Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1153908

57 (2016) 22878–22886
October

Taylor & Francis
Taylor & Francis Group

Ibuprofen degradation in aqueous solution by using UV light

Simeone Chianese[a], Pasquale Iovino[b], Silvana Canzano[b], Marina Prisciandaro[c,*], Dino Musmarra[a]

[a]*Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Seconda Università degli Studi di Napoli, Real Casa dell'Annunziata, Via Roma 29, 81031 Aversa (CE), Italy*
[b]*Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Seconda Università degli Studi di Napoli, Via Vivaldi 43, 81100 Caserta, Italy*
[c]*Dipartimento di Ingegneria Industriale e dell'Informazione e di Economia, Università dell'Aquila, viale Giovanni Gronchi 18, 67100 L'Aquila, Italy, Tel. +39 0862 434241; Fax: +39 0862 434203; email: marina.prisciandaro@univaq.it*

Received 31 May 2015; Accepted 8 February 2016

ABSTRACT

Recent regulation policies are focusing on the presence of priority and emerging pollutants in water, among them, pharmaceutical residues are of particular public concern since trace of these molecules is commonly found in drinking and superficial waters. Progresses in innovative technologies for wastewater treatment are mandatory in order to improve their abatement efficiencies for water source prevention and reclamation. The OH$^\cdot$-based technologies, a group of different techniques usually called advanced oxidation processes (AOPs), can be used to mineralize organic pollutants. In particular, combined treatments based on UV light appear to be more eco-friendly, also giving very interesting removal efficiencies if opportunely devised. Moreover, many of the commonly detected pharmaceutical compounds are susceptible to degradation by UV at disinfection doses. In this paper, the removal of ibuprofen (IBP)—a widely used non-steroidal anti-inflammatory drug (NSAID)—from synthetic water streams was explored using a lab-scale experimental device, consisting of a batch reactor equipped with a lamp emitting monochromatic UV light at fixed wavelength and intensity (254 nm; 400 mJ m^{-2}). IBP initial concentration (C_{IBP_0}) was varied in the range 30–60 mg L^{-1}. The treatment time, the initial IBP concentration, pH and the presence of nitrates were investigated by several sets of experiments in order to study their effect on IBP degradation, showing very promising results. IBP removal of 75% was obtained at pH 6.0 with a concentration of $NaNO_3$ of 10 mg L^{-1} and at pH 6.6 with an initial concentration of ibuprofen of 60 mg L^{-1}. Moreover, a reaction mechanism has been proposed, which fits well in the experimental results, and the kinetic constants of 0.026 and 0.015 were statistically evaluated.

Keywords: Ibuprofen; Photodegradation; Nitrates; Advanced oxidation processes; Modelling; Wastewaters

---

*Corresponding author.

Presented at EuroMed 2015: Desalination for Clean Water and Energy Palermo, Italy, 10–14 May 2015. Organized by the European Desalination Society.

1. Introduction

Solving water quality problems requires strategies to prevent, treat and remediate water pollution [1]. The cheapest and most effective strategy to protect water quality is reducing or removing contaminants at the source, before they get into natural water bodies (prevention). Unfortunately, nowadays, the quality of many water sources and watersheds has already been compromised; therefore, a second-order intervention (treat wastewater before it is discharged) or third-order intervention (physically restore the biological integrity of polluted watercourses through remediation) are mandatory [2–7].

Anthropogenic activities release numerous pollutants in the environment: industries discharge about 300–500 million tons of heavy metals, organics (persistent organic pollutants—POPs), toxic sludge and other wastes into the world's waters every year [8]. Moreover, about 700 new chemicals are introduced into commerce every year in the United States alone [1], and most of them are discharged, modified or not, in public sewers, without considering the combination of these pollutants that cause worse, or different, impacts than the cumulative effects of a single one.

Among those substances, pharmaceutical residues (pharmaceutical compounds, PhACs), excreted after application in their native form or as metabolites, strongly contribute to the water pollution problem, together with the disposal of unused medicines of households and manufacturing facilities. PhACs residues, together with illicit drugs, endocrine disruptors, personal care and home products constitute the group of the so-called *emerging pollutants* [9]. Despite their widespread use, the fate of many of these new chemicals is still mostly unknown since till now chemical measurement techniques have been unable to detect contaminants at low concentrations in the environment. The presence of trace pharmaceuticals and other xenobiotic compounds in drinking and superficial waters is a major public health concern, since little is known about the potential chronic effect on human health associated with long-term ingestion of mixtures of these substances [10]. Thus, over the past few years, both the occurrence and fate of pharmaceutical residues have attracted the interest of the scientific community [11,12].

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 [12]. 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} [13–15]. Particularly, IBP is the sixth most abundant pharmaceutical detected in the inlet of wastewater treatment plants (WWTPs) in Italy [16].

In order to improve the removal efficiency of this compound, for water source prevention and reclamation, the development of innovative technologies is therefore mandatory. Among the technologies aimed at the oxidization of organic pollutants, advanced oxidation processes (AOPs) are a group of different techniques based on the generation of extremely reactive species, the $OH^{\cdot}$. Over the past two decades, the AOP treatments have been studied from both the experimental and the theoretical point of view [17,18]. 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 the high costs (considering the equipment and the process). Furthermore, AOP efficiency is influenced by the wastewater composition and often their residual streams need to be further treated and managed, requiring the combination of several removal techniques [19–21].

Photo-oxidation process presents several disadvantages, since they can be energy consuming and material intensive [22]; however, combined treatments based on UV light appear to be more eco-friendly, with a reduced energy demand, also with very interesting removal efficiencies if opportunely devised [23,24].

Many of the commonly detected pharmaceutical compounds can be degraded by UV at disinfection doses. It is to point out that photodegradation of every molecule dissolved in water is strongly dependent on many experimental factors such as the volume of solution, the turbidity, and in real waters, the presence of other species may enhance photodegradation by generative strong active species when irradiated [25] or acting as $OH^{\cdot}$ scavengers, such as nitrite/nitrate, dissolved organic matter, carbonates [26].

The degradation of IBP by hydrodynamic cavitation was investigated by Musmarra et al. [27]. They observed an ibuprofen removal close to 60% with an initial concentration of IBP of 200 μg L^{-1}, a run time of 60 min, an electrical energy per order (EEO) of 10.77 kWh m^{-3} and a relative inlet pressure of 0.35 MPa.

Quero-Pastor and co-workers [28] found IBP removal over 99% using ozonation, with O_3 flow stream of 50 g h^{-1} and a run time of 20 min.

Scheers et al. [29] studied ibuprofen removal using H_2O_2-based AOPs, observing the complete degradation of IBP, at an initial concentration of

22 mg L^{-1}, by the application of a H_2O_2 concentration of 0.024 mg L^{-1} for the photo-assisted Fenton oxidation.

Scheideler et al. [30] combined O_3/H_2O_2 and UV light to investigate the degradation of atrazine, bromacil, ibuprofen and NDMA (10–20 µg L^{-1}). They found 59, 85 and >99% removal of ibuprofen by UV/H_2O_2, O_3/H_2O_2 and O_3/H_2O_2/UV, respectively.

In this paper, the removal of ibuprofen from synthetic water streams was explored by using a lab-scale experimental apparatus, consisting of a batch reactor equipped with a lamp emitting monochromatic UV light at fixed wavelength and intensity (254 nm; 400 mJ m^{-2}).

The IBP initial concentration (C_{IBP_0}) was varied in the range 30–60 mg L^{-1}. Several sets of experiments were carried out to study the effect of different parameters on IBP degradation, such as the treatment time, the initial IBP concentration, the pH, the presence of nitrates, showing very promising results. In particular, the presence of NO_3^- ions, instead of acting as OH· scavenger [31], seems to enhance the photodegradation of IBP, in agreement with the literature findings [32,33]. Moreover, a reaction mechanism is suggested, which fits well in the experimental results.

2. Materials and methods

An ibuprofen sodium salt (Na-IBP) of analytical grade with purity higher than 98% from Sigma–Aldrich (UK) was used. The presence of nitrate was simulated by adding powder sodium bicarbonate ($NaNO_3$) of analytical grade with purity higher than 99.5% from Sigma–Aldrich (UK) to the ibuprofen solution. Solutions were made using MilliQ water.

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 cc, 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 gentle 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 conducted in capped vials at 60˚C for 90 min. Then, they were cooled down quickly and the extracts were transferred into GC vials which were then 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 (20 mL, containing 30–60 mg L^{-1} IBP) 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 UV-Crosslinker BLX-E254 with exposure chamber dimensions of 14.5 cm× 36 cm× 35 cm ($H \times D \times W$), five UV tubes of ultraviolet wavelength of 254 nm was used. The temperature was measured and kept constant at 20˚C in all experiments. A simplified sketch of the experimental apparatus is shown in Fig. 1.

3. Results and discussion

3.1. Experimental results

A parametric investigation was carried out to study IBP removal as a function of the irradiation time. The effects of IBP initial concentration (C_{IBP_0}) and nitrate presence (NO_3^-) were studied in two series of experiments, respectively. In both cases, a solution volume of 20 mL, an irradiation wavelength of 254 nm and an UV-light intensity of 400 mJ m^{-2} were used. Experimental runs were performed in triplicate; however, the average values are reported.

The influence of IBP initial concentration is sketched in Fig. 2, which shows the IBP removal vs. the irradiation time (0–60 min). Three IBP initial concentrations were used (30, 45.9 and 60 mg L^{-1}), while the initial pH of the solution was kept constant at the value of 6.6. The ibuprofen removal increases monotonically with irradiation time and higher the C_{IBP_0} concentration, higher is the IBP degradation, as highlighted by Mendez-Arriaga et al. [34] and Achilleos et al. [35]. At a runtime of 60 min, an IBP removal close to 75% was found with C_{IBP_0} = 60 mg L^{-1}. Removals of about 66 and 71% were observed with C_{IBP_0} = 45.9 and 30 mg L^{-1}, respectively.

As shown in Fig. 3, the absolute removal of ibuprofen increases rapidly by achieving the maximum value upon which a slow decrease can be observed. The lower the IBP concentration, the higher will be the IBP absolute removal. The pick values were found at a runtime in the range 10–15 min, while the lowest values were found at a runtime in the range 55–60 min. The highest IBP absolute removal

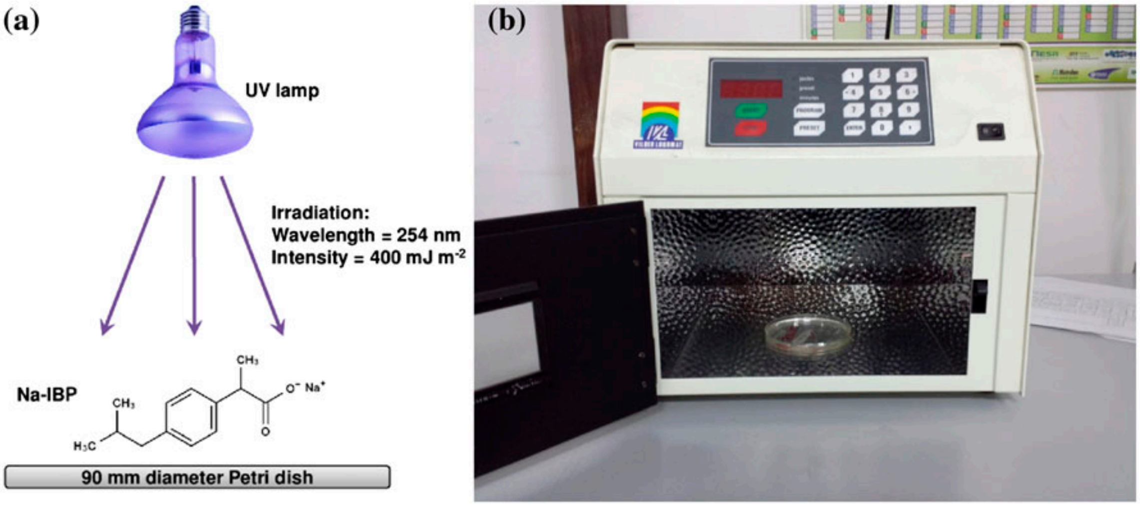

Fig. 1. Experimental apparatus: (a) simplified sketch and (b) Vilber-Lourmat BLX-E254.

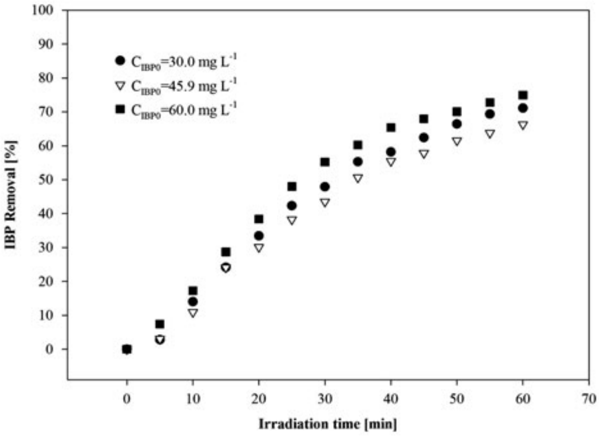

Fig. 2. IBP initial concentration effect on IBP removal.

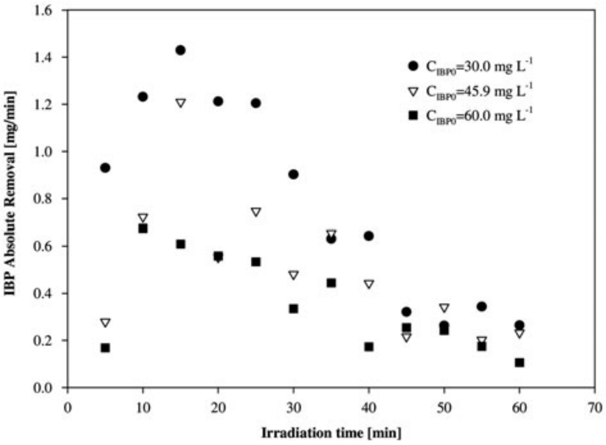

Fig. 3. IBP absolute removal.

close to 1.4 mg min^{-1} was observed at a runtime of 15 min with $C_{\text{IBP}_0} = 30$ mg L^{-1}.

The influence of the presence of nitrate is sketched in Fig. 4, which shows the comparison between the

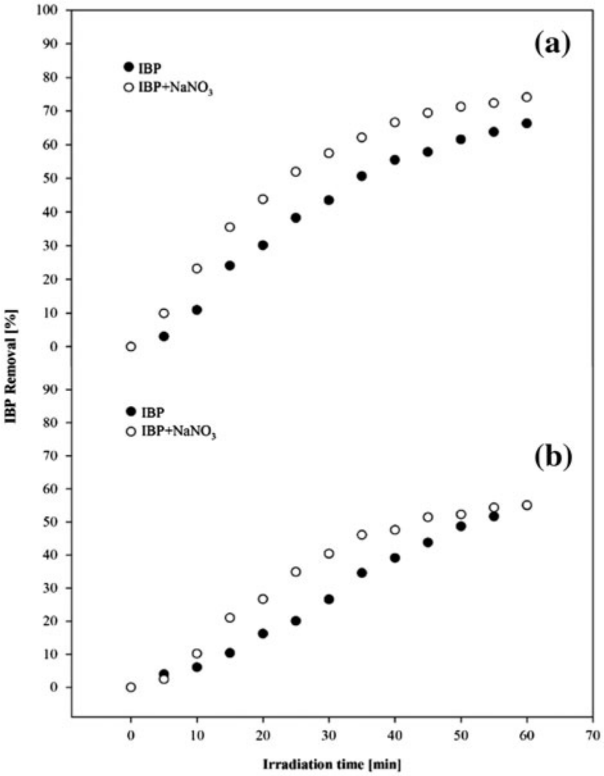

Fig. 4. Nitrate effect on IBP removal: (a) initial pH 6.0 and (b) initial pH 2.25.

IBP removal with and without NO_3^- as a function of the irradiation time (0–60 min). Nitrate was added as $NaNO_3$, a concentration of 10 mg L^{-1} was considered and two initial pH of the solution were used (2.25 and 6.0). After an hour of treatment, at the initial pH of six, an increase in ibuprofen removal was observed with the presence of NO_3^-, passing from 66%, without nitrate, to 75%, with nitrate, while at the pH of 2.25, after an irradiation time of 30 min, IBP degradation passes from 25 to 45%, in agreement with literature results [16]. Ibuprofen degradation increases monotonically with irradiation time and higher the solution pH, the higher will be the IBP removal, in agreement with literature findings [36].

Some literature can be found regarding the influence of the variation of NO_3^- concentration on photodegradation efficiency. Wang et al. [37] recently investigated the effect of the variation of the NO_3^- concentration on the photocatalytic process applied to a secondary effluent of an urban wastewater treatment plant. They showed that the higher the NO_3^- concentration, the higher will be the photocatalytic activity.

The removal of ibuprofen and others emerging pollutants by natural sunlight was lately studied by Koumaki et al. [38]. They observed that the removal efficiency improved due to the presence of NO_3^- and increased with increasing NO_3^- concentrations.

In water solution, an anionic (A^-) and a molecular (HA) species of IBP coexist, depending on the solution pH and temperature [39]. The anionic and molecular concentrations can be evaluated according to the Henderson–Hasselbalch equation, valid for dilute solutions [40]:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \tag{1}$$

As shown in Eq. (1), the Ibuprofen dissociation constant ($\mathrm{p}K_\mathrm{a}$) influences the concentration ratio between anionic and molecular IBP forms. In particular, with $\mathrm{pH} < \mathrm{p}K_\mathrm{a}$, IBP is mostly in its molecular form, while with $\mathrm{pH} > \mathrm{p}K_\mathrm{a}$, IBP is mainly in its anionic form. Since the solution temperature is 20˚C, a dissociation constant of 4.32 was evaluated.

The IBP anionic species seems to be more affected by photodegradation than its molecular species, in agreement with Choina et al. [36].

3.2. Modelling

The photodegradation of Ibuprofen was modelled considering the IBP dissociation forms. As sketched in the kinetic scheme of Fig. 5, the Ibuprofen sodium salt (Na-IBP), used to carry out the experimental activity, was assumed to be completely dissociate in Na^+ and A^- ionic species in aqueous solution, with the A^- ion to form the molecular species of the IBP (HA) due to the hydrolysis equilibrium reactions.

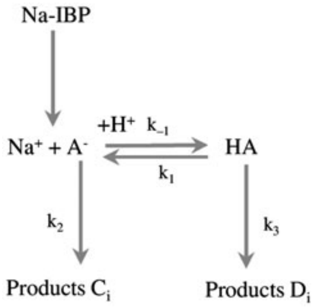

Fig. 5. IBP photodegradation kinetic scheme.

The Henderson–Hasselbalch equation (see Eq. (1)) was used to calculate the IBP molecular/anionic species concentration ratio, assuming an instantaneous hydrolysis equilibrium condition.

Moreover, the UV-light irradiation direct photolysis and the indirect photolysis reaction with transient species, such as $OH^\cdot$ produced by nitrate, may be involved during photodegradation [16,33,41].

The following equation can be used to state the initial IBP concentration, the molecular and the anionic IBP species mass balance, at the initial irradiation time (i.e. $t = 0$):

$$C_\mathrm{IBP} = C_{\mathrm{IBP}_0} = [\mathrm{A}^-]_0 + [\mathrm{HA}]_0 \tag{2}$$

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

According to the proposed reaction pattern (Fig. 4), parallel reactions [42,43] with different reaction rates can occur during oxidation of IBP anionic and molecular compounds, producing different reaction products. Anionic and molecular species photodegradation processes were assumed to be first-order reactions and studied by Eqs. (3) and (4), respectively:

$$\mathrm{A}^- \xrightarrow{k_2} \text{Products } C_\mathrm{i} \tag{3}$$

$$\mathrm{HA} \xrightarrow{k_3} \text{Products } D_\mathrm{i} \tag{4}$$

where k_2 and k_3 are the kinetic constant reaction rates. It is worth highlighting that the influence of the nitrate presence on the IBP removal can be included in the kinetic constants [35]. Numerous studies were focused on the nitrate photolysis, showing that the photodegradation reaction consists in the hydroxyl radical formation [34,44,45], by favouring an indirect photolysis mechanism. As reported by Xu et al. [44], the overall rate constants (k_2 and k_3) can be calculated as the sum of the direct and the indirect reaction rates, according to the following equations:

$$k_2 = k_2^{\mathrm{dir}} + k_2^{\mathrm{ind}} \tag{5}$$

$$k_3 = k_3^{\mathrm{dir}} + k_3^{\mathrm{ind}} \tag{6}$$

As shown, without nitrate presence, the direct photolysis only occurs.

The IBP, A^- and HA concentrations as functions of the irradiation time can be calculated by the equations as follows:

$$\frac{\mathrm{d}C_{\mathrm{IBP}_t}}{\mathrm{d}t} = -k_2 \cdot [\mathrm{A}^-]_t - k_3 \cdot [\mathrm{HA}]_t \tag{7}$$

$$C_{\mathrm{IBP}_t} = C_{\mathrm{IBP}_0} - [\mathrm{A}^-]_t - [\mathrm{HA}]_t \tag{8}$$

$$\frac{[\mathrm{A}^-]_t}{[\mathrm{HA}]_t} = \frac{[\mathrm{A}^-]_0}{[\mathrm{HA}]_0} = 10^{(\mathrm{pH}-\mathrm{p}K_\mathrm{a})} = K_1 \tag{9}$$

where C_{IBP_t}, $[\mathrm{HA}]_t$ and $[\mathrm{A}^-]_t$ are the total IBP, the molecular and the anionic IBP species concentrations at time t, respectively.

IBP, A^- and HA concentrations were calculated by numerically solving the three equation systems (7–9), through a first-order finite difference forward scheme method and using the following initial conditions (10):

$$\left\{ t = 0 \quad \begin{array}{c} C_{\mathrm{IBP}} = C_{\mathrm{IBP}_0} \\ [\mathrm{A}^-] = [\mathrm{A}^-]_0 \\ [\mathrm{HA}] = [\mathrm{HA}]_0 \end{array} \right. \tag{10}$$

A series-parallel reaction mechanism was used to model the IBP removal by photodegradation. According to the photodegradation modelling, the IBP, considered at the equilibrium, is dissociated and the IBP species degradation occurs in series. The dissociation of ibuprofen is influenced by the pH of the solution. A first-order parallel reaction was used to study the degradation of dissociated forms. Finally, both the direct photolysis by UV-light irradiation and the indirect photolysis reaction with OH· produced by nitrate were considered.

Table 1
Equilibrium constants

pH	K_1
6.61	190.9
6.00	45.95
2.25	0.0085

Table 1 shows the equilibrium constants (K_1) as a function of the solution initial pH. As previously indicated, at a solution temperature of 20°C, a dissociation constant of 4.32 was calculated.

The reaction rate constants were statistically calculated by the best-fit line of the experimental data (Fig. 6). In particular, direct reaction rate constants

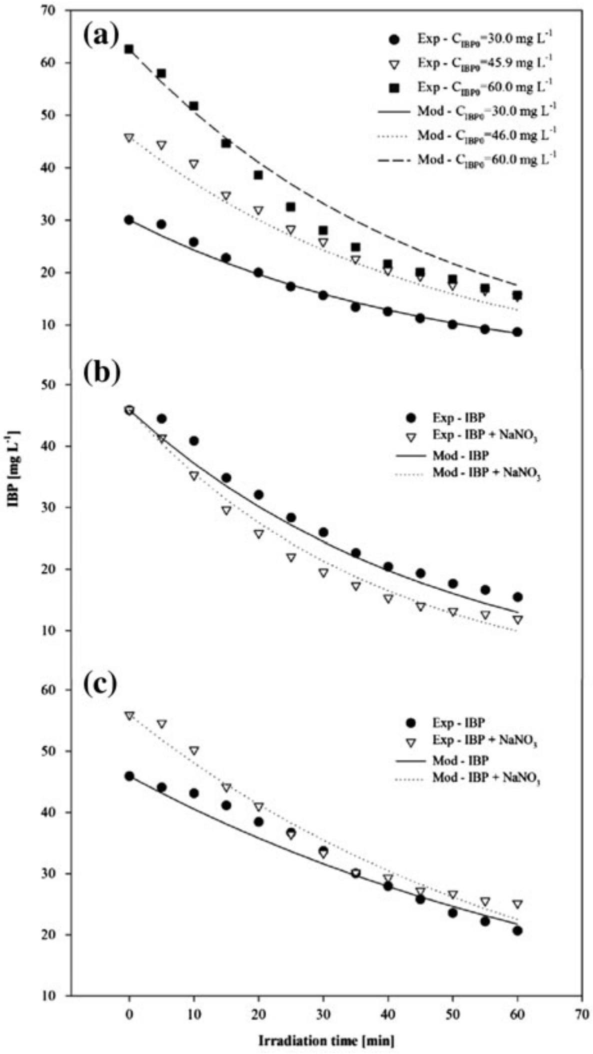

Fig. 6. IBP time evolution fitting (Exp = experimental; Mod = model): (a) IBP concentration influence (pH 6.6), (b) nitrate influence (pH 6.0) and (c) nitrate influence (pH 2.25).

Table 2
Kinetic constants

k_2 (min^{-1})	k_3 (min^{-1})	k_2^{dir} (min^{-1})	k_3^{dir} (min^{-1})	k_2^{ind} (min^{-1})	k_3^{ind} (min^{-1})
0.026	0.015	0.021	0.012	0.005	0.003

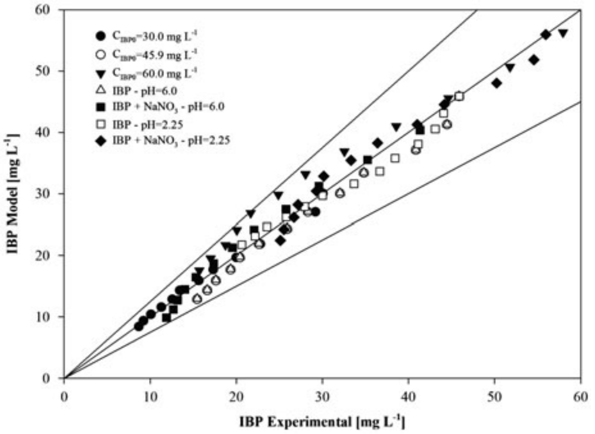

Fig. 7. Parity diagram ±25% variation range.

were determined by fitting IBP concentration experimental data (Fig. 6(a)) [28], while overall kinetic constants were determined by fitting nitrate experimental data (Fig. 6(b) and (c)). Indirect reaction rate constants were computed as difference between overall and direct reaction rate constants. Overall, direct and indirect kinetic constants are reported in Table 2. As the kinetic constant k_2 is almost twice as much as k_3, the IBP anionic species can be more quickly photodegraded than the molecular IBP species.

The comparison between the model predictions and the experimental findings is shown in Fig. 6. The model seems to well fit the investigation results even if some divergences can be observed at C_{IBP_0} = 30 mg L^{-1} (Fig. 6(a)). The validity of the reaction mechanism hypothesized was assessed through the parity diagram (Fig. 7). Fig. 7 shows that all the points fall within variation range of ±25%, demonstrating the best fit of the model to the experimental observations and verifying the reaction mechanism suggested.

4. Conclusions

The degradation of Ibuprofen from simulated water streams via UV-light irradiation was investigated on a lab-scale batch reactor, equipped with a lamp emitting monochromatic UV-light at a wavelength of 254 nm and an intensity of 400 mJ m^{-2}.

The IBP photodegradation was studied by varying different parameters, such as the treatment time, the initial concentration of IBP, the nitrate presence and the solution pH. Moreover, a reaction pattern was hypothesized and the reaction rate constants were statistically estimated.

After an irradiation time of an hour, a reduction in Ibuprofen concentration higher than 55% and up to 75% was achieved. The best results were obtained for the experiments carried out at pH 6.0 with a concentration of NaNO$_3$ of 10 mg L^{-1} and at pH 6.6 with an initial IBP concentration of 60 mg L^{-1}.

The photodegradation mechanism was modelled as a series-parallel reaction system, in which the IBP dissociation, considered at the equilibrium, and the IBP species degradation occur in series. The degradation of dissociated forms is considered as first order parallel reactions and both the UV-light irradiation direct photolysis and the indirect photolysis reaction with OH$^{\cdot}$ produced by nitrate were considered. The reaction rate constants were determined by fitting the IBP oxidation findings. The model, supported by a parity diagram with a variation range of ±25%, well describes the experimental results highlighting the effectiveness of the IBP decay pattern hypothesized and the validity of the assumption made.

References

[1] UNEP (United Nations Environment Programme), Division of Environmental Policy Implementation. Clearing the Waters. A focus on water quality solutions, 2010. Available from: <www.unep.org>.
[2] I. Bortone, A. Di Nardo, M. Di Natale, A. Erto, D. Musmarra, G.F. Santonastaso, Remediation of an aquifer polluted with dissolved tetrachloroethylene by an array of wells filled with activated carbon, J. Hazard. Mater. 260 (2013) 914–920.
[3] A. Salladini, M. Prisciandaro, D. Barba, Ultrafiltration of biologically treated wastewater by using backflushing, Desalination 207 (2007) 24–34.
[4] P. Iovino, S. Canzano, S. Capasso, A. Erto, D. Musmarra, A modeling analysis for the assessment of ibuprofen adsorption mechanism onto activated carbons, Chem. Eng. J. 277 (2015) 360–367.
[5] M. Prisciandaro, A. Lancia, D. Musmarra, Gypsum nucleation into sodium chloride solutions, AIChE J. 47 (4) (2001) 929–934.
[6] M. Prisciandaro, E. Olivieri, A. Lancia, D. Musmarra, Gypsum precipitation from an aqueous solution in the presence of nitrilotrimethylenephosphonic acid, Ind. Eng. Chem. Res. 45 (2006) 2070–2076.

[7] A. Di Zio, M. Prisciandaro, D. Barba, Disinfection of surface waters with UF membranes, Desalination 179 (2005) 297–305.

[8] UN WWAP (United Nations World Water Assessment Program) Water and Industry. Available from: <http://webworld.unesco.org/water/wwap/facts_figures/water_industry.shtml> 2009–2014.

[9] M. Capocelli, E. Joyce, A. Lancia, T. Mason, D. Musmarra, M. Prisciandaro, Sonochemical degradation of estradiols: Incidence of ultrasonic frequency, Chem. Eng. J. 210 (2012) 9–17.

[10] F. Yuan, C. Hu, X. Hu, J. Qu, M. Yang, Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H_2O_2, Water Res. 43 (2009) 1766–1774.

[11] L. Araujo, M.E. Troconis, M.B. Espina, A. Prieto, Persistence of ibuprofen, ketoprofen, diclofenac and clofibric acid in natural waters, J. Environ. Human 2014 (2014) 32–38.

[12] I. Georgaki, E. Vasilaki, N. Katsarakis, A study on the degradation of carbamazepine and ibuprofen by TiO_2 & ZnO photocatalysis upon UV/visible-light irradiation, Am. J. Anal. Chem. 05 (2014) 518–534.

[13] F. Méndez-Arriaga, S. Esplugas, J. Giménez, Degradation of the emerging contaminant ibuprofen in water by photo-Fenton, Water Res. 44 (2010) 589–595.

[14] J.L. Santos, I. Aparicio, E. Alonso, Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain), Environ. Int. 33 (2007) 596–601.

[15] M. Skoumal, R.M. Rodríguez, P.L. Cabot, F. Centellas, J.A. Garrido, C. Arias, E. Brillas, Electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton degradation of the drug ibuprofen in acid aqueous medium using platinum and boron-doped diamond anodes, Electrochim. Acta 54 (2009) 2077–2085.

[16] D. Vione, P.R. Maddigapu, E. De Laurentiis, M. Minella, M. Pazzi, V. Maurino, C. Minero, S. Kouras, C. Richard, Modelling the photochemical fate of ibuprofen in surface waters, Water Res. 45 (2011) 6725–6736.

[17] M. Capocelli, D. Musmarra, M. Prisciandaro, A. Lancia, Chemical effect of hydrodynamic cavitation: Simulation and experimental comparison, AIChE J. 60 (2014) 2566–2572.

[18] M. Capocelli, M. Prisciandaro, A. Lancia, D. Musmarra, Hydrodynamic cavitation of p-nitrophenol: A theoretical and experimental insight, Chem. Eng. J. 254 (2014b) 1–8.

[19] M.V. Bagal, P.R. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: A review, Ultrason. Sonochem. 21 (2014) 1–14.

[20] P. Zeng, J. Du, Y. Song, Y. Liu, R. Liu, P. Zhang, S. Xiao, Efficiency comparison for treatment of amantadine pharmaceutical wastewater by Fenton, ultrasonic, and Fenton/ultrasonic processes, Environ. Earth Sci. 73 (2015) 4979–4987.

[21] H. Suzuki, S. Araki, H. Yamamoto, Evaluation of advanced oxidation processes (AOP) using O_3, UV, and TiO_2 for the degradation of phenol in water, J. Water Process Eng. 7 (2015) 54–60.

[22] Z. Shu, J.R. Bolton, M. Belosevic, M.G. El Din, Photodegradation of emerging micropollutants using the medium-pressure UV/H_2O_2 advanced oxidation process, Water Res. 47 (2013) 2881–2889.

[23] R. Mudliar, S.S. Umare, D.S. Ramteke, S.R. Wate, Energy efficient—Advanced oxidation process for treatment of cyanide containing automobile industry wastewater, J. Hazard. Mater. 164 (2009) 1474–1479.

[24] M.I. Badawy, M.Y. Ghaly, T.A. Gad-Allah, Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater, Desalination 194 (2006) 166–175.

[25] D. Fatta-Kassinos, M.I. Vasquez, K. Kümmerer, Transformation products of pharmaceuticals in surface waters and wastewater formed during photolysis and advanced oxidation processes—Degradation, elucidation of byproducts and assessment of their biological potency, Chemosphere 85 (2011) 693–709.

[26] G.V. Buxton, Q.G. Mulazzani, A.B. Ross, Critical review of rate constants for reactions of transients from metal ions and metal complexes in aqueous solution, J. Phys. Chem. Ref. Data 24 (1995) 1055–1349.

[27] D. Musmarra, M. Prisciandaro, M. Capocelli, D. Karatza, P. Iovino, S. Canzano, A. Lancia, Degradation of ibuprofen by hydrodynamic cavitation: Reaction pathways and effect of operational parameters, Ultrason. Sonochem. 29 (2016) 76–83.

[28] M. Quero-Pastor, A. Valenzuela, J.M. Quiroga, A. Acevedo, Degradation of drugs in water with advanced oxidation processes and ozone, J. Environ. Manage. 137 (2014) 197–203.

[29] T. Scheers, L. Appels, B. Dirkx, L. Jacoby, L. Van Vaeck, B. Van der Bruggen, J. Luyten, J. Degrève, J. Van Impe, R. Dewil, Evaluation of peroxide based advanced oxidation processes (AOPs) for the degradation of ibuprofen in water, Desalin. Water Treat. 50 (2012) 189–197.

[30] J. Scheideler, K. Lekkerkerker-Teunissen, T. Knol, A. Ried, J. Verberk, H. van Dijk, Combination of O_3/H_2O_2 and UV for multiple barrier micropollutant treatment and bromate formation control—An economic attractive option, Water Pract. Technol. 6 (2011) 1–8.

[31] M. Taghi Ghaneian, M. Hassan Ehrampoush, T. Jasemizad, M. Kheirkhah, R. Amraei, F. Sahlabadi, The effect of nitrate as a radical scavenger for the removal of humic acid from aqueous solutions by electron beam irradiation, J. Commun. Health Res. 1 (3) (2013) 134–143.

[32] J. Mack, J.R. Bolton, Photochemistry of nitrite and nitrate in aqueous solution: A review, J. Photochem. Photobiol., A 128 (1999) 1–13.

[33] J. Peuravuori, K. Pihlaja, Phototransformations of selected pharmaceuticals under low-energy UVA–vis and powerful UVB–UVA irradiations in aqueous solutions—The role of natural dissolved organic chromophoric material, Anal. Bioanal. Chem. 394 (2009) 1621–1636.

[34] F. Mendez-Arriaga, S. Esplugas, J. Gimenez, Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO_2 and simulated solar irradiation, Water Res. 42 (2008) 589–594.

[35] A. Achilleos, E. Hapeshi, N.P. Xekoukoulotakis, D. Mantzavinos, D. Fatta-Kassinos, UV-A and solar photodegradation of ibuprofen and carbamazepine catalyzed by TiO_2, Sep. Sci. Technol. 45(11) (2010) 1564–1570.

[36] J. Choina, H. Kosslick, C. Fischer, G.U. Flechsig, L. Frunza, A. Schulz, Photocatalytic decomposition of pharmaceutical ibuprofen pollutions in water over titania catalyst, Appl. Catal. B: Environ. 129 (2013) 589–598.

[37] D. Wang, Y. Li, G. Li Puma, C. Wang, P. Wang, W. Zhang, Q. Wang, Mechanism and experimental study on the photocatalytic performance of Ag/AgCl @ chiral TiO_2 nanofibers photocatalyst: The impact of wastewater components, J. Hazard. Mater. 285 (2015) 277–284.

[38] E. Koumaki, D. Mamais, C. Noutsopoulos, M.C. Nika, A.A. Bletsou, N.S. Thomaidis, A. Eftaxias, G. Stratogianni, Degradation of emerging contaminants from water under natural sunlight: The effect of season, pH, humic acids and nitrate and identification of photodegradation by-products, Chemosphere 138 (2015) 675–681.

[39] S. Canonica, L. Meunier, U. von Gunten, Phototransformation of selected pharmaceuticals during UV treatment of drinking water, Water Res. 42 (2008) 121–128.

[40] J. Reijenga, A. van Hoof, A. van Loon, B. Reijenga, Development of methods for the determination of pK_a values, Anal. Chem. Insights 8 (2013) 53–71.

[41] J. Hoigné, Formulation and Calibration of Environmental Reaction Kinetics: Oxidations by Aqueous Photooxidants as an Example, Aquatic Chemical Kinetics, Wiley, New York, NY, 1990.

[42] A. Lancia, D. Musmarra, Calcium bisulfite oxidation rate in the wet limestone−gypsum flue gas desulfurization process, Environ. Sci. Technol. 33(11) (1999) 1931–1935.

[43] D. Karatza, M. Prisciandaro, A. Lancia, D. Musmarra, Reaction rate of sulfite oxidation catalyzed by cuprous ions, Chem. Eng. J. 145(2) (2008) 285–289.

[44] Y. Xu, T. Nguyen, M. Reinhard, K. Gin, Photodegradation kinetics of p-tert-octylphenol, 4-tert-octylphenoxy-acetic acid and ibuprofen under simulated solar conditions in surface water, Chemosphere 85 (2011) 790–796.

[45] O.C. Zafiriou, J. Joussot-Dubien, R.G. Zepp, R.G. Zika, Photochemistry of natural waters, Environ. Sci. Technol. 18 (1984) 358A–371A.