versus Vis light, in the presence and absence of photocatalyst, $[CBZ]_0$ = 10 mg/L; [TiO_2-P25] = [ZnO] = 100 mg/L.

Table 7. Apparent first-order rate constant for aqueous CBZ degradation upon different irradiation source (UV-A, Vis.) $[CBZ]_0$ = 10 mg/L; $[TiO_2$-P25] = [ZnO] = 100 mg/L.

Lamp	Catalyst	k (min^{-1}) × 10^{-3}
UV-A	none	31
	TiO_2	97
	ZnO	81
Vis	none	0
	TiO_2	57
	ZnO	49

Table 8. Apparent first-order rate constant for aqueous IBP degradation upon different irradiation source (UV-A, Vis.) $[IBP]_0$ = 10 mg/L; $[TiO_2$-P25] = [ZnO] = 100 mg/L.

Lamp	Catalyst	k (min^{-1}) × 10^{-3}
UV-A	none	140
	TiO_2	382
	ZnO	326
Vis	none	0.73
	TiO_2	199
	ZnO	144

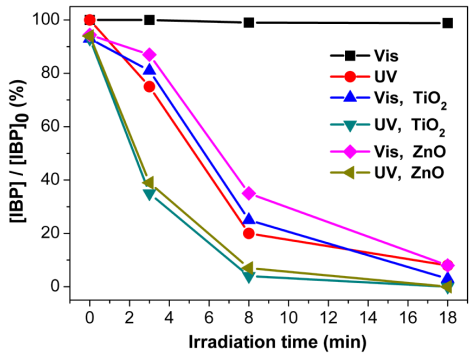


Figure 10. Comparison of IBP degradation upon irradiation with UV versus Vis light, in the presence and absence of photocatalyst, $[IBP]_0$ = 10 mg/L; $[TiO_2$-P25] = [ZnO] = 100 mg/L.

and the extent of the overall process. However, under visible-light exposure, where photolysis is negligible, the use of catalysts is most crucial for drug degradation.

3.1.5. Effect of Isopropanol (*i*-PrOH) Addition

In the photocatalytic degradation, one of the main uncertainty is whether oxidation proceeds via direct electron transfer between substrate and positive holes, or via an HO• radical-mediated pathway. As direct oxidation of short aliphatic alcohols by photogenerated holes may be considered negligible, having a very weak adsorption power on TiO_2 surface in aqueous media, alcohols are usually used as a diagnostic tools of HO• radicals mediated mechanism [34]. The contribution of hydroxyl radicals to the photocatalytic degradation of CBZ and IBP was evaluated by addition of isopropanol at a molar concentration of 10^3 times higher than the initial concentration of 10 mg/L of the pharmaceutical. The diffusing hydroxyl radicals (desorbed from the catalyst surface, where were formed by the reaction of holes (h^+) with adsorbed OH^-/H_2O) would be scavenged by excess iso-

propanol in the solution, and the influence in the reaction rate would suggest the extent of HO• participation in the removal mechanism.

The addition of isopropanol to the solution containing CBZ in the presence of TiO_2, irradiated with simulated UV light, modifies the reaction course. Due to its low affinity to the TiO_2 surface, isopropanol was expected to compete mainly for HO• radicals [34] [35] [40], by which it is easily oxidized. **Figure 11** shows the strong influence in the CBZ removal efficiency upon the presence of isopropanol, *i.e.*, the 80% removal with no addition dropped to 35% within only 15 min of photocatalysis when the alcohol was added. The result overall suggests the important contribution of free hydroxyl radicals in the reaction mechanism.

In the case where the reaction is catalysed by ZnO, the effect of HO• scavenger is also pronounced (**Figure 11**), indicating again that hydroxyl radicals probably play determinant role in CBZ photooxidation. This result is concordant with the mechanism proposed by Daneshvar *et al*. [48] where small amounts of ethanol inhibited the photocatalytic degradation of an azo dye (Acid Red 14, AR14) on ZnO.

In the current work, after addition of the HO• scavenger (*i*-PrOH) the rate constant k, for the photodegradation of $[CBZ]_0$ of 10 mg/L catalysed by TiO_2, dropped from 0.097 to 0.016 min^{-1}, while from 0.081 to 0.022 min^{-1} in the case of ZnO. Degradation kinetics are well described by a pseudo-first-order model (R^2 = 0.98) (see **Table 9**). For the first 5 minutes since the onset of the irradiation time, initial reaction was slow (despite the presence or absence of the hydroxyl scavenger), possibly owing to the time that takes for the formation of the surface-bound hydroxyl radicals ($HO•_{ads}$) on the catalyst surface and their diffusion into the bulk solution, to react with the alcohol (in alcohol addition) or to participate in a series of hydroxylation reactions for the initial molecule break down (in case of no addition).

However, in the case of IBP degradation, **Figure 12** shows that after the addition of isopropanol the degradation rates decreased but not drastically, indicating this time the minimal alcohol inhibitory effect. In other words, in this case, the results suggested that HO• radicals played a minor role during photocatalytic oxidation and that the hole (h^+) mechanism may then be prevailing. The finding is in agreement with another study [34] on the photocatalytic oxidation of AO7 where after addition of isopropanol (*i*-PrOH) in air equilibrated TiO_2 suspension, the degradation rate only slightly decreased concluding that *i*-PrOH had little influence on the photodegradation of the tested dye.

Comparing the above results observed for IBP versus CBZ degradation process, it could be suggested in a word that the degradation of IBP seems to be a result of a hole-dominated surface reaction, while in the case of CBZ the initial process is shifted to a homogeneous radical reaction in the bulk solution. In the following section a possible drug degradation mechanism based on this suggestion is described.

3.1.6. Proposed Reaction Mechanism for the Photocatalytic Drug Removal

The hydroxyl radicals, strongly active and degrading, react very rapidly with aromatic ring compounds [31] [32], such as in the CBZ molecule, resulting in a series of hydroxylation—dehydroxylation reactions, followed by the ring opening and the step by step breakdown of the initial molecule. However, in the case of IBP photocatalytic process, the hydroxyl radicals showed to have only slight contribution to the initial molecule conversion upon

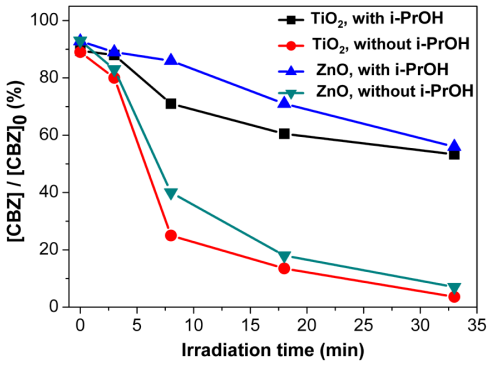


Figure 11. Effect of *i*-PrOH on degradation rates of CBZ in aqueous TiO_2 and ZnO suspensions, $[CBZ]_0$ = 10 mg/L; $[TiO_2]$ = [ZnO] = 100 mg/L.

Table 9. Apparent first-order rate constant for aqueous CBZ and IBP degradation upon UV-A irradiation, under addition of isopropanol $[CBZ]_0 = [IBP]_0 = 10$ mg/L; $[TiO_2\text{-P25}] = [ZnO] = 100$ mg/L.

Aqueous matrix	k_1 (min^{-1}) × 10^{-3} (for TiO_2)	k_2 (min^{-1}) × 10^{-3} (for ZnO)
CBZ without addition	97	81
CBZ + *i*-PrOH	16	22
IBP without addition	382	326
IBP + *i*-PrOH	160	215

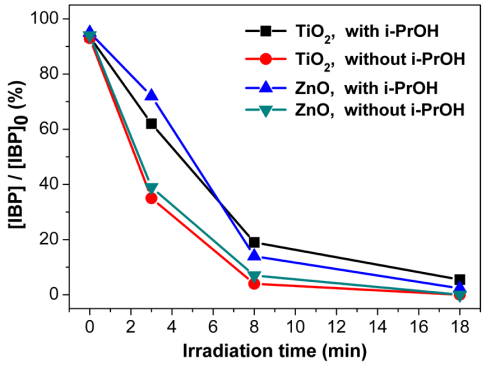


Figure 12. Effect of *i*-PrOH on degradation rates of IBP in aqueous TiO_2 and ZnO suspensions, $[IBP]_0 = 10$ mg/L; $[TiO_2] = [ZnO] = 100$ mg/L.

UV irradiation. IBP having a more open chemical structure with only one aromatic ring and carboxyl in its structure, may be oxidised preferentially by the photogenerated holes, mainly involved in the decarboxylation reaction ("photo-kolbe"), rather than by the non selective HO• radicals. Arriaga *et al*. [24] state in their work that high oxidation levels can be assured by direct decarboxylation avoiding the hydroxylation step. In the same work though, it is suggested that in the presence of excess hydroxyl radicals, such as in aerated conditions, IBP acts more efficiently as a scavenger of those hydroxyl radicals and diminishes almost totally its concentration by the hydroxylation process.

According to the overall experimental findings in this study and a general literature review on photocatalytic processes, a proposed mechanism of IBP-TiO_2 catalysis may be described as follows: The anionic IBP molecules under acidic conditions (pH of solution ca. 4) are first adsorbed on the cationic TiO_2 surface (the IBP molecule is linked to the Ti surface metallic cation through one oxygen atom of carboxyl group) where the degradation reaction is mostly initiated by the direct electron transfer reaction between a positive hole and a surface-bound IBP molecule. The Ti-O bond has a relatively high covalent character, and the oxygen atoms of IBP, being relatively strong electron donors, are able to direct interact with valence band photogenerated holes. As the valence band hole migrates to the surface, it is primarily captured by the adsorbed IBP molecules, rather than by the adsorbed water or hydroxyl groups, testified by the fast initial drug removal. Of course, the photo-produced HO• ads/free could not be excluded, attacking as well the drug molecule, but their role in the degradation process would not be the major one, and certainly not the one to initiate the oxidation reaction, as the process proceeds with a fast rate in their absence too (see **Table 9**).

It must though be clear that the deduction to this theory is valid for an aqueous matrix, given the specific experimental conditions, where there is not: 1) any catalyst surface modification in process (either by the presence of a hole scavenger, such as iodide, and/or by the presence of surface site inhibitors, such as F^- or SO_4^{2-}); 2) saturation/supply of dissolved oxygen (due to higher hydroxyl radical concentrations that would be then able to react), as could be the case in environmental aerated water matrices.

The mechanism proposed in this paper unifies literature findings for the photodegradation of organic pollutants by titania semiconductor photocatalysis [20] [34]. Nevertheless, semiconductor photocatalysis varies upon the different experimental conditions, as its character is multivariant, controlled by several parameters, which have an either synergistic or antagonistic effect to the overall process.

4. Conclusions

The degradation of two typical pharmaceuticals, Carbamazepine (CBZ) and Ibuprofen (IBP), was studied by means of the two most common type commercial photocatalysts, TiO_2 (P-25) and ZnO using both UV-A and visible-light irradiation. Operational parameters, such as type and catalyst loading and initial drug concentration were complementary assessed. To complete this study, the oxidative role of the photocatalytically generated hydroxyl radicals in the bulk solution was investigated by addition of isopropanol scavenger. The main remarks are summarized as follows:

- In the case of irradiation under visible-light, the contribution of the photochemical degradation for both pharmaceuticals tested is negligible and hence it can be assumed that catalysis in visible-light exposure takes place as a pure photocatalytic degradation reaction (photocatalytic regime).
- Regarding the pharmaceuticals, IBP photocatalytic conversion was found to be overall faster in relation to CBZ, in the presence of either P-25 or ZnO catalyst, under either UV or visible light, indicating that it is highly reactive especially under photocatalytic conditions.
- Comparing the catalysts, TiO_2 (the type of P-25) showed generally better photocatalytic efficiency in the degradation of both pharmaceuticals compared to ZnO.
- Addition of isopropanol (HO• quencher) showed a significant inhibition effect on the CBZ degradation, taken as an evidence of a solution-phase mechanism. In the case though of IBP degradation, the negligible effect upon addition of isopropanol drives to the conclusion that a direct electron transfer between holes and surface-bound IBP molecules dominates the degradation pathway, *i.e*., the hole mechanism may be prevailing. A plausible photocatalytic mechanism was proposed and described in details.

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