Understanding the effects of mineral water matrix on degradation of several pharmaceuticals by ultrasound: Influence of chemical structure and concentration of the pollutants

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Abstract
Degradation of seven relevant pharmaceuticals with different chemical structures and properties: acetaminophen (ACE), cloxacillin (CXL), diclofenac (DCF), naproxen (NPX), piroxicam (PXC), sulfacetamide (SAM) and cefadroxil (CDX), in distilled water and mineral water by ultrasound was studied herein. Firstly, proper conditions of frequency and acoustic power were determined based on the degradation ability of the system and the accumulation of sonogenerated hydrogen peroxide (24.4 W and 375 kHz were found as the suitable conditions for the sonochemical treatment of the pharmaceuticals). Under such conditions, the pharmaceuticals degradation order in distilled water was: PXC > DCF > NPX > CXL > ACE > SAM > CDX. In fact, the initial degradation rate showed a good correlation with the Log P parameter, most hydrophobic compounds were eliminated faster than the hydrophilic ones. Interestingly, in mineral water, the degradation of those hydrophobic compounds (i.e., ACE, SAM and CDX) was accelerated, which was attributed to the presence of bicarbonate ions. Afterwards, mineral water containing six different initial concentrations (i.e., 0.331, 0.662, 3.31, 16.55, 33.1, and 331 µM) of selected pharmaceuticals was sonicated, the lowest concentration (0.331 µM) always gave the highest degradation of the pollutants. This result highlights the great ability of the sonochemical process to treat bicarbonate-rich waters containing pollutants at trace levels, as pharmaceuticals. Finally, the addition of ferrous ions to the sonochemical system to generate a sono-Fenton process resulted in an acceleration of degradation in distilled water but not in mineral water. This was attributed to the scavenging of sonogenerated HO• by bicarbonate anion, which decreases H2O2 accumulation, thus limiting the Fenton reaction.

1. Introduction

Currently, the pharmaceuticals are considered as contaminants of emerging concern [1,2]. Many of these pharmacological-type pollutants are released through human and animal excretions to the sewage system [3–5]. As conventional municipal treatment plants are unable to efficiently eliminate the pharmaceuticals, these recalcitrant substances then enter the environment [2,4,6]. Most pharmaceuticals also persist in the aquatic environment at trace levels and they can show noxious effects against diverse life-forms [2,7–10]. Hence, the continuous exposure to these compounds induces a negative impact on the ecosystems [10].

Pharmaceuticals have been found in diverse aqueous environments such as natural mineral water (which is highly consumed around the world as bottled mineral water [11–14]. Thus, the presence of pharmaceuticals in these matrices represents a potential risk, which demands strategies to remove these pollutants from mineral water.

Advanced oxidation processes (AOPs) have proven to be efficient for degrading persistent compounds in water. Specifically, AOPs based on ultrasound have been successfully utilized for degrading pharmaceuticals in diverse aqueous matrices [12]. The processes based on ultrasound (also called sonolysis or sonochemistry) involve waves that interact with dissolved gases in the liquid medium, inducing the formation of cavitation bubbles. These bubbles grow by the diffusion of vapor or gas from the liquid until the bubbles reach a critical size, which provokes their violent implosion. The implosion generates very high temperatures and pressures (5000 K and 1000 bar) in the medium (the so-called “hot spots”), allowing the decomposition of water and oxygen molecules to produce radicals as HO• and HO2•. These species can...
oxidize/degrade the organic compounds present in the aqueous medium [10,12].

When the radicals reach the aqueous solution and do not react with organic compounds, they can combine to produce H₂O₂ [13,15,16]. Indeed, the H₂O₂ accumulated during the ultrasound process can be used as an indicator of the production of HO• [16].

In the sonochemical system, three reaction zones are recognized: a) inside the cavitation bubble, b) the bubble-solution interface, and c) the bulk of solution [17,18]. The zone where degradation occurs is strongly dependent on the pollutant nature; volatile compounds react inside the cavitation bubbles, while non-volatile hydrophobic substances mainly react at the bubble/water interface. Meanwhile, non-volatile hydrophilic pollutants react within the bulk solution [15,18–20]. Additionally, the matrix components may modify both the rate and routes of pollutants elimination by ultrasound [17,21,22].

The effect of organic and inorganic constituents of natural water on the degradation of some pharmaceuticals by ultrasound has been previously studied by Nasseri et al [17]. Also, other works have tested the treatment of pharmacological substances (e.g., dicloxacillin, fluoxetine, and acetaminophen) in mineral water by sonochemistry [16,23,24]. However, to the best of our knowledge, a systematic study on the treatment of mineral water, comparing the degradation of several pharmaceuticals and variations of the pollutants concentrations, has not been reported. Thus, the main objective of this work was to analyze the effect of chemical structure and concentration of pharmaceuticals on their sonochemical degradation in mineral water. The target pharmaceuticals were chosen because they are the most consumed pharmaceuticals worldwide; additionally, compounds such as acetaminophen [25], diclofenac [26], naproxen [27] and cloxacillin [28] have been detected in superficial, ground and even potable water bodies. Furthermore, their different chemical characteristics allow us to obtain a wide panorama of the sonochemical degradation of pharmaceuticals in mineral water.

Therefore, primary sonochemical parameters (frequency and power) were initially varied, to establish the proper conditions for degrading the pharmaceuticals. Afterward, the treatment of the pollutants in distilled water and mineral water was performed. It was determined the correlation among the initial degradation rate of the target pharmaceuticals (in both distilled and mineral water) and several physicochemical properties. An accelerating effect on the removal of hydrophilic pharmaceuticals in mineral water was found. Then, the role of each mineral water component was evaluated to determine the component responsible for the enhancing effect. Subsequently, to better understand the relationship between nature (hydrophilic/hydrophobic) and the amount of pollutant, degradation of some representative pharmaceuticals in the mineral water at different concentrations of the pollutant was tested. Finally, the effect of iron addition (at 1 and 5 mg L⁻¹) to improve the sonochemical system (generating a sono-Fenton process) was also evaluated.

2. Materials and methods

2.1. Reagents

Acetaminophen (ACE) was purchased from Bell Chem International S.A.S. Cefadroxil monohydrate (CDX) and sodium cloxacillin (CXL) were obtained from Syntofarma S.A. Naproxen (NPX) and sodium diclofenac (DCF) were provided by Laproff. Piroxicam (PXC) was purchased from TCI. Sulfacetamide (SAM) was provided by Corpaul. Tetrahydrate ammonium heptamolybdate, potassium bicarbonate, magnesium sulfate heptahydrate, sulfuric acid, sodium hydroxide and sodium nitrate were provided by Merck. Calcium chloride dihydrate, iron sulfate heptahydrate, and potassium iodide were purchased from PanReac. Acetonitrile, formic acid, methanol, sodium hydroxide, and sulfuric acid were purchased from Scharlau.

The mineral water was prepared in the laboratory (Table 1) based on the chemical composition of bottled mineral water [29], by adding the reagents to distilled water. It is important to indicate that distilled water has some ions (at very low concentrations, i.e., below mg L⁻¹ levels, [30–32] intrinsically. Therefore, the effects in the synthetic mineral water respect to the distilled water can be associated to the presence of the extra ions concentrations (at mg L⁻¹ levels) in the mineral matrix.

2.2. Reaction system

Degradation experiments were carried out in a Meinhardt multi-frequency ultrasound laboratory reactor, conditioned with a water-cooling jacket, which kept the temperature at 20 ± 2 °C through a Huber Minichiller. All experiments were performed at least in duplicate, using a working volume of 250 mL and initial pH 7.2, adjusted with H₂SO₄ (0.1 M) or NaOH (0.1 M). A treatment time of 30 min was considered and the sampling was carried out at times 0, 3, 5, 10, 15, 20, and 30 min. The real acoustic power provided by the reactor was quantified using the calorimetric method, according to reference [33].

To test the role of physical effects of ultrasound (turbulence/stirring) on pollutants, experiments in silent conditions were performed, the target pharmaceuticals were submitted to mechanical stirring at 750 rpm as described in our previous work [34].

2.3. Analyses

The degradation of pharmaceuticals was quantified using a Thermo Scientific Dionex UltiMate 3000 UHPLC instrument equipped with an Acclaim™ 120 RP C18 column (5 μm, 4.6 × 150 mm) and a diode array detector. In the mobile phase, the formic acid solution was used at 10 mM and pH 3.0. Table 2 summarizes the specific conditions for each pharmaceutical.

The accumulation of sonogenerated hydrogen peroxide in the reaction system was quantified by iodometry method. For this analysis, samples of the 600 μL experimental solution were taken, mixed in a quartz cell containing 1350 μL of potassium iodide (0.1 M) and 50 μL of

Table 1

Chemical composition of synthetic mineral water used in sonochemical experiments. Concentrations added to distilled water, including the amounts of sodium and sulfate ions provided by the pH adjustment.

| Component | Concentration (mg L⁻¹) |
|-----------|------------------------|
| Ca²⁺      | 5.7                    |
| Mg²⁺      | 2.5                    |
| Na⁺       | 2.8                    |
| K⁺        | 228                    |
| HCO₃⁻ (mg L⁻¹) | 357                  |
| SO₄²⁻ (mg L⁻¹) | 19.6              |
| Cl⁻       | 5                      |
| NO₃⁻ (mg L⁻¹) | 3.8                 |

Table 2

Specific chromatographic conditions for the pharmaceuticals.

| Pharmaceutical | Wavelengths of detection (nm) | Mobile phase | Flow in isotropic mode (mL min⁻¹) | Retention time (min) |
|----------------|------------------------------|--------------|-----------------------------------|----------------------|
| ACE            | 243                          | 85/15        | 0.45                              | 7.0                  |
| DGF            | 260                          | 30/70        | 0.5                               | 7.5                  |
| NPX            | 227                          | 65/35        | 1                                 | 5.2                  |
| PXC            | 340                          | 40/60        | 0.6                               | 7.4                  |
| CDX            | 254                          | 80/20        | 0.5                               | 4.2                  |
| SAM            | 280                          | 60/40        | 0.5                               | 4.2                  |
| CXL            | 225                          | 50/50        | 0.7                               | 6.1                  |
ammonium heptamolybdate (0.01 M), before leaving it to react for 5 min. Subsequently, the absorbance at 350 nm was measured using a Mettler Toledo UV5 spectrophotometer.

3. Results and discussion

3.1. Determination of proper operating conditions for pharmaceuticals degradation

Frequency and acoustic power are recognized as the primary operation parameters that determine the efficiency of the sonochemical system [35]. Thus, experiments to establish the suitable settings of both parameters for the degradation of pollutants were initially performed using diclofenac (DCF) as a model compound. This substance was chosen because it is a pharmaceutical frequently found in diverse waters and it has shown a good susceptibility to the sonochemical degradation according to the literature [18,36,37].

The performance of the sonochemical system was followed in terms of the pollutant removal and accumulation of hydrogen peroxide. Two experimental sets were developed by modifying a single factor at a time (frequency or power). Fig. 1 shows the DCF removal under different experimental sets were developed by modifying a single factor at a time (frequency or power). Here, the lowest pollutant removal was obtained at 40 kHz (44% at 30 min of treatment). For 1175 and 990 kHz, comparable DCF removal were obtained (84% and 88% at 30 min, respectively). The highest removal was obtained at 375 kHz of frequency, ~100% of the pharmaceutical was removed in the same treatment time.

The inset in Fig. 1 depicts the rate of H$_2$O$_2$ accumulation (Ra, in µM min$^{-1}$, see Text S1 in Supporting information) at the different frequencies in the presence of DCF-H$_2$O$_2$ accumulated is attributed to the combination of sonoenergated radicals. As seen in Fig. 1, using a frequency value of 375 kHz the greatest rate of H$_2$O$_2$ accumulation was observed. It was also found that the frequencies of 990 kHz and 1175 kHz exhibit a similar Ra. Meanwhile, at 40 kHz there was a very low peroxide accumulation rate.

Ultrasound frequency influences both cavitation collapse time and bubble size [38,39]. It is estimated that between 200 and 500 kHz occurs the greatest formation of radicals [40,41]. This explains the highest DCF degradation and Ra at 375 kHz under the tested conditions. Considering the above result, the following experiments were performed by using 375 kHz.

Fig. 2 presents the results for the DCF degradation under different levels of acoustic power (at 375 kHz). As this factor increased, the degradation of the pollutant was also augmented. Indeed, for ~1.0, 4.0, and 11.2 W of power, the removals were 1%, 32%, and 80%, respectively. The highest removal of DCF was obtained at 24.4 W (~100% of degradation was achieved after 30 min of treatment). Similarly, the Ra was the highest at 24.4. W of power (see inset in Fig. 2). Raising the ultrasonic power increases the number of cavitation bubbles and consequently, the production of HO• is augmented [42–44]. This is traduced in higher values of both removal of pollutants as DFC and sono-generation of H$_2$O$_2$. Considering that at 24.4 W of acoustic power gave the greatest production of HO• and higher degradation of the reference pollutant, this power was used for the development of the subsequent experiments.

3.2. Effect of the chemical structure of the contaminant on the sonochemical degradation in distilled and mineral water

After the determination of the proper frequency and acoustic power for the sonochemical system, seven target pharmaceuticals (substances highly consumed and commonly found in diverse water matrices, [1,43]) were individually treated in distilled water and their evolutions were compared. Fig. 3 depicts the removal curves at 30 min of
treatment. It can be observed significant differences among the pharmaceuticals. CXL, NPX, DCF, and PXC exhibited a fast degradation with respective removal of 62, 69, 69, and 83% obtained after 10 min of treatment. In contrast, CDX was the compound with the lowest removal, with percentages of 14 and 28% at 10 and 30 min, respectively. Meanwhile, SAM and ACE presented intermediate removals of 43 and 50% at 10 min and 71 and 80% at 30 min, respectively.

The chemical nature of the compounds directly influences their removal through sonochemistry [20,42]. Considering that none of the seven molecules is volatile, a pyrolysis route is not expected. On the other hand, it is well-known that during ultrasound action, physical effects (i.e., turbulence and stirring) can also take place, solutions of the target pollutants were subjected to mechanical stirring at 750 rpm during 30 min to test the contribution of such effects. The results (data not shown) indicate that, under mechanical effects, the degradation of these pollutants is negligible. This agrees with previous works dealing with the elimination of pharmaceuticals by ultrasound and mechanical stirring [45]. Consequently, under our experimental conditions, the degradation of the pharmaceuticals can be mainly associated to their reaction with the sonogenerated HO• [13].

To verify the degrading role of the hydroxyl radical, the accumulation rate of hydrogen peroxide (Ra) was measured during pharmaceuticals degradation and compared with the Ra obtained from a blank experiment (i.e., sonication of distilled water without pollutants).

Inset in Fig. 3 contains values for the Ra in absence of pollutants and in presence of two illustrative pharmaceuticals SAM (which had a medium removal) and DCF (which presented a fast removal). As observed, when pollutants were not present, the accumulation rate of H₂O₂ was higher (4.72 µmol L⁻¹ min⁻¹) than that obtained in the presence of SAM (4.22 µmol L⁻¹ min⁻¹) or DCF (3.71 µmol L⁻¹ min⁻¹). The lower accumulation of hydrogen peroxide in the presence of the pharmaceutical suggests the reaction of hydroxyl radical with these pollutants, which decreases the combination of sonogenerated HO• [46].

To understand the degradation order observed in Fig. 3, it was tested the relationship among the initial degradation rate of the pollutants (Rd, see Text S2) and the second-order rate constant of the pharmaceutical with the HO• (k_{HO•}) taken from literature [47–52]) (Fig. 4A). It can be noted that the degradation rate (Rd) does not correlate well with the k_{HO•} for the pharmaceuticals (as evidenced by a low correlation coefficient, R²: 0.11, in Fig. 4A). This means that the degradation rate (Rd) of the target molecules cannot be explained solely through the reaction with the HO•, and k_{HO•} does not determine which molecule is degraded fastest through ultrasound.

Therefore, to find a clearer explanation of the elimination order obtained in Fig. 3, it was evaluated the correlation with some properties that offer information about hydrophobicity/hydrophilicity of the

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**Fig. 4.** Relationship between the initial degradation rate (Rd, µM min⁻¹) and different physicochemical parameters of pharmaceutical. A. Reaction rate constant with HO•, B. Henry’ s Law constant, C. Topological Polar Surface Area (TPSA), D. Water solubility, and E. Octanol/water partition coefficient (Log P). Conditions: Initial pollutant concentration: 3.31 µM, initial pH: 7.2 ± 0.1, Frequency: 375 kHz, Acoustic power: 24.4 W, Temperature: 20 °C and Volume: 250 mL. Note: The values of k_{HO•}, Log (P), S_W, TPSA, k_H were taken from references [47–56].
pharmaceuticals. Such properties were: octanol/water partition coefficient (Log P), solubility in water (Sw), Henry’s Law constant (kH) and topological polar surface area (TPSA) [47–56]. The relationship between the initial degradation rate (Rd) and each one of these parameters is presented in Fig. 4B-E.

In the case of Henry’s law constant, no correlation was found with the initial degradation rates ($R^2 = 0.01$, Fig. 4B). The kH represents the fugacity, which indicates the trend of molecules to escape from aqueous media to the gas phase. Although this parameter has been useful to rationalize sono-degradation of some phenolic compounds [57], for the tested pharmaceuticals this is not the key parameter. kH was not a determining parameter since the considered pharmaceuticals are not volatile substances; therefore, they have a low capability to escape from aqueous media to the gas phase (low fugacity). Regarding the topological polar surface area (TPSA), no correlation was observed either ($R^2 = 0.04$, Fig. 4C). Despite TPSA represents the polar part of the surface of the molecule, and therefore, certain hydrophilicity of the substances [58], this parameter does not explain the behavior of the target pollutants in the sonochemical process. This because TPSA parameter denotes the relative propensity for polar interactions in biological systems or affinity of the pollutant toward the water in our case [59] more than the interaction with the interface or cavitation bubble where the degrading agents are placed mainly in the sonochemical process.

In turn, a moderate correlation ($R^2 = 0.68$) between the logarithm of water solubility (Log Sw) and Rd is observed in Fig. 4D. In this figure it can be noted two groups of compounds, in the first one are those pharmaceuticals that have low solubility and a high initial degradation rate (i.e., CXL, NPX, and PXC) and the second group is composed with greater solubility in water and medium or low Rd (i.e., CDX, SAM, ACE, and DCF). Noting that CDX has a low Rd and far from the trend line, despite being very soluble in water it degrades slowly by ultrasound. For such reason, the Log Sw parameter had a moderate correlation with Ra for the treatment of the pharmaceuticals. Solubility in water is a direct indicator of hydrophilicity, also it is recognized that high soluble substances are far from the cavitation bubbles and are slowly degraded by sonochemistry [39].

Interestingly, a high correlation ($R^2 = 0.90$) between the octanol/water partition coefficient (Log P) and the initial degradation rate (Rd) was observed (Fig. 4E). In fact, CXL, NPX, and PXC, which have a high Log P (2.48, 3.18, and 3.06, respectively) achieved a faster removal (Rd: 0.2762, 0.3089 and 0.3442 $\mu$mol L$^{-1}$ min$^{-1}$, respectively). Meanwhile, CDX, SAM, ACE and DCF, the pharmaceuticals with low Log P (i.e., −0.4, −0.96, 0.46 and 0.7, respectively) had 0.0748, 0.1386, 0.1597 and 0.2201 $\mu$mol L$^{-1}$ min$^{-1}$ values for Rd, respectively. The octanol/water partition coefficient is a physicochemical property indicative of compounds hydrophobicity [60–62]. This property is influenced by the geometric, constitutional, electronic and electrostatic characteristics of the molecules [34]. Hydrophobic pharmaceuticals are closer to the cavitation bubble, and therefore, they have a faster interaction with the sonogenerated H•. On the contrary, the hydrophilic compounds are placed away from the cavitation bubble, which limits their reaction with the sonogenerated radicals [39,60,63,64]. This explains the good correlation between Log P and Rd for the considered pharmaceuticals.

Once considered the degradation of the pollutants in distilled water, it was studied the treatment of the pharmaceuticals in mineral water (Fig. 5A). As seen, the degradations of CDX, SAM, ACE, and DCF were accelerated in the mineral water, achieving removal percentages of 23, 60, 73, and 82% at 10 min of treatment and 42, 99, 100, and 100% at 30 min, respectively. In turn, the most hydrophobic pharmaceuticals (e.g., CXL, NPX, and PXC) exhibited removal percentages very close to those obtained in the distilled water (Fig. 3), having values of 61, 68 and 81% at 10 min of treatment and 90, 96 and 100% at 30 min, respectively.

To better compare the results in mineral water and distilled water, the ratio between the initial degradation rates in mineral water and in distilled water was calculated (i.e., $R_{MW}/R_{DW}$, Fig. 5B). If such ratio is lower than one indicates that the effect of mineral water matrix is inhibitory, whereas a ratio greater than one means that the pharmaceutical degradation was favored by the matrix. When the ratio is equal to one indicates that similar pollutant degradation in the mineral water and distilled water occur. ACE, SAM, DCF, and PXC showed a ratio higher than one (Fig. 5B), thus confirming the positive effect of the mineral water matrix. On the other hand, PXC, NPX, and CXL present ratios close to one, which means that their initial degradation rates in both matrices were similar. Thus, the physicochemical properties such as Log P and Sw, in addition to the effect of the ionic constituents of the mineral water were considered to interpret these results.

In an analogous way to developed for distilled water, it was evaluated the correlation of initial degradation rate (Rd) in mineral water (Fig. 6) with the two physico-chemical properties (Log Sw and Log P, same values used for distilled water) that exhibited the best fits before. It can be noted a difference between the slopes of the Log P graphs for distilled water and mineral water (Fig. 4E and 6A). In mineral water, a more horizontal behavior of the slope is evidenced in comparison with that obtained in distilled water. This ratifies that there was an increase in the initial degradation rate of some pollutants (those with the lower degradation rate: SAM, ACE, and CDX) when it was treated in mineral water. However, unlike the observed for experiments in distilled water, in the mineral water matrix, the Log P and Log Sw parameters did not offer so good correlations with Rd ($R^2$: 0.67 and 0.32 were obtained for Log P and Log Sw, respectively). Moreover, the mineral water components may modify Log P and Log Sw of the pollutants with respect to their values in distilled water ($S_0$ could decrease and P may be increased slightly in the mineral water [65]). Consequently, the parameters which were useful in distilled water cannot be utilized to explain the order of degradation of the pharmaceuticals in the mineral water. Hence, in addition to hydrophobicity, other criteria must be considered.

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Fig. 5. Degradation of the target pollutants in mineral water. A. Pharmaceuticals evolution. B. Ratio between the initial degradation rate in mineral water and distilled water. Conditions: Initial pollutant concentration: 3.31 µM, initial pH: 7.2 ± 0.1, Frequency: 375 kHz, acoustic power: 24.4 W, Temperature: 20 °C and Volume: 250 mL.
As the mineral water is rich in ionic species (e.g., HCO$_3^-$, SO$_4^{2-}$, Cl$^-$ and NO$_3^-$), the acceleration of degradations of some pharmaceutical compounds could depend on these species. Indeed, some previous works on degradation of other organic pollutants in mineral waters have suggested a particular effect of bicarbonate/carbonate ions [16,22,64]. Then, the role of matrix components on the sono-degradation of the pharmaceuticals was studied (such topic is detailed in Section 3.3).

3.3. Understanding the role of the mineral water matrix components in pharmaceuticals degradation.

To understand the role of the constituents of mineral water on the degradation of the pharmaceuticals, individual experiments in distilled water with each ion (at the same concentration that in mineral water, Table 1) were carried out. SAM was chosen as a probe molecule for this purpose, due to its relative high acceleration by the mineral water matrix in the previous experiments (see Fig. 5B).

The SAM removal curves in the presence of the different ions are shown in Fig. 7. It can be noted that there were no significant differences in the degradation obtained in the presence of nitrate, sulfate, chloride and distilled water alone, indicating that these ions did not contribute to the degradation of SAM. Interestingly, the removal of SAM in the presence of bicarbonate was greatly accelerated in comparison to that obtained in distilled water alone (and in presence of the other ions), achieving a degradation of 97% of the pollutant at 30 min of treatment.

Indeed, the degradation evolution in the presence of only bicarbonate is very similar to the obtained in the mineral water (Fig. 7).

It is recognized that bicarbonate anion scavenges HO• (Eq. (1)), and this substance is very concentrated in the water (5300 µM), which should affect the degradation of the pharmaceutical. However, as seen in Fig. 7, this ion favored the degradation of SAM, moving from an initial degradation rate in distilled water of 0.1997 µM min$^{-1}$ to one of 0.2495 µM min$^{-1}$ in bicarbonate-containing water. Similar results were found in previous works [16,22,64], during the degradation of other organic pollutants in the presence of bicarbonate. In addition to the SAM evolution, the Ra in the presence of the anions was also established and compared with distilled water. Inset in Fig. 7 contains the ratio between the accumulation rates of H$_2$O$_2$ in water with the ions and distilled water. It was observed that for water with bicarbonate ions there was an inhibitory effect on the accumulation of H$_2$O$_2$ because that relationship is below one; while for the other ionic constituents this ratio was very close to one.

The inhibition of H$_2$O$_2$ accumulation supports that HO• is captured by the bicarbonate (Eq. (1)), decreasing the combination of radicals to form H$_2$O$_2$. The formed CO$_3^{2-}$ is an oxidizing agent. Thereby, it is proposed that the formed carbonate radical attacks to the compounds. Although the carbonate radical (E$: 1.78$ V) is less powerful than hydroxyl radical (E$: 2.8$ V), it has a lower recombination rate (1.2x10$^{7}$ M$^{-1}$ s$^{-1}$) than HO• (5.5x10$^{8}$ M$^{-1}$ s$^{-1}$) and it can easily migrate to the solution bulk [39,64,66,67] reaching hydrophilic substances as SAM, which are further away from the cavitation bubble. Consequently, this enhances the pollutant degradation respect to water without bicarbonate ions (Fig. 7). Similarly, it can be proposed that the presence of bicarbonate in mineral water (which promotes the formation of CO$_3^{2-}$) is also the responsible for the improvement in the degradation of ACE, DCF, and CDX, observed in Fig. 5B.

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\text{HCO}_3^- + \text{HO} \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad k = 8.5 \times 10^7 \text{ L mol}^{-1}\text{s}^{-1}
\]  

3.4. Effect of pharmaceutical concentration on its removal in mineral water.

To study the enhancement effect exerted by the mineral water matrix as a function of the concentration of pollutants, three representative pharmaceuticals with different behavior were chosen. These substances were SAM (which has a pronounced acceleration of degradation in mineral water), CDX (pharmaceutical with a low acceleration in mineral water), and CXL (with no acceleration in mineral water). Fig. 8 presents the ratio between the initial degradation rates in mineral water and distilled water, for diverse concentrations of the pharmaceuticals. Again, if the ratio is lower than one, the effect of the mineral water is inhibitory. Meanwhile, if the ratio is greater than one it indicates acceleration of the degradation, and a ratio equal to one means that the matrix has no net effect on the degradation.
For SAM, it was found that the lowest concentrations of the pollutant (i.e., 0.331, 0.662, and 3.31 µM) had a ratio greater than one (Fig. 8A), indicating an acceleration of degradation in the mineral water. At the concentrations of 16.55 and 33.10 µM, it is observed that the ratio is very close to one, and for the highest concentration used in the experiments (331 µM) a negative effect on the degradation by the mineral water matrix is found. As SAM has a hydrophilic nature, this pharmaceutical is far away from the cavitation bubble, and a decrease of its concentration further limits the diffusion toward the interfacial zone. This allows the majority of produced HO• to react with the bicarbonate, leading to a high participation of CO$_3^-$ as a degrading agent of SAM in the bulk of the solution (where typically arrive low amounts of HO•). On the contrary, when the concentration of SAM in the mineral water is relatively high (e.g., 331 µM) the diffusion is favored, causing that more molecules of this pharmaceutical locate closer to the cavitation bubble. Then, a competition among the constituents of the matrix and the target compound for HO• occurs, which decreases the SAM degradation as observed in Fig. 8A.

CXL shows a very small positive effect by the mineral water matrix only at the lowest concentration of CXL (0.331 µM, Fig. 8B). For the concentrations of 0.662, 3.31, 16.55, and 33.1 µM, the degradation rates in distilled water and mineral water were similar. On the contrary, at the highest concentration (331 µM) of CXL, a small inhibitory effect was observed. Unlike SAM, CXL has a hydrophobic behavior. Therefore, CXL is closer to the cavitation bubble, this allows it to react more quickly with hydroxyl radicals than the ionic constituents of mineral water (which are very hydrophilic). This justifies the non-competing effect for the concentrations of 0.662, 3.31, 16.55, and 33.1 µM, which allow the compound to be mainly placed at the interfacial reaction zone and available for the attack of sonogenerated hydroxyl radicals. However, at the lowest concentration of CXL, the result can be rationalized considering the greater dilution of the pollutant. In such condition, the pharmaceutical is far away from the cavitation bubble, so the bicarbonate radical may take an important role in the degradation as in the case of very hydrophilic pollutants. Regarding the highest concentration, it could be indicated that a competition between the CXL and the bicarbonate ions for the HO• occurs [24], leading to a ratio lower than one (Fig. 8B).

In the case of CDX (Fig. 8C), the ratios show that for almost all concentrations (0.331, 0.662, 3.31, 16.55 and 33.1 µM) there was an accelerating effect by mineral water matrix. Taking into account that CDX is a compound with a low degradation rate in ultrasound (Fig. 1), because of its high hydrophilicity this pharmaceutical would be far of the cavitation bubbles. Thus, in the mineral water, the carbonate radical improves the CDX degradation even in CDX concentrations as high as 33.1 µM. Nevertheless, for a very high concentration (331 µM), an inhibitory effect is observed, which can be attributed to the competition of CDX with the matrix components (mainly bicarbonate, the most concentrated anion in the mineral water) for HO•.

On the other hand, the value of the ratio of the initial degradation rates for the lowest concentration of CDX was higher compared with that obtained for SAM and CXL. This could be explained considering that in addition to the hydrophilic nature of CDX (Figs. 1 and 4E), this has a reactivity toward carbonate radical higher than SAM and CXL. As CDX is far from the cavitation bubble, and the generated carbonate radical migrates more easily than the hydroxyl radical to the solution, the pollutant degradation by CO$_3^-$ is favored. Moreover, carbonate radical could present a greater opportunity to oxidize CDX compared with SAM and CXL because the cephalosporin antibiotic has three moieties (phenol, amine structure close to the aromatic ring, and thioether) that activates this molecule for the attack of such radical [68]. In turn, SAM has an aniline group which can be attacked by carbonate radicals but this pharmaceutical has a carbonyl group attached to the sulfonamide structure, which may make SAM less reactive to CO$_3^-$ than CDX. Meanwhile, CXL possesses a thioether moiety that is active for the reaction with carbonate radical, and at the same time this penicillin

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**Fig. 8.** Effect of pharmaceuticals concentration on the degradation in mineral water. RdMW/RdDW: Relationship between the initial degradation rate in mineral water and in distilled water for different concentrations. A. SAM, B. CXL, and C. CDX. Conditions: initial pH: 7.2 ± 0.1, Frequency: 375 kHz, Acoustic power: 24.4 W, Temperature: 20 °C and Volume: 250 mL.
antibiotic has a chlorine atom and a carbonyl bonded to its electron-rich system (i.e., benzene ring plus isoxazole group). These two last electron withdrawing substituents could limit the CLX interaction with the carbonate radical [68]. Hence, the reactivity of CLX to CO$_3^{2-}$ is lower compared with CDX.

From the above results, it is evident that the mineral water matrix (mainly the bicarbonate anion) plays a dual role (i.e., enhancer or inhibitor of degradation) with respect to a simpler medium as distilled water. The specific role depends on two characteristics of the pollutants: the hydrophilic/hydrophobic nature, chemical structure, and concentration. At this point, it is also important to highlight that the predominance of the degradation enhancing effect by the mineral water occurs at very low concentrations (Fig. 8). This is an interesting result considering that the contaminants of emerging concern, such as pharmaceuticals, are at trace levels in aqueous media as mineral water, which indicates the high potentiality/usefulness of the sonochemical process to successfully degrade pollutants in bicarbonate-rich water.

3.5. Effect of iron addition to the sonochemical system (Sono-Fenton process) to improve the degradation of hydrophilic substances

The results in previous sections showed that the ultrasound process was more efficient for degrading hydrophobic contaminants in water. However, the removal of hydrophilic pollutants as CDX is limited even in mineral water (see Figs. 1 and 5A). A possible solution for such limitation is the combination of ultrasound with other advanced oxidation processes [66,69]. In this work, the addition of ferrous ions to the sonochemical reactor, to produce a Sono-Fenton process, was performed. This system was chosen to take advantage of the H$_2$O$_2$ accumulated in the sonochemical system.

As an illustrative case of the hydrophilic pharmaceuticals, the treatment of CDX was considered. Initially, the effect of the concentration of iron was tested. Fig. 9 compares the CDX degradation in distilled water at different additions of iron (0, 1.0, and 5.0 mg L$^{-1}$). It can be noted the presence of ferrous ions at 1 mg L$^{-1}$ leads to an increasing of in the CDX degradation. Indeed, the Rd values for sonochemistry and sono-Fenton (1 mg L$^{-1}$) were calculated as 0.0908 and 0.1975 $\mu$M min$^{-1}$, respectively. Furthermore, when a higher dose of Fe$^{2+}$ (5 mg L$^{-1}$) was considered, removal of 57% after 30 min of treatment was achieved, indicating a stronger acceleration of the pharmaceutical removal (with a Ra of 0.2774 $\mu$M min$^{-1}$).

The presence of iron in the solution, induces the formation of extra hydroxyl radicals in the bulk of the solution, through reaction with the H$_2$O$_2$ accumulated (Eq. (2), Fenton reaction), thus increasing the rate of degradation of the contaminant. The interaction between iron and hydrogen peroxide is confirmed through the measurement of the accumulation rates of H$_2$O$_2$ (Ra). Inset in Fig. 9 shows that Ra in the presence of iron (4.6 and 3.9 $\mu$M min$^{-1}$, for 1.0 and 5.0 mg L$^{-1}$, respectively) are lower than in absence (4.7 $\mu$M min$^{-1}$).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^\cdot + \text{HO}^-$$ (2)

On the other hand, when CDX in the mineral water was treated by the sono-Fenton systems, it was no observed improvement of the pollutant degradation respect to the sonochemical system alone (Fig. 10).

Due to the high concentration of the bicarbonate anion, this can scavenge the HO$^\cdot$ sonogenerated, decreasing the accumulation of H$_2$O$_2$, and then limiting the Fenton reaction (Eq. (2)). Additionally, if hydroxyl radicals are produced by the interaction of ferrous ions with some of the accumulated hydrogen peroxide from the sonolysis, the bicarbonate anion may also induce trapping of such radicals in the bulk of solution (where is mainly placed the hydrophilic pollutants as CDX). Hence, there is no improvement of CDX removal in the mineral water by the addition of ferrous ions to the sonochemical system. Here, it is important to remark that the role of carbonate radical in the sono-Fenton system is still unclear. Thus, future works should research more deeply on this topic, also detailing aspects such as the effect of different amounts of iron, diverse pH levels and initial concentrations of contaminants, and diverse kinds of pharmaceuticals.

4. Conclusions

After the study of degradation of the target pollutants by the sonochemical process, it can be concluded that:

- The degradation of the seven representative pharmaceuticals in distilled water is highly dependent on their hydrophobic nature. Indeed, the most hydrophobic pharmaceuticals showed faster removals by the process. Additionally, the initial degradation rate correlated well with the Log P property of pollutants.
- In the mineral water, degradation of the hydrophilic substances is significantly accelerated in comparison to the removal in distilled water.

Fig. 9. Removal of CDX through sono-Fenton (SF) process in distilled water. Inset: comparison of H$_2$O$_2$ accumulation rates (in $\mu$M min$^{-1}$) for individual sonolysis, sono-Fenton (Fe$^{2+} = 1.0$ mg L$^{-1}$) and sono-Fenton (Fe$^{2+} = 5.0$ mg L$^{-1}$). Conditions: initial CDX concentration: 3.31 $\mu$M, pH: 7.2 ± 0.1, frequency: 375 kHz, acoustic power: 24.4 W, temperature: 20 °C and volume: 250 mL.

Fig. 10. Degradation of CDX in mineral water by the sono-Fenton process. Conditions: Initial pharmaceutical concentration: 3.31 $\mu$M, pH: 7.2 ± 0.1, Frequency: 375 kHz, acoustic power: 24.4 W, Temperature: 20 °C and Volume: 250 mL.
• The bicarbonate anion present in the mineral water reacts with the hydroxyl radical to form the carbonate radical, which can migrate to the solution, favoring/enhancing the degradation of the molecules placed far away from the cavitation bubble.

• When the concentration of the pharmaceutical is varied, the mineral water matrix (mainly the bicarbonate anion) exhibits a dual role (i.e., enhancer or inhibitor of degradation), which depends on the hydrophilic/hydrophobic nature of the pollutant. In fact, the degradation of hydrophobic pharmaceuticals at a very low concentration is strongly accelerated, whereas the removal of hydrophobic pollutants at high concentrations is inhibited by the mineral water matrix.

• The predominance of the degradation enhancing effect by the mineral water occurs at very low concentrations, which indicates the high potentiality/usefulness of the sonochemical process to treat bicarbonate-rich waters containing the contaminants of emerging concern (as pharmaceuticals) at trace levels.

• The addition of ferrous ions to the sonochemical system (i.e., sono-Fenton process) accelerates the removal of the most hydrophilic pharmaceutical (CDX) in distilled water, thanks to extra production of hydroxyl radical by the Fenton reaction. However, such addition does not affect the removal of pollutants in mineral water, which may be associated to the scavenger effect of bicarbonate ions.

CRediT authorship contribution statement

Ana L. Camargo-Perea: Investigation, Methodology, Formal analysis, Writing - original draft. Efraín A. Serna-Galvis: Conceptualization, Formal analysis, Writing - review & editing. Judy Lee: Conceptualization, Funding acquisition, Writing - review & editing.

Ricardo A. Torres-Palma: Conceptualization, Writing - review & editing, Funding acquisition, Resources.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultrason.2021.105500.

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