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UV-A and Solar Photodegradation of Ibuprofen and Carbamazepine Catalyzed by TiO_2

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The objective of this study was to investigate the efficiency of solar and UV-A photocatalysis with suspended TiO_2 to degrade ibuprofen and carbamazepine in aqueous matrices. Emphasis was given on the effect of various operating conditions such as catalyst type (six commercially available titanium oxide samples were tested) and concentration (50–3000 mg/L), initial drug concentration (5–20 mg/L), solution pH (3–10), the addition of hydrogen peroxide (0.07–1.4 mM), and the matrix (pure water and treated domestic wastewater) on degradation and mineralization. The former was assessed monitoring sample absorbance at each drug's characteristic wavelength, while the latter measuring dissolved organic carbon. The best performance was achieved at lower drug concentrations irradiated by UV-A in the presence of Degussa P25 catalyst and hydrogen peroxide in pure water.

Keywords carbamazepine; ibuprofen; pharmaceuticals; photocatalysis; wastewater

INTRODUCTION

The occurrence of pharmaceuticals residues in the environment has been frequently reported in the literature, receiving increasing attention as an emerging environmental problem (1,2). Although pharmaceutical residues are present at low levels in the aquatic environment, their continuous input into the environment is characterized as persistence and may result in toxic effects. The main source of such compounds is the excretion in urine or feces, both in unchanged form and as metabolites due to the incomplete absorption in humans and veterinary medicine.

Most frequently, conventional treatment processes applied at domestic wastewater treatment plants fail to remove completely pharmaceutical substances. Therefore, the integration of conventional wastewater treatments with advanced technologies has become of great interest (3).

In recent years, photocatalysis has gained considerable attention due to its ability to degrade a wide class of pollutants. Irradiating aqueous TiO_2 suspensions with photons with energy greater than the band gap of titanium oxide (i.e., 3.2 eV) results in the generation of a charge carrier pair (e^-/h^+), which eventually leads to the formation of strong oxidants, such as hydroxyl radicals and superoxide radical anions (4).

The preference to use solar or UV lamps as the irradiation source depends largely on illumination intensity and the cost of the light-producing or light-collecting equipment. Solar photochemical systems are based on the collection of only high-energy short-wavelength UV or near UV sunlight (300–400 nm) to promote photochemical reactions especially with TiO_2 as the catalyst (5). Solar systems have been used with much success for the degradation of both common water pollutants and pharmaceuticals and endocrine disrupting compounds (EDCs) with reaction rates comparable to UV lamp systems (6).

The limited part of the solar spectrum (<400 nm) that can be used in photocatalysis with TiO_2 can be a disadvantage (7). Since titanium dioxide has a wide band gap of 3.2 eV only light below 400 nm is absorbed and capable of forming the e^-/h^+ pairs necessary for the heterogeneous photocatalytic decomposition. More importantly, in solar applications where only less than 5% of the solar energy reaching the surface of the earth can be used, it is crucial to avoid any loss of the solar irradiation needed for the photoexcitation of TiO_2. This means that the whole system, including light collectors, reactor materials, pollutant solutions, and even the dispersion state of the photocatalyst itself have to be tested and optimized (8).

Non-steroidal anti-inflammatory drugs (NSAIDs) are a special group of widely available pharmaceuticals that are often found in waters and wastewaters. Ibuprofen (IBP), a typical NSAID, is prescribed for skeletal-muscle pain and inflammatory rheumatic disorders. It is also used for analgesic and antipyretic purposes (9). The main common

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characteristic of NSAIDs is the carboxylic aryl acid moiety that provides their acidic properties (10). In this view, NSAIDs are commonly detected at the outlets of domestic wastewater treatment plants and in the receiving aquatic bodies since their biodegradation and/or natural attenuation are limited (11).

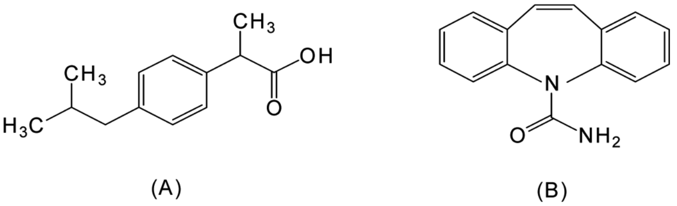
Carbamazepine (CBZ) is an anticonvulsant and mood stabilizing drug used primarily in the treatment of epilepsy and bipolar disorder. It is also used to treat schizophrenia, phantom limb syndrome, paroxysmal extreme pain disorder, and trigeminal neuralgia.

The aim of this work was to study the degradation and mineralization of IBP and CBZ in aqueous matrices by means of TiO_2 photocatalysis initiated by UV-A and simulated solar irradiation; emphasis was given on the effect of operating conditions such as titanium oxide type and loading, initial drug concentration, solution pH, the addition of hydrogen peroxide, and the water matrix (i.e., pure water and domestic wastewater) on the kinetics of pharmaceuticals degradation. The aim of this work was to investigate in a systematic way the effect of the various operating conditions, something that has not been carried out for the particular compounds so far.

MATERIALS AND METHODS

Chemicals

IBP and CBZ (their molecular structures are presented in Scheme 1), both of 99% purity, were purchased from Dr. Ehrenstorfer GmbH (Germany) and Sigma Aldrich, respectively and used as received. Their main properties are shown in Table 1, while their structures in Schematic 1. Hydrogen peroxide (35% w/w solution) was supplied by Merck. Six commercially available TiO_2 samples were employed in the present study, namely Aeroxide P25 (Degussa P25) supplied by Degussa AG (anatase:rutile 75:25, 21 nm particle size, 50 m^2/g BET area); Hombikat UV 100 supplied by Sachleben Chemie GmbH (anatase, 5 nm particle size, >250 m^2/g BET area); Tronox A-K-1 (anatase, 20 nm particle size, 90 m^2/g BET area); Tronox TR (rutile, 300 nm particle size, 5.5 m^2/g BET area); and Tronox TR-HP-2 (rutile, 7 m^2/g BET area) supplied by Kerr-McGee Chemicals LLC; Aldrich (anatase, 15 nm particle size, 190–290 m^2/g BET area).



SCH. 1. Chemical structures of (A) IBP; (B) CBZ.

TABLE 1
Main properties of the pharmaceuticals used in this study

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
CAS No.	15687-27-1	298-46-4
Solubility in water (mg/mL)	0.021 (25°C)	0.015 (25°C)
pK_a	4.9	7

Photocatalytic Experiments

Photocatalytic experiments were carried out as follows: 0.35 L of an aqueous drug solution was added to the appropriate amount of TiO_2 (in the range 50–3000 mg/L) and the resulting mixture was loaded in the photochemical reactor (ACE Glass Inc.) which is described in detail elsewhere (12). The suspension was magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption of the drugs on the catalyst surface. After that period, the solution was irradiated by a 9 W UV-A lamp (Radium Ralutec lamp, 9 W/78, 350–400 nm) at 3.2 W/m^2 intensity under continuous oxygen flow. The photon flux of the lamp was determined actinometrically using the potassium ferrioxalate method (13) and it was found $3.37\ 10^{-6}$ einstein/s. For runs conducted under artificial sunlight conditions, solar irradiation was provided by a Phillips xenon lamp (Xe-OP) of 1000 W nominal power in a Newport (91193) solar simulator. Reactions were conducted in a glass vessel illuminated from the top (at a distance of 8 cm). An average irradiation intensity of 272.3 W/m^2 was maintained throughout the experiments and was measured by a radiometer (Newport model 70260). Periodically, samples were taken from the reactor and filtered with 0.22 μm filters to remove catalyst particles.

TABLE 2
Characterization of tertiary wastewater spiked with pharmaceuticals. *Mean value of three separate measurements before spiking

Parameter	*Value
Temperature, °C	19.7
Conductivity, μS/cm	1424
Dissolved oxygen, mg/L	4
pH, –	8.2
Turbidity, NTU	1.9
DOC, mg/L	11
COD, mg/L	6
TSS, mg/L	4.6
Chlorides, mg/L	196

Experiments were conducted with spiked solutions prepared with either Milli-Q water or wastewater samples; the latter were collected from a domestic wastewater treatment plant (WWTP) which applies conventional activated sludge treatment. The sample was collected after sand filtration and chlorination and its main properties are given in Table 2.

Analytical Techniques

Changes in the concentration of the pharmaceuticals were monitored using a UV-Vis Jasco V-530 spectrophotometer. The absorbance was measured at the wavelength that corresponds to the maximum absorbance for each compound, i.e., 220 nm for IBP and 284 nm for CBZ. Conversion refers to the degradation of the parent compound, but also to that of the IBP or CBZ oxidation intermediate products, which contribute to the absorbance at the characteristic wavelength of the parent compound. In order to determine the extent of mineralization, dissolved organic carbon (DOC) was measured by a TOC analyzer (TOC-VCPH/CPN Shimadzu with autosampler ASI-V). Potassium hydrogen phthalate standards were used for the calibration curves.

RESULTS AND DISCUSSION

Screening of Catalysts

To assess the relative catalytic activity of various titanium oxide samples, screening experiments were performed with 10 mg/L initial drug concentration and 250 mg/L catalyst loading under UV-A irradiation. Figure 1 clearly shows that Degussa P25 exhibits higher photoactivity than all other samples employed in this study. This is believed to be due to the slow recombination of the e^-/h^+ pair taking place on the surface of Degussa P25, different from other photocatalysts. Its higher activity may also be attributed to its structure containing both anatase and rutile, being the activity of the mixed phase greater than the activities of the pure crystalline phases (14). Figure 1 also shows that pure anatase TiO_2 is more active than pure rutile for the drugs oxidation. This behavior is attributed to the different position of the conduction band, the higher aptitude of anatase to photoadsorb oxygen, and the lower relative electron/hole recombination rate in anatase. With regard to these findings, subsequent runs were done with Degussa P25.

To confirm the beneficial role of titanium oxide in the photocatalytic degradation, experiments were performed under UV-A irradiation in the absence of a catalyst. The extent of photolytic degradation was marginal, i.e., only about 4% for IBP and 7% for CBZ after 120 min of reaction and this was accompanied by an insignificant DOC removal of about 2%. This implies that the oxidative role of the photocatalytically generated hydroxyl radicals and other reactive moieties in degrading the drugs is crucial; this most likely occurs in the vicinity of the catalyst since dark adsorption onto the catalyst surface was negligible (i.e., about 1%) for either substrate.

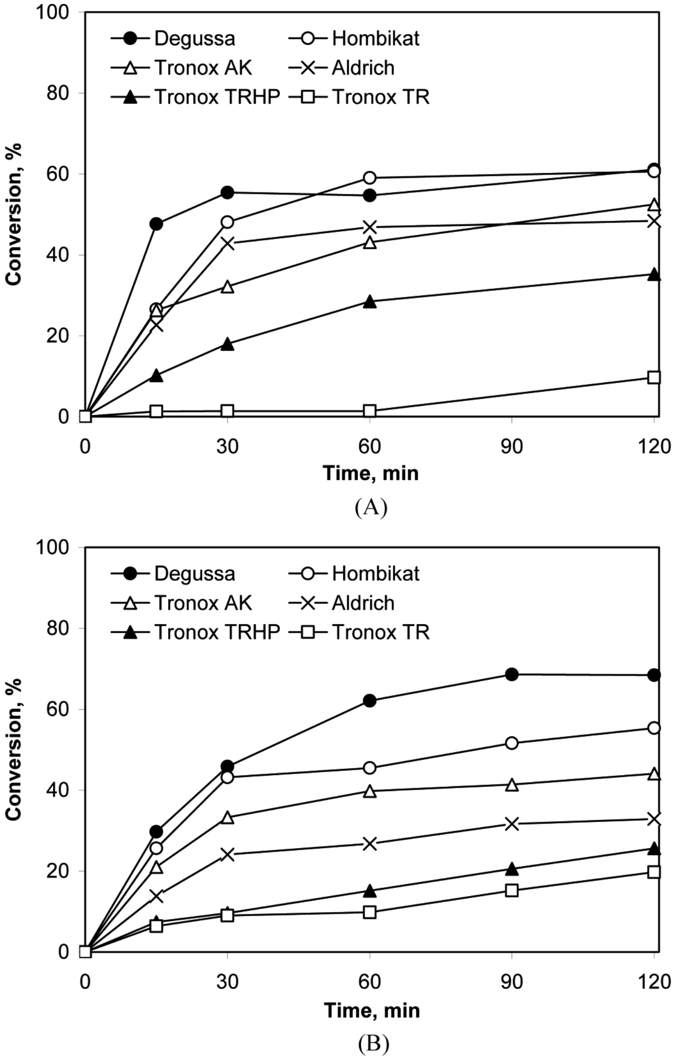
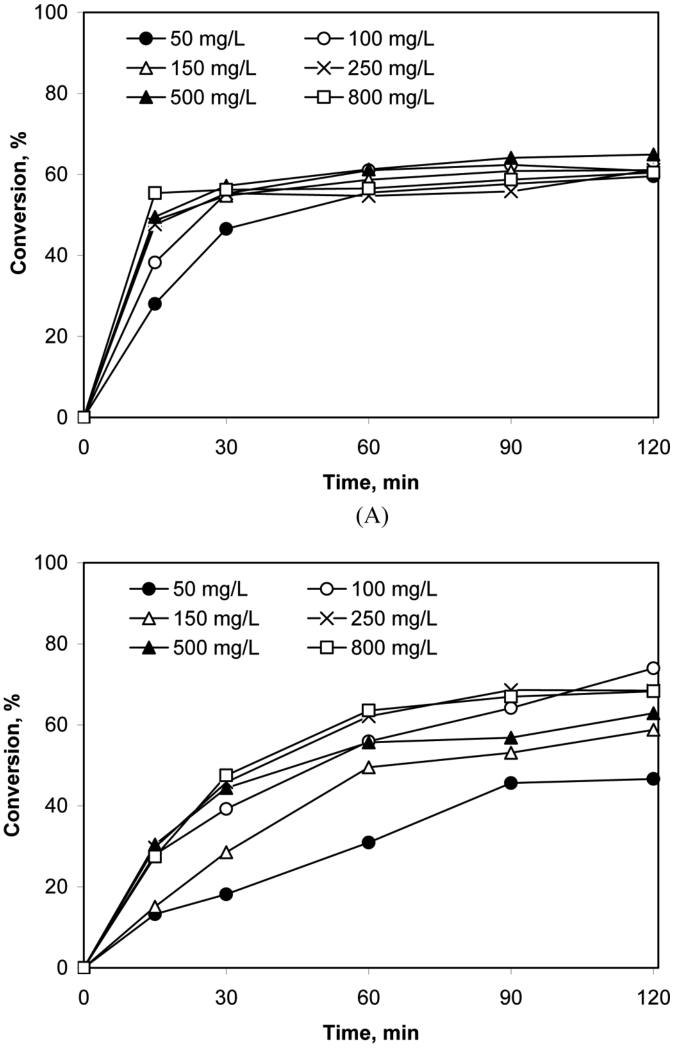


FIG. 1. Effect of titanium oxide type (250 mg/L) on the degradation of 10 mg/L (A) IBP; (B) CBZ under UV-A irradiation in pure water.

Effect of Catalyst Loading

Figure 2 shows the effect of the catalyst loading, in the range 50–800 mg/L, on drug degradation under UV-A irradiation. Regarding IBP degradation, catalyst loading appears to affect the early stages of the reaction (i.e., 15–30 min), after which the reaction reaches a plateau; the final (i.e., 120 min) conversion is 62 ± 3% regardless of the catalyst loading used. After 120 min of reaction at 500 mg/L Degussa P25, a 65% IBP conversion was accompanied by 46% DOC removal (DOC data are shown in Fig. 4a). The experiment was repeated under solar



(A)

(B)

FIG. 2. Effect of Degussa P25 loading on the degradation of 10 mg/L (A) IBP; (B) CBZ under UV-A irradiation in pure water.

irradiation leading to comparable results, i.e., 61% IBP conversion and 46% DOC removal after 120 min of reaction (data not shown).

CBZ degradation appears to be more sensitive in changes in the catalyst loading; after 120 min of reaction at 100 mg/L Degussa P25, a 74% CBZ conversion was accompanied by 40% DOC removal (DOC data are shown in Fig. 4b). However, when the experiment was performed under solar irradiation, CBZ conversion dropped to 35%, while DOC removal to 16% (data not shown). This can be explained as follows:

i. the spectrum of the xenon lamp consists of just about 5% UV irradiation and, consequently, the degree of photoactivation is expected to be limited (15), and
ii. reactor setups for UV-A and solar irradiation experiments are totally different.

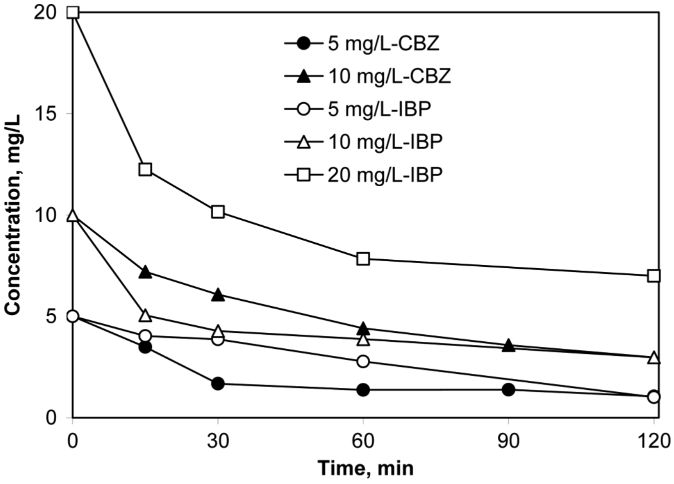


FIG. 3. Concentration-time profiles during the UV-A degradation of IBP and CBZ at 250 mg/L Degussa P25 loading and various drug concentrations in pure water.

The former offers full and uniform illumination of the reaction mixture since the lamp is located inside the vessel, while the latter yields partial illumination since the source is outside the vessel.

Effect of Initial Drug Concentration

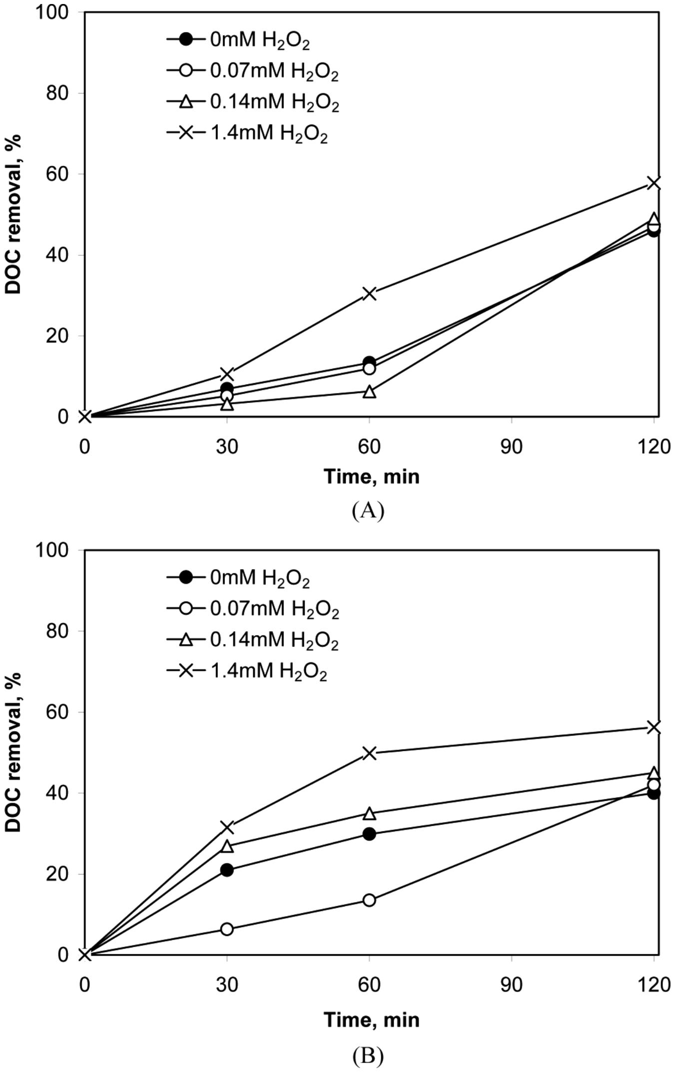
The influence of initial drug concentration on degradation was examined in the range 5–20 mg/L at 250 mg/L catalyst loading under UV-A irradiation and representative concentration-time profiles are shown in Fig. 3. It should be noticed that the range of IBP and CBZ concentrations employed is substantially higher than those typically found in environmental samples which are at the μg/L level (16). This was done though to allow

i. the assessment of treatment efficiency within a measurable time scale, and
ii. the accurate determination of residual concentrations with the analytical techniques employed in this work.

Conversion expectedly decreased with increasing initial concentration, i.e., after 120 min of reaction it became 80%, 70%, and 65% at 5, 10, and 20 mg/L initial IBP concentration, respectively; the corresponding values for 5 and 10 mg/L CBZ were 79% and 70%.

Effect of Oxidant Addition and Initial Solution pH

The effect of adding H_2O_2, in the range 0.07–1.4 mM, on drug mineralization was tested during the photocatalytic degradation of 10 mg/L IBP or CBZ under UV-A irradiation and the results are shown in Fig. 4. For instance, DOC removal increased from 46% (without oxidant) to 58% and from 40% (without oxidant) to 56% after



(A)

(B)

FIG. 4. Effect of H_2O_2 addition on mineralization during the UV-A degradation of 10 mg/L (A) IBP (with 500 mg/L Degussa P25); (B) CBZ (with 100 mg/L Degussa P25) in pure water.

120 min of reaction in the presence of 1.4 mM H_2O_2 for IBP and CBZ, respectively. Under solar irradiation, DOC removal increased from 46% to 55% for IBP and from 16% to 42% for CBZ (data not shown). The beneficial role of H_2O_2 can be attributed to its reaction with electrons, which

i. yields extra hydroxyl radicals, and
ii. prevents electron holes from recombining with electrons, a major cause for reduced photocatalytic activity (17).

All the experiments described so far were executed at the solution's ambient pH; this was 5.5 and 5.9 for 10 mg/L IBP and CBZ, respectively. A set of experiments was conducted adjusting the initial solution pH to 3 and 10 with the addition of the appropriate amount of HCl and NaOH, respectively. The extent of DOC removal decreased in either acidic or alkaline conditions compared to experiments at ambient pH and this was more pronounced at alkaline conditions; for instance, the extent of IBP mineralization after 120 min of reaction at the experimental conditions of Fig. 4a was 9% and 21% at pH 10 and 3, respectively (data not shown). The solution pH is a complex factor that can affect photocatalytic reactions in many ways, i.e., in relation to

i. the ionization state of titanium oxide surface (i.e., negative at pH greater than about 6 and positive below this value (18,19), as well as the organics present in the reaction mixture,
ii. the relative contribution of electron holes and hydroxyl radicals in degrading organic species; the former are believed to dominate at acidic environments, while the latter at neutral or high pH levels (20), and
iii. the fact that titanium oxide particles may agglomerate under highly acidic conditions, thus reducing the surface area available for photochemical reactions (21).

Effect of Water Matrix

All runs described so far were carried out in pure water. In order to evaluate the effect of water matrix on mineralization, wastewater samples were spiked with 10 mg/L of IBP or CBZ, added varying loadings of Degussa P25 in the range 500–3000 mg/L and subject to UV-A or solar irradiation; results are shown in Fig. 5 alongside data from runs in pure water (denoted by an asterisk).

As clearly seen, mineralization increased with increasing catalyst loading and under UV-A rather than solar irradiation. More importantly though, the matrix appears to have a detrimental effect on mineralization and this can be explained in terms of

i. increased initial carbon concentration. The wastewater sample already has 11 mg/L of DOC (Table 2) which accounts for about 150% of the organic carbon contained in 10 mg/L substrate; as has already been discussed in section titled "Effect of Initial Drug Concentration" conversion decreases with increasing initial concentration,
ii. the presence of species like chlorides and carbonates/bicarbonates that may act as scavengers of hydroxyl radicals and other reactive moieties, and
iii. the increased solution pH (the wastewater sample is alkaline) which, as discussed in section titled "Effect of Oxidant Addition and Initial pH" affects mineralization adversely.

Experiments were also carried out in the presence of 0.07–3 mM H_2O_2. The addition of H_2O_2 did not practically improve the reduction of DOC (i.e., only about 3% greater

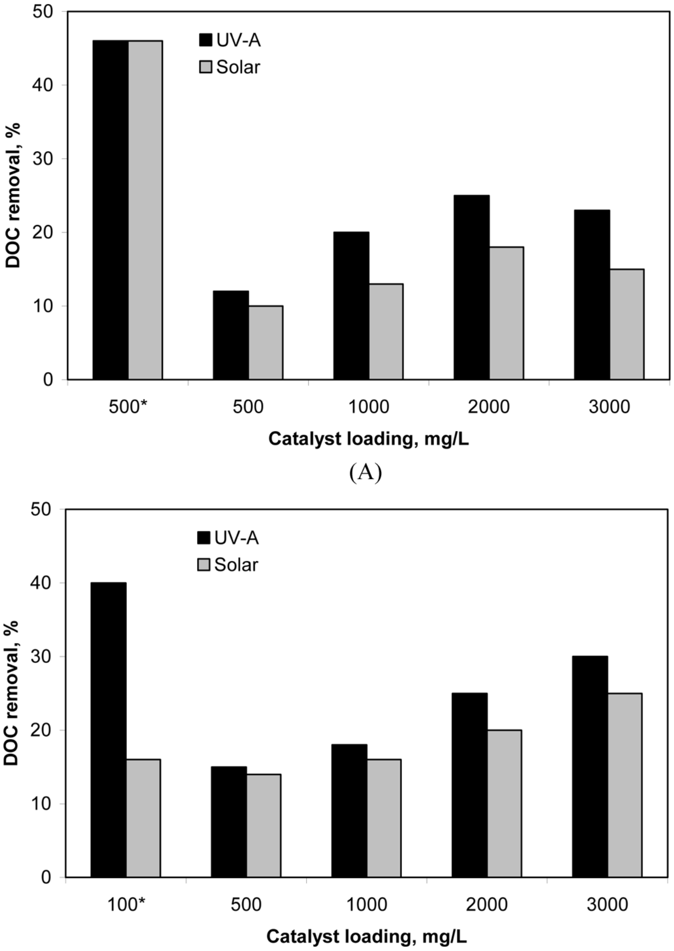


FIG. 5. Mineralization of wastewater samples spiked with 10 mg/L of (A) IBP; (B) CBZ as a function of Degussa P25 loading and illumination source. Reaction time is 120 min. Asterisk denotes run in pure water.

than without peroxide), thus indicating the stability of the wastewater matrix (data not shown).

FINAL REMARKS

The degradation of IBP and CBZ, a NSAID and an anticonvulsant and mood-stabilizing drug, respectively was studied by means of TiO_2 photocatalysis using both UV-A and solar light. The study included the investigation of the effect of various parameters such as type and loading of the catalyst, initial substrate concentration, addition of hydrogen peroxide, the pH, and the water matrix. The main conclusions drawn from this study are summarized as follows:

- The extent of photolytic degradation was found to be marginal, i.e., only about 4% for IBP and 7% for CBZ after 120 min of reaction and this was accompanied by an insignificant DOC removal of about 2%.
- The oxidative role of the photocatalytically generated hydroxyl radicals and other reactive moieties in degrading the drugs is crucial; this most likely occurs in the vicinity of the catalyst since dark adsorption onto the catalyst surface was negligible (i.e., about 1%) for either substrate.
- Photocatalysis using UV-A or solar irradiation appears to be a promising treatment method for the removal of IBP and CBZ, particularly taking into account that the actual concentrations of the pharmaceuticals in WWTPs will be much lower than those studied in this work. Heterogeneous photocatalysis could be employed as a post-secondary treatment to remove residual drugs, as well as inactivate waterborne pathogens.
- Process performance is affected by several factors including the type and concentration of the catalyst, initial drug concentration, solution pH and the water matrix (i.e., the addition of extra oxidants, the presence of other organics, etc).

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