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RESEARCH ARTICLE

Ibuprofen photodegradation in aqueous solutions

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Abstract The advanced treatment of polluted liquid streams containing traces of pharmaceutical compounds is a major issue, since more and more effluents from pharma labs and wastewaters containing the excretions of medically treated humans and animals are discharged in the conventional wastewater treatment plants without previous effective treatments. Ibuprofen is a widely used non-steroidal anti-inflammatory drug (NSAID), which explains why it is found in wastewaters so often. In this paper, the removal of IBP from simulated water streams was investigated by using a lab-scale experimental device, consisting of a batch reactor equipped with a lamp emitting monochromatic UV light at a fixed wavelength (254 nm) and various intensities. Three sets of experiments were carried out: the first to study IBP concentration as a function of time, at different volumes of treated solutions ($V = 10$–30 mL); the second to explore the effect of pH on IBP degradation as a function of time (pH = 2.25–8.25) and the third to evaluate the effect of different UV light intensities on IBP degradation ($E = 100$–400 mJ m^{-2}). The IBP initial concentration (IBP_0) was varied in the range 30–60 mg L^{-1}.

The results obtained show that the concentration of IBP decreases along with treatment time, with a negative effect of the treated volume, i.e. smaller volumes, such as lower liquid heights, are more easily degraded. Moreover, the higher the pH, the better the IBP degradation; actually, when pH increases from 2.25 to 6.6 and 8.25, the IBP concentration, after an hour of treatment, decreases respectively to 45, 34 and 27 % of its initial value. In addition, as the intensity of light increases from 100 to 400 mJ m^{-2}, the IBP concentration decreases to 34 % of its initial value. A reaction scheme is put forward in the paper, which well describes the effects of volume, pH and light intensity on the IBP degradation measured experimentally. Moreover, the IBP degradation by-products have been identified.

Introduction

The residues of the pharmaceutical compounds (PhACs) administered to humans and animals—excreted as metabolites or in their native form—certainly contribute to water pollution (Kaur et al. 2016). Furthermore, the disposal of unused medications from households and manufacturing facilities also contributes to the spreading of PhACs in the environment. These residues fall within the group of the so-called emerging pollutants (Capocelli et al. 2012; Lapworth et al. 2012; Pereira et al. 2015), together with illegal drugs, endocrine disruptors, personal care products and household substances. Since PhACs are not easily degraded by the typical biological treatments in the municipal wastewater treatment plants (Miralles-Cuevas et al. 2015; Zheng et al. 2011), together with all the toxic substances discharged from a treatment

Responsible editor: Roland Kallenborn

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plant or a septic system, they can end up in surface waters or groundwaters that may ultimately be used as a source of drinking water (Bortone et al. 2013; Erto et al., 2009; Salladini et al. 2007).

Therefore, the effective removal of PhACs and other priority pollutants from wastewaters before they are discharged is an emerging topic in environmental science and engineering (Rivera-Utrilla et al. 2014). Non-steroidal anti-inflammatory drugs (NSAIDs) are among the most frequently detected pharmaceuticals in environmental samples and among the most widespread drugs in the world (Georgaki et al. 2014; Kaur et al. 2016). Ibuprofen (2-(4-(2-methylpropyl)phenyl)propanoic acid, hereinafter IBP) belongs to this family of medicines, and its concentration in the environment is reported to be between 10 and 160 ng L^{-1} (Mendez-Arriaga et al. 2010; Santos et al. 2007; Skoumal et al. 2009). Particularly, IBP is the sixth most abundant pharmaceutical detected in the inlet of wastewater treatment plants (WWTPs) in Italy (Vione et al. 2011), and in general, in the effluents of WWTPs the IBP concentration ranges from 0.4 μg L^{-1} (Thokchom et al. 2015) up to 4.2 μg L^{-1} (Pedrouzo et al. 2011).

It is worth developing new and innovative technologies for the effective and efficient removal of this compound from wastewaters to avoid water source contamination.

The techniques based on advanced oxidation processes (AOPs) result in the oxidization of organic pollutants by generating extremely reactive species, the OH radicals. Over the past two decades, the AOP-based treatments have been studied from both the experimental and the theoretical point of view (Barndõk et al. 2013; Capocelli et al. 2014a, b; Karatza et al. 2010; Musmarra et al. 2016; Rioja et al. 2014; Trapido et al. 2014). Despite their great potential in the field of WWT and the recent advances of scientific knowledge, AOPs are still scarcely employed on pilot and industrial scales, particularly because of their cost (considering the equipment and the process). Actually, they can be energy- and material-intensive, and their residual streams often need further treatment and management (Shu et al. 2013).

On the other hand, combined treatments based on UV light, including TiO$_2$ photocatalysis, appear to be more eco-friendly, also show very interesting removal efficiencies if properly designed. UV light at disinfection doses degrades many of the commonly detected PhACs.

The effect of IBP initial concentration (5–20 mg L^{-1}) was investigated by Achilleos et al. (2010) by adding a titania catalyst concentration of 250 mg L^{-1}. After a treatment time of 60 min, they found IBP removals close to 60, 55 and 50 % at 20, 10 and 5 mg L^{-1} IBP initial concentrations, respectively.

Mendez-Arriaga et al. (2008) studied IBP photodegradation by varying initial concentrations of IBP in the range 25–200 ppm and using 1 g L^{-1} of TiO$_2$. After an irradiation time of 60 min, the maximum degradation (≈ 99 %) was observed for the lowest initial concentration.

Choina et al. (2013) investigated the effect of initial pH of the solution on the IBP removal by catalysed photodegradation (irradiation power = 60 W; TiO$_2$ = 20 mg L^{-1}). After a treatment time of 60 min, they observed IBP degradations close to 70, 65 and 55 % at pH of 9, 7 and 3, respectively. The effect of the initial pH of the solution (pH = 3–7) on ibuprofen photodegradation was also studied by Zhang et al. (2015). Experiments were performed with a visible light incubator intensity of 10.000 lx, by adding titania (TiO$_2$ = 20 mg L^{-1}). IBP removals close to 35, 40, 45, 50 and 42 % were observed at initial pH of 3, 4, 5, 6 and 7, respectively.

Photolysis removal efficiency and phototrasformation of organic compounds dissolved in aquatic environments are strongly influenced by environmental elements, both abiotic and biotic, and operative factors. In particular, the design of operative units on pilot and industrial scales necessarily requires variation in parametric experimentations on a lab scale in order to preliminary investigate the effect of the main working parameters on the photodegradation efficiency, such as pH and light intensity. Moreover, wastewater composition can play an important role in the oxidation of organic pollutants, since several compounds, such as dissolved organic matter and nitrate, can act as photosensitizers of the photolysis degradation efficiency (Bolton et al. 2015).

In this paper, the removal of ibuprofen from synthetic water streams was explored by using a lab-scale experimental device, consisting of a batch reactor equipped with a lamp emitting monochromatic UV light at a fixed wavelength (254 nm) and variable intensity. The effect of the main working parameters on IBP degradation, such as IBP initial concentration (IBP$_0$ 30–60 mg L^{-1}), treatment time (t 0–60 min), solution initial pH (pH 2.25; 6.6; 8.25), solution volume (V 10–30 mL) and light intensity (E 100–400 mJ m^{-2}), was studied by several sets of experiments, showing very promising results. In particular, this paper was aimed at defining working conditions allowing to improve IBP removal to point out the effective application of photolysis. As well known in literature, anionic species (pH > pKa) and molecular species (pH < pKa) are different compounds which have a different behaviour when exposed to the same stress, such as UV irradiation. As a consequence, the importance to investigate the effect of solution pH on the photoremoval efficiency and to propose a reaction modelling able to predict it was considered fundamental for the proper definition of the best conditions for IBP photodegradation. A new model, based on parallel reactions, is proposed to describe the experimental findings, and the model results well fit the experimental results. Eventually, the ibuprofen degradation by-products were identified.

Experimental

Materials

An ibuprofen sodium salt (Na-IBP) of analytical grade with purity higher than 98 % from Sigma-Aldrich (UK) was used. Sample solutions were made by dissolving Na-IBP in Milli-Q water.

Experimental methods

The analytical measurement of the total IBP in solution was performed by gas chromatography coupled with mass spectrometry (GC/MS), preceded by a solid phase extraction (SPE) step. The pharmaceuticals were isolated from the water samples through a reverse-phase cartridge (Oasis HLB 1 cm^3, Waters). Each cartridge was pre-conditioned with 3 mL of methanol (analytical grade, Fluka) followed by 5 mL of ultra-pure water. The samples were extracted under vacuum at a flow rate of 5 mL min^{-1}. After extraction, the cartridges were dried under vacuum for 10 min. Ibuprofen was eluted with 3 mL of methanol. The extracts were dried under a stream of nitrogen. The final volume extracted was 100 μL.

The dried extracts were derivatized by adding 200 μL MTBSTFA + 1 % TBDMSCl (Fluka). The derivatization was carried out in capped vials kept at 60 °C for 90 min and then quickly cooled down, after which the extracts were transferred into GC vials and analysed by GC/MS (1 μL sample volume).

The trimethylsilyl (TMS) derivatives of IBP were analysed on a GC/MS system consisting of a 7890A gas chromatograph with a mass spectrometric detector MSD5975C (Agilent Technologies, USA), equipped with a capillary column HP-5ms (capillary column, 5 % phenyl–95 % methylsiloxane, length 30 m, internal diameter 0.25 mm, film thickness 0.25 μm).

The irradiation of the aqueous samples was carried out in plastic Petri dishes of 90 mm diameter. The sample pH was adjusted by addition of NaOH or HCl. For the irradiation, a Vilber Lourmat BLX-254 with ultraviolet wavelength of 254 nm was used. The intensity of the incident light was varied in the range 100–400 mJ m^{-2}. The temperature was measured and kept constant at 20 °C in all the experiments. A simplified sketch of the experimental apparatus is shown in Fig. 1, while the experimental conditions are summarized in Table 1.

Experimental results

Ibuprofen photodegradation was studied through parametric variation experiments. The effects of initial concentration of IBP (IBP$_0$), volume of the solution (V), initial pH of the
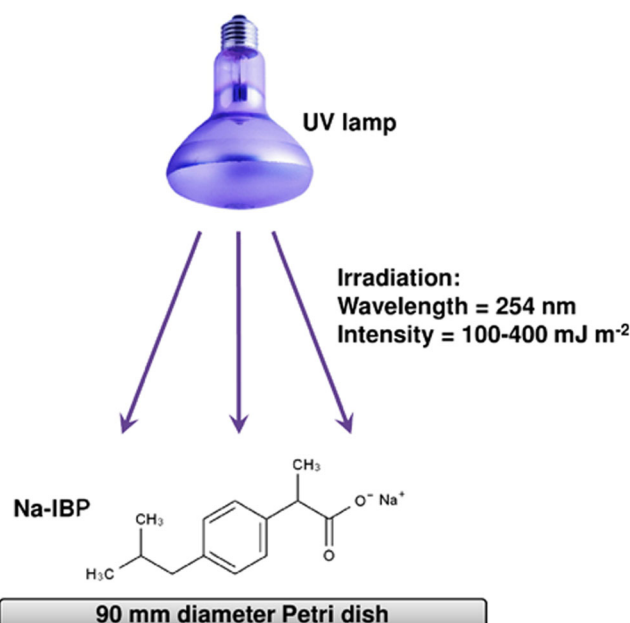

Fig. 1 Sketch of the experimental apparatus (Chianese et al. 2016)

solution (pH) and UV-light irradiation intensity (E) were investigated. The tests were performed using a UV-light irradiation wavelength at 254 nm, and the IBP concentration trend as a function of irradiation time was evaluated. Furthermore, the ibuprofen removal, normalized to the initial concentration (IBP/IBP$_0$), was assessed.

Investigations were performed in triplicate; however, the average values were only reported.

Figure 2 shows the IBP concentration vs. irradiation time, in the range 0–60 min, as a function of IBP initial concentration (test no. 1). IBP$_0$ varied in the range 30–60 mg L^{-1}. For these experiments, 20 mL solution volume, 6.6 initial pH and 400 mJ m^{-2} UV-light irradiation intensity were used.

In agreement with literature findings (Mendez-Arriaga et al. 2008), the analysis of the figure shows that the ibuprofen concentration decreases monotonically with time and that the higher the IBP$_0$ concentration, the higher the IBP removal.

Table 1 Experimental conditions

Test no.	Parameter	Constants
1	IBP$_0$ = 30; 45.9; 60 mg L^{-1}	V = 20 mL pH = 6.6 E = 400 mJ m^{-2}
2	V = 10; 20; 30 mL	IBP$_0$ = 45.9 mg L^{-1} pH = 6.6 E = 400 mJ m^{-2}
3	pH = 2.25; 6.6; 8.25	V = 20 mL IBP$_0$ = 45.9 mg L^{-1} E = 400 mJ m^{-2}
4	E = 100; 200; 400 mJ m^{-2}	V = 20 mL pH = 6.6 IBP$_0$ = 45.9 mg L^{-1}

Fig. 2 IBP concentration trend vs. irradiation time for different IBP initial concentrations (IBP_0): $V = 20$ mL, pH = 6.6, $E = 400$ mJ m^{-2}
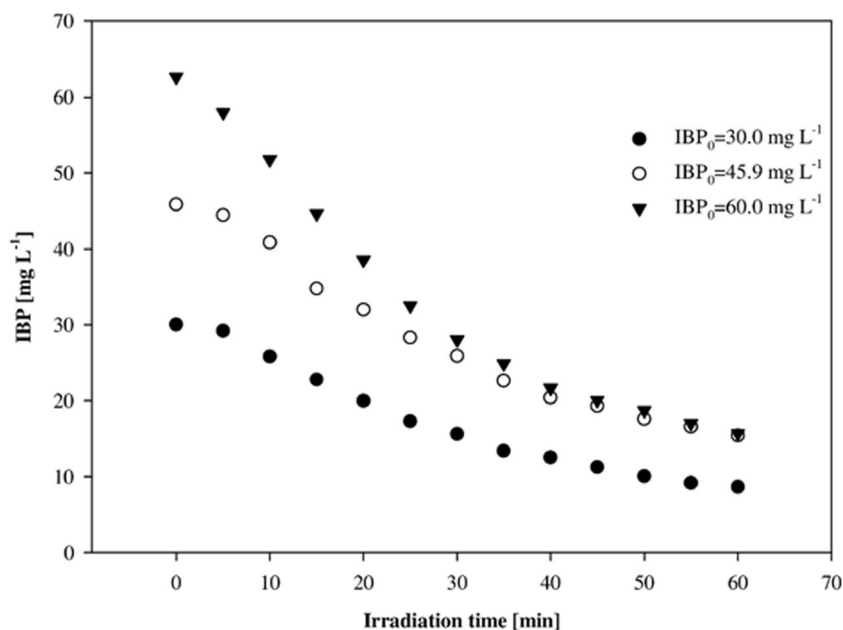
After an hour of treatment at an initial IBP concentration of 60 mg L^{-1}, a final ibuprofen concentration of 15.7 mg L^{-1} was found and an IBP removal close to 75 % was observed. With an initial IBP concentration of 45.9 and 30 mg L^{-1}, the final IBP concentrations were equal to 15.5 and 8.7 mg L^{-1} and removals of about 66 and 71 % were reached, respectively. The effect of IBP initial concentration on photodegradation removal efficiency seemed to be strongly influenced by the irradiation time, since after 60 min to UV irradiation exposition, quite similar final IBP concentrations of 15.7 and 15.5 mg L^{-1} were achieved at IBP initial concentrations of 45.9 and 60 mg L^{-1}, respectively. In particular, IBP concentration decreased most rapidly at 60 mg L^{-1} than at 45.9 mg L^{-1}, without achieving asymptotic values.

Similar results were found by Achilleos et al. (2010) studying the IBP photodegradation in conjunction with titania catalyst.

Figure 3 shows the IBP irradiation time profile, in the range 0–60 min, with the solution volume *V* as parameter (test no. 2). *V* varied in the range 10–30 mL, while IBP initial concentration (IBP_0) of 45.9 mg L^{-1}, initial pH = 6.6 and $E = 400$ mJ m^{-2} UV were used.

The effect of the solution volume is well visible in the figure: the lower the *V*, the lower the IBP concentration, with a monotonically decreasing trend. At $t = 60$ min with a solution volume of 10 mL, the lowest ibuprofen concentration was observed (14 mg L^{-1}) and an IBP removal close to 69 % was found. With $V = 20$ and 30 mL, the final IBP concentrations were equal to 15.5 and 17.6 mg L^{-1} and removals of about 66 and 62 % were reached, respectively.

Assuming the Petri dish as a completely stirred reactor, the irradiation available for the IBP photochemical degradation is the average irradiation of the solution volume (E_V) (Bolton and Stefan 2003). As reported by Bolton and Linden (2003), E_V can be calculated by considering a number of corrective coefficients, such as the Reflection Factor, to take the light reflection at the solution/air interface into account; the Petri Factor, to take the radiation non-uniformity across the dish into account; the Water Factor, to take the water adsorption of the light into account and the Divergence Factor, to take the lamp incomplete collimation into account. Assuming that the Reflection and Petri Factors are constant, E_V varies with the Water and Divergence Factors, which are influenced by the solution depth; in particular, the lower the solution depth, the higher the Water and Divergence Factors and the higher the effective irradiation. Since the surface area exposed to UV irradiation was kept constant, the lower the solution volume, the lower the solution depth available for the photodegradation reaction, thus increasing the effective irradiation and the IBP removal.

Figure 4 shows the IBP irradiation time profile, in the range 0–60 min, with the initial pH of the solution as parameter (test no. 3). pH varied in the range 2.25–8.25, while $V = 20$ mL, $IBP_0 = 45.9$ mg L^{-1} and $E = 400$ mJ m^{-2} were used.

The solution pH seems to strongly influence the IBP reduction as shown by the experimental results. The higher the solution pH, the lower the IBP concentration with a monotonically decreasing trend. At a time of 60 min with a solution pH of 8.25, the lowest ibuprofen concentration was observed (12.4 mg L^{-1}) and an IBP removal close to 73 % was found. With a pH of 6.6 and 2.25, the final IBP contents were equal to 15.5 and 20.7 mg L^{-1} and removals of about 66 and 55 % were reached, respectively. Thus, a decrease in initial pH of the solution drastically increases the residual IBP concentration.

Fig. 3 IBP trend vs. irradiation time for different solution volumes: $IBP_0 = 45.9$ mg L^{-1}, pH = 6.6, $E = 400$ mJ m^{-2}
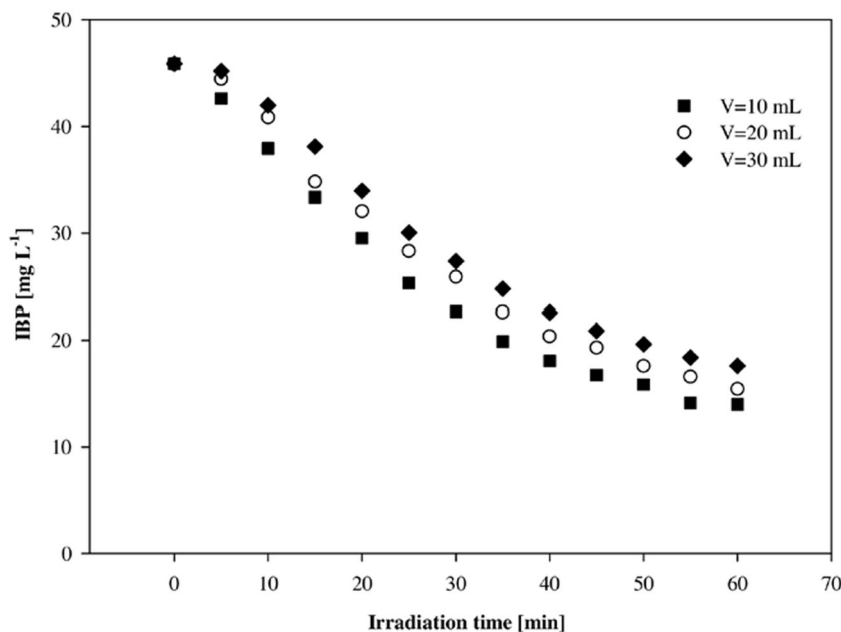
This behaviour can be explained by considering that an anionic species (A^-) and a molecular (HA) IBP species may coexist in aqueous solutions, with their ratio varying as a function of the solution pH and temperature (Canonica et al. 2008). The anionic/molecular IBP ratio can be calculated considering the IBP pKa. In particular, the molecular IBP species prevails for pH < pKa, while the anionic IBP species is prevalent for pH > pKa (Iovino et al. 2015). Assuming dilute solutions, the anionic and molecular species concentration (Reijenga et al. 2013) can be assessed by the Henderson–Hasselbalch equation:
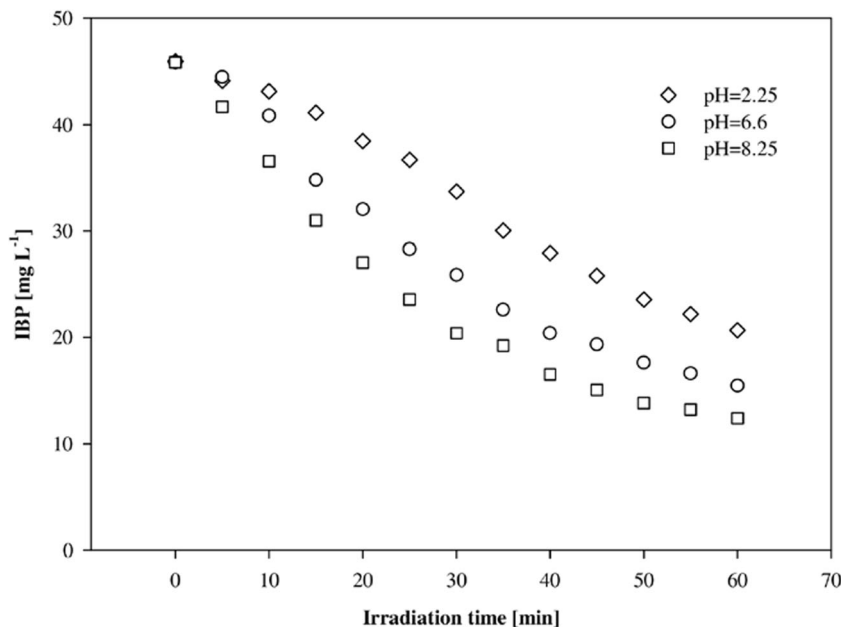
$$pH = pKa + \log \frac{[A^-]}{[HA]} \tag{1}$$

A pKa value of 4.32 was assumed for solution temperature equal to 20 °C (Vicenteño-Vera et al. 2010).

Photodegradation seems to be more effective for the IBP anionic compound (pH > pKa) than for its molecular

Fig. 4 IBP trend vs. irradiation time for different initial pH of the solution: $V = 20$ mL, $IBP_0 = 45.9$ mg L^{-1}, $E = 400$ mJ m^{-2}

compound (pH < *pKa*); this finding is in agreement with recent results proposed by Choina et al. (2013) and by Zhang et al. (2015) which studied IBP photodegradation in the presence of titania as catalyst. In both papers, the IBP removal efficiency decreases as the pH decreases and the lowest values are attained at pH = 3.

It is worth highlighting that IBP photodegradation investigations, reported in this paper, were performed without any catalyst; a similar pH influence on IBP photodegradation was obtained.

Figure 5 shows the IBP irradiation time profile, in the range 0–60 min, with UV-light irradiation intensity as a parameter (test no. 4). *E* varied in the range 100–200 mJ m^{-2}, while V = 20 mL solution volume, initial concentration of IBP (IBP$_0$) of 45.9 mg L^{-1} and initial pH of the solution (pH) of 6.6 were used.

The IBP reduction is strongly affected by the irradiation intensity as shown by the experimental results. The higher the irradiation intensity, the lower the IBP concentration with a monotonically decreasing trend, in agreement with Yuan et al. (2009). At a time of 60 min with an irradiation intensity of 400 mJ m^{-2}, a final IBP concentration of 15.5 mg L^{-1} was observed and an IBP removal close to 66 % was found. With irradiation intensities of 200 and 100 mJ m^{-2}, final IBP concentrations were equal to 28.7 and 38.1 mg L^{-1} and removals of about 37 and 17 % were reached, respectively.

This result is straightforward, since as the UV-light intensity increases, also the effective irradiation available for the IBP degradation increases, when the other parameters are kept constant.

Modelling

The IBP photochemical removal modelling was carried out considering the IBP dissociation species. The ibuprofen sodium salt used for the experiments (Na-IBP) is assumed to completely dissociate in Na$^+$ and A$^-$ ionic species in an aqueous solution. The anionic IBP species (A$^-$) undergoes the hydrolysis equilibrium reaction to form the molecular species of the IBP (HA). As highlighted by literature findings (Iovino et al. 2015), ibuprofen removal from water is strongly influenced by its dissociation grade. Starting from this evidence, the proposed model reflects the importance to take into account the effect of ibuprofen dissociation on photodegradation, since IBP photolysis was investigated by considering two parallel reactions which involve anionic and molecular forms of ibuprofen as reagents. The IBP molecular/anionic species concentration ratio was calculated according to the Henderson–Hasselbalch equation (see Eq. (1)), and it was assumed that the hydrolysis equilibrium condition was instantaneously established. A sketch of the reaction scheme is shown in Fig. 6.

At the initial irradiation time (i.e. $t = 0$), the material balance between the initial IBP concentration and the molecular and the anionic IBP compounds can be expressed by the following equation:

$$\text{IBP} = \text{IBP}_0 = [\text{A}^-]_0 + [\text{HA}]_0 \qquad (2)$$

where [HA]$_0$ and [A$^-$]$_0$ are the initial molar concentrations of molecular and anionic IBP species.

As reported in the reaction scheme of Fig. 6, both IBP forms can be oxidized by the UV light at different reaction

Fig. 5 IBP trend vs. irradiation time for different irradiation intensities: V = 20 mL, IBP$_0$ = 45.9 mg L^{-1}, pH = 6.6
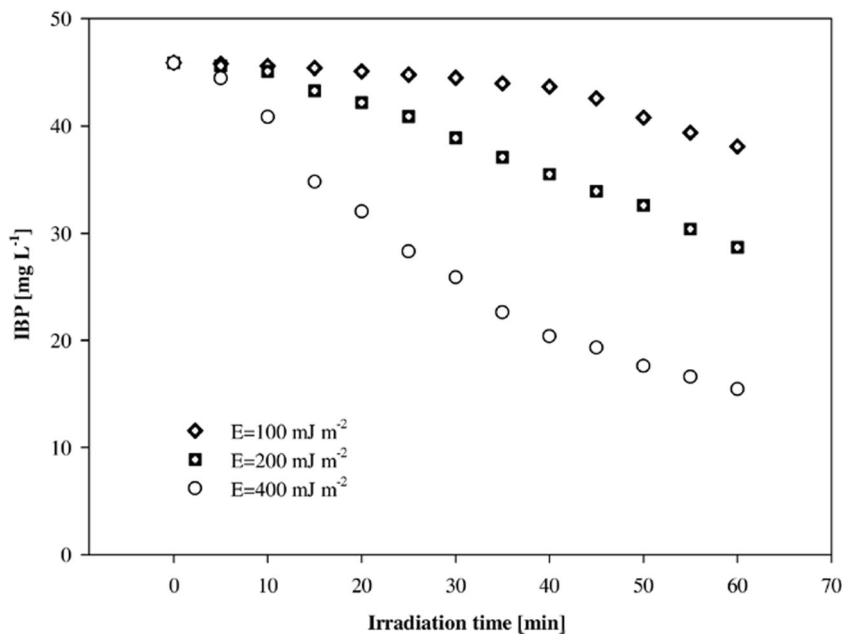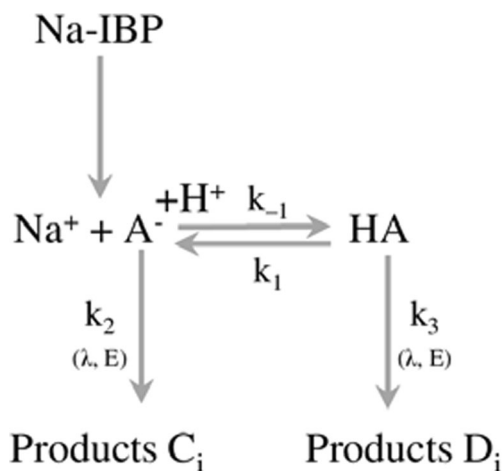
Fig. 6 IBP photodegradation reaction scheme (Chianese et al. 2016)

rates, yielding different reaction products (Karatza et al. 2008). First-order reactions for the molecular and the anionic IBP species photodegradation were assumed and reported below:

$$A^- \xrightarrow{k_2} \text{Products } C_i \tag{3}$$

$$HA \xrightarrow{k_3} \text{Products } D_i \tag{4}$$

where k_2 and k_3 are the kinetic constants of the anionic and molecular IBP form reaction rates, respectively. The irradiation time dependence of the IBP, A^- and HA concentrations can be evaluated by the following equations (Chianese et al. 2016):

$$\frac{dIBP_t}{dt} = -k_2 \times [A-]_t - k_3 \times [HA]_t \tag{5}$$

$$IBP_t = IBP_0 - [A-]_t - [HA]_t \tag{6}$$

$$\frac{[A^-]_t}{[HA]_t} = \frac{[A-]_0}{[HA]_0} = 10^{(pH-pKa)} = K_1 \tag{7}$$

where IBP_t, $[HA]_t$ and $[A^-]_t$ are the total IBP and the molecular and anionic IBP species concentrations at time t, respectively. It is worth specifying that the total IBP concentrations in solution at several irradiation times were measured, as described in the section Modelling, while molecular and anionic IBP species concentrations at time t were theoretically calculated.

A first-order finite difference forward scheme method was used to numerically solve the system of Eqs. 5–7, by using initial conditions (8) to assess the three variables: IBP, A^- and HA concentrations.

$$\begin{cases} & IBP = IBP_0 \\ t = 0 & [A^-] = [A^-]_0 \\ & [HA] = [HA]_0 \end{cases} \tag{8}$$

The molecular and the anionic IBP species ratio (K_1) as a function of the initial pH of the solution is reported in Table 2.

Table 2 Molecular and anionic IBP species ratio

pH	K_1
2.25	0.0085
6.6	190.9
8.25	8527.1

As previously indicated, at a solution temperature of 20 °C, a *pKa* value of 4.32 was assumed (Vicenteño-Vera et al. 2010).

The data collected in the experimental tests (numbers 1–4) have been used to estimate the reaction rate constants, k_2 and k_3, by a non-linear regression analysis. The values of these constants are collected in Table 3. As reported, IBP photodegradation rate can be enhanced at pH > *pKa*, since the kinetic constant of photolysis of IBP anionic form, k_2, which prevails at this condition, is almost twice as much as the kinetic constant of photolysis of IBP molecular form, k_3.

It is to be highlighted that the values of the kinetic constants reported in this paper cannot be really compared with the data in the literature since the reaction scheme proposed is innovative as the dissociated species of IBP were considered. However, some similarities can be found in Li et al. (2015) where a photodegradation scheme for the direct photolysis based on the excitation of IBP and its sensitization is suggested. Moreover, a pseudo-first order reaction rate is proposed and a value of the rate constant of 0.0134 min^{-1} is estimated. A first-order mechanism to model IBP direct photodegradation is also presented by da Silva et al. (2014) who find a kinetic constant of 0.037 min^{-1}.

It is worth emphasizing that the influence of the UV-light irradiation intensity on the IBP degradation is included in the kinetic constants (Nick et al. 1992). According to Bolton and Stefan (2003), k can be defined by using the equation reported below:

$$k = k^* \cdot E^* \tag{9}$$

where k^* and E^* are the fluence-based first-order rate constant [m^2 W^{-1} s^{-1}] and the volume averaged fluence rate [W m^{-2}], respectively. The former depends on the quantum yield, the molar photon energy and the molar absorption coefficient, at a fixed irradiation wavelength; the latter depends on the UV-light irradiation, the reflection coefficient, the absorption coefficient of the solution, the depth of the solution and the distance between the UV source and the Petri dish (Bolton and Linden 2003; Bolton and Stefan 2003).

Figure 7a–d illustrates how the model predictions fit to the experimental findings. The model predictions seems to fit well

Table 3 Kinetic constants

k_2 [min^{-1}]	k_3 [min^{-1}]
0.021	0.012
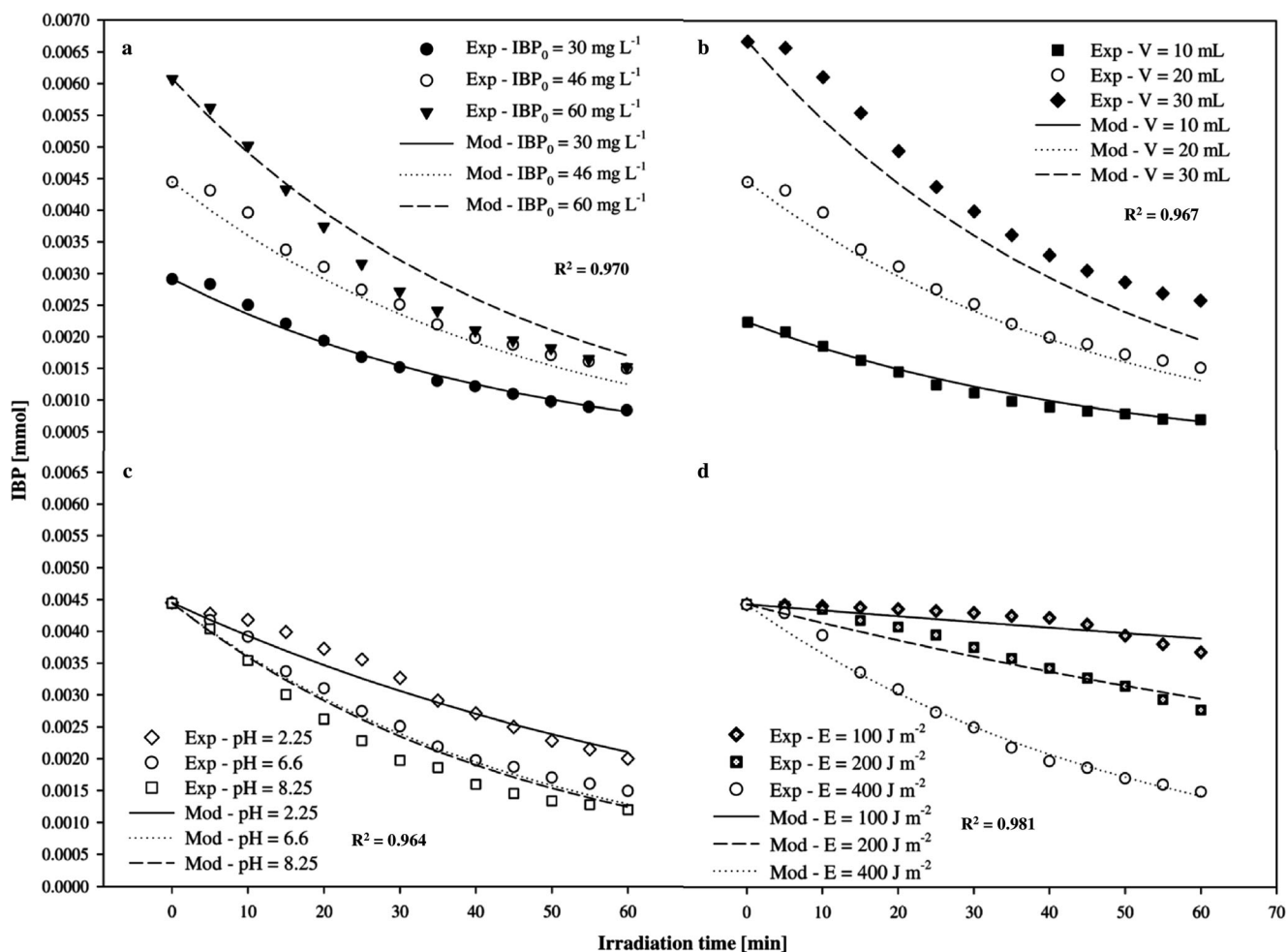
Fig. 7 IBP time evolution fitting (*Exp* experimental; *Mod* model). **a** IBP initial concentration influence (test no. 1). **b** Solution volume influence (test no. 2). **c** Solution initial pH influence (test no. 3). **d** Irradiation intensity influence (test no. 4)

to the results of the investigations even if for the data at $IBP_0 = 30$ mg L^{-1} (Fig. 7a), $V = 30$ mL (Fig. 7b) and pH = 8.25 (Fig. 7c), some divergences can be observed.

This model was assessed by calculating the determination coefficient (R^2), as reported in Fig. 7. R^2 ranges between 0.964 and 0.981, which confirms that the reaction scheme suggested is verified and that the model can well predict IBP photodegradation. Furthermore, the validity of the model is underlined in Fig. 8, showing the comparison between the model predictions and the experimental results. As all the points fall within a variation range of ±25 %, the best fit of the model to the experimental observations is demonstrated and the reaction scheme hypothesis is corroborated.

Photodegradation by-products

A GC/MS, preceded by derivatization (TMS esters), was used to identify the by-products of IBP photodegradation. It is

worth specifying that reaction products were experimentally determined through qualitative analysis.

An example of mass spectrum of trimethylsilyl ester of ibuprofen is reported in Fig. 9. Ibuprofen molecular ion is seen at $m/z = 278$. Fragment ion at $m/z = 263$ represents the fragmentation of methyl group from molecular ion, while $m/z = 205$ shows trimethylsilyl group fragmentation. Ion at $m/z = 160$ is developed with sequential fragmentation of trimethylsilyl and carboxyl groups. The base ion is present at $m/z = 73$ and is typical for MSTFA derivatisation.

The samples at the irradiation times of 0 and 60 min were analysed (Fig. 10). As shown by the chromatographs reported in Fig. 10, after an hour of treatment two prevailing by-products were identified while IBP decreased by half in the photolysis solution, which validates the kinetic model hypothesised. In agreement with the results by Castell et al. (1987), 1-(4-isobutylphenyl)ethanol (IBPE) and 4-isobutylacetophenone (IBAP) were identified, with IBPE as the dominant by-product in agreement with Jacobs et al. (2011).

Fig. 8 Parity plot ±25 %
variation range
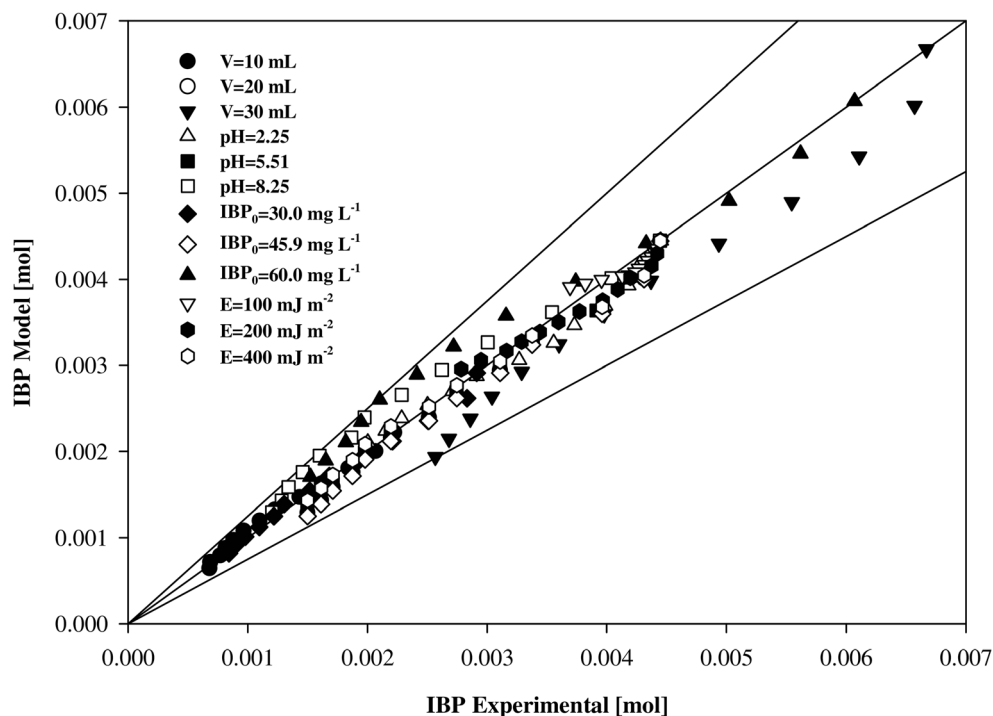
IBP decarboxylation in non-aqueous systems with for-
mation of IBPE and IBAP was demonstrated by Castell
et al. (1987); nevertheless, IBP decarboxylation can also
be observed in aqueous systems as both IBPE and

IBAP were found (Jacobs et al. 2011; Mendez-Arriaga
et al. 2008).

A possible IBP degradation pathway by photolysis is
sketched in Fig. 11. As shown, IBPE and IBAP formation
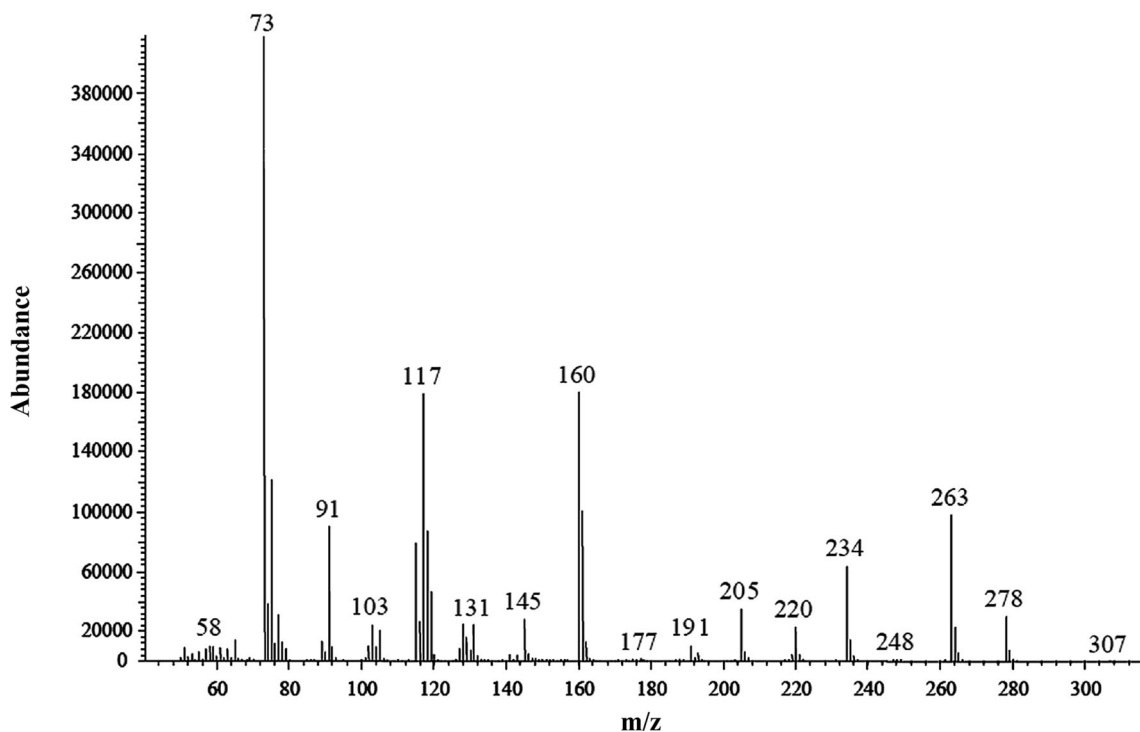
Fig. 9 Mass spectrum of ibuprofen-trimethylsilyl
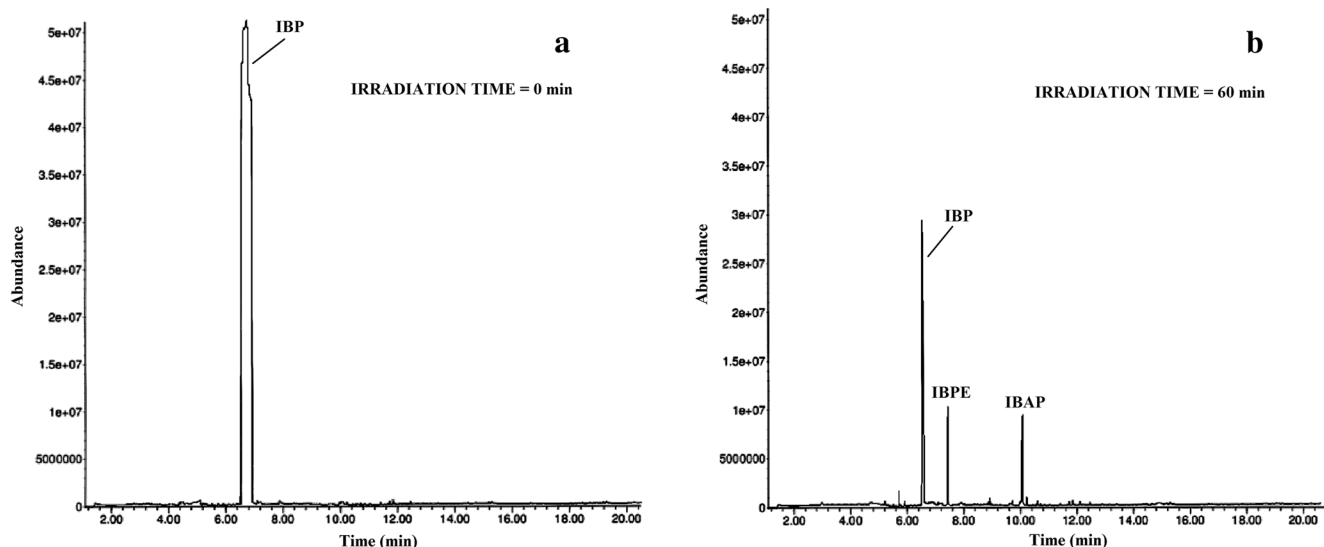
Fig. 10 Total ion chromatograms of IBP photodegradation. **a** IBP solution. **b** Photolysis by-products (*IBPE* 1-(4-isobutylphenyl)ethanol; *IBAP* 4-isobutylacetophenone)

can occur starting from IBP decarboxylation, with the subsequent reaction between O_2 and the carbon radical, followed by the hydroxylation of the benzene ring (Castell et al. 1987; Jacobs et al. 2011).

IBP photodegradation by-product toxicity was investigated by several studies (Li et al. 2015; Mendez-Arriaga et al. 2008; da Silva et al. 2014). An increase of the inhibition of the bacteria test due to intermediate products (ibuprofen hydroxylated) was observed until a peak value was achieved, following inhibition reduction by increase of the irradiation time. This behaviour suggests that photodegradation by-products could be more toxic than IBP but they can be removed by photodegradation itself.

Conclusions

A lab-scale experimental apparatus, consisting of a batch reactor equipped with a lamp emitting monochromatic UV light at a fixed wavelength of 254 nm was used to investigate the photochemical degradation of ibuprofen from simulated water streams.

The influence of the irradiation time, the initial IBP concentration, the volume and initial pH of the solution and the UV-light irradiation intensity were studied.

In an hour of irradiation time, the ibuprofen removal efficiency varied in the range 20–75 %. Experiments performed at initial pH of the solution of 8.25 and at initial concentration of
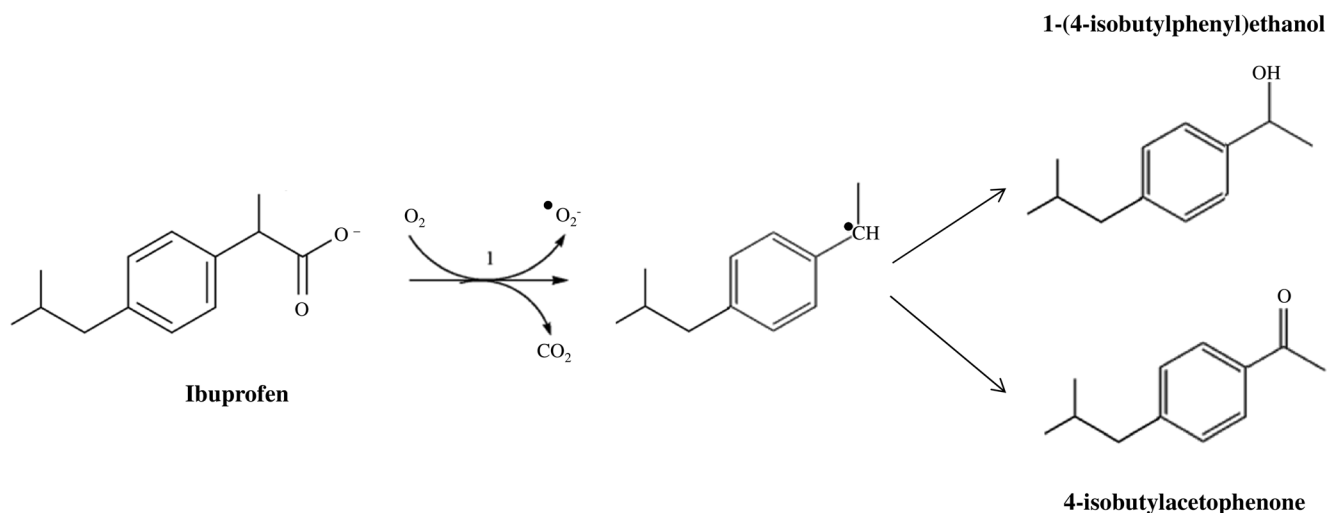
Fig. 11 Possible IBP degradation pathway by photolysis

IBP of 60 mg L^{-1} showed the best results as IBP removals close to 75 % were achieved.

Working conditions for IBP photodegradation enhancement was found as when the IBP anionic form prevails into the solution (pH > pKa), IBP photolysis rates doubled, highlighting the effectiveness of photodegradation process.

A new reaction scheme was defined, and the statistical estimation of the reaction rate constants was carried out.

A series–parallel reaction system was used to model the photodegradation mechanism, with the IBP dissociation at equilibrium in the first step, while first-order photochemical reactions of the IBP molecular and anionic forms were assumed as parallel reactions. The fit of the IBP oxidation measurements was used to determine the reaction rate constants. The experimental results are well interpreted by the model, and the efficiency of the IBP decay mechanism and the validity of the model proposed are supported by an R^2 in the range 0.964–0.981 and a parity plot with a variation range of ±25 %.

Finally, a possible ibuprofen degradation pathway by photolysis was put forward and 4-isobutylacetophenone and 1-(4-isobutylphenyl)ethanol were identified as by-products after an hour of treatment.

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