Heliyon 9 (2023) e13678

Contents lists available at ScienceDirect

Heliyon

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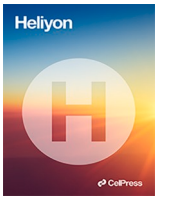

Research article

Pharmaceutical compounds photolysis: pH influence

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ARTICLE INFO

Keywords:
Emerging contaminants
Drugs
Photolysis
P25 catalysts

ABSTRACT

The operating parameters of photolytic and photocatalytic reaction processes directly affect the efficiency in the degradation of compounds. In particular, pH is a variable that needs to be considered as it exerts great influence on adsorption, absorption, solubility, among others. This study describes the application of the photolytic process, at different pHs, in the degradation of different pharmaceutical compounds. Photolytic reactions were performed with the following contaminants: acetylsalicylic acid (ASA), ibuprofen (IBP) and paracetamol (PAR). In addition, a comparison was performed using the commercial catalyst P25. The results indicated a great influence of the pH in the kinetic constant of the photodegradation and in the UV absorbance of the species. In particular, the degradation of ASA and PAR were favored with the reduction of pH, while the degradation of IBU and SA were favored by increasing. Also, the chromatograms indicated that pH may affect the by-products formed. In comparison, the photocatalysis process in the presence of P25 proved to be much more effective, but it was not possible to achieve complete mineralization of the compounds.

1. Introduction

Photolysis refers to any chemical process in which a compound is directly or indirectly decomposed by the action of light [1]. Photolysis can occur directly by absorbing light chromophores or indirectly following the release of reactive species, which are formed via photosensitization. In the aquatic environment these processes are of great importance. This is due to being a source of HO• generation. In fact, the absorption of water constantly increases from approximately 190 to 120 nm [2], and its electronic excitation may result in the formation of hydrogen atoms and hydroxyl radicals, as represented by Equations (1) and (2).

$$H_2O + hm\ (V - UV) \rightarrow \mathrm{HO}\bullet + \mathrm{H}\bullet \quad (1)$$

$$H_2O + hv(< 190nm) \rightarrow H^+ + e^- + \mathrm{HO}\bullet \quad (2)$$

This technique has the advantage of producing HO• without adding any oxidant. Reaction (1) in which HO• and H• are produced, can be used to oxidize inorganics and initiate oxidative degradation and mineralization of organic compounds [3]. In reactions (1) and

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https://doi.org/10.1016/j.heliyon.2023.e13678
Received 8 November 2022; Received in revised form 26 January 2023; Accepted 7 February 2023
Available online 11 February 2023

(2), intermediates are generated with relatively high efficiency. These reactive species are capable of initiating a series of diffusion-controlled secondary reactions leading to the formation of more stable ions and molecules, such as H_2O_2.

However, the study of processes can be carried out by combining other supplementary agents such as: hydrogen peroxide, oxygen and photocatalysts. Currently, pollutants of emerging concern, or micropollutants, are being the focus of studies on these processes.

Micropollutants, including pharmaceutical waste, personal care, endocrine-disrupting chemicals, pesticides and chemicals, are frequently detected in the aquatic environment. In particular, drugs with active principles are metabolized after administration and unmetabolized active substances are excreted either unchanged compounds, or conjugated with a deactivating agent or a combination of metabolites bound to the molecule. For example, urine accounts for 55–80% of the total unmetabolized active ingredients, and thus enters the water cycle [4]. Most drugs are not removed in conventional wastewater treatment plants (WWTPs) and are discharged to receiving water bodies [5–8]. The great diversity of these compounds, the variety of processes and conditions applied by the various research groups active in the field, and the large list of potential outcomes, together with the limitations related to the analytical resources currently available, are some of the important parameters that characterize this research as challenging [9]. Thus, studies on the degradation of pharmaceutically active compounds have aroused great interest. In this work, the contribution is the study of the photolysis of different drugs: ibuprofen (IBU), salicilyc acid (SA), Acetylsalicylic acid (ASA) and paracetamol (PAR), considering the effect of pH on a variation of acid-base pHs. Also, a comparison when we insert a supplementary agent, photocatalyst (P25, degussa).

2. Experimental procedure

2.1. Chemicals

Acetylsalicylic acid (ASA, ≥98%-supplied by Biotec, São Paulo, Brasil), Ibuprofen (IBU, ≥98% GC-supplied by Sigma-Aldrich, St Louis, USA), Paracetamol (PAR, ≥98% GC-supplied by Sigma-Aldrich, St Louis, USA), Acetonitrile (HPLC–supplied by J.T. Barker, Ciudad de México, México), titanium dioxide (P25 Aeroxide, Evonik), Phosphoric acid (P.A. supplied by Biotec); Potassium phosphate monobasic (KH_2PO_4) (supplied by Dinâmica) and Potassium phosphate dibasic (K_2HPO_4) (supplied by Reagen).

2.2. Photolysis tests

Photolysis tests were carried out in a glass reactor with temperature control (25 °C) containing the solution of the pharmaceutical in ultrapure water to be degraded (200 mL). The solution was irradiated with a 250 W mercury vapor lamp, without bulb (34.10 mW/cm^2), for 120 min, under constant magnetic stirring and atmospheric air bubbling. During this period, samples were collected for later determination of the pharmaceutical concentration. The entire apparatus described was located inside a metallic photocatalysis chamber. The photodegradation of each drug was studied separately, using four different solutions with the following initial concentrations: 5 mg L^{-1} of ASA, 10 mg L^{-1} of IBU, 10 mg L^{-1} of PAR and 50 mg.L^{-1} of SA [10,11]. Different pH conditions were studied (3, 5, 7 or 9), and the pH of the solution was adjusted with addition of HCl or NaOH solutions.

2.3. Photocatalysis tests

The photocatalytic tests were carried out following the same configuration and procedures described for the photolysis tests, with the difference that TiO_2 P25 (1 g L^{-1}) was suspended in the pharmaceutical solution, acting as a photocatalyst. Before irradiation, the suspension was kept in the dark for 60 min (adsorption test). The collected samples were filtered with syringe filters (Nylon, diameter 13 mm, pore size 0.22 μm).

2.4. High performance liquid chromatography (HPLC)–method and validation

The drug concentration in the samples collected in the photolysis and photocatalysis tests was determined in a high-performance liquid chromatograph (YL Clarity 9100) equipped with a pre-column, and visible ultraviolet detector (UV-VIS). The column used was a C-18 column (Luna, 5 μm, 150 × 4.6 mm, Phenomenex). The conditions used in the analysis are described in Table 1. The methodologies applied in the present study were adapted from Refs. [12,13], respectively.

Based on the conditions described in Table 1, analyzes were performed to determine the calibration curves for each analyte, as represented in Fig. 1(a–d). All pharmaceuticals, within their respective quantification intervals (Table 2), showed good results regarding the linear relationship between the concentration and the analytical signal, with correlation coefficients greater than 0.99.

Based on the parameters of the calibration curves linear regressions, it was possible to determine the LOD (Equation (3)) and LOQ

Table 1
Operational conditions of the HPLC analysis.

Mobile phase	Flow (mL.min^{-1})	T (°C)	Wavelength	Analyte	Retention time (min)
40:60 Acetonitrile and Phosphate buffer (pH = 2.8, 50 mM)	1	30	210 nm	ASA	3.3
				PAR	1.95
				SA	3.7
60:40 Acetonitrile and Phosphate buffer (pH = 7.0, 40 mM)	0.8	30	225 nm	IBU	2.2

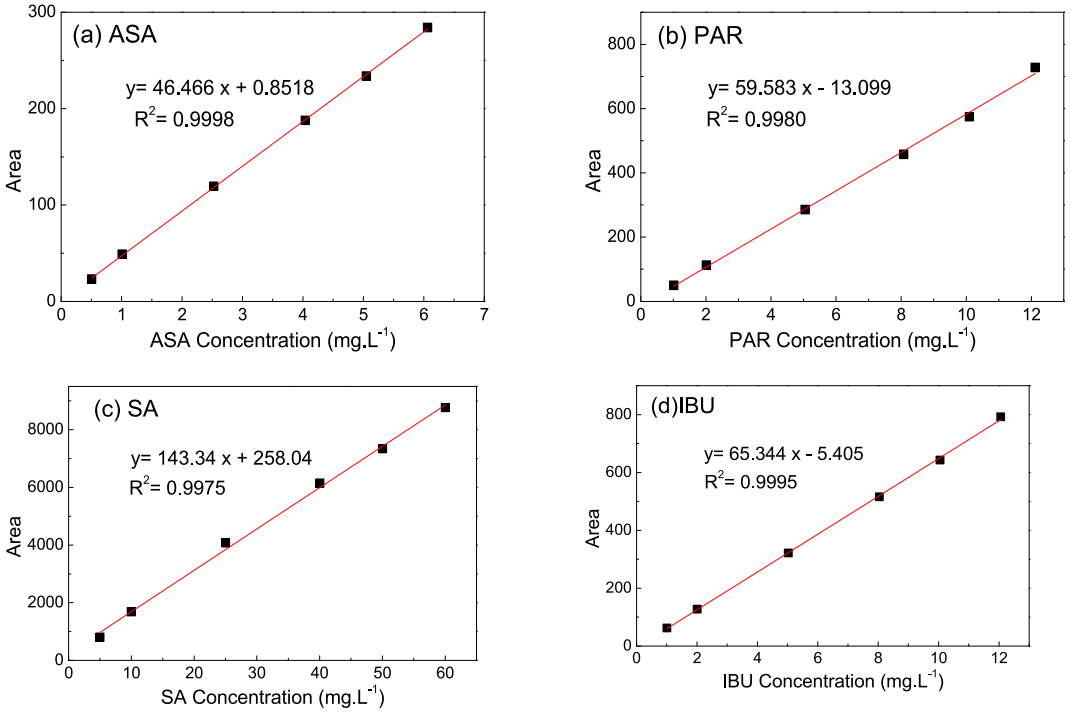

Fig. 1. Calibration curves of: (a) ASA, (b) PAR, (c) SA and (d) IBU.

Table 2
Quantitative ranges, calibration curve equations and correlation coefficients of each analyte.

Analyte	Quantitative Range (mg.L^{-1})	Equation	R^2
ASA	0.5–6	y = 46.466 x + 0.8518	0.9998
PAR	1–12	y = 59.583 x − 13.099	0.998
SA	5–60	y = 143.34 x + 258.04	0.9975
IBU	1–12	y = 65.344 x − 5.405	0.9995

(Equation (4)) values for each drug, considering the standard deviation of the intercept (SD) and the slope of the curve (S) as follows:

$$LOD = 3,3 * SD/S \quad (3)$$

$$LOQ = 10 * SD/S \quad (4)$$

The obtained results are described in Table 3.

Additional information regarding method precision and recovery are described in Tables S1–S4 and Tables S5–S8 of the Supplementary Material, respectively.

3. Results and discussion

3.1. Photolysis tests

As can be seen in the photolysis curves and rate constants of each drug at different pHs (Fig. 2), the increase of pH affected directly the photodegradation of all the studied pharmaceuticals, albeit in different ways. The apparent first order rate constant was

Table 3
LOD and LOQ values of each analyte.

Analyte	LOD (mg L^{-1})	LOQ (mg L^{-1})
ASA	0.09	0.27
PAR	0.56	1.70
SA	3.09	9.35
IBU	0.27	0.81

determined by the plot of $\ln(C_0/C)$ versus irradiation time [14].

Photocatalytic ASA degradation tests indicated complete degradation of the compound within 60 min of irradiation, regardless of pH (Fig. 2a). When comparing the pHs, decreasing the pH favored the ASA removal, as observed in the variation of the photodegradation rate (Fig. 2b). Similarly, PAR photolysis was more efficient at pH 3 (Fig. 2e), and the removal rate decreased as the pH increased up to 7, followed by an improvement in removal at pH 9 (Fig. 2f). On the other hand, IBU photodegradation considerably increased as the pH increased from 3 to 9 (Fig. 2c and d). Iovino et al. also observed an increase in the removal of ibuprofen by photolysis as the pH increased from 2.25 to 8.25 [15].

The photocatalytic test performed with P25 in the best pH of each pharmaceutical's photolysis indicated a considerable increase in the drugs degradation, remarkably, in the ASA case, increasing from $k_{ASA,pH3} = 0.1142\ min^{-1}$ to $k_{ASA,P25,pH3} = 0.6045\ min^{-1}$. The difference was not restricted to the reaction rate, but also had an impact on the formation of by-products, as it can be seen in Fig. 3. In the comparison between Fig. 3a and b it is possible to notice a difference in the by-products formed in photolysis at pHs 3 and 5, identified in the chromatograms between 2 and 2.4 min. Interestingly, in the photocatalytic process it was possible to observe a considerable formation of a by-product in 1.5 min (Fig. 3c), which was not identified in the photolysis tests. The same by-product was

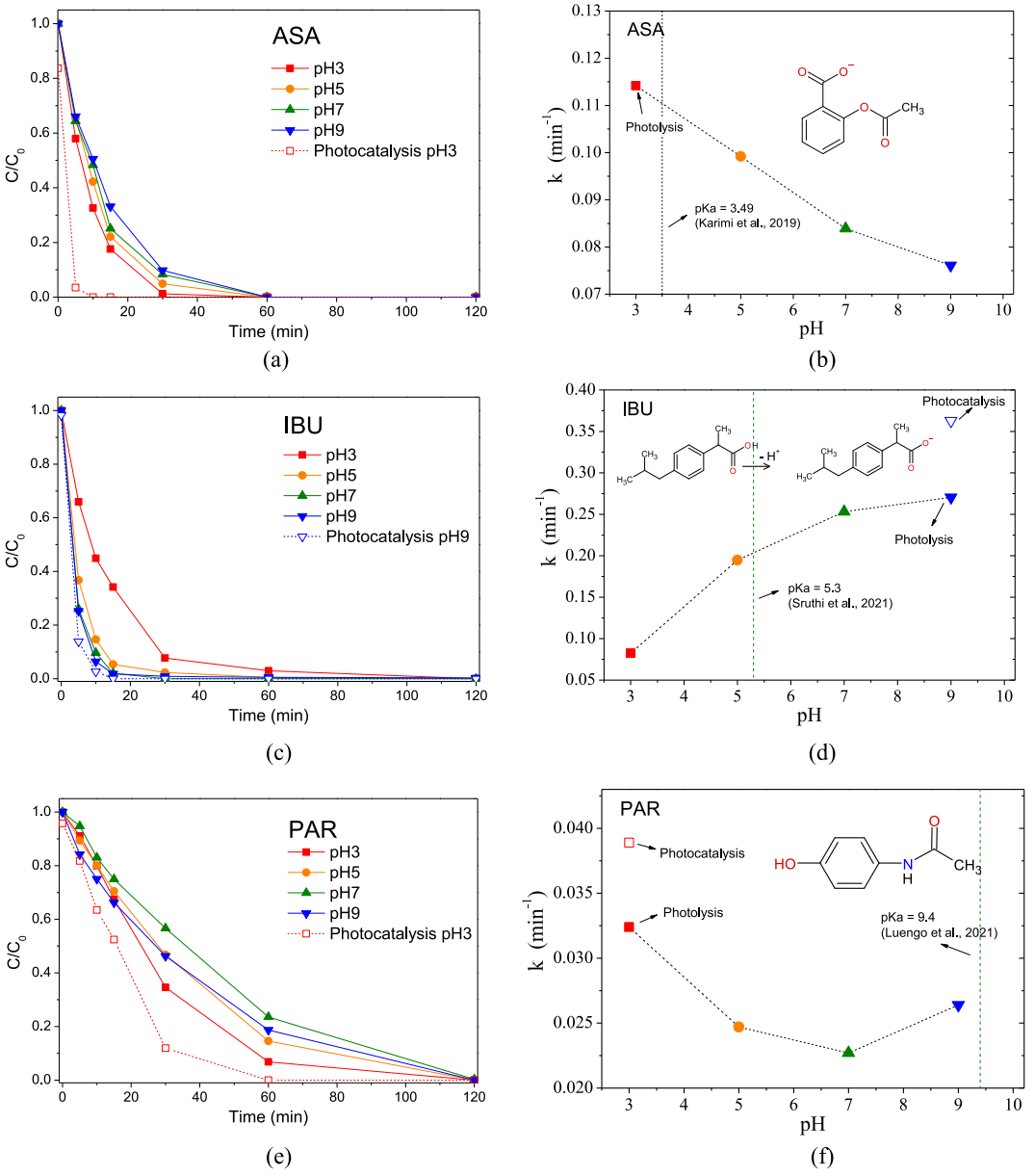

Fig. 2. Effect of pH in: ASA photolysis curves (a) and rate constants (b); IBU photolysis curves (c) and rate constants (d); PAR photolysis curves (e) and rate constants (f). $[ASA]_0 = 5\ mg\ L^{-1}$; $[IBU]_0 = 10\ mg\ L^{-1}$; $[PAR]_0 = 10\ mg\ L^{-1}$.

also observed in PAR and IBU photocatalytic tests (Figs. 4b and 5b) but was less prominent in their respective photolysis tests (Figs. 4a and 5a). In any case, the chromatograms showed that it was not possible to achieve complete mineralization in any of the processes carried out in the present work.

Mukherjee et al. studied the photocatalytic process for ASA degradation using titanium dioxide (TiO_2) as a photocatalyst, and initially observed salicylic acid and acetic acid formation by aspirin hydrolyzation in water. In the whole process, the main products described were salicylic acid, acetic acid, fumaric acid/maleic acid, malic acid and malonic acid [16]. These are probably the compounds identified in the ASA degradation chromatograms (Fig. 3a and b). According to the schemes presented by Moctezuma et al., the formation of carboxylic acids such as maleic acid and malonic acid is also expected in the photocatalytic degradation of paracetamol [17]. In addition, the photocatalytic process studied by Moctezuma et al. in aqueous solution using TiO_2/UV system indicated that complete mineralization of PAR is not easily achieved. HPLC analysis indicated the formation of several intermediate compounds such as hydroquinone, benzoquinone, *p*-aminophenol and *p*-nitrophenol. In addition, some aromatic compounds (*p*-aminophenol and *p*-nitrophenol) are produced and eventually mineralized [17].

Silva et al. studied direct photocatalytic and photolytic processes operating under UV-C irradiation evaluating IBU removal with high efficiencies, at rates that reached 100% and 98.9%, respectively (120 min exposure). The high-resolution MS analysis results allowed the detection and characterization of 11 by-products. These intermediates were proposed to be formed through an immediate attack of hydroxyl radicals, reactive species produced in situ under the conditions of photocatalytic and photolytic processes [18].

3.2. *Effect of pH on ionization and UV absorbance*

In their study with *p*-arsanilic acid, Xu et al. pointed out that two possible causes for the pH-dependent photolysis of the compound were (I) the molecule ionization and (II) changes in absorbance at the irradiation wavelength as the pH varies [19]. As highlighted by Iovino et al., a compound can behave differently when exposed to UV radiation if it is found in the molecular form (pH $<$ pKa) or in the anionic form (pH $>$ pKa) [15]. That said, ASA, IBU and PAR absorbance spectra in different pH were obtained (Double beam UV-VIS spectrophotometer N6000) and are shown in Fig. 6.

ASA absorption spectra at different pH indicated a decrease in the UV absorption around 225 nm when the pH increased from 3 to 5 (Fig. 6a). Such behavior can be related to the greater presence of the deprotonated form of ASA in conditions of pH $>$ pKa $=$ 3.49 [20], leading to a reduction in absorbance around 225 nm. Consequently, this reduction in absorbance affects the photodegradation process, causing the reaction rate to drop with the increasing of pH from 3 to 5, which is in agreement with what was observed experimentally in ASA photolysis tests (Fig. 2b).

IBU absorption spectra (Fig. 6b), on the other hand, indicated that the increase in the pH caused an increase in the absorption around 222 nm, probably related to the predominant presence of IBU anionic form in pH $>$ pKa. In the literature, there are reports of

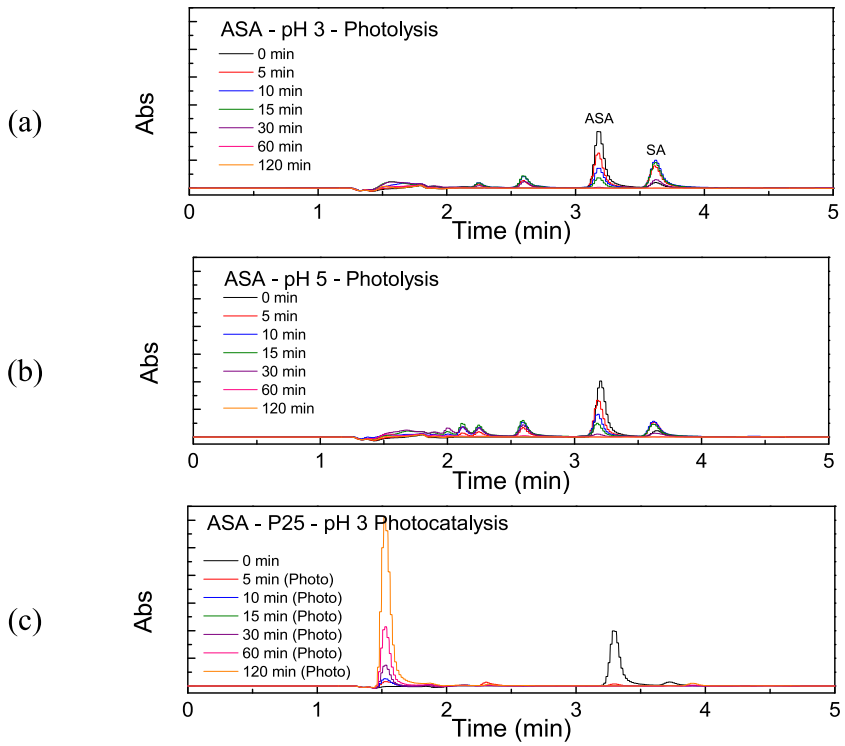

Fig. 3. ASA Chromatograms of (a) photolysis at pH 3, (b) photolysis at pH 5 and (c) photocatalysis at pH 3.

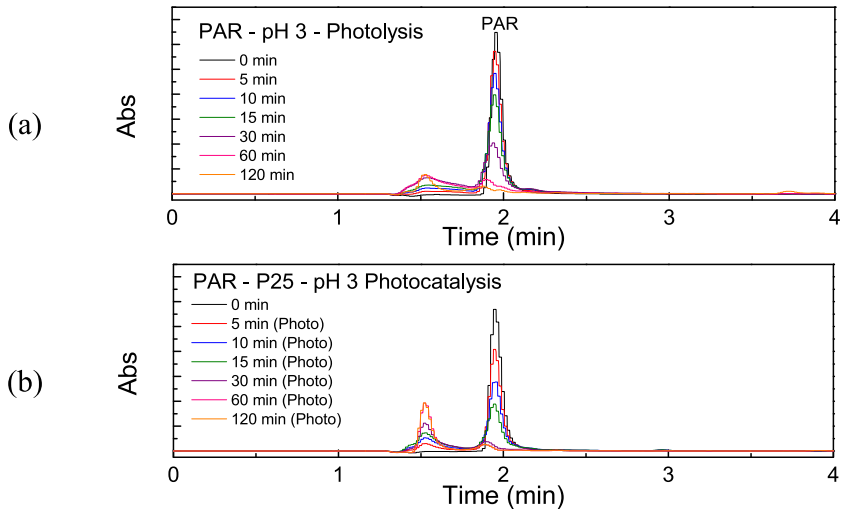

Fig. 4. PAR Chromatograms of (a) photolysis at pH 3, (b) photocatalysis at pH 3.

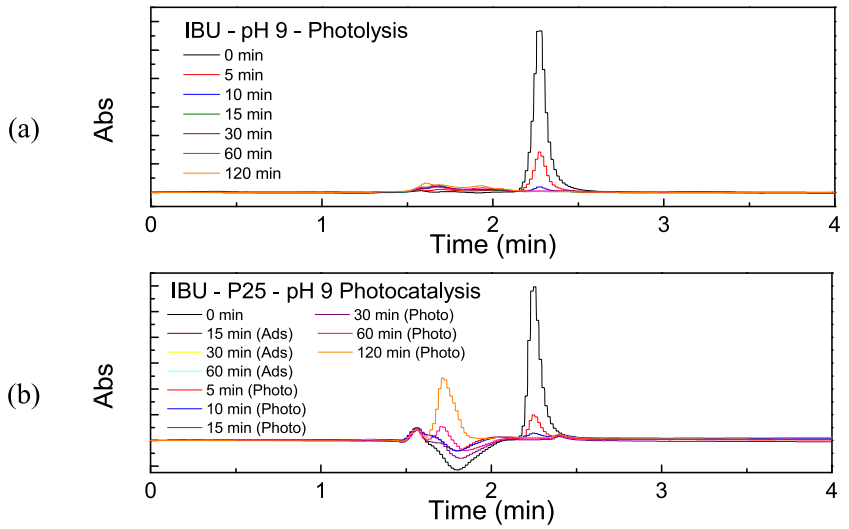

Fig. 5. IBU Chromatograms of (a) photolysis at pH 9, (b) photocatalysis at pH 9.

IBU pKa value around 4.59 [21], 4.91 [22] and 5.3 [23], to name a few. Iovino et al. stated that IBU anionic form kinetic constant can be nearly twice the value of the molecular form rate constant [15], which agrees with the experimental results presently obtained (Fig. 2d). Musa and Eriksson point out that the first step in the photodegradation of ibuprofen, whether of its molecular or anionic form, is its excitation to the first excited singlet state S_1. In their theoretical study, the authors reported that the neutral form of IBU requires 121 kcal/mol for the $S_0 \rightarrow S_1$ excitation, while the deprotonated form requires only 82.3 kcal/mol. Another difference is the elongation of the C–C bond corresponding to decarboxylation in the deprotonated form of the IBU, which is further elongated in the passage to the triplet state [22].

In the case of paracetamol, it was possible to observe a redshift in the absorption spectrum as the pH approaches the value of pKa = 9.4 [24], the redshift being much more pronounced for the case pH = 11 (pH > pKa), inserted in the graph for comparison purposes (Fig. 6c).

3.3. Salicylic acid photolysis and photocatalysis

For comparison purposes, tests were carried out with salicylic acid as model pollutant (Fig. 7), since this was one of the main products formed in the photolysis and photocatalysis of ASA. In the case of SA photolysis (Fig. 7a), there is a contrasting difference between the removal rate at pH 3 ($k_{AS,pH3} = 0.0088\ min^{-1}$) and at other pHs ($k_{AS,pH5} = 0.0179\ min^{-1}$, $k_{AS,pH7} = 0.0213\ min^{-1}$ and $k_{AS,pH9} = 0.0193\ min^{-1}$), the latter presenting very similar behaviors, with a slightly better result at pH 7. It is interesting to note that SA

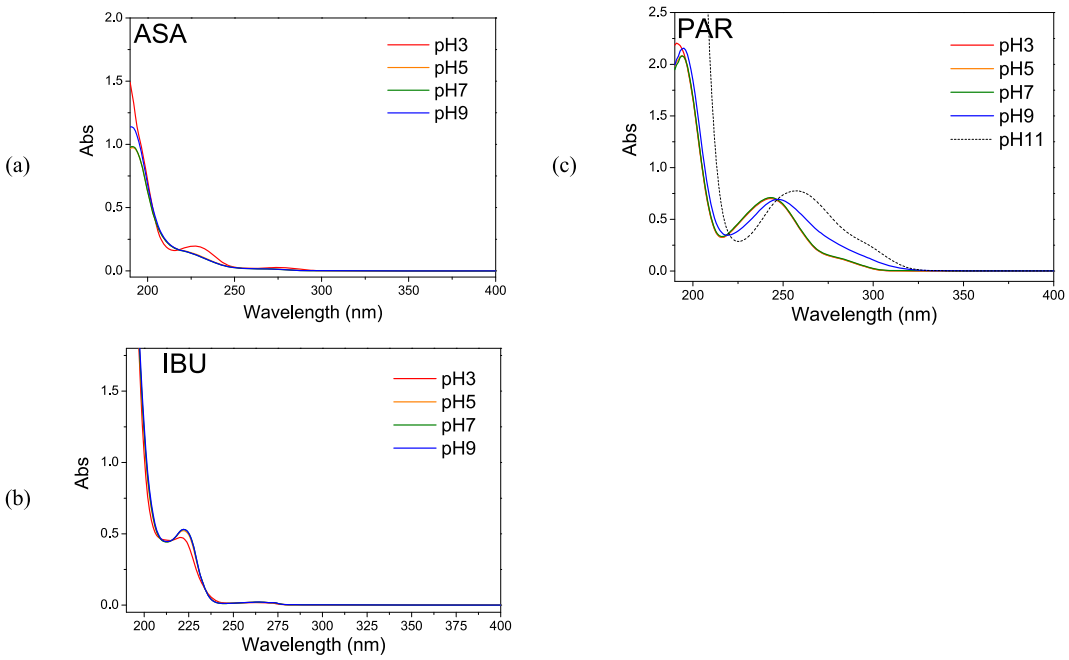

Fig. 6. UV spectra of (a) Acetylsalicylic acid, (b) Ibuprofen and (c) Paracetamol and different pH, in the range from 190 nm to 400 nm.

showed an opposite behavior to ASA with respect to pH (Fig. 2a and b).

Conducting the SA photodegradation process in the presence of P25 (photocatalysis) led to a drastic increase in the removal rate of the compound, being possible to promote its complete degradation within 60 min of irradiation, in contrast to the photolysis tests which did not reach the total degradation even in 120 min of irradiation (Fig. 7b). As for the effect of pH on photocatalysis, it was also possible to observe a clear distinction between the result obtained at pH 3 and the results obtained at pHs 5, 7 and 9, similar to what was noticed in the photolysis tests. The degradation process was considerably slower at pH 3 ($k_{AS,P25,pH3} = 0.0161\ min^{-1}$) than at pH 5 ($k_{AS,P25,pH5} = 0.0446\ min^{-1}$), pH 7 ($k_{AS,P25,pH7} = 0.0395\ min^{-1}$) or pH 9 ($k_{AS,P25,pH3} = 0.0926\ min^{-1}$).

Comparing photolysis (Fig. 8a–d) and photocatalysis (Fig. 8e–h) chromatograms in different pHs, a contrast can be observed in the by-product detected around 1.5 min. Talking about the photocatalysis tests, it is important to note that although at a lower speed, the photocatalysis test conducted at pH 3 (Fig. 8e) was also able to achieve complete SA degradation, but unlike the tests conducted at other pHs (Fig. 8(f–h)), it produced a signal less prominent for by-products between 1.5 and 2.5 min (Fig. 8e). It is probably related to the more intense interaction at pH between the SA, negatively charged (pH > pKa = 2.98 [25]), and the positively charged surface of the catalyst (pH < $pH_{PZC,\ P25}$ = 5.65 [26]), which favored adsorption (Fig. 7b) and the photodegradation process of SA and its by-products.

4. Conclusions

The results indicated the possibility of photolytic degradation of the studied compounds (ASA, SA, PAR and IBU) and that the pH of the solution during the process has a direct impact on the photodegradation reaction rate. Within the pH range studied (3–9), the degradation of ASA and PAR were favored with the reduction of pH, while the degradation of IBU and SA were favored by increasing the pH. The analysis of the absorption spectra showed the impact of molecular and anionic species on the absorption in the UV region and consequently on the photolytic efficiency.

In comparative photocatalysis tests carried out in the presence of P25, a drastic increase in the photodegradation rate was observed, with it not being possible to achieve complete mineralization. In common, all compounds indicated in their chromatograms the formation of a common by-product.

Due to the complexity involving the process and the analysis of products and intermediates, the future direction is tests involving other parameters, such as radiation intensity, different geometry of reactors and continuous processes.

Author contribution statement

Maria Eduarda Fuziki: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Laura S. Ribas: Performed the experiments; Wrote the paper.

Ângelo Marcelo Tusset; Rodrigo Brackmann: Analyzed and interpreted the data; Wrote the paper.

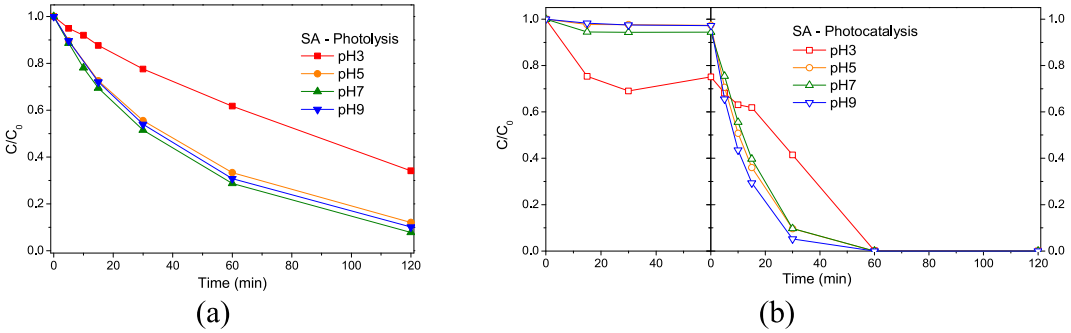

Fig. 7. Salicylic acid tests of (a) photolysis and (b) photocatalysis.

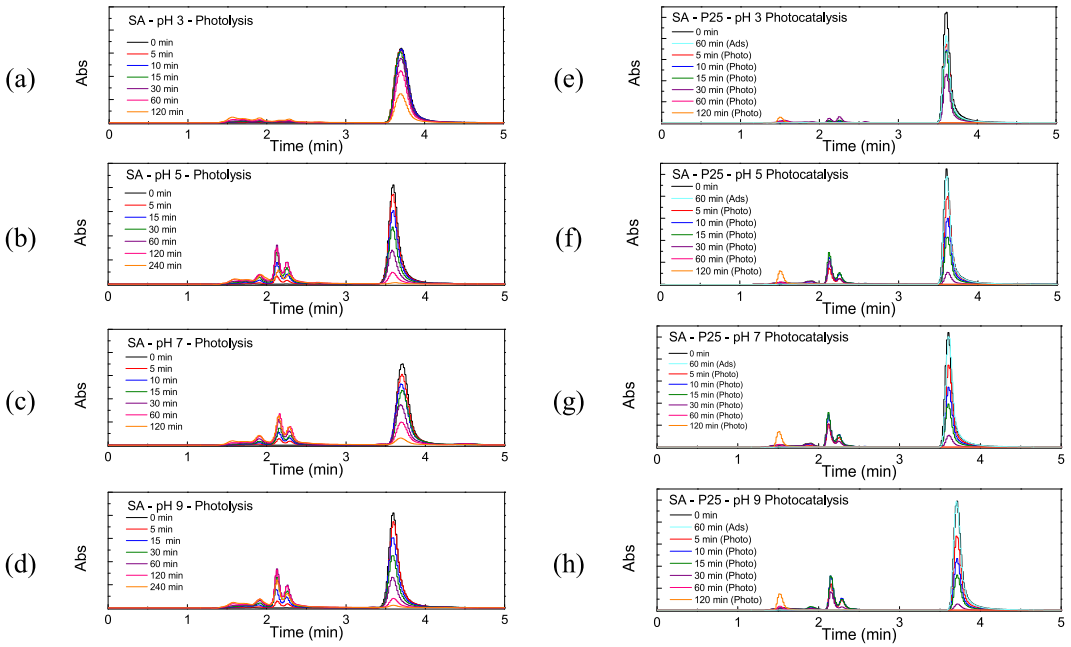

Fig. 8. Chromatograms of salicylic acid tests of (a–d) photolysis and (e–f) photocatalysis in different pHs.

Onelia A. A. Dos Santos: Conceived and designed the experiments; Wrote the paper.

Giane Gonçalves Lenzi: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability statement

Data included in article/supp. material/referenced in article.

Additional information

Supplementary content related to this article has been published online at [URL].

Declaration of interest's statement

The authors declare no competing interests.

Acknowledgements

Analysis Center laboratory of UTFPR-PG (C^2MMa) and Brazilian agencies CNPq, CAPES and Fundação Araucária for financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e13678.

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