

Heterogeneous photocatalytic degradation of ibuprofen in ultrapure water, municipal and pharmaceutical industry wastewaters using a UV-LEDs/TiO₂ system

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Abstract

Degradation and mineralization of ibuprofen (IBU) was investigated by UV-Light Emitting Diodes (LEDs)/TiO₂ photocatalysis, using spiked ultrapure water and secondary treated effluent collected in a municipal wastewater treatment plant (WWTP), as well as a highly concentrated IBU (230 mg L⁻¹) pharmaceutical industry wastewater (PIWW). The work was carried out to optimize three operating variables: pH, catalyst load and number of LEDs. The process efficiency was evaluated through high performance liquid chromatography (HPLC), ultra-high performance liquid chromatography coupled to high-resolution mass spectrometry (LC-MS/MS) and dissolved organic carbon (DOC) content. Formation of transformation products (TPs) was also investigated and their chemical structures were proposed based on the data from ion trap combined with time-of-flight (LC-MS-IT-TOF) analyses. A possible pathway of IBU degradation was accordingly proposed. Bioassays were performed using the marine bacterium *Vibrio fischeri* to evaluate the potential acute toxicity of original and treated wastewaters. TiO₂ heterogeneous photocatalysis was efficient for when using ultrapure water or the pharmaceutical

industry wastewater, but IBU removal was more difficult in municipal wastewater, even if the acute toxicity decreased after treatment (by ca. 40%) regardless of the studied matrix.

Keywords: ibuprofen; TiO₂; municipal wastewater; pharmaceutical industry wastewater; UV-LEDs; acute toxicity.

1. Introduction

In the last two decades, the presence of pharmaceuticals in the environment has been reported worldwide in many types of environmental matrices, such as wastewaters, surface, groundwater and even drinking water (Garcia-lor et al., 2011, Matongo et al., 2015, Caban et al., 2015, Sim et al., 2013). These compounds may enter into the water resources through wastewaters generated in hospitals and houses, containing parent molecules or metabolites excreted by animals and humans, effluents of pharmaceutical industries, or from the disposal of unused medicines (Santos et al., 2010; Sim et al., 2011; Zylan et al., 2011). The pharmaceutical industry aims at producing increasingly stable molecules to achieve the wanted pharmacological effect. However, as result, pharmaceuticals are more persistent in the environment, where they appear in part due to the limited efficiency of current full-scale wastewater treatment technologies that have been applied in some pharmaceutical industries. Moreover, as conventional municipal wastewater treatment plants (WWTPs) are not specifically designed to degrade pharmaceutical compounds, they also are recognized as one of the entryways of these substances into the aquatic environment (Gros et al., 2010; Nakada et al., 2006). In fact, several studies demonstrated that drugs are not completely removed after biological treatment in municipal WWTPs and, subsequently, might contaminate the natural aquatic compartments (Fernando-Lopez et al., 2016; López-Serna et al., 2013; Rivera-Utrilla et al., 2013).

Ibuprofen (IBU), 2-[3-(2-methylpropyl)phenyl] propanoic acid, is a non-steroidal anti-inflammatory (NSAID) drug and it is one of the most used active pharmaceutical ingredients worldwide, especially prescribed for the treatment of fever, migraine, muscle aches, arthritis and

tooth aches (Skoumal et al., 2009; Madhavan et al., 2010). Carballa et al. (2004) reported that more than 70% of IBU can be removed by classical biological treatments. Recently, some studies revealed the detection of IBU in effluents of municipal WWTPs and in surface waters at levels of concentrations between ng L^{-1} and $\mu\text{g L}^{-1}$ (Ferrando-Climent et al., 2012; Elorriaga et al., 2012; Ziylan et al., 2011). The constant introduction of IBU at these concentrations into the environment, together with many other drugs and their human metabolites, and the intermediate products produced in WWTPs, may cause harmful implications to human health, climate and aquatic environments (Li et al., 2015; Focazio et al., 2008).

In order to avoid these problems, tertiary processes such as advanced oxidation processes (AOPs), have arisen as alternative options for the degradation of different types of persistent organic pollutants present in wastewaters, such as pharmaceutical compounds, and as far as possible to promote their complete mineralization. AOPs are characterized by the formation of active and non-selective oxidizing species, like hydroxyl radicals ($\cdot\text{OH}$), which can oxidize most of the organic compounds in water (Oppenländer, 2003). Among the different AOPs, heterogeneous TiO_2 photocatalysis is reported to be one promising technology for the degradation of organic compounds (Gaya and Abdullah, 2008; Lamsal et al., 2011; Shu et al., 2013; Matilainen et al., 2010). Photocatalysis has shown a great potential as a low-cost, environmental friendly and efficient treatment technology (Giraldo et al., 2010).

The degradation of IBU has already been studied using UV/chlorine (Xiang et al., 2016), the photo-Fenton process (Méndez-Arriaga et al., 2010), electro-peroxone (Li et al., 2014), ultrasound (Méndez-Arriaga et al., 2008), homogenous photocatalysis (Loaiza-Ambuludi et al., 2014) and (sono)photocatalysis (Michael et al., 2014), among others. Zwiener et al. (2000) reported that simple ozonation was ineffective to totally remove IBU, achieving only ca. 12% of IBU degradation. However, a high IBU removal (i.e. 99%) was achieved with the application of the combined $\text{O}_3/\text{H}_2\text{O}_2$ process (Quero-Pastor et al., 2014). Studies with TiO_2 heterogeneous catalysts have also been reported for the degradation of IBU (Candido et al., 2016; Hama Aziz

et al., 2017; Gongora et al., 2017). Méndez-Arriaga et al. (2008) reported the photocatalytic degradation of highly concentrated IBU solutions (200 mg L^{-1}) over TiO_2 aqueous suspension under simulated solar irradiation. The results showed an increase in IBU removal and biodegradability index after the photocatalytic treatment. Oxidation of IBU is achieved by means of $\bullet\text{OH}$ radicals photo-generated through the h^+ and e^- produced pairs when the TiO_2 semiconductor is exposed to UV radiation.

Only a few studies have been conducted with industrial wastewater of pharmaceutical origin employing the TiO_2 -UV system (Ahmadi et al. 2017; Boroski et al. 2017; Solís-Casados et al. 2017; Wang et al. 2013). The main purpose of this work was to study the UV-LED/ TiO_2 photodegradation of IBU in ultrapure water, municipal wastewater (MWW) and pharmaceutical industry wastewater (PIWW). The effect of operating conditions, such as pH, catalyst load and number of LEDs, on IBU removal and mineralization was assessed and discussed. Identification of the major reaction intermediates and acute toxicity evaluation were also investigated.

2. Materials and Methods

2.1. Chemicals

IBU (2-methyl-4-(isobutyl) phenylacetic acid) sodium salt ($\geq 98\%$ purity) was purchased from Sigma-Aldrich (Steinheim, Germany). Degussa (Aeroxide) TiO_2 P25 (80% anatase and 20% rutile crystalline phases) was obtained from Evonik Corporation (Germany). Sodium dihydrogen phosphate and *o*-phosphoric acid 99% were respectively supplied by Sigma-Aldrich (Steinheim, Germany) and Merck (Darmstadt Germany). Methanol (HPLC and MS grade) was acquired from Fisher Scientific UK Limited (Leicestershire, UK) and ultrapure water was supplied by a Milli-Q water system. The pH of the solutions was adjusted using H_2SO_4 (0.1 and 0.01 M) or NaOH (0.1 and 0.01 M). The aqueous IBU solution was prepared by dissolution of a known amount of IBU in ultrapure water. MWW samples were collected (May 2015) after secondary treatment (conventional activated sludge) of a WWTP located in Northern Portugal,

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using pre-rinsed amber glass bottles (2.5 L), which were transported at 4 °C to the laboratory. The PIWW was collected from a pharmaceutical manufacturer located in Sfax, Tunisia (April 2016).

2.2. Experimental set-up and procedure

2.2.1. Photodegradation of IBU in ultrapure water and spiked municipal wastewater (MWW)

The photocatalytic experiments of both IBU-spiked solutions prepared in ultrapure water and using MWW were conducted at room temperature (25 °C) in a lab-scale photoreactor (**Figure 1a**). The reactor was equipped with four 10 W UV high intensity LEDs (16 × 23 mm), placed perpendicularly, with a maximum irradiance wavelength at 382 nm (ca. 375 W m⁻² each at 5 cm away from the photoreactor) and long service life (intensity remains above 70% after 10,000 h work). The reactor was filled with 250 mL of ultrapure water (6 mg L⁻¹, 60 mg L⁻¹ or 213 mg L⁻¹ of spiked IBU) or MWW (6 µg L⁻¹, 6 mg L⁻¹ or 213 mg L⁻¹ of spiked IBU), and the solution maintained under magnetic stirring and aeration during the experiments. For the photocatalytic experiments, a known amount of TiO₂ Degussa (P25) was added to the aqueous solutions to achieve a catalyst load of 0.5, 1.0 or 1.5 g L⁻¹. The experiments were performed at natural pH (5.3) and also at lower (3.0) and higher (9.0) pH. The suspension was kept in the dark under stirring during 30 min (adsorption phase) and afterwards the LEDs (n = 1, 2 or 4) were switched on. At certain times, 1 mL aliquots were withdrawn, centrifuged and filtered using PTFE syringe filters for HPLC analysis.

2.2.2. Photodegradation of pharmaceutical industry wastewater (PIWW)

The experiments with PIWW, consisting of 213 mg L⁻¹ of IBU concentration, were performed at room temperature (25 °C) in a quartz cylindrical reactor filled with 7.5 mL of the wastewater (**Figure 1b**). This different configuration was used in this particular case to expend a lower amount of the sample that was collected. The appropriate amount of TiO₂ P25 was added

to achieve the desirable catalyst load (0.5, 1.0, 2.0, 2.5, 3.0 or 4.0 g L⁻¹). The suspension was magnetically stirred and continuously purged with oxygen. The irradiation source consisted in a LED similar to those used for experiments with IBU spiked in ultrapure water and MWW. In this case, a single LED is enough considering the lower volume to be treated. The experiments were performed at natural pH of wastewater (7.9) and also at acidic pH (3.0 and 5.0) and alkaline pH (10.0). For comparison purposes, one experiment with spiked MWW was also performed in this photoreactor (**Figure 1b**) under the same operating conditions tested for PIWW.

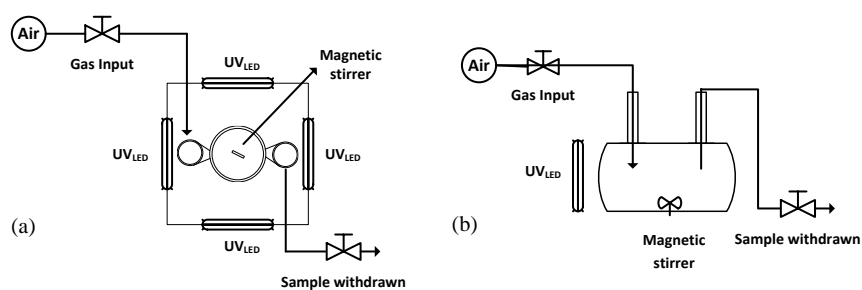


Figure 1. Experimental set-up of the photocatalytic reactors equipped with (a) 4 LEDs (top view) and (b) 1 LED.

2.3. Analytical procedures

The IBU concentration was determined by HPLC using a Hitachi Elite LaChrom system equipped with a diode array detector (DAD). The column employed was a Hydrosphere C18 (250 × 4.6 mm) at room temperature. The analyses were performed under isocratic mode, employing a mobile phase that consisted of a mixture of 30:70 (v/v) of sodium dihydrogen phosphate aqueous solution (pH 2.8, adjusted with *o*-phosphoric acid): acetonitrile. In the particular case of MWW samples spiked with 6 μg L⁻¹ of IBU, they were analysed by ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS), using a Shimadzu Corporation apparatus (Tokyo, Japan), consisting of a Nexera UHPLC equipment and a LCMS-8040 triple quadrupole mass spectrometer detector with an electrospray ionization

source operating in negative ionization mode. The column used was a Kinetex™1.7 µm XB-C18 100 Å (100 × 2.1 mm i.d.) supplied by Phenomenex, Inc. (California, USA). It was operated under reversed mode with a mobile phase consisting of a mixture of ethanol and water (50/50, v/v). A Shimadzu LC-MS-IT-TOF (ion trap combined with time-of-flight), under the same chromatographic conditions, was used for analysis of reaction intermediates, after photocatalytic degradation of IBU spiked in ultrapure water.

The dissolved organic carbon (DOC) content was determined using a Shimadzu TOC-L analyser equipped with autosampler. Ion chromatography analyses were performed in a Metrohm 881 Compact IC Pro apparatus equipped with a Metrosep A Supp 7 Anionic Exchange Column (250 mm × 4.0 mm) for quantification of sulphates and chlorides.

2.4. Toxicity assessment

For the purpose of assessing the acute toxicity of the original (213 mg L⁻¹ of IBU) and treated MWW (spiked) and PIWW (non-spiked) samples, experiments were performed at room temperature (25 °C) in the quartz cylindrical reactor (7.5 mL) shown in **Figure 1b**. Microtox acute toxicity tests were carried out according to the standard (ISO/DIS 11348-3, 2007) method using the Microtox basic test (Azure Environmental, USA). The toxicity assessment was based on the inhibition of the bioluminescence of the selected strain of the marine bacterium *Vibrio fischeri* (*Photobacterium phosphoreum*) (Hach Lange) using a Microtox® M500 analyzer, after mixing 0.5 mL of the sample with 0.5 mL of the bacterial suspension and incubation at 15 °C during 30 min. For osmotic protection, during sample and reagent dilutions, 2 and 22% NaCl solutions were prepared. The pH was adjusted (6.8 – 7.2) by using 0.1 mol L⁻¹ NaOH or 0.1 mol L⁻¹ HCl solutions. The acute toxicity was expressed as the percentage of the bioluminescence inhibition with relation to a control sample.

3. Results and discussion

3.1. Photocatalytic degradation of IBU in ultrapure water

3.1.1. Effect of catalyst load

The photocatalytic degradation of IBU was evaluated using different catalyst loads of TiO₂ P25 at natural solution pH (5.3) with 4 LEDs (**Figure 2**). IBU is very refractory to photolysis. IBU degradation significantly increased with the catalyst load up to 1.0 g L⁻¹. However, very similar results were obtained with catalyst loads of 1.0 and 1.5 g L⁻¹, complete IBU photocatalytic degradation being achieved after 30 min of reaction. Regarding the mineralization (**Figure 2**), DOC removal increased with the catalyst load and the highest mineralization was obtained for the catalyst load of 1.5 g L⁻¹, achieving values of 70% of DOC reduction. The mineralization was incomplete even until the end of the experiments (90 min), indicating that IBU by-products were produced and accumulated, after the removal of IBU to levels below the detection limit.

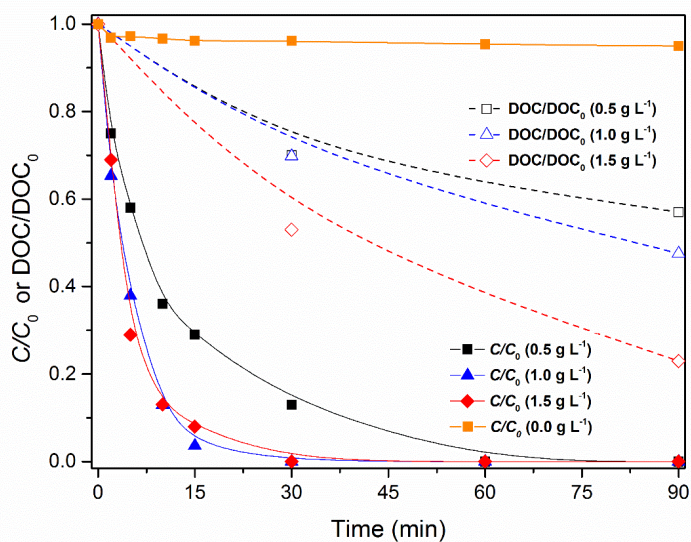


Figure 2. Effect of catalyst load (0.5, 1.0 and 1.5 g L⁻¹) on the IBU photocatalytic degradation and DOC abatement, using IBU in ultrapure water ($C_0 = 60 \text{ mg L}^{-1}$) at natural pH (5.3). Irradiation source: 4 LEDs. Results with photolysis (i.e. without catalyst) are also shown for comparison.

3.1.2. Influence of the initial pH

The photocatalytic degradation of IBU was studied varying the initial pH of the IBU solution (i.e. 3.0, natural pH and 9.0) at a catalyst load of 1.0 g L⁻¹ with 4 LEDs (**Figure 3**). The highest degradation rate was observed at natural pH (5.3). This result can be explained by the point of zero charge (pH_{PZC}) of TiO₂ (6.6) and the pK_a of IBU (4.8), as shown in the speciation diagram (**Figure 4**). It is well known that the photocatalytic degradation efficiency can be related to the distribution of IBU species and the state of TiO₂ P25 surface according to the pH value. At natural solution pH (5.3), the IBU molecules are negatively charged (IBU⁻) while the TiO₂ surface is positively charged according to its pH_{PZC} (6.6). In this case, there is an increase of electrostatic attractions between the positively charged surface of TiO₂ P25 and the negatively charged IBU molecules, favoring the photocatalytic degradation. At pH 3.0, the interaction between the molecules and the photocatalysts is lower, because at pH below 4.8, the IBU molecules are undissociated whereas the TiO₂ surface is positively charged, decreasing the electrostatic attraction. The lower photocatalytic degradation obtained at pH 9.0 can be due to the predominant electrostatic repulsion among the IBU molecules and the TiO₂ surface, both negatively charged, when the pH is above 6.6. The DOC reduction follows the trends observed for IBU degradation in the photocatalytic experiments, and the higher DOC reduction was found at the natural pH (53%).

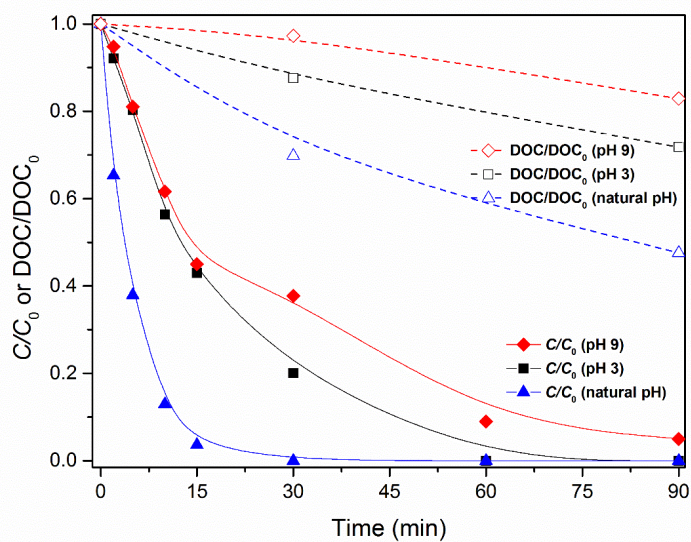


Figure 3. Effect of initial solution pH (3, natural, 9) on the IBU photocatalytic degradation and DOC abatement, using an IBU aqueous solution ($C_0 = 60 \text{ mg L}^{-1}$) and a catalyst load of 1 g L^{-1} . Irradiation source: 4 LEDs.

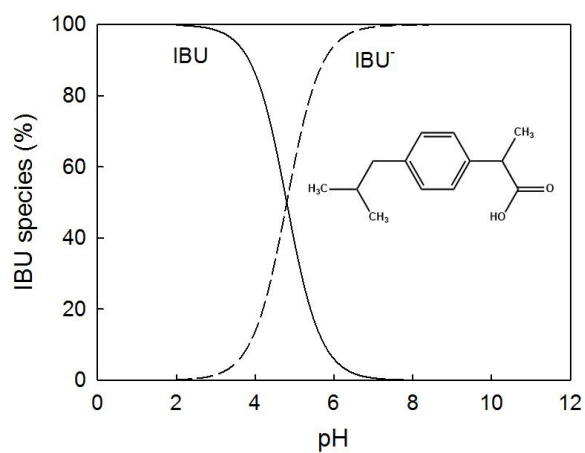


Figure 4. Speciation diagram of IBU in aqueous solution at $25 \text{ }^\circ\text{C}$ (inset: chemical structure of IBU).

3.1.3. Influence of the number of LEDs

The IBU photocatalytic degradation was also studied varying the number of LEDs (i.e. 1, 2 or 4 LEDs) using the natural solution pH (5.3) and a catalyst load of 1.0 g L^{-1} , as shown in **Figure 5**. Higher degradation rates were observed when 4 LEDs were used (100% IBU degradation being obtained after 60 min of irradiation). It can be observed, that the removal rate of IBU increased with the number of UV-LEDs (i.e. up to 4), as expected since light intensity increases with the number of LEDs employed (Dominguez et al., 2015). The light irradiation produces the photons required for the electron transfer from the valence band of the TiO_2 photocatalyst to the conduction band. When the irradiance increases until a certain value, more $\cdot\text{OH}$ radicals are expected to be catalytically generated, increasing the removal rate of IBU (Dong et al. 2010). The mineralization was also enhanced by increasing the number of LEDs (15, 43 and 53% for 1, 2, and 4 LEDs, respectively), as observed in **Figure 5**.

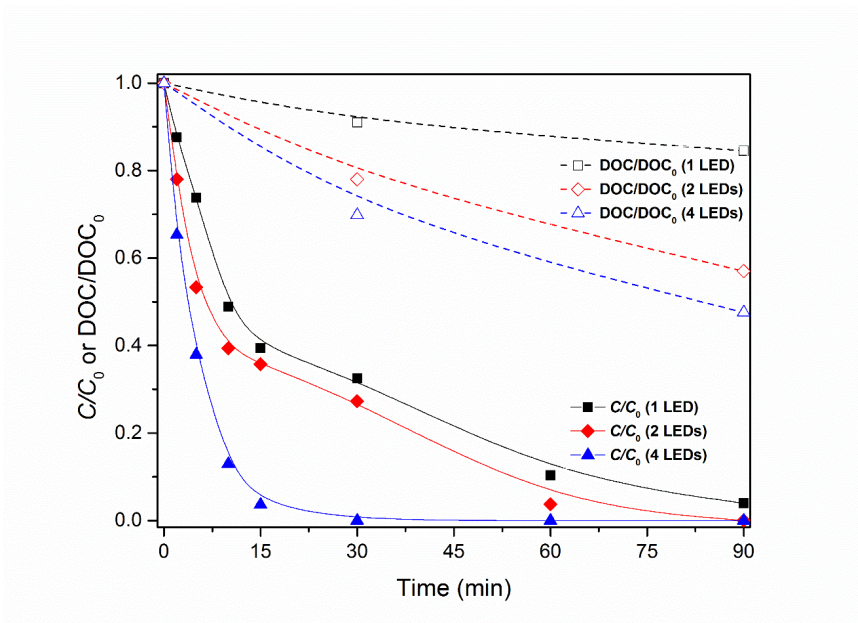


Figure 5. Effect of number of LEDs (1, 2 or 4) on the IBU photocatalytic degradation and DOC abatement, using IBU in ultrapure water ($C_0 = 60 \text{ mg L}^{-1}$) at natural solution pH (5.3), and a catalyst load of 1 g L^{-1} .

3.1.4. Formation of oxidation products and proposed degradation pathways

In order to identify the reaction intermediates and to understand the degradation mechanism of IBU during photocatalytic treatment, samples collected after 30 min were also analyzed by means of LC-MS-IT-TOF. The results indicate that photocatalysis is efficient to degrade IBU, but leads to the formation of a number of products such as substituted phenolic compounds, aromatic carboxylic acids, among others. Molecular structures were proposed for each intermediate on the basis of the molecular ion masses and MS fragmentation patterns. **Figure 6a** shows the total ion chromatogram of the following m/z : 177 and 221. Although tandem mass spectrum of TP1 had no fragments, the determined exact molecular weight under negative ionization was 177.128 (**Figure 6b**). According to other works reported in the literature, this TP probably might be 1-(4-isobutyl-phenyl)-ethanol with an elementary composition of $C_{12}H_{18}O$ and a molecular weight of $178.27 \text{ g mol}^{-1}$ (Da Silva et al., 2013, Szabó et al., 2011). The determined exact molecular weight of TP2 under negative ionization was 221.117 (**Figure 6c**), which corresponds to hydroxy-ibuprofen, with an elementary composition of $C_{13}H_{18}O_3$ and molecular weight of $222.28 \text{ g mol}^{-1}$. This intermediate has already been identified by other authors (Zheng et al., 2011, Illés et al., 2013). The tandem mass spectra showed its fragments at m/z 177 and 134 which correspond respectively to 1-(4-ethyl-phenyl)-2-methyl-propan-1-ol and 4-ethyl-benzaldehyde (**Figure 6d**), as reported previously by Huang et al. (2015).

Based on these results and the well-known reactivity of $\bullet OH$ radical towards organic compounds in aqueous medium, a photodegradation pathway of IBU with the corresponding intermediates was therefore proposed (**Figure 7**).

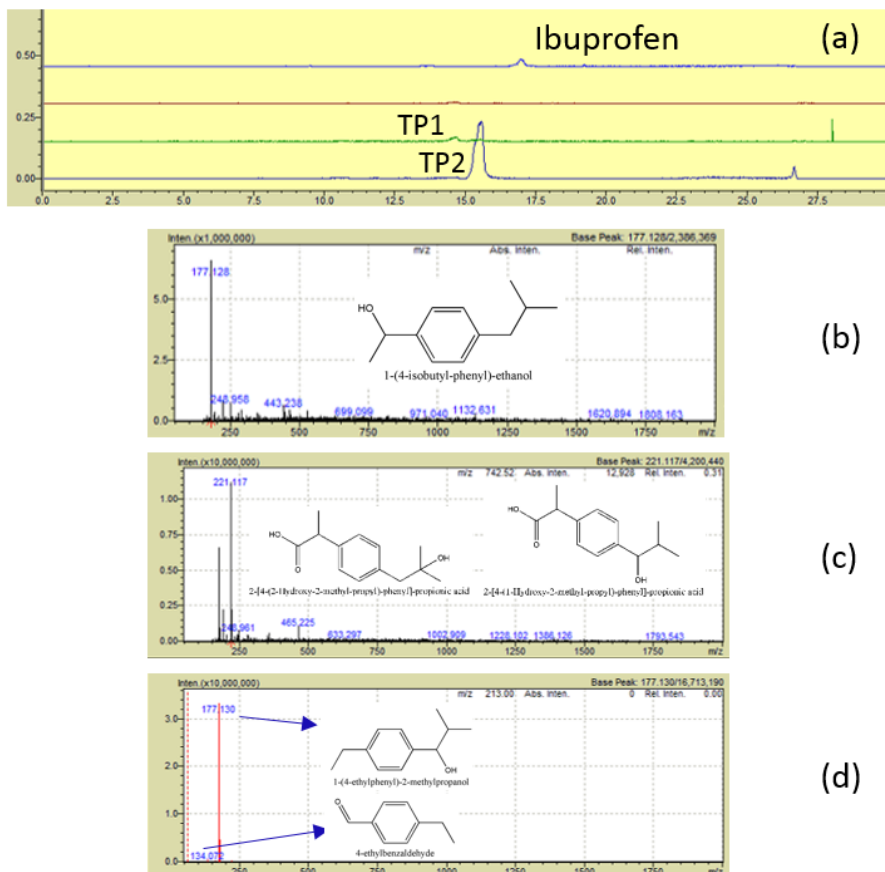


Figure 6. LC-MS-IT-TOF of a sample collected after 30 min of photocatalytic IBU degradation (initial IBU concentration of 60 mg L⁻¹, natural pH, 4 LEDs and 1.0 g L⁻¹ of TiO₂). (a) Total ion chromatogram of the following m/z: 177 and 221; (b) mass spectrum at retention time 14.64 min; (c) mass spectrum at retention time 15.53 min; (d) MS² of TP2 at retention time 15.53 min.

3.2. Photocatalysis of IBU in a spiked municipal wastewater (MWW)

In order to study the matrix effect, the photocatalytic degradation of different concentrations of IBU was carried out in spiked ultrapure water, UP (i.e. 6 mg L⁻¹, 60 mg L⁻¹ and 213 mg L⁻¹), and MWW (i.e. 6 µg L⁻¹, 6 mg L⁻¹ and 213 mg L⁻¹), as shown in **Figure 8**, with 1.0 g L⁻¹ catalyst load. The IBU concentration in non-spiked MWW is below 1 µg L⁻¹.

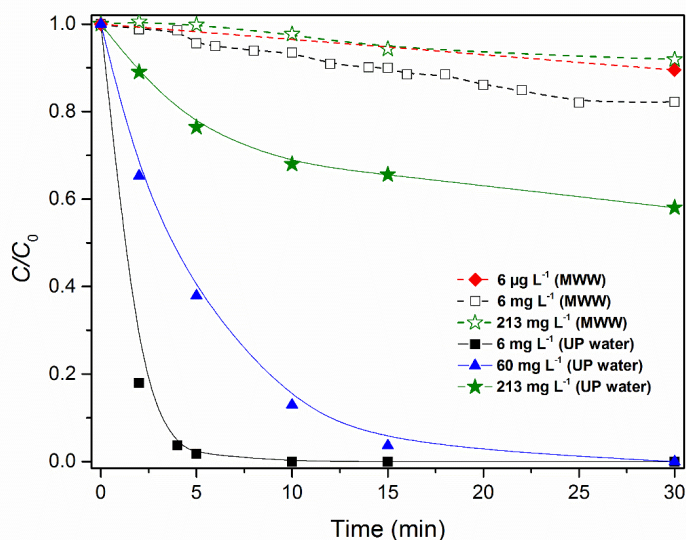


Figure 8. Comparison between photocatalysis of IBU spiked in ultrapure water and MWW.

It could be observed that the photocatalytic degradation of IBU (6 mg L^{-1}) in MWW reached 18% of degradation after 30 min of treatment while the IBU degradation was complete in ultrapure water when the same IBU concentration was spike (6 mg L^{-1}). Similarly, the photocatalytic degradation of IBU at a higher initial concentration (213 mg L^{-1} MWW) in a secondary treated wastewater achieved ca. 9% of IBU degradation after 30 min of treatment and nearly 42% in ultrapure water (213 mg L^{-1} UP water). The significantly lower IBU removal efficiency in realistic wastewater (MWW) was expected due to the complexity of this matrix (Table 1). Other studies have shown that the presence of anions and natural organic matter in water matrices can influence the photocatalytic degradation efficiency (Pereira et al., 2013; Sheng et al., 2013; Uyguner-Demirel et al., 2017). These anions are capable to compete for the same adsorption sites with organic compounds in the photocatalytic oxidation of IBU (Calza and

Pelizzetti, 2001; Dionysiou et al., 2000), negatively affecting the IBU photocatalytic degradation.

Table 1. Main characteristics of spiked municipal (MWW) and pharmaceutical industry (PIWW) wastewaters.

Characteristics	MWW	PIWW
DOC (mg L ⁻¹)	215	170
pH	7.3	7.9
Conductivity (µs/cm)	610	3770
Chlorides (Cl ⁻) (mg L ⁻¹)	58	978
Sulphates (SO ₄ ²⁻) (mg L ⁻¹)	34	661
Nitrites (NO ₂ ⁻) (mg L ⁻¹)	30	< LOQ
Nitrates (NO ₃ ⁻) (mg L ⁻¹)	19	< LOQ
Phosphates (PO ₄ ³⁻) (mg L ⁻¹)	7	< LOQ
Sodium (Na ⁺) (mg L ⁻¹)	40	310
Ammonium (NH ₄ ⁺) (mg L ⁻¹)	22	< LOQ
Calcium (Ca ²⁺) (mg L ⁻¹)	21	< LOQ
Potassium (K ⁺) (mg L ⁻¹)	10	< LOQ
Magnesium (Mg ²⁺) (mg L ⁻¹)	< LOQ	27

3.3. Photocatalysis of IBU in pharmaceutical industry wastewater (PIWW)

The photocatalytic degradation of IBU ($C_0 = 213 \text{ mg L}^{-1}$) in a real PIWW (i.e. non-spiked) was then compared with that using MWW spiked with IBU ($C_0 = 213 \text{ mg L}^{-1}$), using the photoreactor equipped with 1 LED under the same conditions (Figure 1b; 2.5 g L^{-1} of catalyst load and natural pH). The lower performance obtained with MWW (**Figure 9**) can be attributed to the complexity of this matrix and the higher DOC content in comparison to PIWW (Table 1).

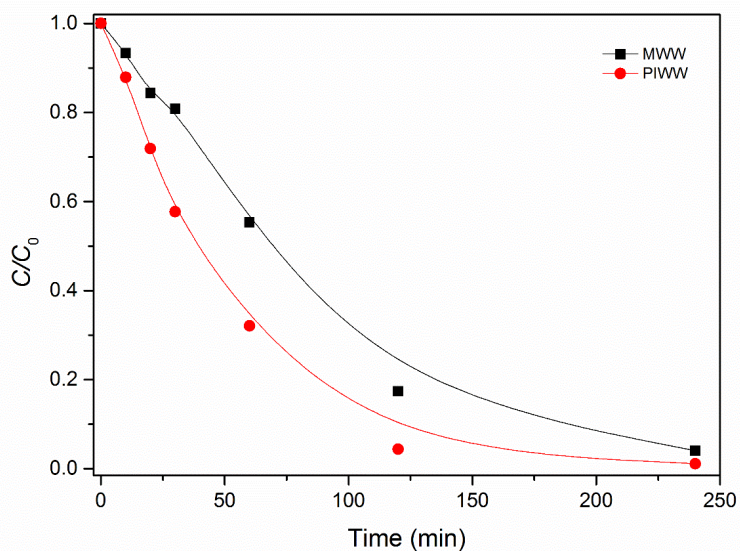


Figure 9. Comparison between photocatalytic treatment of MWW (spiked with 213 mg L^{-1} of IBU), and PIWW (non-spiked, 213 mg L^{-1} of IBU), at natural pH and 2.5 g L^{-1} catalyst load in both cases.

3.3.1. Influence of catalyst load

The effect of catalyst load on the photocatalytic degradation of IBU in the real PIWW was then examined using the same photoreactor (Figure 1b). The characteristics of the PIWW are summarized in Table 1. The respective k constants of IBU within 240 min of irradiation at different catalyst loads (i.e. 0.5 , 1.0 , 2.0 , 2.5 , 3.0 and 4.0 g L^{-1}) can be found in **Table 2**. The direct photolysis of IBU was investigated, achieving a 9% of IBU removal under these non-catalytic conditions. Jacobs et al. (2011) had already reported the photolysis of IBU in solutions also containing fluvic acids isolated from surface waters, and no effective IBU removal was observed. A conversion far superior to that obtained in the non-catalytic conditions was observed in the presence of all catalyst loads. IBU degradation increased with the catalyst load, a complete conversion of IBU (100%) being achieved with catalyst loads equal or above 2 g L^{-1} . The lowest

conversion (55.9%) was observed for 0.5 g L⁻¹ of catalyst. A single exponential decay model fitted the IBU degradation versus reaction time data (not shown), with good coefficients of correlation, which suggests a pseudo-first order kinetics reaction. The values of the rate constants (k_{app}) were obtained from the slope of the plot representing $\ln(C/C_0)$ versus time (**Table 2**). It could be found that the rate constant increases with the increase of the catalyst load up to 2.5 g L⁻¹ ($k_{app} = 0.024 \text{ min}^{-1}$). A TiO₂ load higher than 2.5 g L⁻¹ led to a decrease of the rate constant ($k_{app} = 0.013 \text{ min}^{-1}$ for 4 g L⁻¹ of catalyst). It is well known that the increase of concentration of TiO₂ can either improve the degradation efficiency by increasing the overall available catalyst surface area and therefore the number of active sites, or reduce the degradation rate by limiting UV light penetration as a result of opacity (Yang et al., 2008). **Table 2** also shows the respective DOC removals after 240 min of treatment. The highest mineralization, namely 57% of DOC abatement, was observed with 2.5 g L⁻¹ of catalyst.

Table 2. IBU removal, apparent pseudo-first order rate constants (k_{app}) and DOC abatement after photocatalytic treatment of PIWW when using different catalyst loads (0.5, 1.0, 2.0, 2.5, 3.0 and 4.0 g L⁻¹). Results obtained in photolysis (non-catalytic) are also shown for comparison.

TiO ₂ load (g L ⁻¹)	IBU removal (%) after 240 min	Correlation coefficient (R^2)	$k_{app} \times 10^3$ (min ⁻¹)	DOC abatement (%)
0.5	55.9	0.973	5	3.0
1.0	95.9	0.991	9	34.0
2.0	100	0.989	23	55.2
2.5	100	0.967	24	57.3
3.0	100	0.965	17	45.8
4.0	100	0.983	13	5.6
Photolysis	9	0.953	2	-

3.3.2. Influence of pH on the photocatalytic degradation kinetics of IBU

The effect of the initial pH (3.0, 5.0, natural pH (7.8) and 10.0) was also examined on the photocatalytic degradation of IBU ($C_0 = 213 \text{ mg L}^{-1}$) in PIWW, using a catalyst load of 2.5 g L^{-1} (**Figure 10**). The reaction rate constant (k_{app}) increased when the solution pH increased from 3.0 ($k = 0.026 \text{ min}^{-1}$) to 5.0 ($k_{app} = 0.029 \text{ min}^{-1}$). This effect can be explained by the higher amount of dissociated IBU species (IBU⁻) when the pH is superior, favoring the electrostatic attraction among the negatively IBU molecules and positively charged TiO₂ ($\text{pH}_{PZC} = 6.6$). At higher pH values (pH 10) a decrease of the rate constant was observed ($k_{app} = 0.013 \text{ min}^{-1}$). In this case, it could occur an increase of electrostatic repulsions among the negatively surface of TiO₂ and the IBU molecules, also negatively charged in this case. In addition, the maximum DOC reduction (59%) was achieved for pH 5.0.

Regarding the results obtained with UP water (section 3.1.2), k_{app} was 0.989 min^{-1} at pH 5 in ultrapure water, while a 34-fold decrease in k_{app} was observed in PIWW. Thus, the decrease in photocatalytic degradation rates might be caused by the presence of inorganic and organic species, acting as $\bullet\text{OH}$ and hole scavengers. Therefore, the adsorption of inorganic anions on the surface of TiO₂ could lead to a decrease of active sites for the oxidation of organic molecules (Chen et al., 1997).

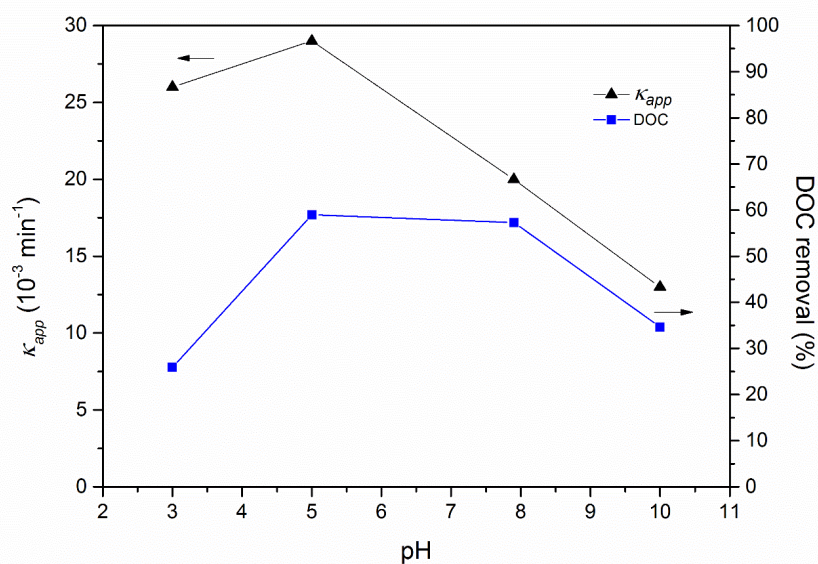


Figure 10. Pseudo-first order reaction rate constant (k_{app}) and DOC removal for different initial pH of PIWW at 2.5 g L^{-1} catalyst load.

3.4. Toxicity measurements

Microtox assays were performed to evaluate the acute toxicity of treated and non-treated MWW spiked with 213 mg L^{-1} of IBU, and PIWW (non-spiked) samples (Figure 11), under the experimental conditions used before (Figure 9). After 30 min exposition, high inhibition in the *Vibrio fischeri* luminescence was verified for non-treated MWW and PIWW samples (78.3 and 73.9%, respectively). Luminescence inhibition was reduced to values as low as 40.8% for MWW and 30.3% for PIWW after 240 min of TiO_2 photocatalytic treatment, together with more than 50% of sample mineralization. These results are in agreement with those reported by (Illés et al., 2012; Illés et al., 2013) and by Kim et al. (2006), where photocatalysis was found to be able to decrease the toxicity with increasing mineralization rates. Slight toxicity increase has been

observed after application of other treatment options (gamma radiolytic), the 1,2-dihydroxy-IBU intermediate being considered more toxic than IBU (Zheng et al., 2011; Marco-Urrea et al., 2009).

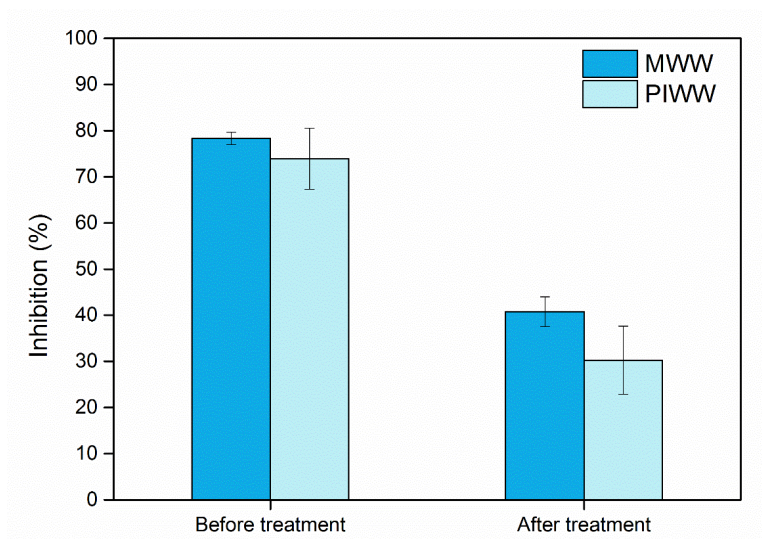


Figure 11. *Vibrio fischeri* bioluminescence inhibition rate (%) before and after photocatalytic treatment of MWW (spiked with 213 mg L⁻¹ of IBU), and PIWW (non-spiked, 213 mg L⁻¹ of IBU), at natural pH and 2.5 g L⁻¹ catalyst load in both cases.

3. Conclusion

IBU was successfully removed to levels below the detection limit in ultrapure water and in a pharmaceutical industry wastewater, by using TiO₂ heterogeneous photocatalysis with UV-LEDs. However, IBU was more difficult to be removed in the case of a secondary treated effluent collected in a municipal wastewater treatment plant, probably due to its complex matrix containing species interfering with the photocatalytic process. Natural pH (5.3) was found to be the most efficient for the degradation of IBU, in comparison with acidic and alkaline pH. This is explained by considering the pHPZC of TiO₂ (6.6) and the pK_a of IBU (4.8), IBU molecules being negatively charged while the TiO₂ surface is positively charged at pH 5.3, thus enhancing

electrostatic attractions. Two intermediates produced during TiO₂ photocatalysis were suggested by LC-MS-IT-TOF analysis, namely 1-(4-isobutyl-phenyl)-ethanol and 2-[4-(hydroxyl-2-methyl-propyl)-phenyl]-propionic acid. Moreover, acute toxicity assays confirmed that the TiO₂ photocatalytic treatment decreased the toxicity of the wastewaters, while the mineralization rates increased.

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