Journal of Environmental Chemical Engineering 13 (2025) 118295

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Contrasting sonochemical with electrochemical and catalytic processes for degrading representative pharmaceuticals in synthetic urine – Treatment of binary mixtures, theoretical calculations, and life cycle assessment

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ARTICLE INFO

Keywords:
Advanced oxidation processes
Electrochemistry
Fenton reaction
Pharmaceuticals degradation
Ultrasound
Urine matrix

ABSTRACT

Active pharmaceutical ingredients (API) in urine are recognized as a primary source of environmental contamination. Thereby, the effective treatment of urine could limit the pollution by pharmaceuticals. Herein, three advanced oxidation processes (a sonochemical, a catalytic, and an electrochemical system) to deal with API in synthetic fresh urine were contrasted. Acetaminophen, losartan, and levofloxacin were considered as representative pharmaceuticals. Effects of operational parameters and the main species responsible for API removal were established. API degradation at a frequency of 582 kHz in the sonochemical process was favored, while 500 μmol L^{-1} of H_2O_2 and 90 μmol L^{-1} of Fe^{2+} were proper conditions for the catalytic process (Fenton). In turn, a low current (9 mA) and the presence of NaCl led to good degradation by the electrochemical process employing a BDD anode. Also, it was found that $HO^{\bullet}$ played the principal degrading role in the three systems. Theoretical calculations allowed for the identification of the moieties on the API susceptible to transformations by $HO^{\bullet}$. The treatments in the urine matrix showed that the sonochemical system was more selective than Fenton and electrochemical processes for degrading API. The treatment of binary mixtures of API in urine evidenced more superiority and selectivity of sonochemistry for degrading hydrophobic pharmaceuticals. The sonochemical process transformed API into simple structures having less phytotoxic effects than the parent pharmaceutical or initial by-products. Moreover, a brief life cycle analysis on sonochemical treatment revealed that the highest environmental impact is attributed to the electricity required for operating the ultrasound.

1. Introduction

Pharmaceuticals are widely used worldwide for the treatment of diseases and control of other biological processes (e.g., contraception). After being consumed, the pharmaceuticals experience the pharmacokinetic process recognized by the acronym ADME (i.e., absorption, distribution, metabolism, and excretion) [1]. Thus, a portion of the ingested pharmaceuticals are excreted from the human body mainly through urine, or a smaller percentage in feces [2,3]. In fact, urine is one of the chief media for the pharmaceuticals input to the sewage systems [4], in places where they are available; and, in places where they are not, it is directly discharged into natural water sources (rivers, lakes, or waterfalls).

Among the active pharmaceutical ingredients (APIs) frequently detected/found in municipal sewage systems are the highly consumed analgesics (e.g., acetaminophen [5]), sartan-type antihypertensives (e.g., losartan [5]), and antibiotics such as those belonging to the fluoroquinolones class (e.g., levofloxacin [6]). Those APIs are not completely eliminated by conventional methods (such as filtration, sedimentation, coagulation, and aerobic or anaerobic biological processes) in municipal wastewater treatment plants (WWTP) [5]. For instance, Botero-Coy et al. (2018) evaluated the presence of acetaminophen, losartan, some fluoroquinolones, and other pharmaceuticals in influents and effluents of wastewater treatment plants in Colombia. After conventional treatments at the WWTPs, the presence of acetaminophen changed from 39.25 μg L^{-1} to 29.66 μg L^{-1}, losartan from 2.18 μg L^{-1} to 1.97 μg L^{-1}, and in the case of fluoroquinolones, changes were reported from 2.29 μg L^{-1} to 0.81 μg L^{-1}. It can be noted that the

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https://doi.org/10.1016/j.jece.2025.118295
Received 9 May 2025; Received in revised form 14 July 2025; Accepted 24 July 2025
Available online 25 July 2025
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concentrations of pharmaceutical pollutants did not decrease completely in the treated wastewater, thus evidencing little efficiency of conventional processes [5]. Therefore, APIs enter the environment, where they can experience bioaccumulation and biomagnification through aquatic species, in addition to the induction of toxic effects for diverse environmental species [7]. In this regard, reproductive problems, cardiac abnormalities, and liver and kidney damage have been reported in fish due to analgesic medications (e.g., acetaminophen, ibuprofen, diclofenac) [8]. Regarding antihypertensives (e.g., losartan), acute and chronic damage (cardiac, liver, and metabolic) has been found, which can lead to the death of aquatic species [9]. Meanwhile, in the case of antibiotics (e.g., levofloxacin), their environmental input can contribute to the development and proliferation of antibiotic-resistant bacteria, which is a major public health problem [7]. All these problems require the search for alternative solutions to decrease the entry of pharmaceuticals into the environment. Thus, the treatment of APIs in the initial pollution sources, such as urine, could be an option.

The literature informs the application of advanced oxidation processes (AOPs, which are based on the use of degrading radicals) for removing APIs in urine. These AOPs include homogeneous or heterogeneous processes based on photochemical, catalytic, and electrochemical systems, and, to a lesser extent, other systems such as ultrasound [4,10–18]. Such works are mainly focused on the individual treatment of diverse APIs. Most of them lack aspects such as the comparison with other AOPs or the evaluation of the environmental impacts of the AOPs through life cycle assessment. Moreover, a few reports show the treatment of pharmaceutical mixtures in the urine matrix [19]. Hence, this research covers those missed aspects.

Herein, we considered three AOPs: sonochemistry, electrochemistry, and Fenton processes. Then, it should be mentioned that high-frequency ultrasound (200–1000 kHz) can be used for the generation of highly reactive species (such as $HO^{\bullet}$) from the acoustic cavitation phenomenon that cleavages water vapor molecules (Eq. 1). Also, in this AOP, in addition to the generation of $HO^{\bullet}$, the radical combination can occur, leading to the production of hydrogen peroxide (Eq. 2). So, H_2O_2 can be considered an indicator of the generation of radicals in the process. The sonogenerated $HO^{\bullet}$ can degrade organic contaminants (Eq. 3), leading to innocuous products [4,20].

$$H_2O +))) \rightarrow H^{\bullet} + HO^{\bullet} \quad (1)$$

$$2HO^{\bullet} \rightarrow H_2O_2 \quad (2)$$

$$HO^{\bullet} + \text{Contaminants} \rightarrow \text{Transformation products} \quad (3)$$

Among catalytic AOPs, we can find the Fenton process, which is based on the reaction between hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) to produce radical species such as the hydroxyl radical ($HO^{\bullet}$) (Eq. 4). Other radical species such as the hydroperoxyl radical ($HOO^{\bullet}$), can be produced in the Fenton process by the interaction of Fe^{3+} with H_2O_2 (Eq. 5) [21,22].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\bullet} + H^{+} \quad (5)$$

The hydroxyl radical can also be produced by electro-oxidation of water. Electrochemical AOPs are termed clean technologies in which green reagents, such as electrons, participate in the $HO^{\bullet}$ formation from the water molecule. However, it should be considered that the generation of $HO^{\bullet}$ radicals is dependent on the type of anode used in the process. Boron-doped diamond (BDD) anodes are typical for producing $HO^{\bullet}$ electrochemically since they have a high overpotential (1.59–2.80 V) for oxygen evolution [23,24]. BDD anodes possess the capacity to generate physisorbed radical species (Eq. 6). Additionally, if chloride anions are present in the aqueous solution, BDD has also the tendency to generate other non-radical oxidizing species such as hypochlorous acid (HClO) (Eqs. 7–8) [25], which can also act as degrading agents toward organic pollutants (Eq. 9) [25–27].

$$\text{BDD anodes} + H_2O \rightarrow \text{BDD}(HO^{\bullet})_{ads} + H^{+} + e^{-} \quad (6)$$

$$2Cl^{-} \rightarrow Cl_2 + 2e^{-} \quad (7)$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \quad (8)$$

$$Cl_2/HClO + \text{Contaminants} \rightarrow \text{Transformation by-products} \quad (9)$$

As mentioned above, this research studied the degradation of pharmaceuticals in synthetic fresh urine by three different POAs (catalytic, electrochemical, and sonochemical systems). Three different pharmaceuticals were considered: an analgesic (acetaminophen), an antihypertensive (losartan), and an antibiotic (levofloxacin); some of their physicochemical properties are shown in Table 1. Initially, the effect of parameters and degradation routes in the processes was established. Then, the degradations by the three AOPs were compared, showing ultrasound to have the highest selectivity for the degradation in urine. Thereby, this process was used to deal with the binary mixtures of the target pharmaceuticals. Besides, to better understand the action of sonogenerated $HO^{\bullet}$ on the target APIs, theoretical calculations about the regions susceptible to the degrading species attacks were carried out. Also, a phytotoxicity test for the urine treated by ultrasound was performed to evaluate the potential reuse for crop irrigation. Finally, the evaluation of the environmental impacts of the sonochemical system was determined through a life cycle assessment.

Values taken from the references [14,28,29].

2. Materials and methods

2.1. Reagents and samples

Acetaminophen (ACE) from Laproff (Medellín, Colombia), losartan (LOS) from La Santé S.A. (Bogotá, Colombia), and levofloxacin (LEV) from Chemo-laboratories (São Paulo, Brazil) were used. Commercial tomato seeds (*Solanum lycopersicum*) of ANASAC® (Santiago de Chile, Chile) were used for the phytotoxicity test. For the preparation of synthetic urine, substances such as urea, sodium chloride, potassium chloride, calcium chloride dihydrate, magnesium chloride hexahydrate, sodium phosphate, and D-glucose from Merck and sodium sulfate from Fisher Chemical were used. In addition, methyl orange from Merck was used. Iron sulfate heptahydrate (as the Fe (II) source for the Fenton reaction) was purchased from Sigma. The pH of distilled water (DW) and synthetic urine was adjusted to 6.5 with sodium hydroxide and sulfuric acid as needed.

For the experiments, distilled water (DW) was used in the preparation of the synthetic urine matrix according to the composition indicated in Table 2 (which was adapted from reference [10]). The concentration of all active pharmaceutical ingredients for the degradation tests corresponded to 66.2 μmol L^{-1} (amount at mg L^{-1} levels), which is a concentration that could be found in human urine typically [10,30,31].

2.2. Reaction systems

For the sonochemical process, a Meinhardt-Ultrasonics® bath apparatus was used, carrying out 200 mL of the liquid sample in a glass cylindrical reactor. The reaction temperature was controlled and

Table 1
Physicochemical properties of the target APIs.

Properties	ACETAMINOPHEN	LOSARTAN	LEVOFLOXACIN
Water solubility in the molecular form (mg mL^{-1})	14.0	< 1.0	1.44
pKa	9.46	5.5	6.25
$LogK_{o/w}$ (LogP)	0.46	4.01	−0.4

Table 2
Composition of synthetic fresh urine.

Substance	Molecular weight (g mol^{-1})	Concentration (mol L^{-1})	Log P*
Urea	60.1	0.2498	−2.59
NaCl	58.4	0.0440	−0.46
Na_2SO_4	142.0	0.0150	−0.84
KCl	74.6	0.0400	−0.46
$MgCl_2.6H_2O$	203.3	0.0040	0.61
NaH_2PO_4	119.9	0.0199	−1.0
$CaCl_2.2H_2O$	147.0	0.0040	−0.57
Glucose	180.2	0.0005	−2.6
Methyl Orange**	327.3	0.000003	2.74
pH: 6.5 ± 0.1			
Electrical conductivity: 14.1 mS cm^{-1}			

**This compound was used as a model of a nitrogen-containing organic molecule responsible for color in the synthetic urine.
* Values taken from the references [10,33–35];

maintained at 20°C utilizing a Huber Minichiller [4]. This sonochemical reactor allowed for varying the frequency and power. The actual ultrasound power was determined by the calorimetric method according to Kimura et al. [32]. In this system, the effect of frequency and power parameters on the APIs degradation was assessed initially.

In the case of the Fenton process, a volume of 50 mL of sample was placed in a beaker. The concentrations of reagents (iron and hydrogen peroxide) were varied to determine their effects on the degradation of pollutants. For the electrochemical system, an undivided electrolytic cell, with 150 mL of sample and magnetic stirring, was used. The system was composed of a boron-doped diamond anode (BBD, 1.9 cm^2) and a titanium cathode (Ti, 4.25 cm^2). In this process, the effects of the current density and supporting electrolyte type were considered.

It is relevant to mention that as the reaction systems involve different sample volumes, the comparison of the process was done in terms of a parameter that is independent of the volume of the reactor, which is the selectivity factor (ρ). This selectivity factor (ρ = %Removal in urine/% Removal in distilled water) is influenced by the intrinsic properties of the processes (e.g., their ability to produce degrading species such as radicals and the action routes involved in the pollutants degradation) [4].

2.3. Analyses

The degradation of the target APIs was followed by high-performance liquid chromatography (HPLC), using equipment with the following specifications: Thermo Scientific Dionex UltiMate 3000 HPLC with diode array detector and an Agilent 120 RP C18 column (5 μm, 4.6 ×150 mm). The mobile phases used were: formic acid buffer with acetonitrile in a ratio 85/15 for acetaminophen at a flow rate of 0.45 mL min^{-1} and a wavelength (λ) of 243 nm; the same buffer, acetonitrile and methanol (MeOH) 46/44/10 for losartan at a flow rate of 0.7 mL min^{-1} and λ of 230 nm; and, formic acid buffer with acetonitrile in a ratio 85/15 for LEV at a flow rate of 1.0 mL min^{-1} at a λ of 278 nm. A volume of 20 μL was injected. Experiments were performed at least in duplicate. A Shimadzu TOC-L Total Organic Carbon Analyzer Instrument (using the platinum combustion technique) was utilized for the mineralization analysis, following the procedure of the Standard Methods SM5310.

For the phytotoxicity test, commercial tomato (*Solanum lycopersicum*) seeds were subjected to four manual washing cycles for 15 min (the first with 2 % hydrogen peroxide solution and the other three with distilled water) to eliminate residues present on the seed surface. Then, the seeds were left to dry on a paper towel and, in different Petri dishes (60 mm diameter), 7.0 mL of the samples were added, taken at times 0T (non-treated), 1T (100 % removal of the contaminant) and 2 T (double the time T), respectively, with previous adjustment of pH to 7.0. In each petri dish with the sample, 5 seeds were added and distributed as uniformly as possible, and growth was expected for 7 days. Finally, the length of each germinated seed was measured (considering radicle and hypocotyl). Positive control samples in distilled water and a negative control with glyphosate were included. The experiments were performed in duplicate.

The life cycle analysis (LCA) was carried out using OpenLCA 2.1 software and the Ecoinvent v 3.7 database, with which the inventory was constructed. This approach was carried out considering the work of Paredes-Laverde et. al. [36]. Meanwhile, the identification of the moieties on the target APIs more susceptible to radical attacks was done through theoretical calculations of the f^0 (Fukui index) [37]. Such calculations were carried out on the Software Rowan available online. This software utilizes the xTB family of semi-empirical methods (geometry optimization: GFN2-xTB, and level of theory: GFN1-xTB) developed by Stefan Grimme and co-workers at the University of Bonn [38]. All the specific details about the calculations can be found on the Rowan *Scientific* platform at https://www.rowansci.com (accessed 2025–04–03).

3. Results and discussion

3.1. High-frequency ultrasound for degrading ACE

The effects of frequency and ultrasound power for the treatment of ACE in distilled water (DW) were initially evaluated. Two frequency levels (582 kHz and 1144 kHz) and two power levels (7.6 W and 20.1 W) were studied (Fig. 1a). The effect of the ultrasound power (keeping the frequency at 582 kHz) was tested, showing that as the actual acoustic power augmented from 7.6 W to 20.1 W, the removal of ACE increased from 13.5 % to 55.3 % in 30 min of sonication. It should be considered that the generation of cavitation events (which lead to the production of degrading species) is directly proportional to the acoustic power. So, the higher the working power, the more ACE degradation is favored [39].

When the ultrasound frequency increased from 582 to 1144 kHz (operating at 20.1 W of acoustic power (Fig. 1a)), the degradation efficiency diminished to 18 %. Such a result can be explained by considering that the predominance of the chemical effects that lead to the sonogeneration of degrading agents occurs in a frequency range between 200 and 600 kHz [39]. Some previous papers have shown that the degradation of pharmaceuticals like ACE by ultrasound is more efficient if the working frequency belongs to such a range [40,41]. Hence, based on our results, 582 kHz of frequency (at 20.1 W of actual acoustic power) was selected to perform the subsequent degradation experiments for the sonochemical system (SC).

For the determination of the sonochemical degradation route, the accumulation of H_2O_2 in the presence and absence of ACE in distilled water was compared (Fig. 1b). Also, degradation experiments with ACE were performed using methanol [39]; which is a scavenger of hydroxyl radicals ($k_{MeOH/HO\bullet}$: 9.7×10^8 L mol^{-1} s^{-1}, [42]). The comparative results of ACE degradation in the absence and presence of the scavenger are shown in Fig. 1c. It was evidenced that in the ACE presence, the hydrogen peroxide accumulation was lower than the absence (i.e., distilled water alone, Fig. 1b), this suggests the reaction of ACE with the sonogenerated hydroxyl radical. Furthermore, the degradation of the pharmaceutical was lowered by approximately 36 % by adding methanol (MeOH, Fig. 1c), thus confirming the main degrading action of the hydroxyl radical in the sonochemical process [10].

3.2. Degradation of ACE in DW by other oxidation processes

3.2.1. Catalytic process (Fenton) for degrading ACE

3.2.1.1. Parameters effects on the catalytic process. The degradation of ACE in distilled water was also tested by the catalytic process. In such a process, the effect of the concentration of the main reagents involved in the Fenton reaction was studied. From Fig. 2a, it is evident that when we

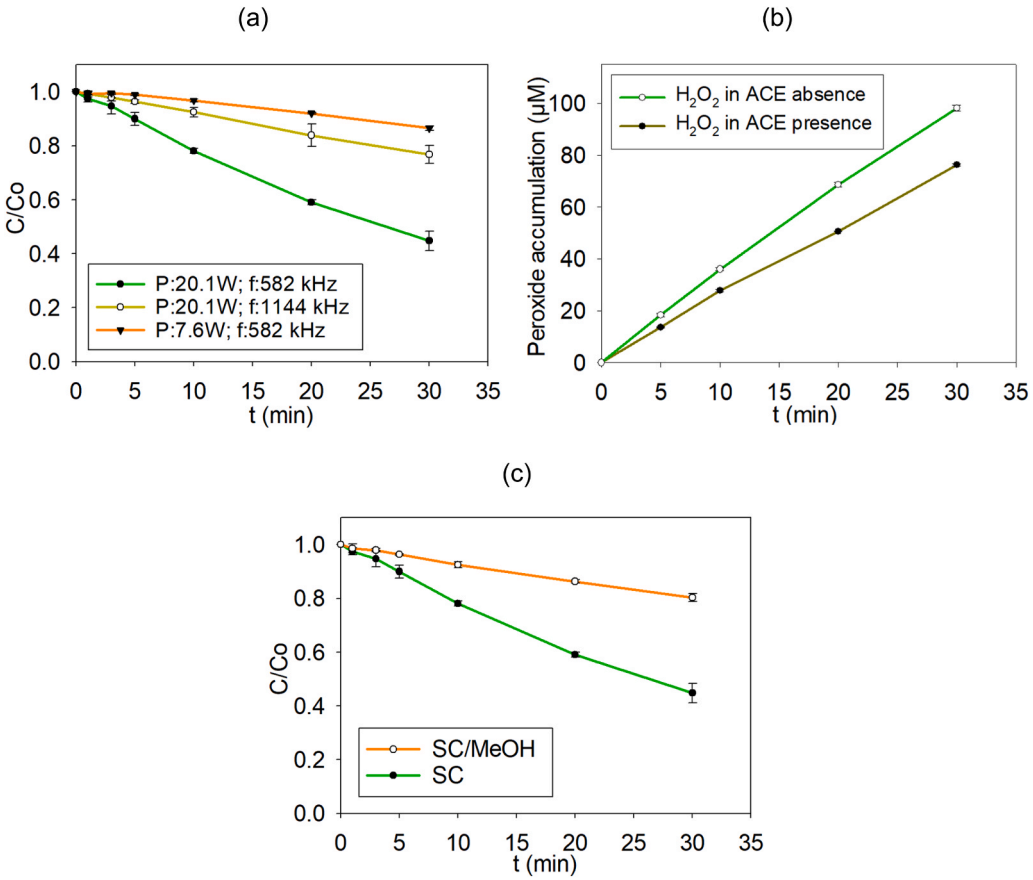


Fig. 1. Results of ACE degradation in DW by the sonochemical process (SC). **(a)** Evaluation of experimental parameters (P: acoustic power, f: frequency), **(b)** hydrogen peroxide accumulation in the absence and presence of ACE, and **(c)** treatment of ACE in the presence of the $HO^{\bullet}$ scavenger (MeOH: 6600 μmol L^{-1}). Experimental conditions: [ACE]: 66.2 μmol L^{-1}, volume: 200 mL, and initial pH: 6.5.

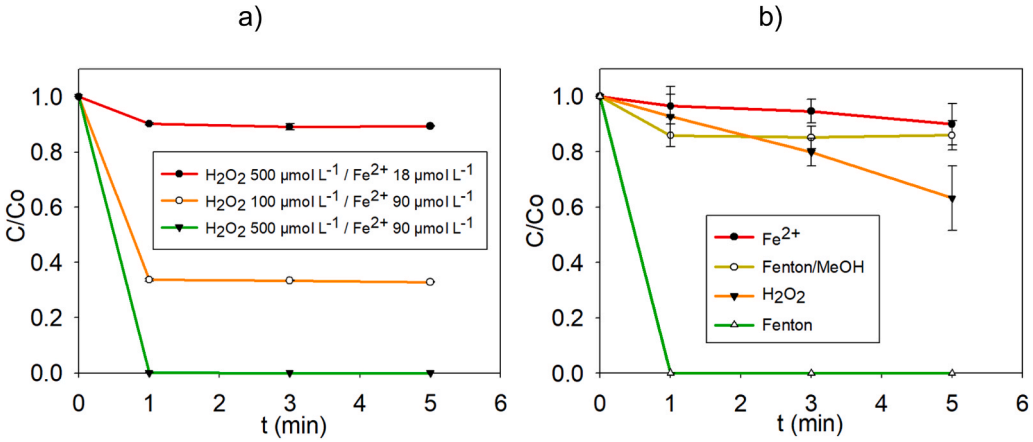


Fig. 2. ACE degradation in DW by the Fenton process. (a) Evaluation of experimental parameters and (b) degradation routes involved in the catalytic process. Experimental conditions: [ACE]: 66.2 μmol L^{-1}, volume: 50 mL, initial pH: 6.5.

used low concentrations of H_2O_2 or Fe^{2+}, less than 20 % of the pharmaceutical degradation was achieved. Nevertheless, when the reagent concentrations were increased up to 90 μmol L^{-1} Fe^{2+} and 500 μmol L^{-1} H_2O_2, in 5 min of treatment, the ACE was completely decreased. This may be associated with the fact that the concentration increase of the reagents is directly proportional to the production of species that exert degradative action on ACE [43]. Thus, based on the results in Fig. 2a, the conditions of 90 μmol L^{-1} Fe^{2+} and 500 μmol L^{-1} H_2O_2 were selected for the subsequent experiments.

3.2.1.2. Routes involved in the sonochemical process. To establish the degradation routes involved in the catalytic process, control experiments for ACE degradation, using each component of the Fenton system (i.e., H_2O_2 and Fe^{2+} acting individually), were carried out (Fig. 2b). By performing these experiments, it was observed that in 5 min of treatment, iron alone has no significant effect on degradation. Meanwhile, hydrogen peroxide only removed 36.7 % of ACE (H_2O_2 is an oxidizing agent (E°: 1.76 V [44]) capable of inducing some oxidation of organic compounds [45]).

These results for H_2O_2 and Fe^{2+} acting individually contrast with 100 % degradation achieved within 1 min of treatment when applying the Fenton system. In addition to the control experiments, the participation of the hydroxyl radicals in the Fenton process was verified by the treatment of ACE in the presence of methanol (at 6.6 mM), obtaining an evident inhibition of ACE degradation (Fig. 2b). Hence, the degradative effect in this catalytic system was associated with the main action of the generated $HO^{\bullet}$ and moderate participation of the direct oxidation by H_2O_2.

3.2.2. Electrochemical process for the ACE degradation

3.2.2.1. Parameters in the electrochemical process. The electrochemical treatment of ACE in distilled water using an electrolytic cell with a BDD anode and a titanium cathode (BDD/Ti system) was performed. The effects of the type of supporting electrolyte and current density were studied. Sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) at 0.1 mol L^{-1} were individually tested in distilled water (DW) (Fig. 3a). It was observed that the highest degradation value was found when using NaCl, obtaining a 100 % elimination in 30 min of treatment, while only 20 % of ACE degradation was observed when Na_2SO_4 was used.

In the presence of sulfate anion, the BDD anode can promote the formation of persulfate anion (which is also an oxidizing agent) [46,47]. Thus, the determination of the persulfate accumulated during the electrolysis of the sulfate anion in the absence of ACE was carried out (persulfate quantification was done following the reference [48]. It can be mentioned that the persulfates formation is more favored at high concentrations of sulfate (> 1.0 mol L^{-1}) and high current densities (e.g., 100 mA cm^{-2}) [46,47]. Under our experimental conditions, a low current density (4.7 mA cm^{-2}) and a moderate sulfate concentration (0.1 mol L^{-1}), we found that only ~ 41 μmol L^{-1} of persulfate was accumulated after 30 min of electrolysis. Thus, the contribution of electrogenerated persulfate to the ACE degradation is very low.

The results in Fig. 3a suggest that in the NaCl solution, more degrading species can be formed. Then, using NaCl as a supporting electrolyte, the role of the current density on the ACE degradation was assessed (Fig. 3a). It was noted that the increase in the current density did not improve the pharmaceutical elimination. This last result can be associated with the enhancement of side parasitic electrochemical reactions, such as oxygen evolution, which does not influence the ACE degradation (Eqs. 10–11) [49]. Also, it should be taken into account that at high current densities, the BBD anode can promote the formation of highly oxidized chlorine species (e.g., chlorate and perchlorate anions). Such highly oxidized chlorine species could act as degrading species, but they are not reactive under low temperature (~25°C) and pressure (~1 atm) conditions [31], as these were used in our work. Therefore, based on the above-mentioned aspects, the subsequent electrochemical tests were carried out at 4.7 mA cm^{-2} of current density with sodium chloride.

$$\textit{Acid solution}: 2\,H_2O \rightarrow O_2 + 4\,H^+ + 4e^- \quad (10)$$

$$\textit{Alkaline solution:}\ 4\,OH^- \rightarrow O_2 + 2\,H_2O + 4e^- \quad (11)$$

3.2.2.2. Routes in the electrochemical process. In the electrochemical process involving BDD and NaCl, three routes are plausible (*i.* attacks of hydroxyl radical from the water cleavage (Eq. 6), *ii.* direct oxidation of the pollutant on the anode surface, and *iii.* the attacks of the electrogenerated Cl_2/HClO species (Eqs. 7–8). Then, to elucidate the contribution of the hydroxyl radical to the ACE, the API treatment using methanol as an $HO^{\bullet}$ scavenger (Fig. 3b) was evaluated. It was found that the elimination of ACE in DW decreased by more than 50 % when methanol was added. This indicated the participation of radical species in the process. Additionally, the results when Na_2SO_4 was used as a supporting electrolyte indicated that the direct oxidation of ACE on the BDD surface (Eq. 12, [50]) was low (~15 %, Fig. 3a).

$$ACE + BDD_{surface} \rightarrow \text{By-products} + BDD + e^- \quad (12)$$

$$HClO + H_2O \leftrightarrows H_3O^+ + ClO^- \quad (13)$$

The ACE degradation in the scavenger presence was not completely inhibited (Fig. 3b), indicating that the electrogenerated Cl_2/HClO species also participated in the process. As mentioned above, the interaction of Cl^- with the BDD surface produces active chlorine species, such as molecular chlorine, hypochlorous acid, and hypochlorite anion (Eqs. 7–8,13) [25]. These species can also attack organic pollutants such as ACE [30]. Thereby, in the tested electrochemical system, the main degradation routes were the attacks of hydroxyl radicals and chlorine species.

3.3. Matrix effects on the degradation of ACE

3.3.1. Effect of synthetic fresh urine matrix on the degradation of ACE

The degradation of ACE by ultrasound in the urine matrix was assessed (Fig. 4a). For ACE, a 55.26 % removal was obtained in distilled water (DW), while, in the urine matrix, the removal percentage obtained was 36.40 %. Degradation of ACE decreased when changing from DW to the more complex urine matrix. The effectiveness of the sonochemical system is related to the hydrophobic character of the treated substances, and high hydrophobicity allows them to be located near the interface of the cavitation microbubbles, which favors their interaction with the $HO^{\bullet}$

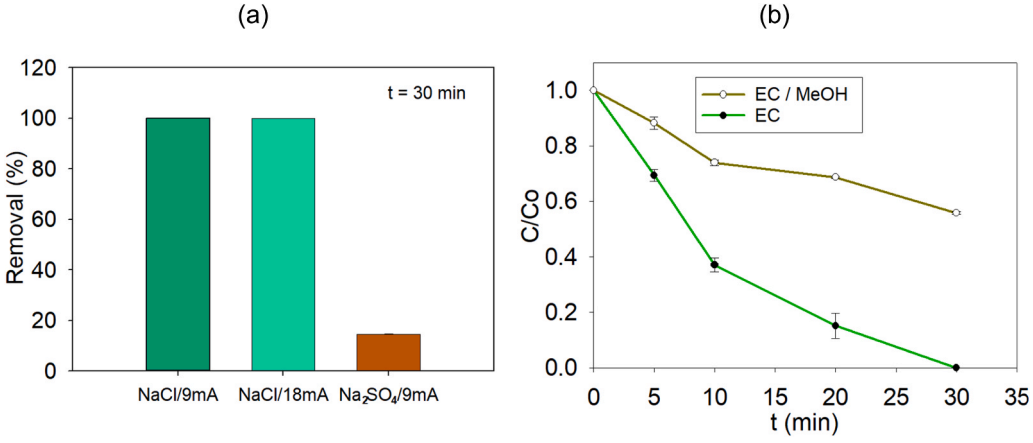


Fig. 3. ACE treatment in DW by the electrochemical system. **(a)** Evaluation of experimental parameters and **(b)** Determination of the degradation routes. Experimental conditions: [ACE]: 66.2 μmol L^{-1}, volume: 150 mL, and initial pH: 6.5.

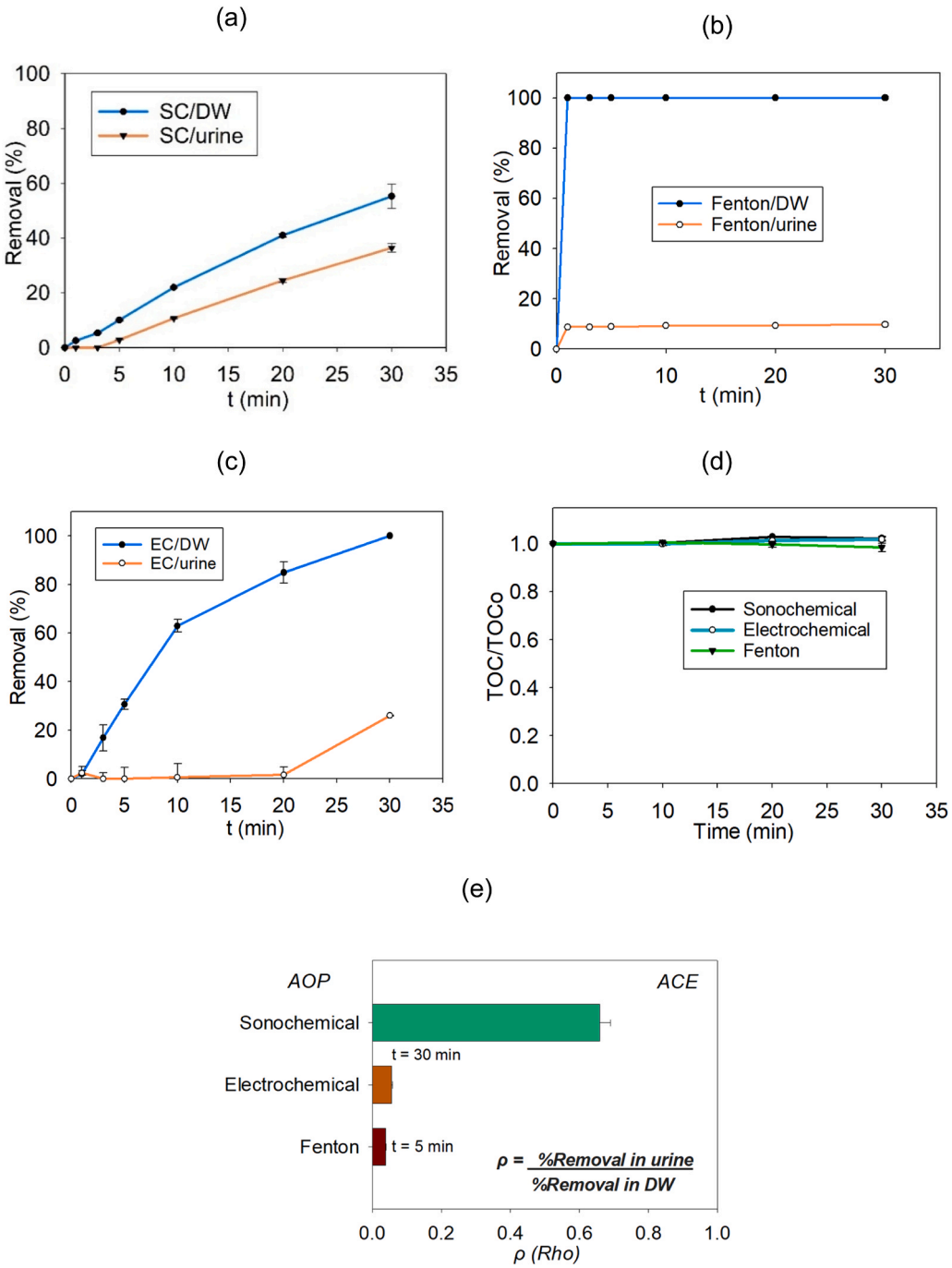


Fig. 4. Urine matrix effect on the degradation of ACE. (a) Sonodegradation (SC) of ACE in urine, (b) degradation in urine by Fenton, (c) electrochemical process (EC) with BDD anode, (d) TOC evolution under the different processes, and (e) comparison of the selectivity parameter (ρ) in the removal of ACE in urine among the studied AOPs. Experimental conditions: as described in Figs. 1–3 previously.

generated at the moment of the bubble implosion [20,51]. Thus, although the hydroxyl radical is not selective, the sonochemical process applied has a certain selectivity against hydrophobic compounds; therefore, degradation is more affected by the more hydrophilic the substance treated is. In the case of ACE, since it is moderately hydrophobic according to its Log P (0.46), it would probably not be found in the interfacial zone; thus, a partial inhibition in degradation occurs in the urine matrix [28,41].

The degradation experiments of ACE in the urine matrix were carried out, using the Fenton process, and the results are presented in Fig. 4b. It is observed that when moving treatment to a more complex matrix such as urine, the degradation of the pharmaceutical is significantly inhibited, obtaining removal percentages lower than 10 %. This could be explained because the hydroxyl radical, a species that acts in the Fenton process, is not selective, so when changing to a complex sample such as urine, competition for the radicals between the urine components and the pharmaceuticals occurs. The non-selective hydroxyl radical generated from the Fenton reaction can attack components of synthetic urine, such as urea, glucose, methyl orange, and even inorganic ions (e.g., Cl^-). Therefore, competition among the target pharmaceutical and the substances that constitute the study matrix occurs, which can be related to the kinetic constants and concentration factors shown in Table 3 [4].

ACE degradation experiments in urine by the electrochemical

Table 3
Rate constants between HO• and the components of urine and concentration factors.

Substance	M (mol L^{-1})	Concentration factor (substance/ACE)	$k^{2nd}_{HO\bullet\ -\ substance}$*
ACE	66.2×10^{-6}	1	$\sim 1.78 \times 10^{9}$ $L\ mol^{-1}\ s^{-1}$
Urea	0.2498	3776.3	7.9×10^{5} $L\ mol^{-1}\ s^{-1}$
Cl^-	0.1000	1510.6	4.3×10^{9} $L\ mol^{-1}\ s^{-1}$
SO_4^{2-}	0.0150	226.8	6.5×10^{2} $L\ mol^{-1}\ s^{-1}$
$H_2PO_4^-$	0.0199	300.8	$\sim 2.0 \times 10^{4}$ $L\ mol^{-1}\ s^{-1}$
Glucose	0.0005	7.6	$\sim 2.0 \times 10^{9}$ $L\ mol^{-1}\ s^{-1}$
Methyl Orange**	3.0×10^{-6}	0.05	$\sim 2.0 \times 10^{10}$ $L\ mol^{-1}\ s^{-1}$

* Rate constants were taken from the references [11,53–55]; **model compound as a source of nitrogen and color for the urine matrix.

process were carried out. At 30 min of treatment, less than 30 % of degradation was obtained (Fig. 4c). This contrasts with the treatment in DW, which had a contaminant elimination higher than 90 %. This is due to the urine components competing with the contaminant in the interaction with HO• and chlorine species [4,39]. For instance, urea degradation can occur through the reaction with HO•, since this interaction has a high kinetic constant (kHO•-urea= 7.9×10^5 L mol^{-1} s^{-1}) [10]. Moreover, the mediated route can also be affected by the urea presence, since it has high reactivity with chlorine species such as HClO (Eq. 8), which predominates at the working pH [52].

$$(NH_2)_2CO + 3HClO \rightarrow CO_2 + N_2 + 3Cl^- + 2H_2O + 3H^+ \quad (14)$$

On the other hand, to evaluate the mineralization, the total organic carbon (TOC) was analyzed for ACE in the urine samples treated by the three processes (Fig. 4d). It can be noted that none processes induced mineralization. This can be explained considering that the short treatment time (i.e., 30 min, which is the focus of our work), there is not enough time to promote the mineralization of the pharmaceutical or other urine matrix components. Then, to better compare the three AOPs at short treatment time, the selectivity index (ρ, Removal in urine/removal in DW (%)) was used.

The results for the selectivity index for the three processes are shown in Fig. 4e. It was observed that the sonochemical (SC) process shows lower matrix interference thanks to urine components being so hydrophilic ([10], Table 2). Thus, matrix components are less likely to react with the HO• generated, compared to the organic pharmaceutical under study. The Fenton (F) and electrochemical (EC) processes showed the lowest selectivity. This evidenced the great potential of the sonochemical AOP for ACE degradation in urine. Therefore, the subsequent experiments were focused on this last AOP.

The present study focused on the approach to the initial stage of removal of APIs by the three processes (sonochemical, electrochemical and Fenton), so the comparison between them was based on the capacity of the reactors in terms of selectivity, rather than on kinetic aspects; for this reason, the difference between the volumes used in the different systems does not interfere in the approach given to the results.

3.3.2. Comparison of the sonochemical degradation of ACE with other relevant pharmaceuticals

To determine the role of the pharmaceutical nature on the sonodegradation process, two other pharmaceuticals were considered; i.e., losartan (LOS) and levofloxacin (LEV). These compounds were selected considering that they belong to three relevant pharmaceutical classes and have diverse functional groups. The sonodegradation of the three active pharmaceutical ingredients (i.e., ACE, LOS, and LEV) in distilled water is compared in Fig. 5a. From this figure was noted that after 30 min of treatment, the degradation of the target APIs followed the order: LOS > ACE > LEV.

The observed order for the sonodegradation can be linked to the hydrophobicity of pharmaceuticals, which is directly linked to the octanol/water partition coefficient (Log P) [10]. For LOS, ACE, and LEV, the Log P values are 4.01, 0.46, and −0.4, respectively [10,28,29]. Hence, the antihypertensive is the most hydrophobic, while the antibiotic is the most hydrophilic compound. Considering this, the results in Fig. 5a make sense, since the most hydrophobic API (i.e., LOS) has more possibilities of being degraded by the sonochemical process (followed by ACE) because it is closer to the bubble interface, and consequently closer to the sonogenerated radicals [10].

On the other hand, as shown in Section 3.1 above, the main degrading species involved in the sonochemical process is the hydroxyl radical. Hence, to better understand the action of such a species on the target APIs, theoretical calculations about the regions susceptible to HO• attacks were carried out. Herein, the Fukui function for radical interactions (f^0) for ACE, LOS, and LEV was calculated [38]. The f^0 index brings information about the moieties of the organic compounds more reactive to radical species [37]. Table 4 presents the f^0 index values for the three target APIs.

The results for ACE in Table 4 show that the central amide (f^0: 0.058) and the ortho-positions (f^0: 0.062) to the hydroxyl moiety on the benzene ring of ACE had high f^0 index values (i.e., these are the electron-rich

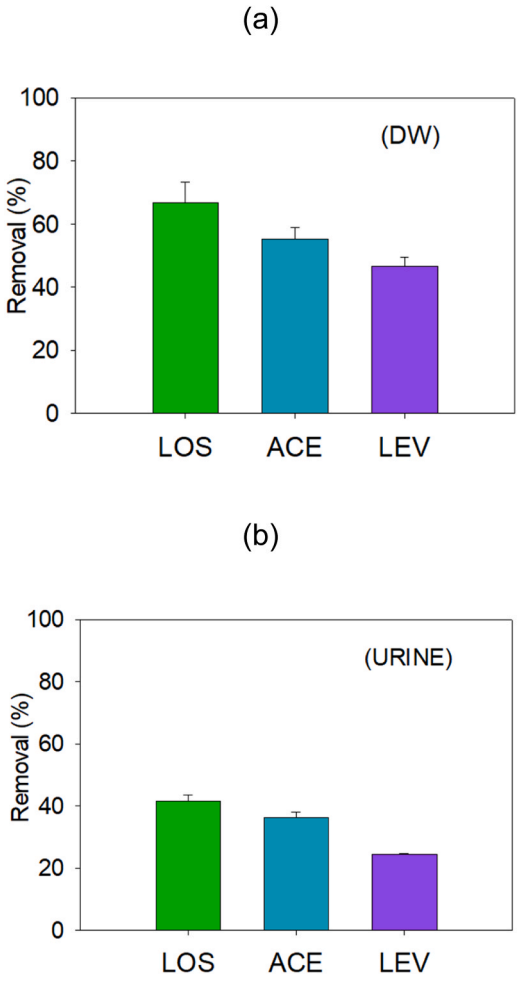
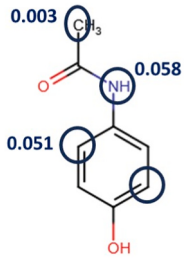
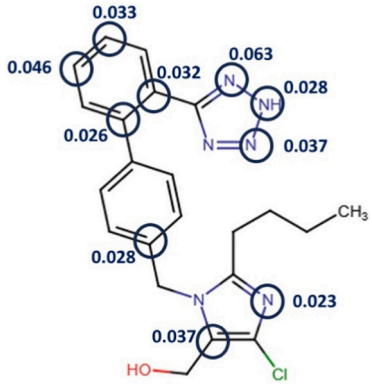
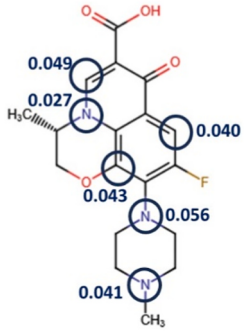


Fig. 5. Treatment of the three APIs by the sonochemical process. (a) APIs degradation by sonochemical AOP in DW at 30 min of treatment, and (b) APIs degradation by sonochemical AOP in urine at 30 min of treatment. Experimental conditions: as described in Fig. 1.

Table 4
Fukui index (f^0) values for the three target APIs and their possible transformations by the HO• attacks.

API	f^{0*}	Possible transformations
ACE		Cleavage of the central amide and hydroxylation of the aromatic ring at the ortho position to the initial OH [56–58].
LOS		Imidazole ring cleavage and hydroxylations of the biphenyl moiety [10,59].
LEV		Demethylation and opening of the piperazyl ring, in addition to hydroxylation and/or oxidation of the C=C bond close to the carboxylic acid [60–62].

* Higher f^0 values on the API denote more reactive moieties toward HO•.

regions). Thus, such moieties can be more easily transformed by the action of the sonogenerated hydroxyl radical. Indeed, the literature reports that acetaminophen can undergo the cleavage of the central amide and hydroxylation of the aromatic ring at the ortho position to the initial OH by the initial HO• action in distilled water [56–58].

In the case of LOS, the theoretical analyses revealed that atoms in the imidazole group, aromatic rings, and tetrazole moiety have the highest values for the f^0 index. Thereby, such structures on LOS are very susceptible to the attacks of HO•. Thereby, the sonochemical treatment of LOS in distilled water can generate stable transformation products coming from imidazole ring cleavage and hydroxylations of the biphenyl moiety [10,59]. Meanwhile, high f^0 values for LEV are placed on the nitrogen atoms (0.041–0.056) of the piperazyl ring and other atoms on the morpholine moiety (0.027–0.043), in addition to the double bonds (0.040–0.049) on the quinolone core; thus, suggesting the involvement of such atoms in the primary transformations of LEV in distilled water. The literature has informed that the piperazyl moiety of the fluoroquinolone antibiotics is very reactive toward HO•, which produces demethylation and intermediates of opened rings [60–62]. Also, the C=C bond close to the carboxylic acid can experience modifications by the HO• attacks [61].

Regarding the treatment of the three pharmaceuticals in the urine matrix (Fig. 5b), we should mention that the sonochemical process led to degradations between 24.3 % and 41.5 % at 30 min of treatment. As mentioned above (Table 1 and Table 2), the target pollutants are more hydrophobic than the matrix components; thus, the sonochemical system was able to achieve high degradation percentages. Also, it is important to highlight that our results agree with those found by Guateque-Londoño et al. (2020), who also evaluated the degradation of LOS, evidencing a favorable sonochemical elimination of this pharmaceutical thanks to its high hydrophobicity [10]. These results confirm the relevance of hydrophobicity on the sonochemical treatment of pharmaceuticals and compounds, such as ACE, which exhibit a medium hydrophobic character, and have the chance to be degraded.

3.3.3. Sonochemical degradation of binary pharmaceutical mixtures

As the main focus of this research was on the selectivity at the primary stages of the processes (more than only the degradation percentage), and the sonochemical process showed a higher/good performance in term of the selectivity at short treatment times for the target pharmaceuticals individually (see previous section), the degradation experiments for rational binary mixtures among ACE, LOS, and LEV, in the urine matrix, were performed using this process.

The results for the treatment of binary mixtures by ultrasound are shown in Fig. 6, where it is observed that the removal of LOS was still higher compared to ACE or LEV, respectively (Figs. 6a-6b). Additionally, it was observed that ACE and LEV removals were lower when found mixture compared to their individual treatment; whereas, LOS is favored when found in mixtures, as its removal was accelerated. Furthermore, the selectivity factor for the APIs degradation in the mixtures was evaluated (it was defined as β the ratio between the percentage removal of API in binary mixtures and the removal alone in solution, Fig. 6d). This shows that the applied sonochemical system also presents greater selectivity for LOS degradation in the binary mixtures in urine (Fig. 6d).

The explanations of results in Fig. 6 are also based on the diverse hydrophobic/hydrophilic nature of the target pharmaceuticals. As LOS is more hydrophobic than ACE and LEV, in the mixture, the former is closer to the cavitation bubble interface, having a higher probability to interact with the sonogenerated HO•, thus affecting the ACE or LEV degradation. Furthermore, as ACE and LEV have more affinity for water than LOS, in the treatment of the binary mixtures, salting-out effects toward the antihypertensive are plausible. I.e., in the binary mixtures with LOS, the water molecules can surround ACE or LEV molecules more effectively, thus pushing LOS closer to the cavitation bubbles interface [10,39]. Otherwise, when ACE and LEV are in the mixture (Fig. 6c), both are placed far away from the interfacial zone of the cavitation bubble because of their less hydrophobic nature. Consequently, they compete for the hydroxyl radical and decrease the degradation in the individual case.

3.4. Treatment extent

3.4.1. Phytotoxicity

Considering the results in Section 3.3, where LOS presented the highest removals by the sonochemical process, the subsequent tests were done with this pollutant. To go beyond the degradation (i.e., treatment extent), the assessment of the possibility of using the treated urine for crop irrigation was carried out by measuring phytotoxicity toward tomato seeds. For this purpose, the degradation of LOS was evaluated up to 100 % removal (this occurred after 180 min of treatment, which was termed T). Also, the non-treated solution (0 T) and that generated at 360 min of treatment (named 2 T) were considered. The results are shown in Fig. 7. We should mention that the urine matrix itself has some phytotoxicity due to its highly saline nature when compared with distilled water (DW) (Fig. 7a) [63]. Then, the test was performed with samples diluted at a 1/10 ratio.

From Fig. 7b, it can be noted that at 1 T (180 min), the growth of the

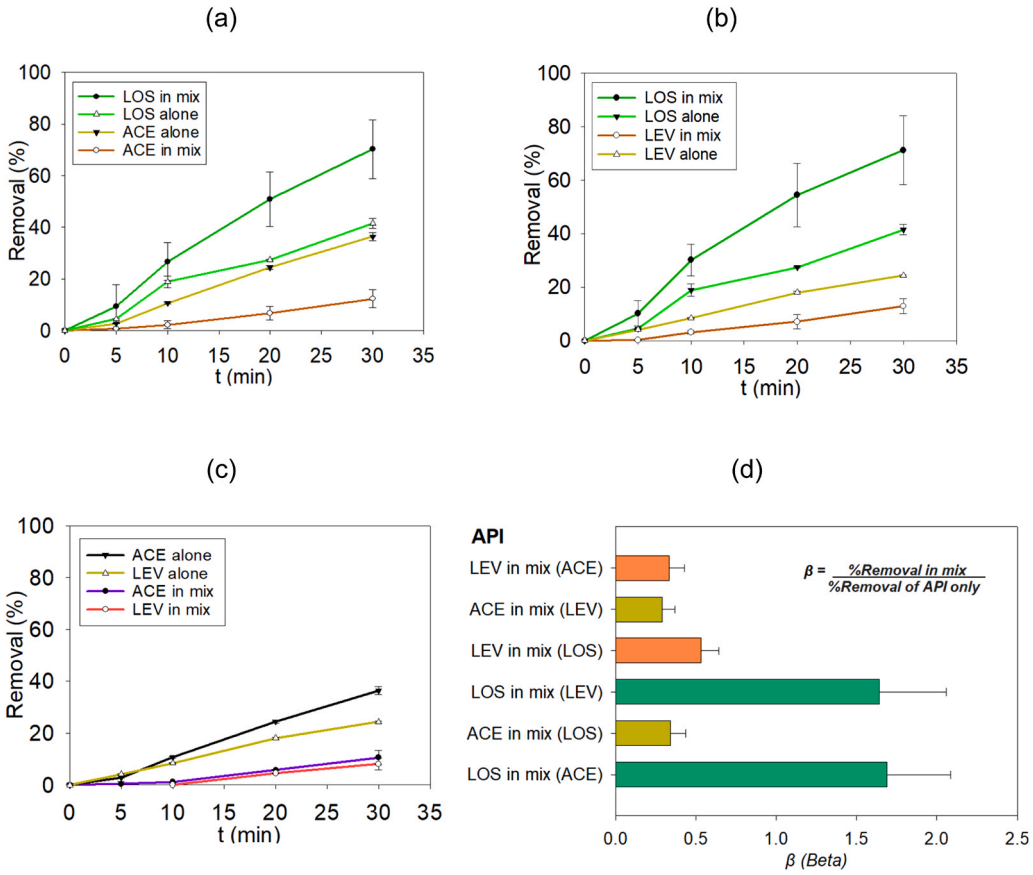


Fig. 6. Removal of APIs in binary mixtures by sonochemical AOP: **(a)** LOS in mixture with ACE, **(b)** LOS in mixture with LEV, **(c)** ACE in mixture with LEV, and. **(d)** Selectivity to the API degradation in the binary mixtures. Experimental conditions: Concentration of LOS, ACE, LEV: 66.2 μmol L^{-1}; frequency: 582 kHz; Power: 20.1 W; volume: 200 mL.

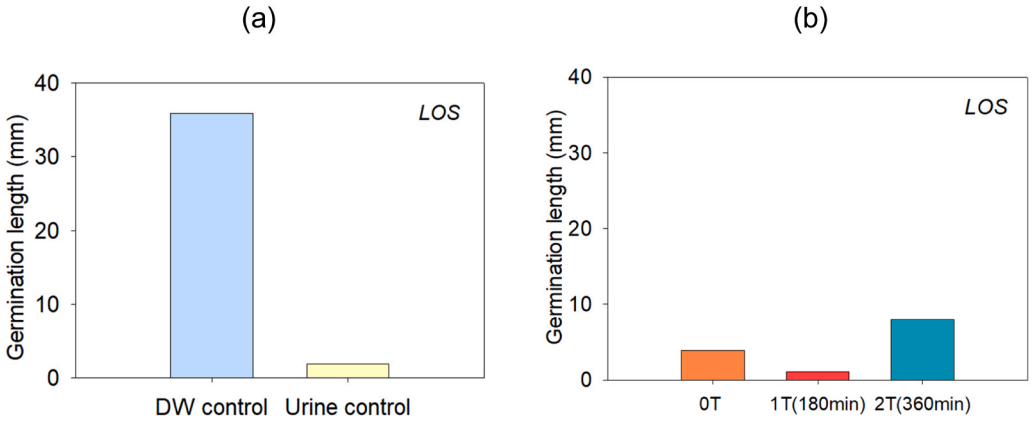


Fig. 7. Phytotoxicity test associated with LOS treatment by the sonochemical process. **(a)** Control experiments in the phytotoxicity test and **(b)** phytotoxicity results for LOS treated at times 0 T, 1 T, and 2 T. Experimental conditions: LOS: 66.2 μmol L^{-1}; urine samples diluted 1/10; tomato seeds; 7 days of germination.

germinate length was lower than the non-treated sample (0 T); i.e., when 100 % of LOS was degraded, an increase in phytotoxicity was evidenced. This indicates that primary degradation by-products have a higher phytotoxicity than the parent pharmaceutical, so it is very important to be concerned about the transformation products generated in the process. Interestingly, when the treatment was 2 T (360 min), the resultant solution had a lower phytotoxicity than both the samples at 0 T and 1 T. Such results suggest that the primary by-products are transformed by the sonochemical process into simple structures that have less phytotoxic effects than the parent pharmaceutical and its initial transformation products. Guateque et al. reported similar results for the treatment of LOS in DW, finding a decrease in phytotoxicity after twice the treatment time applied for the elimination of the active pharmaceutical ingredient [10]. Therefore, our results about the phytotoxicity diminution indicate a positive effect of the sonochemical treatment of LOS in the urine matrix.

3.4.2. *Life cycle assessment*

To determine the environmental impact of the sonochemical process for degrading LOS in urine, an LCA was carried out. Regarding the effect

of this study on the environment, the system and boundaries of the process were established based on the ISO 14040 standard. Subsequently, the inputs/outputs required in the ultrasound treatment of 0.200 L of synthetic urine containing LOS were included in the inventory (see Fig. 8 and Table 5). The calculations were done using the OpenLCA 2.1 software and the Ecoinvent v 3.7 database, and the process impacts were determined for 11 environmental impact categories using the Characterization factors for life cycle impact assessment baseline approach [36,64].

The environmental impacts of the process on global warming (GWP 100a), abiotic depletion, abiotic depletion (fossil fuels), acidification, eutrophication, freshwater aquatic ecotoxicity, human toxicity, marine aquatic ecotoxicity, ozone layer depletion (ODP), photochemical oxidation, and terrestrial ecotoxicity are reported in Table 6. The results for all evaluated categories indicated that the highest impact is almost 100 % attributed to the electricity required for the operation of the ultrasound equipment (Table 6). Consequently, these results motivate the scientific community to search for renewable energy alternatives for the green operation of ultrasound (e.g., solar light/solar panels) for the treatment of pharmaceuticals in complex matrices such as urine.

4. Conclusions

From the development of this research can be concluded that:

-The operational conditions that favored the API degradation by the sonochemical, catalytic (Fenton system), and electrochemical processes were those that increased the hydroxyl radical generation.

-From the theoretical calculations, the central amide and aromatic ring on ACE, the imidazole and byphenyl moieties on LOS, and the piperazyl ring plus the morpholine structure on LEV were recognized as the moieties more susceptible to transformations by the radical attacks due to they are the electron-rich regions on the API.

-The sonochemical system was more selective than the Fenton and electrochemical processes for degrading the target API, because the system based on ultrasound allows matrix components differentiation depending on the hydrophobic nature of the substances.

-The treatment of binary mixtures of API in the urine matrix showed the high suitability of the sonochemical process to deal with hydrophobic pharmaceuticals in complex samples.

-After a long treatment time, the sonochemical process was able to transform LOS into structures less phytotoxic than the parent pharmaceutical and its initial transformation products, thus denoting the relevance of going beyond the decrease in the simple API concentration during the process action.

-The life cycle assessment on the sonochemical treatment uncovered the highest environmental impacts of the electricity required for the operation of the ultrasound equipment, suggesting the need for searching for renewable energy alternatives for the green operation of this process to treat pharmaceuticals in complex matrices such as urine.

-Finally, it is very important to remark that this work presented an initial comparison of three advanced oxidation processes through the approach of selectivity (as a key factor at short treatment times, beyond than the reaction kinetics), thus opening the possibility for future works, where a more exhaustive evaluation of each process at long treatment times, considering degradation by-products, toxicity, and mineralization level must be performed to provide a wider comparison of the environmental relevance and safety of the three tested processes.

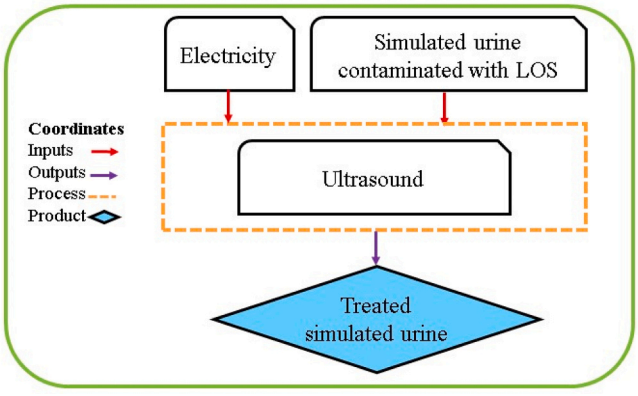


Fig. 8. Schematic representation of ultrasonic treatment for LOS degradation considered for life cycle analysis (gate to gate).

Table 5
Inventory of inflows and outflows considered in the ultrasonic treatment of 0.200 L of LOS-contaminated urine.

Flow	Unit	Sonochemical treatment
Inputs		
Electricity	M.J.	6.2
Synthetic urine (composed of inorganic salts)	L	0.2
Pharmaceutical (LOS)	kg	6.1×10^{-6}
Outputs		
Treated synthetic urine	L	0.2

Table 6
Life cycle analysis for the sonochemical process.

Impact group*	Units	Result of the impact assessment	Percentage contribution
Global warming (GWP 100a)	Kg CO_2eq	6.4	
Abiotic depletion	Kg Sb equivalent	2.5×10^{-9}	
Abiotic depletion (fossil fuels)	M.J.	77.8	
Acidification	kg SO_2 equivalent	0.03	
Eutrophication	kg PO_4 equivalent	0.002	
Aquatic ecotoxicity in freshwater	kg 1,4-DB equivalent	0.01	Electricity: 100 %
Human toxicity	kg 1,4-DB equivalent	0.6	
Marine aquatic ecotoxicity	kg 1,4-DB equivalent	833	
Ozone layer depletion (ODP)	kg CFC−11 equivalent	4.2×10^{-7}	
Photochemical oxidation	kg C_2H_4 equivalent	0.002	
Terrestrial ecotoxicity	kg 1,4-DB equivalent	0.003	

* Environmental assessment of the sonochemical treatment of LOS in synthetic urine in eleven impact categories using the reference method. Conditions: 0.200 L of synthetic urine contaminated with 6.1 mg of LOS, and 3 h of treatment.

CRediT authorship contribution statement

Efraím A. Serna-Galvis: Writing – review & editing, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization. **Ricardo A. Torres-Palma:** Writing – review & editing, Resources, Conceptualization. **Marcela Paredes-Laverde:** Visualization, Methodology, Formal analysis. **Javier Silva-Agredo:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Yudy L. Martínez-Mena:** Writing – original draft, Methodology, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

E. A. Serna-Galvis and Y. L. Martínez-Mena acknowledge the financial support to develop this research work provided by the Universidad de Antioquia UdeA, through the project CODI-UdeA 2022–53586.

Data availability

Data will be made available on request.

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