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Research article

Electrochemical oxidation of acetaminophen and its transformation products in surface water: effect of pH and current density

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ABSTRACT

Several studies have been conducted worldwide to develop effective and affordable methods to degrade pharmaceuticals and their metabolites/intermediates/oxidation products found in surface water, wastewater and drinking water. In this work, acetaminophen and its transformation products were successfully degraded in surface water by electrochemical oxidation using stainless steel electrodes. The effect of pH and current density on the oxidation process was assessed and the oxidation kinetics and mechanisms involved were described. Additionally, the results were compared with those obtained in acetaminophen synthetic solutions. It was found that conducting the electrochemical oxidation at 16.3 mA/cm^2 and pH 5, good performance of the process was achieved and not only acetaminophen, but also its transformation products were totally degraded in only 7.5 min; furthermore, small number of transformation products were generated. On the other hand, degradation rates of acetaminophen and its transformation products in surface water were much faster (more than 2.5 times) and the reaction times much shorter (more than 4.0 times) than in synthetic solutions at all current densities and pH values evaluated. At pH 3 and pH 5, greater soluble chlorine formation due to the higher HCl amount used to acidify the surface water solutions could enhance the degradation rates of acetaminophen and its transformation products. However, constituents of surface water (ions and solids) could also have an important role on the oxidation process because at pH 9 (non-acidified solutions) the degradation rates were also much greater and the reaction times were much shorter in surface water than in acetaminophen synthetic solutions.

1. Introduction

Pharmaceuticals are chemical organic compounds that have contributed to enhance the quality life of human beings. However, potential adverse effects on aquatic ecosystems and human health can be derived when they or their metabolites are excreted into the environment without any treatment and control. Among thousands of pharmaceuticals currently found in surface water, wastewater and drinking water, acetaminophen is one of the most commonly reported [1, 2, 3, 4, 5, 6, 7, 8]. The molecule of acetaminophen is composed of an aromatic group (benzene ring), an amide group (R–CO–N (R_1, R_2)), and a hydroxyl group (R–OH) (Figure 1).

In humans, acetaminophen is metabolized by the liver and excreted into urine as acetaminophen glucuronide (47–62%), acetaminophen sulphate (25–36%), 3-hydroxy-paracetamol and N-acetyl-p-benzoquinone-imine (NAPQI) (8–10%), and unchanged acetaminophen (1–4%) [9]. In advanced oxidation processes (AOPs), the generation of oxidation/intermediates products such as NAPQI, 1,4-benzoquinone, hydroquinone, p-nitrophenol and p-aminophenol has been documented [10, 11, 12]. These products are toxic and difficult to degrade and, therefore, have addressed the interest and attention of the scientific community.

Toxicity of acetaminophen and its transformation products (metabolites/intermediates/oxidation products) in aquatic microorganisms and humans have been documented [10, 13, 14, 15, 16, 17] and now is recognized as an environmental concern and a human health risk. Therefore, worldwide many efforts have been done to find an affordable method to degrade effectively the acetaminophen and its metabolites/intermediates/oxidation products found in surface water, wastewater and drinking water. Among several treatment approaches, the following processes are documented, biological, electrochemical oxidation, H_2O_2/UV oxidation, electrocatalysis, TiO_2 photocatalysis, UVA/-LED/TiO_2, TiO_2/UV, sonolysis, chemical, Fenton, photo-Fenton,

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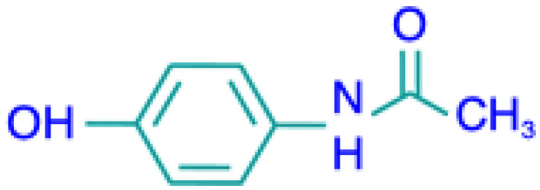

Figure 1. Acetaminophen molecule.

photoelectro-Fenton, nonthermal plasma, reverse osmosis, activated carbon, chlorination and ozonation [2, 10, 16, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45]. However, in most of them only partial mineralization of acetaminophen was obtained, ranging from 14% to 88% [36, 37]. Additionally, in most cases the reaction times were long, up to 6 h [2, 43], the transformation products generated by the processes were not degraded [19, 25, 30, 34, 39], and continuous supply of oxygen to produce H_2O_2 was needed [23]. Due to the high operation costs, the production of derivative pollutants and the complex reaction conditions, such methods are frequently not an affordable solution for degrading the acetaminophen [5].

More recently, electrochemical oxidation process has become attractive and promising because it is versatile, energetically efficient, environmentally friendly, less costly and allows automation [6, 46, 47]. The oxidation of organic compounds by an electrochemical process can involve two different mechanisms, direct anodic oxidation and indirect oxidation. In the first, transfer reactions of the organic compounds occur directly on the anode surface and involves the mediation of the electrons to oxidize the organic compounds. In the indirect oxidation, the electrochemical process is mediated by highly oxidant species such as reactive oxygen species (hydroxyl radical, ·OH) and chlorine active species (ClO^- at pH > 8, HClO in the pH range 3–8, and Cl_2 at pH < 3), which are electro-generated at the anode surface [47]. However, degradation of acetaminophen by this process could potentially generate intermediates/oxidation products such as 4-benzoquinone, hydroquinone, oxalic and oxamic acids, p-aminophenol, p-nitrophenol and NAPQI [6, 10, 11, 12, 20, 48]. These by-products could be more toxic and bio-recalcitrant than the initial compound that are difficult to degrade by using conventional methods [46]. Therefore, if electrochemical oxidation is planned to be used, not only acetaminophen, but also its intermediates/oxidation products must be degraded to ensure that not any ecosystems impact and human health risk will occur.

On the other hand, several electrode materials have been used in electrochemical processes for organic compounds degradation, such as Pt, Au, boron-doped diamond (BDD), mixed metal oxide (MMO), graphite and carbon. For their resistance to dissolution and corrosion and excellent catalytic properties, MMO and BDD electrodes are preferred in the electrochemical oxidation processes of organic compounds such as pharmaceuticals, pesticides, dyes and industrial wastewaters. Unfortunately, those electrodes are expensive, and their catalytic efficacy depends not only on their composition but also on fabrication methods [49]; therefore, these drawbacks limit their use in practical applications. To overcome this weakness, much cheaper electrode materials could be used. In this sense, stainless steel is a common and cheap alloyed material available in the market. It is widely used in the industry sector because of its mechanical workability, extraordinary electrical and thermal conductivities, strength, corrosion resistance and affordability compared to other noble metals such as platinum, gold and tantalum [50, 51]. The use of stainless-steel electrodes in electrooxidation processes has been reported in the literature for the treatment of copper cyanide, nitrites, antibiotics, cinnamic acid and phenol effluents [52, 53, 54, 55]; however, reports where such electrodes have been used to degrade pharmaceuticals is very limited.

Thus, recently López Zavala and Espinoza Estrada [6] achieved promising results degrading successfully synthetic solutions of acetaminophen and its transformation products by using an electrochemical oxidation cell with stainless steel electrodes fed with low direct current densities that can be supplied by photovoltaic cells. However, still remains the question about the performance and effectiveness of the electrochemical oxidation process when, besides the pharmaceutical, other constituents are also present in water, like those in surface water, wastewater and drinking water. Therefore, in this work, performance and efficacy of the electrochemical oxidation process is evaluated when acetaminophen and its oxidation products are degraded in surface water. Effects of pH and current densities on the degradation rates of the acetaminophen and its oxidation products are described. Oxidation kinetics, electrochemical processes and mechanisms are also discussed. Furthermore, the results obtained in this research were compared with those obtained in acetaminophen synthetic solutions reported by López Zavala and Espinoza Estrada [6] and with those reported by other researchers for acetaminophen synthetic solutions using another advanced oxidation processes and electrode materials such as electro-Fenton, photoelectron-Fenton, solar photoelectron-Fenton and Pt/carbon-PTFE gas--diffusion electrodes [56, 57].

The results obtained in this research are relevant and promising from the practical point of view because the electrochemical oxidation process with stainless steel electrodes degraded totally the pharmaceutical and its transformation products in a real surface water, required very short reaction times (even lower than those reported by other researchers for acetaminophen synthetic solutions using another advanced oxidation processes and electrode materials such as electro-Fenton, photoelectron-Fenton, solar photoelectron-Fenton and Pt/carbon-PTFE gas-diffusion electrodes [56, 57]), demanded low DC densities and needed a small pH adjustment. The DC densities can be provided with photovoltaic cells and the pH adjustment does not represent a real challenge in the practice. Therefore, the electrochemical oxidation with stainless steel electrodes could become a viable, feasible, affordable and sustainable technological alternative to degrade pharmaceuticals and their transformation products.

2. Materials and methods

2.1. Chemicals and materials

The chemicals used in this research were hydrochloride acid (HCl, 37%, Fermont, Mexico City, Mexico), methanol (J.T. Baker, Center Valley, PA), potassium hydroxide (KOH, Sigma-Aldrich Toluca, Mexico), acetaminophen (4-acetamidophenol, 98%, Sigma-Aldrich, Toluca, Mexico), sulfuric acid (H_2SO_4, Sigma-Aldrich, Toluca, Mexico), and acetic acid (Fisher Scientific, Monterrey, Mexico). Additionally, ultrapure water (Milli-Q water purification system, Bedford, MA) and surface water from the "Rodrigo Gómez'' dam located in Santiago, Nuevo León, Mexico, were used in this research.

2.2. Experimental device

The experimental device used in this work was similar to the electrochemical oxidation cell reported by López Zavala and Espinoza Estrada [6] but modified to increase its volume up to 200 ml and have a mesh of more resistant electrodes. 15 stainless steel electrodes (type 304, 7 cathodes and 8 "active" anodes) with 2 mm diameter and effective length of 120 mm were spaced approximately 2 mm each. Figure 2 shows the schematic representation of the experimental device.

2.3. Characterization of surface water

Raw surface water was characterized based on parameters such as chemical oxygen demand (COD), total organic carbon (TOC), total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), pH, electrical conductivity (EC) and turbidity. Standard methods for the analysis of water and wastewater [58] were used to determine TS, TSS,

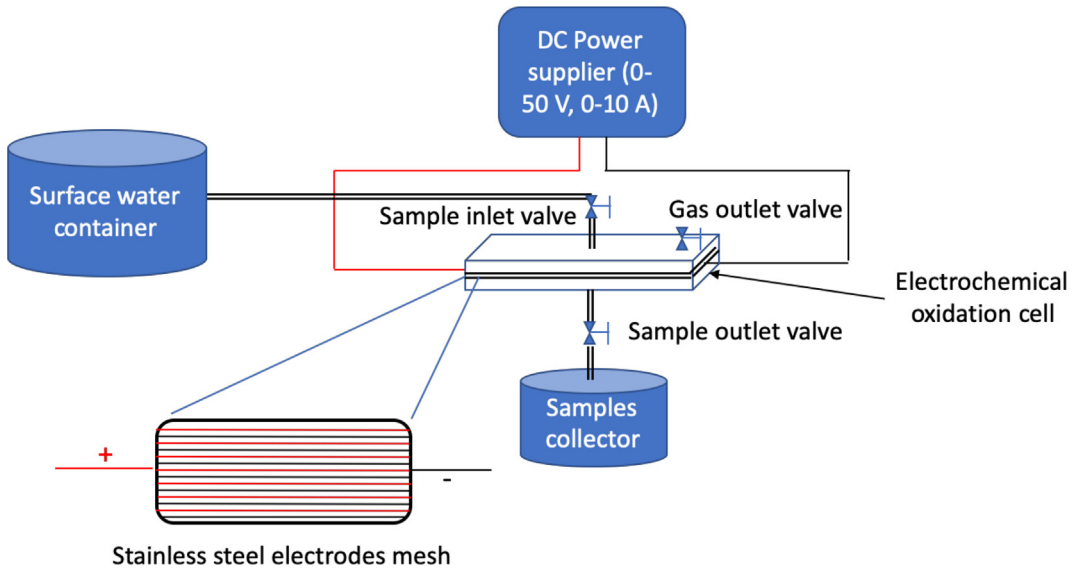

Figure 2. Schematic representation of the experimental device.

TDS and COD. Thermo Scientific Orion 3-Star equipment (Thermo Fisher Scientific, Waltham, MA) was used to determine EC and pH, and a Hach 2100 N Turbidimeter (USA Hach Company, Loveland, CO) for turbidity. High-performance liquid chromatography using an Agilent 1200 HPLC-DAD equipment (Agilent Technologies, Santa Clara, CA) was used to analyze traces of acetaminophen in surface water.

2.4. Degradation of paracetamol and its oxidation products

Preparation of four surface water solutions of 10 mg/L-acetaminophen was done. By using hydrochloric acid (HCl) and/or potassium hydroxide (KOH), as required, initial pH of the solutions was adjusted to 3, 5, 7 and 9. Then, electrochemical oxidation of samples of each solution was conducted at DC densities of 12.3 mA/cm^2 (8.5 V), 16.3 mA/cm^2 (10 V) and 20.3 mA/cm^2 (12 V), and different reaction times 1, 2.5, 5, 7.5, 10, 15, 20, 25, 30, 35, 40, 50 and 60 min. The current density here is referred to the surface area of "active" anodes. All experiments were conducted on batch configuration. All samples were filtered with 0.45μm polytetrafluoroethylene syringe filters and then analyzed by triplicate using an Agilent 1200 HPLC-DAD equipment (Agilent Technologies, Santa Clara, CA, USA). Analytes were separated by using a 150 × 4.6 mm reverse phase monomeric Zorbax C18 column with 5μm diameter spherical particles (MAC-MOD Analytical, Wilmington, DE, USA). A mobile phase of methanol in ultrapure water (40/60/v/v) was used to analyze the acetaminophen and its oxidation products under the following operating conditions, temperature 30 °C, flowrate 1.0 mL/min, detection 254nm and injection volume 20 μL.

Due to the formation of sludge (iron oxides flocs) during experiments, sludge was drained from the oxidation cell and dewatered using 0.45μm polytetrafluoroethylene syringe filters; then the extracts were analyzed as described before with the aim of detecting the presence of acetaminophen and oxidation products in the sludge extracts.

3. Results and discussion

3.1. Surface water characterization

Raw surface water presented low constituent's loads. Table 1 summarizes the characteristics of raw surface water and two acetaminophen solutions prepared with surface water and MilliQ water at different pH values. Acetaminophen and its oxidation products in raw surface water were not detected by HPLC-DAD at 254 nm.

As seen in Table 1, COD and TOC of surface water increased when the pharmaceutical was added to prepare the 10 mg/L acetaminophen solutions. Cl^- concentration also increased importantly when pH of surface water solutions was adjusted to 3, 5 and 7 with HCl. As seen, resulting concentration of Cl^- in surface water solutions was greater than in synthetic acetaminophen solutions (MQW + Acm) because greater amount of HCl acid was needed to adjust the pH.

Table 1. Constituent's load of raw surface water and acetaminophen solutions.

Parameter	RSW[1]	RSW[1]+Acm[2] Solution				MQW[3]+Acm[2] solution	
		pH 3	pH 5	pH 7	pH 9	pH 3	pH 5
COD (mg/L)	15.7	24.10	24.10	24.10	24.10	—	—
TOC (mg/L)	2.85	10.15	10.15	10.15	10.15	—	—
Chlorides (mg/L)	4.2	322.10	203.17	84.23	4.2	74.3	1.0
pH	8.13	3.0	5.0	7.0	9.0	3.0	5.0
EC (us/cm)	412	902	493	448	420	308	37.5
Turbidity (NTU)	1.24	1.85	1.11	2.32	2.71	—	—
TS (mg/L)	322.4	—	—	—	—	—	—
TSS (mg/L)	61.3	—	—	—	—	—	—
TDS (mg/L)	261.1	—	—	—	—	—	—

Note: [1] RSW: Raw surface water. [2] Acm: Acetaminophen. [3] MQW: Milli Q water.

3.2. Degradation of acetaminophen

Figure 3 shows the acetaminophen degradation for the three current densities and four pH evaluated. As seen, acetaminophen in surface water was totally oxidized. Oxidation was faster at higher current densities and lower pH values. At 20.3 mA/cm^2 and pH 3, acetaminophen was totally oxidized at 2.5 min reaction time. Similar time was required at pH 5; but the oxidation rate was faster at pH 3. At pH 7, the complete oxidation of acetaminophen was achieved at 10 min reaction time; meanwhile at pH 9, the reaction time needed was 30 min. At 16.3 mA/cm^2 and pH 3 and 5, the reaction time required for complete degradation of the pharmaceutical was also 2.5 min, similar to that observed at 20.3 mA/cm^2. At pH 7 and 9, longer reaction times were needed to oxidize totally the acetaminophen, 20 min and 50 min, respectively. Acetaminophen degradation at 12.3 mA/cm^2 was slower; at pH 3, total oxidation of the pharmaceutical was reached at 5 min, meanwhile at pH 5 the required reaction time for complete degradation of the compound was 7.5 min. At pH 7 and 9, total oxidation of acetaminophen was registered at 30 and 120 min, respectively. As explained before, at 20.3 mA/cm^2 and 16.3 mA/cm^2 and at pH 3 and 5, the reaction time was the same, 2.5 min.

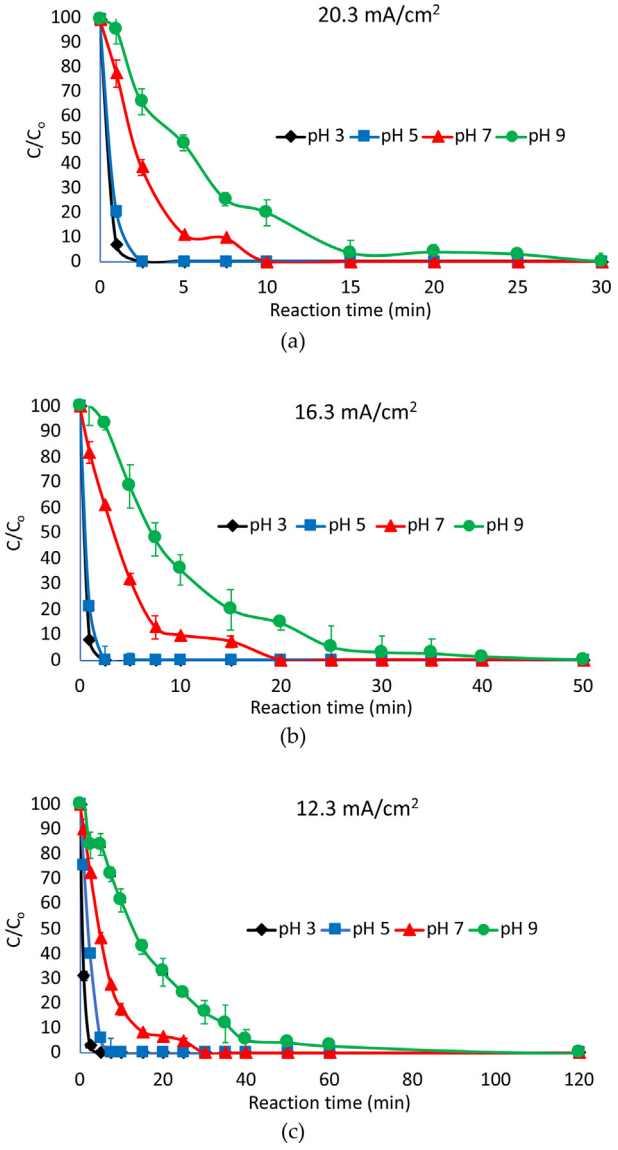

Figure 3. Degradation of acetaminophen at different current densities and pH values. The figure shows the average of three replicates. (a) DC density: 20.3 mA/cm^2; (b) DC density: 16.3 mA/cm^2; (c) DC density: 12.3 mA/cm.^{2}.

These reaction times are shorter than those reported by other researchers (6–55 min) for acetaminophen synthetic solutions using another advanced oxidation processes and electrode materials such as electro-Fenton, photoelectron-Fenton, solar photoelectron-Fenton and Pt/carbon-PTFE gas-diffusion electrodes [56, 57]. This result is very significant from the practical point of view because moderate current density and small adjustment of pH is needed to have very short reaction time. Furthermore, the reaction times at pH 7 were no greater than 30 min for the three reaction times, which are still very attractive values. In comparison with the results reported for synthetic acetaminophen solutions [6], similarly, faster oxidation occurred at higher current densities applied and lower pH values of the solutions. However, reaction times in this study (surface water) were much shorter (See a comparison in Table 2). This was an unexpected result because of the presence of solids, ions, and organic matter in surface water that could affect the effectiveness of the electrochemical oxidation. However, such constituents contributed to have better performance as it is discussed later in this document.

Note: [1] López Zavala and Espinoza Estrada [6] estimated the current densities based on the surface area of all electrodes. In this table, those current densities were recalculated and presented respect to the surface area of "active anodes".

Electrochemical oxidation of acetaminophen was dominated by different mechanisms depending on the pH and concentration of chloride ions in the surface water solutions. In solutions with pH 9, chloride ions were present in very low concentrations (See Section 3.1); therefore, anodic oxidation (AO) dominated the degradation process and the oxidation of acetaminophen occurred by either direct electron transfer to the anode or mediated oxidation with reactive oxygen species (ROS) such as "active oxygen" or hydroxyl radical (·OH) formed from water at the anode [47, 56, 59, 60]. Thus, acetaminophen was electrochemically converted into intermediates (discussed in section 3.3) by chemisorbed "active oxygen" species, and then electrochemically mineralized by physisorbed ·OH.

At high current densities, acetaminophen and water were simultaneously oxidized and the anode activity had a remarkable effect on the selectivity and efficiency of the degradation process resulting either electrochemical conversion or oxidation [47, 56]. By denoting the anode as M, oxidation of water lead to the formation of the hydroxyl radical (M(·OH)) by Reaction (1) [47,59].

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^-, \quad (1)$$

Due to stainless steel electrodes are "active" anodes, the hydroxyl radical (M(·OH)) interacted remarkably with the anode's surface that was transformed into a chemisorbed "active oxygen" specie or superoxide MO according to Reaction (2).

$$M(\cdot OH) \rightarrow MO + H^+ + e^-, \quad (2)$$

As seen in Reactions (1) and (2), formation of H^+ is indicated; this was confirmed by the decrease of the solutions pH, from 9 to 6.2 (12.3 mA/cm^2), 6.4 (16.3 mA/cm^2) and 6.8 (20.3 mA/cm^2).

In addition to the heterogeneous ·OH, in AO other ROS such as H_2O_2 and O_3 are formed from water at the anode surface by Reaction (3) and Reaction (4), respectively; however, the physisorbed ·OH is the strongest.

$$2M(\cdot OH) \rightarrow 2MO + H_2O_2, \quad (3)$$

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^- \quad (4)$$

The electrochemical conversion of acetaminophen (R) was mediated by the pair MO/M, according to Reaction (5)

$$MO + R \rightarrow M + RO, \quad (5)$$

In Reaction (5), the superoxide (MO) reacted with the pharmaceutical forming acetaminophen oxidation products (RO), which were detected, and they are discussed in Section 3.3.

Table 2. Reaction times (min) required to degrade acetaminophen in synthetic solutions (SS) and surface water solutions (SW).

DC density (mA/cm^2)	11.0[1]	12.3	14.6[1]	16.3	18.3[1]	20.3
pH	SS	SW	SS	SW	SS	SW
3	120	5.0	7.5	2.5	2.5	2.5
5	>900	7.5	570	2.5	240	2.5
7	>900	30	>900	20	240	10
9	>900	120	>900	50	540	30

On the other hand, as described in section 2.4, HCl was used to adjust the pH of the surface water solutions to 3, 5 and 7 values. Therefore, chloride ions were available in such solutions due to the HCl dissociation into H^+ and Cl^-. Under these conditions, acetaminophen was electro-oxidized by active chlorine species. Cl^- ion was directly oxidized at the anode to produce soluble chlorine (Cl_2) by Reaction (6), then this diffused away from the anode to be hydrolyzed and converted into hypochlorous acid (HClO) and chloride ion according to Reaction (7):

$$2Cl^- \rightarrow Cl_2\ (aq) + 2e^-, \quad (6)$$

$$Cl_2\ (aq) + H_2O \rightleftharpoons HClO + Cl^- + H^+, \quad (7)$$

At pKa = 7.55, hypochlorous acid is in equilibrium with hypochlorite ion

$$HClO \rightleftharpoons ClO^- + H^+, \quad (8)$$

Under equilibrium conditions, the predominant species are ClO^- at pH > 8, HClO in the pH range 3–8, and Cl_2 until pH near 3 [61]. Due to the higher standard potential of Cl_2 (E^0 = 1.36 V vs SHE) and HClO (E^0 = 1.49 V vs SHE) compared to ClO^- (E^0 = 0.89 V vs SHE), the mediated oxidation with active chlorine species is faster in acid than in alkaline media [47, 56]. Thus, in this work active chlorine species (Cl_2 and HClO) were generated at pH 3, 5 and 7 and attacked the acetaminophen molecule in competition with ROS [60]. Cl_2 and HClO had greater degradative activity than reactive oxygen species (ROS) due to the degradation activity of the "active" anodes (stainless steel electrodes) was remarkably enhanced by the chloride ions present in the surface water solution and generated active chlorine oxidized the pharmaceutical, alone or in combination with hydroxyl radicals. These results agree with those reported by [6] for acetaminophen synthetic solutions and by [62] that degraded 80% and 95% of acetaminophen at 80 mA in 0.1 M NaCl with Ti/RuO_2 and boron anodes doped with diamond (BDD). However, in this study, degradation rates were greater, and the reaction times were faster than those obtained by [6] for acetaminophen synthetic solutions (Table 2) and by [62] that reported 30 min reaction times. Better performance of the electrochemical oxidation process in this research, in comparison with acetaminophen synthetic solutions, was due to the greater amount of HCl used to acidify the surface water, which resulted in a higher chloride concentration and consequently in a greater oxidation of the Cl^- ion at the anode. Thus, greater soluble chlorine formation enhanced the degradation of acetaminophen. However, at pH 9 (non-acidified solutions), the reaction times were also much shorter in surface water than in synthetic solutions (see Figure 3); this means that surface water constituents (ions and solids) also played an important role on the electrochemical oxidation process.

Analysis of degradation rate constants can give more details of the effect of pH and current density on the electrochemical oxidation of acetaminophen in surface water. Rate constants were estimated by linearizing the curves of Figure 3 using a semi-log method ($\ln(C/C_o) = k{\cdot}t + \ln A$). In Figure 4, the effect of pH and current density on degradation rate constants is shown. As seen, for all pH values the rate constants are greater at higher current densities. This means that high current densities enhanced the oxidation of acetaminophen; however, their effect diminished as pH increased, especially remarkable at pH 9. On the other hand, the degradation rate constants are greater at lower pH values, irrespective the current density; however, at 16.3 mA/cm^2 and 20.3 mA/cm^2 the oxidation rate constants of acetaminophen were much greater than a 12.3 mA/cm^2. These results are in agreement with those reported by other researchers for electrochemical oxidation of acetaminophen and other emergent pollutants such as colorants where the optimum pH conditions for the oxidation are in the range of 2.5–3.5 [23, 56].

On the other hand, at pH 3, the rate constants at current densities 16.3 mA/cm^2 and 20.3 mA/cm^2 were very similar, 2.52 min^{-1}and 2.66 min^{-1}, respectively. This means that at pH 3 moderate current density (16.3 mA/cm^2) is required to have high degradation rates.

In comparison with the degradation rate constants obtained by [6] for acetaminophen synthetic solutions; the rate constants obtained in this study (surface water) were much greater (more than 2.5 times) for all pH values and current densities evaluated. As mentioned above, these greater degradation rates might be the result of greater soluble chlorine formation in surface water due to the greater amount of HCl used to acidify the solutions. However, at pH 9 (non-acidified solutions), also the degradation rate constants of acetaminophen were much greater in surface water than in synthetic solutions ($k < 0.01$/min); this confirms that surface water constituents also play an important role on the electrochemical oxidation process, as mentioned above. Nonetheless, it is necessary to conduct additional research to elucidate their contribution.

3.3. Degradation of acetaminophen intermediates/oxidation products

As discussed in section 3.2, depending on the surface water solutions pH, the acetaminophen degradation can be dominated by anodic oxidation or by oxidation with active chlorine species. Under anodic oxidation, acetaminophen intermediates are formed; while, oxidation with active chlorine species generates oxidation products. These transformation

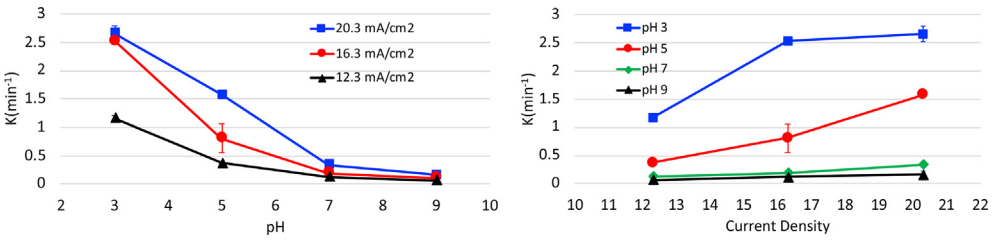

Figure 4. Degradation rate constants of acetaminophen in surface water. (a) effect of pH and (b) effect of current density. The figure shows the average of three replicates.

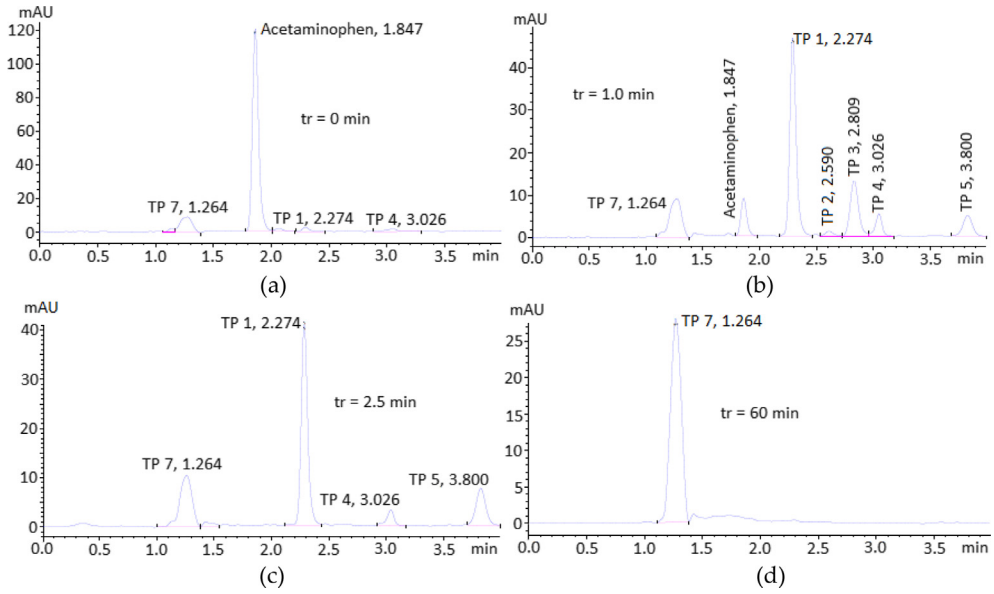

Figure 5. Degradation of acetaminophen and its transformation products at different reaction times at highest current density (20.3 mA/cm^2) and the lowest pH (3). (a) tr = 0 min; (b) tr = 1 min; (c) tr = 2.5 min; (d) tr = 60 min. TP refers to transformation products.

products were detected not only in the treated effluent, but also in sludge generated during the oxidation process. During experiments, the stainless-steel electrodes suffered some level of oxidation that caused formation of iron oxides flocs (sludge). These flocs were settled and analyzed to determine the presence of the acetaminophen intermediates/oxidation products. Because these transformation products are potentially more toxic than the pharmaceutical itself, they must be also completely degraded. Evidence of the formation and total degradation of these compounds is shown in Figure 5 for the treated effluent and in Figure 6 for the sludge. These figures include only chromatograms for the highest current density (20.3 mA/cm^2) and the lowest pH (3), where most of the transformation products were detected; however, similar chromatograms were obtained for other current densities and pH values (not included in this document).

As seen in Figure 5a (tr = 0 min), when the acetaminophen solutions were prepared with surface water, besides the pharmaceutical five additional peaks were detected, especially that at 1.264 min retention time. Indeed, this peak was the only one detected in raw surface water and corresponded to iron oxides. Other traces of compounds were generated during the solution preparation, i.e. surface water constituents and the addition of HCl to adjust the pH of the solution caused immediately some transformations of the acetaminophen. This is can be confirmed because in case of acetaminophen synthetic solutions, traces of transformation products were not detected during the solutions preparation [6]; therefore, surface water constituents had some effect on the acetaminophen oxidation. Once the electrochemical oxidation started (Figure 5b, reaction time tr = 1 min) acetaminophen degraded rapidly and seven transformation products

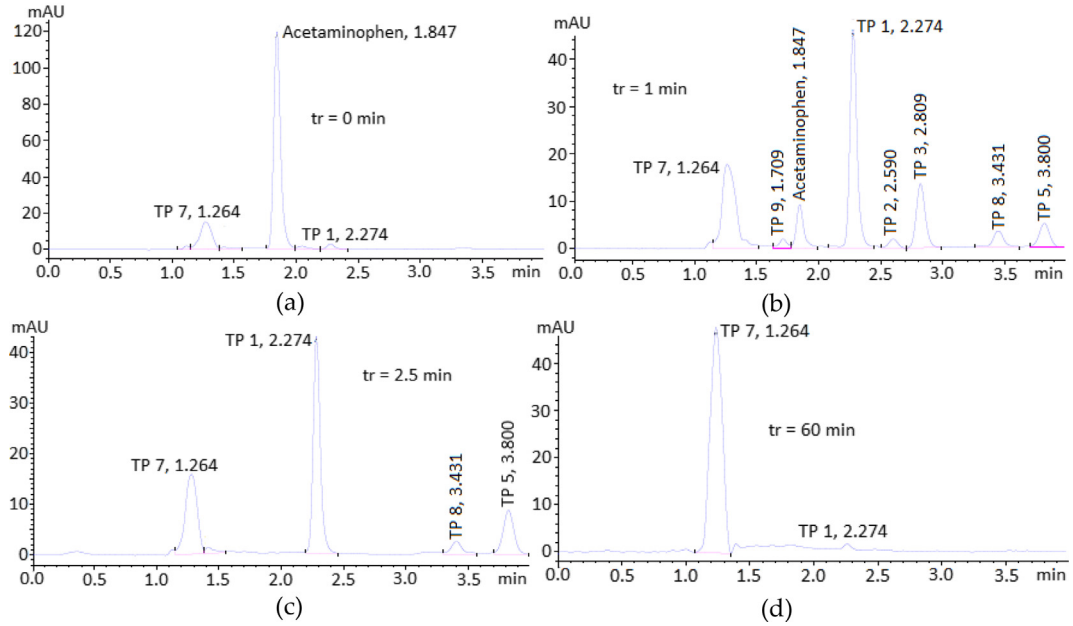

Figure 6. Acetaminophen and its transformation products detected in the sludge at different reaction times at highest current density (20.3 mA/cm^2) and the lowest pH (3). (a) tr = 0 min; (b) tr = 1 min; (c) tr = 2.5 min; (d) tr = 60 min. TP refers to transformation products.

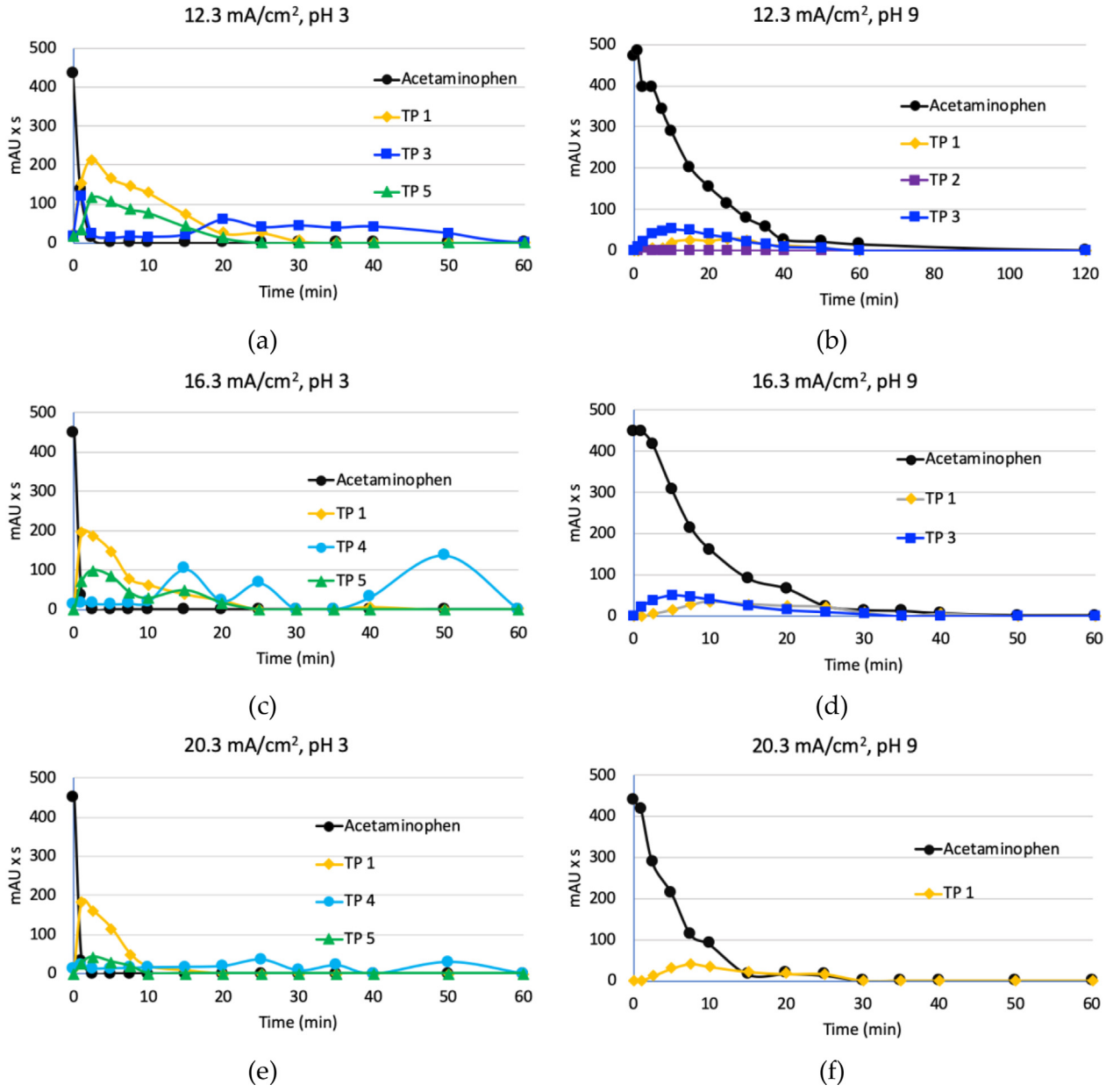

Figure 7. Effects of pH and current density on the degradation of intermediates/oxidation products of acetaminophen in surface water. The figure shows the average of three replicates. (a) 12.3 mA/cm^2 and pH 3; (b) 12.3 mA/cm^2 and pH 9; (c) 16.3 mA/cm^2 and pH 3; (d) 16.3 mA/cm^2 and pH 9; (e) 20.3 mA/cm^2 and pH 3; (f) 20.3 mA/cm^2 and pH 9.

began appearing in the treated effluent. These compounds were designated as TP 1 (2.274), TP 2 (2.590), TP 3 (2.809), TP 4 (3.026), TP 5 (3.800), TP 6 (2.715), and TP 7 (1.264) for the compound detected in surface water. As reported by [6], TP 7 corresponded to iron oxides; therefore, it is not exactly an acetaminophen oxidation byproduct, but it was also considered as a transformation product of the oxidation process because its concentration increased as reaction time increased. As seen, most of the compounds were generated at pH 3, except the TP 6 that was detected at pH 9. This confirms that electrochemical oxidation with active chlorine species generates more byproducts than the anodic oxidation, as reported by [6]. No additional transformation products were found in other pH values and current densities. As seen, all acetaminophen transformation products were not detected at 60 min reaction time.

On the other hand, the transformation products detected in the sludge were TP 1 (2.274), TP 2 (2.590), TP 3 (2.809), TP 5 (3.800), and TP 7 (1.264), also found in the treated effluent; additionally, other two compounds were detected TP 8 (3.431) and TP 9 (1.709), as seen in Figure 6b (tr = 1 min). No additional transformation products were detected at other pH values and current densities. In general, peaks height of transformation products is slightly higher in sludge than in the treated effluent. This means that more than half of transformation products were adsorbed to the flocs formed during oxidation. Similarly to the treated effluent, in sludge most of the acetaminophen transformation products were not detected at 60 min reaction time.

In comparison with acetaminophen synthetic solutions, five additional transformation products were detected in this study (surface water). Such compounds were TP 2, TP 4, TP 6, TP 8 and TP 9. This means that surface water constituents caused the formation of additional intermediates/oxidation products when acetaminophen is electrochemically oxidized. Those compounds, detected in either synthetic or surface water solutions, could be the transformation products reported by literature, such as NH_4^+, NO_3^-, 4-benzoquinone, hydroquinone,

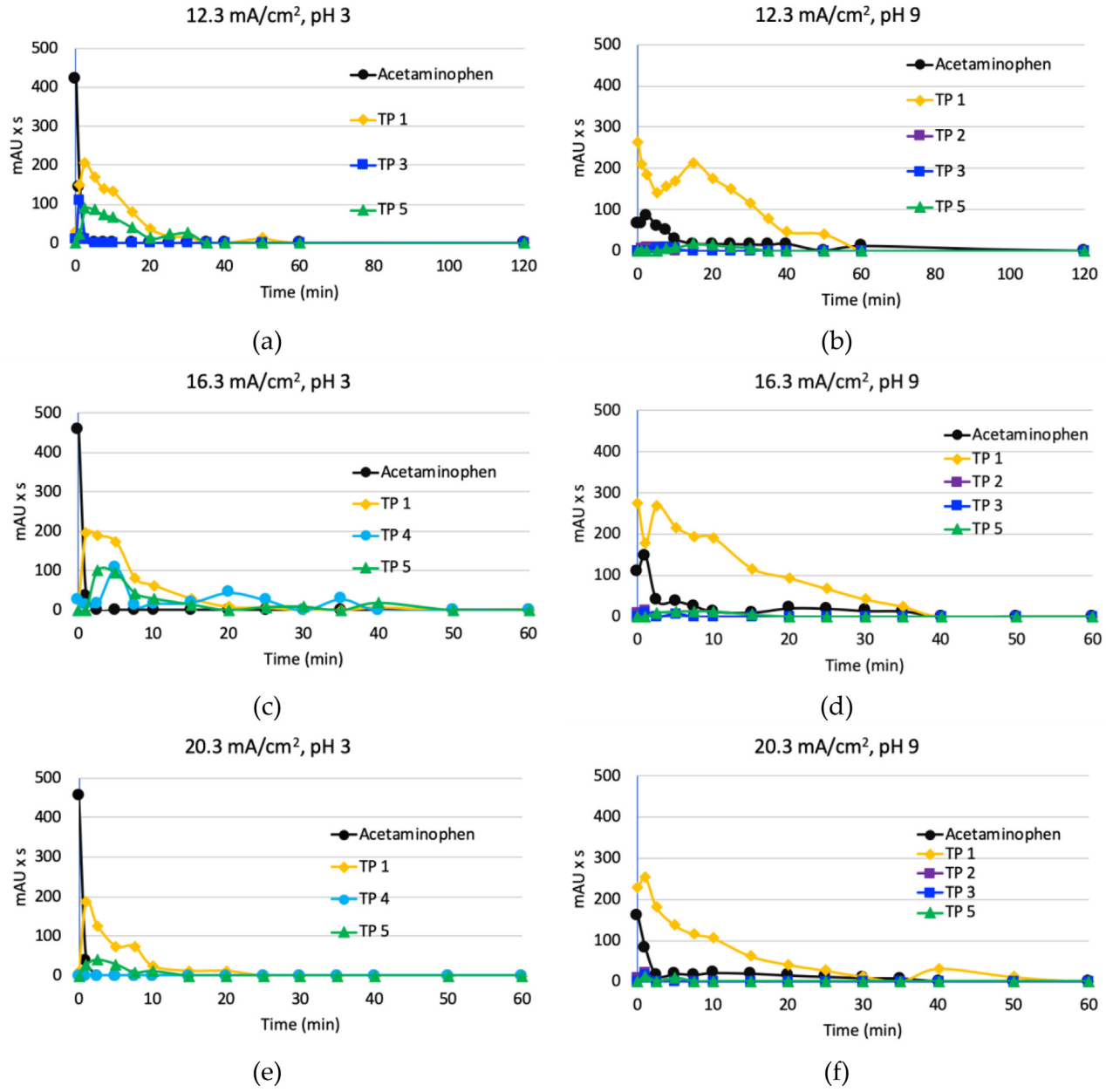

Figure 8. Effects of pH and current density on the degradation of intermediate/oxidation products of acetaminophen detected in the sludge. The figure shows the average of three replicates. (a) 12.3 mA/cm^2 and pH 3; (b) 12.3 mA/cm^2 and pH 9; (c) 16.3 mA/cm^2 and pH 3; (d) 16.3 mA/cm^2 and pH 9; (e) 20.3 mA/cm^2 and pH 3; (f) 20.3 mA/cm^2 and pH 9.

oxalic and oxamic acids, p-aminophenol, p-nitrophenol and NAPQI [6, 10, 11, 12, 20, 47]. However, identification of the transformation products was not the scope of this work; but the assessment of the effects of pH and current density on their detection and degradation was. As observed in chromatograms of Figures 5 and 6, all acetaminophen transformation products were successfully degraded in approximately 60 min reaction time. TP 7, as mentioned above, corresponded to iron oxides; therefore, its detection was expected to increase with the increase of the reaction time. It is important to note that iron oxides do not represent an environment concern neither a human health risk; furthermore, they can be removed effectively from the treated effluent by simple techniques.

Figure 7 presents more details of the effects of pH and current density on the degradation of acetaminophen intermediates/oxidation products in surface water. In general, greater number of transformation products was observed at low pH values; furthermore, higher current densities and lower pH values accelerated the degradation of intermediates/oxidation products. TP 7 was not included in the subsequent figures and discussions because iron oxides were not acetaminophen byproducts. At 12.3 mA/cm^2 and pH 3, most of the transformation products were totally degraded at 30 min, except the TP 3 that took 60 min. At pH 9, complete oxidation of the transformation products was achieved at 60 min reaction time; however, total degradation of acetaminophen was obtained at 120 min. At 16.3 mA/cm^2 and pH 3, the reaction time needed to degrade most of the transformation products was 25 min, except for the TP 4 that required 60 min. At pH 9, longer reaction time (35 min) was required to achieve complete oxidation of the transformation products; meanwhile, acetaminophen required 50 min. At 20.3 mA/cm^2 and pH 3, most of transformation products were completely degraded at 20 min, except the TP 4 that required 60 min reaction time. At pH 9, only the TP 1 was generated. This transformation product and the acetaminophen required 30 min reaction time to be completely degraded.

Table 3. Reaction times (min) required to degrade acetaminophen transformation products in synthetic solutions (SS) and surface water (SW).

DC density (mA/cm^2)	11.0[1]	12.3	14.6[1]	16.3	18.3[1]	20.3
pH	SS	SW[2]	SS	SW[2]	SS	SW[2]
3	360	60	240	35	120	30
5[3]	>900	15	900	7.5	240	7.5
7[3]	>900	25	900	15	240	10
9	>900	60	>900	50	540	35

Note: 1 López Zavala and Espinoza Estrada [6] estimated the current densities based on the surface area of all electrodes. In this table, those current densities were recalculated and presented based on the surface area of "active anodes". 2 The highest values from treated effluent and sludge were selected. 3 Chromatograms and figures not included in this work.

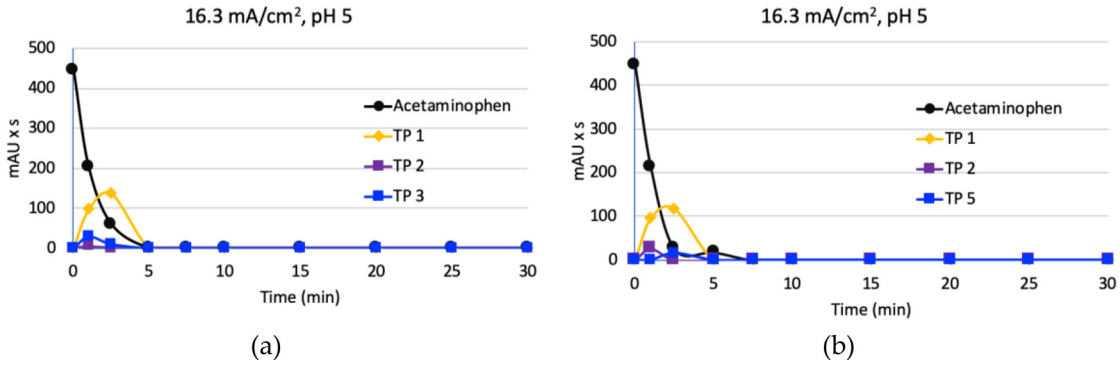

Figure 9. Current density and pH conditions needed to achieve complete degradation of acetaminophen and its transformation products in surface water at the shortest reaction times. The figure shows the average of three replicates. (a) Treated effluent; (b) Sludge.

Regarding the transformation products detected in sludge; as seen in Figure 8, total degradation of the compounds was faster at high current densities and lower pH values, similar to that observed in Figure 7. At 12.3 mA/cm^2 and pH 3, 60 min reaction time was needed to achieve complete degradation of transformation products; same reaction time was required at pH 9. At 16.3 mA/cm^2 and pH 3, total oxidation of transformation products was observed at 35 min; meanwhile, at pH 9 the reaction time required was 40 min. At 20.3 mA/cm^2 and pH 3, the transformation products were totally degraded at 30 min, but at pH 9 the time needed was 35 min. In case of TP 1, some traces of this compound were detected at 40 min and 50 min reaction times; however, these results should be associated to the inappropriate cleaning of the column or contamination of the samples. As seen, the reaction times needed to degrade totally the transformation products in both figures were quite similar. This means that even though the generation of iron oxides, where the transformation products were adsorbed, they were completely degraded in very short reaction times, 60 min (maximum) at the lower current density applied (12.3 mA/cm^2) and at the pH values evaluated (3–9). In comparison with acetaminophen synthetic solutions [6], the reaction times required to achieve complete degradation of transformation products were much shorter in surface. Table 3 summarizes the reaction times for both types of acetaminophen solutions.

As mentioned in Section 3.2, the reason of greater degradation rates of acetaminophen in surface water in comparison with synthetic solutions might be the greater soluble chlorine formation in surface water due to the greater amount of HCl used to acidify the solutions. However, at 9 pH (non-acidified solutions), also the degradation rates of acetaminophen and its transformation products were much greater and the reaction times were much shorter in surface water than in synthetic solutions (see Table 2 and Table 3); this means that surface water constituents also play an important role on the electrochemical oxidation process; therefore, it is necessary to conduct additional research to elucidate their contribution.

As seen from Table 3, the reaction times needed to oxidize totally the transformation products in surface water were, in the worst case, only 25% of those needed in acetaminophen synthetic solutions for all pH and current densities evaluated. In surface water, at pH 5 acetaminophen transformation products were degraded completely in only 7.5 min, at current densities 16.3 mA/cm^2 and 20.3 mA/cm^2. Furthermore, the smaller number of transformation products were also generated at this pH. These results are very promising from the practical point of view because at 16.3 mA/cm^2 and pH 5, not only acetaminophen, but also its transformation products can be totally degraded in only 7.5 min (Table 3 and Figure 9). Moreover, considering that this current density can be supplied by photovoltaic cells, the pH adjustment to 5 is practically feasible, and the removal of iron oxides generated during the oxidation process can be effectively done by simple and conventional settling or granular filtration techniques.

On the other hand, oxidation of stainless electrodes in this study was confirmed by the formation of iron oxide flocs and the deterioration of the "active" anodes after several experiments. Indeed, this drawback is commonly referred by those who prefer to use Pt, Au, boron-doped diamond (BDD), mixed metal oxide (MMO), graphite and carbon as electrode materials; however, it is important to remark that such materials are expensive and their catalytic efficiency depends on their composition and fabrication methods. On the contrary, stainless steel is a common alloyed material available in the market, much cheaper and has properties such as mechanical workability, extraordinary electrical and thermal conductivities, strength and corrosion resistance that make it more affordable than other noble metals such as platinum, gold and tantalum for practical applications. Therefore, electrochemical oxidation with stainless steel electrodes could be a technological alternative with enormous potential for degrading not only pharmaceuticals, but also their intermediates/oxidation products.

4. Conclusions

Acetaminophen and its intermediates/oxidation products in surface water were successfully degraded by electrochemical oxidation using stainless steel electrodes. The effect of pH and current density on the

oxidation process was assessed and the oxidation kinetics and mechanisms involved were described. Additionally, the results of this research were compared with those obtained in acetaminophen synthetic solutions. At alkaline (pH 9) conditions, degradation of acetaminophen was dominated by "active oxygen" species (anodic oxidation); meanwhile, under acidic conditions (pH 3 and pH 5), degradation of acetaminophen was dominated by "active chlorine" species. Thus, electrochemical oxidation generated intermediates and oxidation products (transformation products). In general, degradation of acetaminophen and its transformation products was faster at high current densities and lower pH values; however, conducting the electrochemical oxidation at moderate current density and pH values (16.3 mA/cm^2 and pH 5), good performance of the process was achieved and not only acetaminophen, but also its transformation products were totally degraded in only 7.5 min; furthermore, the smallest number of transformation products were generated.

On the other hand, in surface water the electrochemical oxidation process generated more transformation products (nine, including the iron oxides) than in acetaminophen synthetic solutions (five, including also the iron oxides). However, the degradation rates of acetaminophen and its intermediates/oxidation products in surface water were much faster (more than 2.5 times) and the reaction times much shorter (more than 4.0 times) than in synthetic solutions at all current densities and pH values evaluated. At low pH values (3 and 5), greater soluble chlorine formation due to the higher HCl amount used to acidify the surface water solutions could enhance the degradation rates of acetaminophen and its transformation products. However, constituents of surface water could also have an important role on the oxidation process because at pH 9 (non-acidified solutions) the degradation rates were also much greater and the reaction times were much shorter in surface water than in acetaminophen synthetic solutions. Undoubtedly, additional research is needed to elucidate the chemical interactions and mechanisms that enhanced the performance of the electrochemical oxidation in surface water. However, the results obtained in this research are relevant and promising from the practical point of view because the electrochemical oxidation process with stainless steel electrodes degraded totally the pharmaceutical and its transformation products in a real surface water, required very short reaction times, demanded low DC densities and needed a small pH adjustment. The DC densities can be provided with photovoltaic cells and the pH adjustment does not represent a real challenge in the practice.

Even though stainless steel is less resistance to dissolution and corrosion than other noble metals and carbon derivative materials, its low cost, availability in the market, and other mechanical, electrical, thermal and strength properties make it attractive as electrode material for practical applications. Therefore, the electrochemical oxidation with stainless steel electrodes could become a viable, feasible, affordable and sustainable technological alternative to degrade pharmaceuticals and their transformation products.

Declarations

Author contribution statement

Miguel Ángel López Zavala: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Diego Anglés Vega: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

José Manuel Álvarez Vega, Odwer Francisco Castillo Jerez, Rodrigo Alejandro Cantú Hernández: Performed the experiments.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

[1] A.M. Ganiyat, The Toxicological Evaluation of Sewage Effluents and Pharmaceuticals with the Use of Zebrafish as a Model Organism. Master of Science Programme in Veterinary Medicine for International Students. Faculty of Veterinary Medicine and Animal Science, 7, Swedish University of Agri- cultural Sciences, Uppsala, Sweden, 2008, p. 1403.
[2] L. Yang, L.E. Yu, M.B. Ray, Degradation of paracetamol in aqueous solutions by TiO_2 photocatalysis, Water Res. 42 (2008) 3480.
[3] B.C. Lourençao, R.A. Medeiros, R.C.R. Filho, L.H. Mazo, O.F. Filho, Simultaneous voltammetric determinate on of paracetamol and caffeine in pharmaceutical formulations using a boron-doped diamond electrode, Talanta 78 (2009) 748.
[4] M. Solé, J.P. Shaw, P.E. Frickers, J.W. Readman, T.H. Hutchinson, Effects on feeding rate and bio- marker responses of marine mussels experimentally exposed to propranolol and acetaminophen, Anal. Bioanal. Chem. 396 (2010) 649.
[5] S. Wu, L. Zhang, J. Chen, Paracetamol in the environment and its degradation by microorganisms, Appl. Microbiol. Biotechnol. 96 (2012) 875–884.
[6] M.,Á. López Zavala, E. Espinoza Estrada, Degradation of acetaminophen and its transformation products in aqueous solutions by using an electrochemical oxidation cell with stainless steel electrodes, Water 8 (2016) 383.
[7] N. Villota, J.I. Lombraña, A. Cruz-Alcalde, M. Marcé, S. Esplugas, Kinetic study of colored species formation during paracetamol removal from water in a semicontinuous ozonation contactor, Sci. Total Environ. 649 (2019) 1434–1442.
[8] W.C. Yun, K.Y.A. Lin, W.C. Tong, Y.F. Lin, Y. Du, Enhanced degradation of paracetamol in water using sulfate radical-based advanced oxidation processes catalyzed by 3-dimensional Co_3O_4 nanoflower, Chem. Eng. J. 373 (2019) 1329–1337.
[9] A. Kulo, M.Y. Peeters, K. Allegaert, A. Smits, J. de Hoon, R. Verbesselt, L. Lewi, M. van de Velde, C.A.J. Knibbe, Pharmacokinetics of paracetamol and its metabolites in women at delivery and post-partum, Br. J. Clin. Pharmacol. 75 (3) (2012) 850–860.
[10] M. Bedner, W.A. MacCrehan, Transformation of acetaminophen by chlorination produces the toxicants 1,4-Benzoquinone and N-acetyl-p-benzoquinone imine, Environ. Sci. Technol. 40 (2006) 516–522.
[11] E. Moctezuma, E. Leyva, C.A. Aguilar, R.A. Luna, C. Montalvo, Photocatalytic degradation of paracetamol: intermediates and total reaction mechanism, J. Hazard Mater. 243 (2012) 130–138.
[12] C. Postigo, S.D. Richardson, Transformation of pharmaceuticals during oxidation/disinfection processes in drinking water treatment, J. Hazard Mater. 279 (2014) 461–475.
[13] J.G. Bessems, N.P. Vermeulen, Paracetamol (acetaminophen)-induced toxicity: molecular and biochemical mechanisms, analogues and protective approaches, Crit. Rev. Toxicol. 31 (2001) 55–138.
[14] H. Jaeschke, M.L. Bajt, Intracellular signaling mechanisms of acetaminophen-induced liver cell death, Toxicol. Sci. 89 (2006) 31.
[15] A.M. Brind, Drugs that damage the liver, Medicine 35 (2007) 26.
[16] Y. Xu, Z. Yuan, B.J. Ni, Biotransformation of pharmaceuticals by ammonia oxidizing bacteria in wastewater treatment processes, Sci. Total Environ. 566 (567) (2016) 796–805.
[17] S.C. Antunes, R. Freitas, E. Figueira, F. Gonçalves, B. Nunes, Biochemical effects of acetaminophen in aquatic species: edible clams Venerupis decussata and Venerupis philippinarum, Environ. Sci. Pollut. Res. Int. 20 (2013) 6658–6666.
[18] D. Vogna, R. Marotta, A. Napolitano, M. d'Ischia, Advanced oxidation chemistry of paracetamol. UV/H2O2-induced hydroxylation/degradation pathways and n-aided inventory of nitrogenous breakdown products, J. Org. Chem. 67 (2002) 6143–6151.
[19] R. Andreozzi, V. Caprio, R. Marotta, D. Vogna, Paracetamol oxidation from aqueous solutions by means of ozonation and H_2O_2/UV system, Water Res. 37 (2003) 993–1004.
[20] E. Brillas, I. Sirés, C. Arias, P.L. Cabot, F. Centellas, R.M. Rodríguez, J.A. Garrido, Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode, Chemosphere 58 (2005) 399–406.
[21] P. Westerhoff, Y. Yoon, S. Snyder, E. Wert, Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment, Environ. Sci. Technol. 39 (2005) 66649.
[22] D.C. Hiremath, C.V. Hiremath, S.T. Nandibewoor, Oxidation of paracetamol drug by a new oxidant diperiodatoargentate (III) in aqueous alkaline medium, E. J. Chem. 3 (2006) 13.

[23] I. Sirés, J.A. Garrido, R.M. Rodríguez, P.L. Cabot, F. Centellas, C. Arias, E. Brillas, Electrochemical degradation of paracetamol from water by catalytic action of Fe^{2+}, Cu^{2+}, and UVA light on electrogenerated hydrogen peroxide, J. Electrochem. Soc. 153 (2006) 1–9.

[24] M. Skoumal, P.L. Cabot, F. Centellas, C. Arias, R.M. Rodríguez, J.A. Garrido, E. Brillas, Mineralization of paracetamol by ozonation catalyzed with Fe^{2+}, Cu^{2+} and UVA light, Appl. Catal. B Environ. 66 (2006) 228–240.

[25] K. Waterston, J.W. Wang, D. Bejan, N.J. Bunce, Electrochemical wastewater treatment: electro-oxidation of acetaminophen, J. Appl. Electrochem. 36 (2006) 227–232.

[26] J.H. Al-Rifai, C.L. Gabelish, A.I. Schäfer, Occurrence of pharmaceutically active and nonsteroidal estrogenic compounds in three different wastewater recycling schemes in Australia, Chemosphere 69 (2007) 803.

[27] I. Dalmázio, T.M.A. Alves, R. Augusti, An appraisal on the degradation of paracetamol by TiO_2/UV system in aqueous medium. Product identification by gas chromatography-mass spectrometry (GC-MS), J. Braz. Chem. Soc. 19 (2008) 81–88.

[28] A.G. Trovó, S.A.S. Melo, R.F.P. Nogueira, Photodegradation of the pharmaceuticals amoxicillin, bezafibrate and paracetamol by the photo-Fenton process-application to sewage treatment plant effluent, J. Photochem. Photobiol., A 198 (2008) 215–220.

[29] X. Zhang, F. Wu, X. Wu, P. Chen, N. Deng, Photodegradation of acetaminophen in TiO2 suspended solution, J. Hazard Mater. 157 (2008) 300–307.

[30] D. Nematollahi, H. Shayani-Jam, M. Alimoradi, S. Niroomand, Electrochemical oxidation of acetamino- phen in aqueous solutions: kinetic evaluation of hydrolysis, hydroxylation and dimerization processes, Electrochim. Acta 54 (2009) 7407.

[31] I. Quesada-Peñate, C. Julcour Lebigue, U.J. Jáuregui Haza, A.M. Wilhelm, H. Delmas, Sonolysis of levodopa and paracetamol in aqueous solutions, Ultrason. Sonochem. 16 (2009) 610.

[32] J. Radjenović, C. Sirtori, M. Petrović, D. Barceló, S. Malato, Solar photocatalytic degradation of persistent pharmaceuticals at pilot-scale: kinetics and characterization of major intermediate products, Appl. Catal. B Environ. 89 (2009) 255–264.

[33] A. Rossner, S.A. Snyder, D.R. Knappe, Removal of emerging contaminants of concern by alternative adsorbents, Water Res. 43 (2009) 33787.

[34] L. Yang, L.E. Yu, M.B. Ray, Photocatalytic oxidation of paracetamol: dominant reactants, intermediates, and reaction mechanisms, Environ. Sci. Technol. 43 (2009) 460–465.

[35] L.C. Almeida, S. Garcia-Segura, N. Bocchi, E. Brillas, Solar photoelectro-Fenton degradation of paracetamol using a flow plant with a Pt/air-diffusion cell coupled with a compound parabolic collector: process optimization by response surface methodology, Appl. Catal. B Environ. 103 (2011) 21–30.

[36] M. Basavaraju, S. Mahamood, H. Vittal, S. Shrihari, A novel catalytic route to degrade paracetamol by Fenton pro- cess, Int. J. Res. Chem. Environ. 1 (2011) 157.

[37] A. Durán, J.M. Monteagudo, A. Carnicer, M. Ruiz-Murillo, Photo-Fenton mineralization of synthetic municipal wastewater effluent containing acetaminophen in a pilot plant, Desalination 270 (2011) 124.

[38] M. Sánchez-Obrero, G. Mayén, J.M.R. Mellado, R. Rodríguez-Amaro, Electrocatalytic oxidation of acetaminophen on a PVC/TTF-TCNQ composite electrode modified by gold nanoparticles: application as an amperometric sensor, Int. J. Electrochem. Sci. 6 (2011) 2001.

[39] A.G. Trovó, R.F. Pupo Nogueira, A. Agüera, A.R. Fernandez-Alba, S. Malato, Paracetamol degradation inter- mediates and toxicity during photo-Fenton treatment using different iron species, Water Res. 46 (2012) 5374.

[40] P. Xiong, J. Hu, Degradation of acetaminophen by UVA/LED/TiO_2 process, Separ. Purif. Technol. 91 (2012) 89–95.

[41] D. Kanakaraju, B.D. Glass, M. Oelgemöller, Titanium dioxide photocatalysis for pharmaceutical wastewater treatment, Environ. Chem. Lett. 12 (2014) 27.

[42] Y. Baloul, O. Aubry, H. Rabat, C. Colas, B. Maunit, D. Hong, Degradation of paracetamol in aqueous solution by non-thermal plasma, in: 15th High Pressure Low Temperature Plasma Chemistry Symposium, HAKONE 15), Brno, Czech Republic, 2016.

[43] W.H.A. Edrees, Q.Y.M. Abdullah, A.G. Al-Kaf, K.M. Naji, A review on comparative study between the physicochemical and biological processes for paracetamol degradation, Uni. J. Pharm. Res. 2 (2017) 12.

[44] P. Xiong, J. Hu, Decomposition of acetaminophen (Ace) using TiO_2/UVA/LED system, Catal. Today 282 (2017) 48–56.

[45] S.A. Lozano-Morales, G. Morales, M.Á. López Zavala, A. Arce-Sarria, F. Machuca-Martínez, Photocatalytic treatment of paracetamol using TiO_2 nanotubes: effect of pH, Processes 7 (2019) 319.

[46] A. Anglada, A.M. Urtiaga, I. Ortiz, Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications, J. Chem. Technol. Biotechnol. 84 (2009) 1747.

[47] S. Garcia-Segura, J.D. Ocon, M.N. Chong, Electrochemical oxidation remediation of real wastewater effluents — a review, Process Saf. Environ. 113 (2018) 48–67.

[48] X. Zhao, Y. Hou, H. Liu, Z. Qiang, J. Qu, Electro-oxidation of diclofenac at boron doped diamond: kinetics and mechanism, Electrochim. Acta 54 (2009) 4172.

[49] M. Shestakova, M. Sillanpää, Electrode materials used for electrochemical oxidation of organic compounds in wastewater, Rev. Environ. Sci. Biotechnol. 16 (2017) 223–238.

[50] Y.A. Albrimi, A. Eddib, J. Douch, Y. Berghoute, M. Hamdani, R.M. Souto, Electrochemical behaviour of AISI 316 austenitic stainless steel in acidic media containing chloride ions, Int. J. Electrochem. Sci. 6 (2011) 4614–4627.

[51] I. Iliyasu, D.S. Yawas, S.Y. Aku, Corrosion behavior of austenitic stainless steel in sulphuric acid at various concentrations, Adv. Appl. Sci. Res. 3 (2012) 3909–3915.

[52] L. Szpyrkowicz, F. Zilio-Grandi, S.N. Kaul, S. Rigoni-Stern, Electrochemical treatment of copper cyanide wastewaters using stainless steel electrodes, Water Sci. Technol. 38 (1998) 261–268.

[53] N.S. Abuzaid, Z. Al-Hamouz, A.A. Bukhari, M.H. Essa, Electrochemical treatment of nitrite using stainless steel electrodes, Water, Air, Soil Pollut. 109 (1999) 429–442.

[54] T. Ramachandramoorthy, A. Rajendran, S. Padmavathy, B. Subramanian, Electrochemical oxidation of cinnamic acid using stainless steel electrodes, Ionics 10 (2004) 283–287.

[55] P. Cañizares, F. Martínez, M. Díaz, J. García-Gómez, M.A. Rodrigo, Electrochemical oxidation of aqueous phenol wastes using active and nonactive electrodes, J. Electrochem. Soc. 149 (2002) D118–D124.

[56] I. Sirés, E. Brillas, Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: a review, Environ. Int. 40 (2012) 212–229.

[57] I. Sirés, C. Arias, P.L. Cabot, F. Centellas, R.M. Rodríguez, J.A. Garrido, et al., Paracetamol mineralization by advanced electrochemical oxidation processes for wastewater treatment, Environ. Chem. 1 (2004) 26–28.

[58] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, twentieth ed., APHA, AWWA, WEF, 2005.

[59] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment, Electrochim. Acta 39 (1994) 1857–1862.

[60] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev. 109 (2009) 6541–6569.

[61] C. Boxall, G.H. Kelsall, Hypochlorite electrogeneration. II. Thermodynamics and kinetic model of the anode reaction layer, Inst. Chem. Eng. Symp. Ser. 127 (1992) 59–70.

[62] J. Boudreau, D. Bejan, N.J. Bunce, Competition between electrochemical advanced oxidation and electrochemical hypochlorination of acetaminophen at boron-doped diamond and ruthenium dioxide-based anodes, Can. J. Chem. 88 (2010) 418–425.