Research article

Enhancement of Paracetamol Degradation by Sono-Fenton Process

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Abstract

The study of the advanced oxidation processes involving enough quantities of "in situ" free radicals formation to produce water purification, has become a research topic of special interest in the last years. The paracetamol is one of the pharmaceuticals frequently detected in wastewaters, surface waters, groundwaters, drinking water, soils and sediments. In this work, the intensification of paracetamol degradation in aqueous solution by ultrasound/H_2O_2 and ultrasound/Fenton processes was studied. The paracetamol degradation was strongly affected by the ultrasonic power and frequency, pH and the initial concentrations of Fe^{2+}/H_2O_2. The degradation of paracetamol increases with increasing ultrasonic power. The total degradation of pharmaceutical is obtained at 60 min for all studied concentrations of hydrogen peroxide and ferrum salt. The optimal conditions of sono-Fenton process guarantee a mineralization higher than 60 % are 4.7 mmol L^{-1} of Fe^{2+} and 14.4 mmol L^{-1} H_2O_2.

Keywords: Paracetamol, process intensification, ultrasound, Fenton, advanced oxidation processes

1. Introduction

Submerged contaminants have been present and handled but only have recently been discovered in different water sources due to the advances in detection methods which have made possible to measure these chemicals in very small concentrations. The arising of submerged contaminants such as pharmaceuticals, antibiotics, surfactants, pesticides, among others, generates an additional problem caused by the scarce available information about their impact in the environment or their interferences in the conventional treatment processes [1, 2]. Several researches have shown that many pharmaceuticals are not completely removed during wastewater treatment and, as a result, they are present in wastewater treatment plant effluents, rivers and lakes, and more rarely in groundwater [3, 4]. Paracetamol is one of the most frequently detected pharmaceutical products [5, 6] and its transformation into toxic compounds during chlorination in wastewater treatment plants is well described by Bedner and Maccrehan [7]. Considering the potential impacts of pharmaceutical products, it is highly important to remove them from wastewater before discharge. In this scenario, alternative treatment technologies and the de-

velopment of economical methods should be considered. In recent years, the development and application of Advanced Oxidation Processes (AOPs) for the treatment of pharmaceutical contaminants in water becomes in a subject of considerable interest [4, 8]. Among AOPs, the ultrasound has increased its potential use in water, wastewater and sewage sludge treatment, because it can be used either to enhance the local mixing process or to induce chemical effects, i.e. chemical or sonochemical reactions. The sonochemical oxidation of pollutants in aqueous phase generally occurs as the result of imploding cavitation bubbles which involves several reaction pathways such as pyrolysis inside the bubble and hydroxyl radical-mediated reactions at the bubble–liquid interface and/or in the liquid bulk [9-11].

Several previous publications have been devoted to the study of paracetamol degradation in water using different AOPs like ultrasound, UV radiation, gamma radiation, electrochemistry, pulsed corona discharge and their combination with catalysts and chemical oxydants as ozone, hydrogen peroxide and Fenton reactive [12-27].

Quesada *et al.* [15] evaluated the influence of several parameters of the ultrasound process on the degradation of paracetamol. The sonochemical degradation followed a pseudo-first-order reaction kinetics due to great excess of water. Complete removal of pharmaceutical was achieved in some cases but some dissolved organic carbon remains in solution showing that long lived intermediates were recalcitrant to ultrasound irradiation. Pollutant conversion and Chemical Organic Demand (COD) removal were found to decrease with increasing the initial solute concentration and decreasing power. The best results were obtained at 574 kHz frequency. Investigations using 1-butanol as radical scavenger and H_2O_2 as promoter revealed that pollutants degradation proceeds principally through radical reactions.

On the other hand, single-walled carbon nanotube-catalyzed ultrasonic degradation of acetaminophen was carried out in water by Im *et al.* [22]. In the absence of single-walled carbon nanotubes, maximum degradation of paracetamol occurred at a high frequency (1000 kHz) and under acidic conditions (pH equal to 3) and at different solution temperatures (25°C at 28 kHz and 35°C at 1000 kHz) during ultrasonic reactions. Rapid degradation of pharmaceutical takes place within 10 min at 28 kHz and 1000 kHz at a single-walled carbon nanotube concentration of 45 mg L^{-1} under ultrasound radiation. Degradation was associated with the dispersion of single-walled carbon nanotubes, small particles acted as nuclei during ultrasonic reactions, enhancing the H_2O_2 production yield. Additionally, the degradation of paracetamol at 580 kHz in the presence of biochar and powdered activated carbon was investigated [23]. Biochar was more efficient than powdered activated carbon under ultrasonic irradiation for treating paracetamol, degrading the drug mainly via a combination of adsorption onto the absorbents and reaction with hydroxyl radicals with absorbent particles providing nucleation sites.

Jagannathan *et al.* [17] studied the degradation of paracetamol by sonolysis, photocatalysis and sonophotocatalysis in the presence of homogeneous (Fe^{3+}) and heterogeneous (TiO_2) photocatalysts using 213 kHz ultrasound. The degradation rates obtained for sonolysis, photocatalysis and sonophotocatalysis using TiO_2 (1 g L^{-1}) were about 8.3, 30.2 and 40.2 x 10^{-7} M min^{-1}, respectively. In the case of reactions involving Fe^{3+}, the degradation rates obtained were 26.1, 18.6 and 46.7 x 10^{-7} M min^{-1} for sonolysis, photocatalysis and sonophotocatalysis, respectively. The above results indicate that the combination of sonolysis with photocatalysis (TiO_2 or Fe^{3+}) results in an additive effect from combining the two processes. There was no synergistic effect in total organic carbon removal in sonophotocatalysis with TiO_2, whereas the mineralization process was synergistic when sonophotolysis was carried out in the presence of Fe^{3+}.

Recently, Villaroel *et al.* [27] studied the effect of ultrasonic power, initial paracetamol concentration, pH and water matrix at 600 kHz on paracetamol degradation. High ultrasonic powers (around 60 W) and, low and natural acidic pH values favored the efficiency of the treatment. Effect of initial substrate concentration showed that the Langmuir-type kinetic model fit well the paracetamol sonochemical degradation. Only organic compounds having a higher value of the Henry's law constant than the substrate decrease the efficiency of the treatment. A positive matrix effect was observed at low paracetamol concentrations (1.65 µmol L^{-1}), which was attributed to the presence of bicarbonate ion in solution. However, at relative high paracetamol concentrations a detrimental effect of matrix components was noticed.

To the best of authors' knowledge, there is no previous work where paracetamol degradation from aqueous solutions by ultrasound/Fenton process has been studied. In this work, the effect of several operating conditions - the ultrasonic power and frequency, pH and initial concentrations of Fe^{2+}/H_2O_2, on paracetamol removal efficiency was studied.

2. Materials and Methods

2.1. Materials

The solutions were prepared by dissolving paracetamol 99% (Sigma-Aldrich) in distilled water. The pH adjustment was carried out with 1 mol L^{-1} solutions of H_2SO_4 or NaOH prepared from concentrated sulfuric acid (95-97% purity) and sodium hydroxide (99% purity) from Sigma-Aldrich. For HPLC analysis, acetonitrile (HPLC quality) and orthophosphoric acid 85% were taken from Merck. The other chemicals used were $Fe_2SO_4 \cdot 7H_2O$ (99.5%) and hydrogen peroxide (30%), obtained from Sigma-Aldrich and Fluka, respectively. Potassium iodide (99.5%) and sodium sulfite (98%) were also taken

from Sigma-Aldrich.

2.2. Methods

Sonochemical reactions were carried out in a 0.5 L cylindrical glass reactor with the transducer placed directly inside solution. An ultrasound multi frequency generator (Meinhardt Ultraschalltechnik) operating in continuous mode at frequencies of 580, 862 and 1142 kHz, at variable electric power output was connected to a stainless steel transducer (E 805/T/M) and used in the sonication experiments. The experimental set-up is shown in Figure 1.
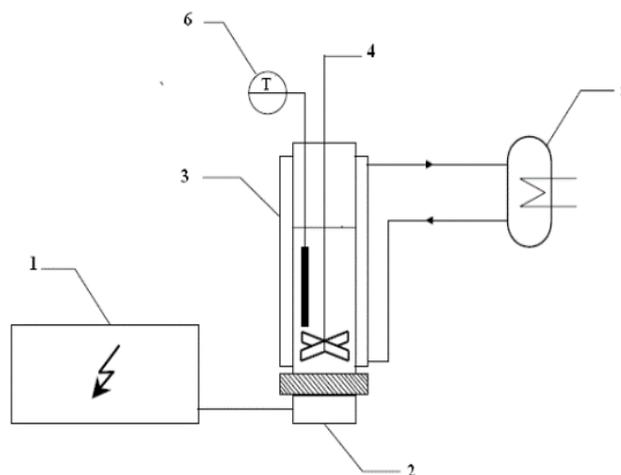

Figure 1. Experimental Set-up: 1 – Ultrasonic Generator, 2 – Transducer, 3 – Glass Reactor, 4 – Stirrer, 5 – Thermostat, 6 – Temperature Measurement

The actual power dissipated into the liquid was measured by the standard calorimetric method according to procedures detailed elsewhere [28], changing in the range from 1 to 30.6 W. Cooling of the reaction mixture was achieved by circulating water through the vessel jacket, in order to maintain an average temperature of $30 \pm 1°C$, which was monitored by a thermometer immersed in the solution. Solution pH was adjusted to the initial desired value (pH_0) but not corrected over reaction time due to the particularities of the reactor. All ultrasonic reactions were performed with 250 mL of aqueous solutions of paracetamol at concentration of 100 mg L^{-1}. A solution containing KI, Na_2SO_3 and NaOH (each 0.1 M) was used to quench the reaction in the samples when H_2O_2 and the Fenton reagent were used. Liquid samples periodically drawn from the vessel were analyzed by HPLC and TOC. An HPLC system (SHIMADZU Prominence High Pressure model), involving a two solvent delivery pump, UV/VIS detector (SHIMADZU SPD-M20A model) and an autosampler was used to follow the concentration-time profiles of paracetamol, which was analyzed on a Shim Pack CLC C8 (M) column (250 mm x 4.6 mm; 5 μm) using 90:10 aqueous solutions of orthophosphoric acid (pH=2): acetonitrile as an isocratic mobile phase respectively at 1 mL min^{-1} and room temperature. The injection volume was 100 μL and detection was achieved at 254 nm. The TOC analyzes were carried out by an SHIMADZU TOC-V CSN total organic carbon analyzer equipped with a non-dispersive infrared detector. The injection volume was 50 μL. The combustion reaction was achieved in a quartz pipe at 680 °C with a regular platinum catalyst. The carried flow was oxygen at 150 mL min^{-1}.

For checking the reproducibility of the evaluated processes, some experiments were triplicated.

3. Results and Discussions

3.1. Influence of Ultrasonic Frequency and Power

The most important parameters for application of sonolysis are the ultrasonic power and frequency employed. Figure 2 shows the influence of frequency and ultrasonic power on paracetamol degradation (Figure 2a) and on pseudo first-order rate constant (Figure 2b). The degradation rate constants were determined assuming pseudo first-order reaction kinetics as follows:

$$\frac{-dc}{dt} = kc; \quad ln\frac{c_0}{c} = kt \qquad\qquad 1$$

where k (min^{-1}) is the pseudo first-order rate constant and c_0 (mg L^{-1}) and c (mg L^{-1}) are the paracetamol concentrations at time zero and t (min), respectively.

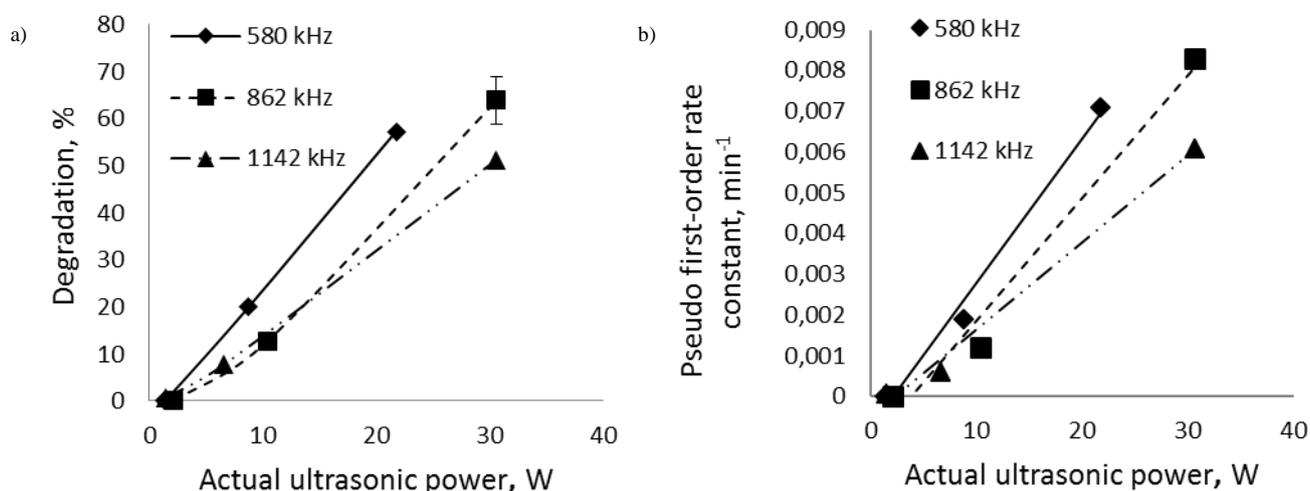**Figure 2.** Influence of Ultrasonic Frequency and Actual Ultrasonic Power on Paracetamol Degradation ([Paracetamol]$_0$: 100 mg L^{-1}, T: 30 °C, pH$_0$=5.5) a) Percent of Degradation after 120 min b) Pseudo First-order Rate Constant

The frequency of the ultrasound has a significant effect on the cavitation process because it changes the critical size of the cavitation bubble. Higher ultrasound frequencies are more useful for the generation of hydroxyl radicals because the collapse of microbubbles takes place rapidly, resulting in an increased efficiency of the $^\bullet$OH radical production. However, it is well known that there exists an optimum frequency beyond which negative effects of frequency on degradation rates are observed [29]. At very high frequencies, the cavitational effect is reduced. This is because the rarefaction cycle of the sound wave produces a negative pressure and/or intensity to initiate cavitation or the compression cycle occurs faster than the time required for the microbubble to collapse [30]. In early studies it was found, by using different types of ultrasound, that the optimal frequency for $^\bullet$OH yield is in the range of 200-400 kHz [31].

At the present experimental conditions, the high degradation was obtained at the frequency of 862 kHz, but this value is statistically similar to the value obtained at 580 kHz. Similar results were obtained by Quesada *et al.* [15] when studying the sonolysis of levodopa (anti-parkinson drug) and paracetamol in aqueous solution at 100 mg L^{-1}. They obtained similar degradation rates at 574 and 860 kHz, but significantly lower at 1134 kHz.

On the other hand, it is well known that sonochemical reactions could be affected by ultrasound power at a fixed frequency. The sonochemical reactivity is increased as the operating power increases. It is widely accepted that the higher ultrasonic power inputs, the higher frequency of cavitation, the higher number of active cavitation bubbles and also the size of the individual bubbles, and the higher concentration of hydroxyl radicals; therefore, the higher pollutant degradation levels [32].

Figure 2a shows that the conversion increases with increasing power. This result is expected because by increasing the magnitude of power dissipation of the horn, there will be an increase in the number of cavities generated and hence the cumulative pressure pulse will also increase. This phenomenon could be explained based on the following argument. During the ultrasonic irradiation two main reactions occur: (1) pyrolysis due to the high temperature and pressure in the gas phase, and (2) hydroxyl radical attack in the bubble-liquid interface and/or in the bulk liquid. In our case, paracetamol is a non-volatile compound and gas phase pyrolytic reactions are known to play a minor role in case of non-volatile solutes. Therefore, the attack of hydroxyl radicals is the dominant reaction. These radicals are produced as a result of the cleavage of H_2O and H_2O_2 molecules. Higher ultrasound power results in higher H_2O_2 molecules breakage and the produced hydroxyl radicals attack paracetamol molecules [33].

The values obtained through pseudo first-order rate constant (Figure 2b) for paracetamol degradation, are in the range of those reported by other authors through several AOPs [15-18, 21-23, 25]. The highest pseudo first-order rate constant obtained in this work when compared with the reported value by Quesada *et al.* [15] can be explained by the increase of temperature from 20 to 30°C. It is well known that the temperature plays an important role in the degradation of pollutant using acoustic cavitation process [11]. In cavitation, the change in operating temperature affects the cavitational intensity due to the change the physiochemical properties of the liquid medium [34].

3.2. Influence of pH

Solution pH is an important factor in determining the physical and chemical properties of the solution. In order to study the sonochemical action on the ionic and neutral forms of paracetamol, pH values between 3 to 9 were chosen. In Figure 3 the pH effect on the degradation of paracetamol (100 mg L^{-1}) at 862 kHz and 30.6 W is depicted. The values of paracetamol

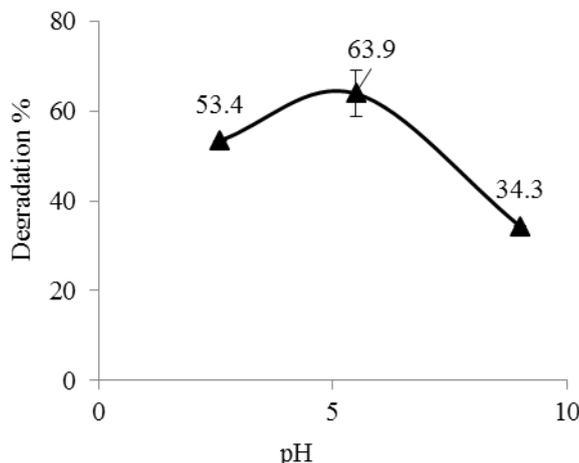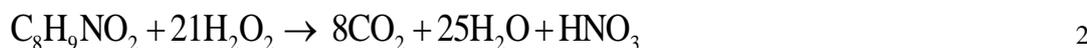percent removal after 2 h followed the order pH 5.5 > pH 3 > pH 9.

Figure 3. Effect of the Initial pH on Paracetamol Degradation (F= 862 kHz, P= 30.6 W, [Paracetamol]$_0$ = 100 mg L^{-1}, T = 30 °C, t = 120 min)

The pH can influence the distribution of non-dissociated (molecular) and dissociated (ionic) species. The pKa value of paracetamol is 9.5. Paracetamol has a superior hydrophobic character in the molecular form (pH < pKa). At this condition, paracetamol is accumulated on the interface of the cavitation bubbles and simultaneous pyrolysis and free radical attack could be observed. In alkaline solutions (pH > pKa), the ionic form of paracetamol is predominant, which is more stable and non volatile. Therefore, the degradation is carried out in the bulk of the solution where there is a lower concentration of $^\bullet$OH [32].

On the other hand, the degradation rate decrease from pH 5 to 9 due to the fact that a higher number of $^\bullet$OH species recombine to H$_2$O$_2$ and do not interact with paracetamol. In acidic conditions, the recombination of $^\bullet$OH radicals is less effective and slower than the $^\bullet$OH attack on pollutant [31]. However, decreasing the initial pH from 5 to 3 resulted in lower paracetamol removals from 63.9% to 53.4%. At low pH values, hydrogen peroxide could gain a proton to form oxonium ion (H$_3$O$_2$$^+$). This ion makes H$_2O_2$ electrophilic and thus enhances its stability lowering H$_2$O$_2$ reactivity and hydroxyl radical production [33]. Similar results have been obtained by other authors where the reduction of target compounds was influenced by the pH of the solution. It was observed that the degradation was higher at lower pH values [31, 33, 35].

3.3. Sonochemical Degradation in the Presence of Hydrogen Peroxide

It is well documented in the literature that during aqueous sonolysis, hydroxyl radicals are produced and recombined into H$_2$O$_2$ at the bubble-liquid interface and/or in the bulk liquid. In general, H$_2$O$_2$ is expected to promote degradation since it may be decomposed by ultrasound to reactive hydroxyl radicals [4, 28, 35]. For this reason, the degradation of organic compounds can be increased by an increase of the H$_2$O$_2$ dose [15, 36]. Then, another set of experiments were carried out in order to study the effects of using ultrasound in combination with an oxidant such as H$_2$O$_2$ at different initial concentrations. The stoichiometric amount of the H$_2$O$_2$ required for the complete oxidation of the paracetamol aqueous solution is calculated as follows:

$$C_8H_9NO_2 + 21H_2O_2 \rightarrow 8CO_2 + 25H_2O + HNO_3 \qquad\qquad 2$$

The effect of added H$_2$O$_2$ on paracetamol sonochemical degradation at 100 mg L^{-1} and pH equal to 5 was investigated. As it can be seen in Figure 4, the degradation of paracetamol increases slightly up to an H$_2$O$_2$ concentration of 3.45 mmol L^{-1}, beyond which it decreases.

Similar results were obtained by Quesada *et al.* [15] who reported that paracetamol shows a dramatic dependence on the hydrogen peroxide concentration present in the reaction medium and there is an optimum concentration of H$_2$O$_2$ to be used. In their work, initial degradation rate increases up to an H$_2$O$_2$ concentration of 3.9 x 10^{-3} mmol L^{-1}, beyond which it decreases. However, the position of this maximum is not very clear; this is due to the low concentration values of H$_2$O$_2$. Im *et al.* [23] studied the degradation of acetaminophen and naproxen under different ultrasound/H$_2$O$_2$ conditions. They found a maximum rate of pharmaceuticals degradation when the H$_2$O$_2$ concentration was set to 5 x 10^{-3} mmol L^{-1}, confirming that depending on the reaction conditions and on the system in question, there is an optimum H$_2$O$_2$ concentration to be used. Despite the generation of hydroxyl radicals by the sonolysis from H$_2$O [9], hydrogen peroxide may act as a hydroxyl radical scavenger, producing the much less reactive hydroperoxyl radicals, according to Equation 3 [36].
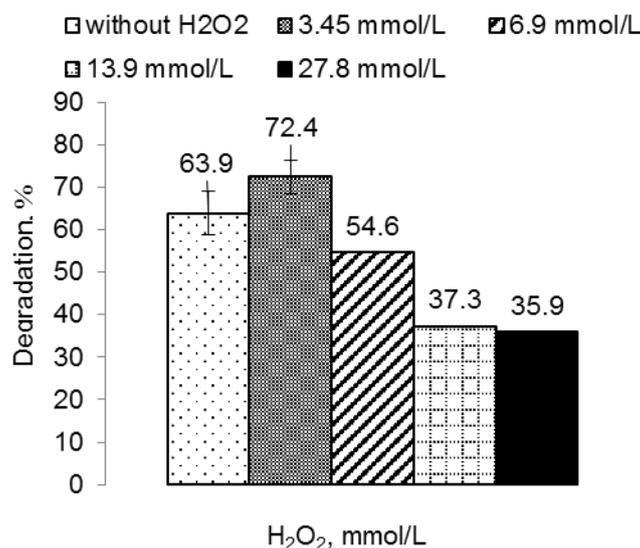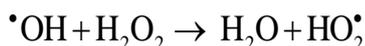
Figure 4. Effect of H_2O_2 on Paracetamol Sonochemical Degradation (F = 862 kHz, P = 30.6 W, [Paracetamol]$_0$ = 100 mg L^{-1}, T = 30°C, pH$_0$ = 5.5, t = 120 min)

$$^\bullet OH + H_2O_2 \rightarrow H_2O + HO_2^\bullet \qquad\qquad 3$$

Several authors have reported the negative influence of H_2O_2 in organic pollutants sonodegradation. Manousaki *et al.* [36] studied the degradation of sodium dodecylbenzene sulfonate in water by ultrasonic irradiation at 20 and 80 kHz and found a detrimental effect of H_2O_2 on the substrate degradation for all studied conditions. Besides the above-mentioned scavenging effect, these authors argue that pollutant removal occurred mainly in the interfacial region, and thus the beneficial effect of extra $^\bullet OH$ radicals generated would be of marginal importance, even close to the cavitation bubbles, due to the thermal decomposition of H_2O_2 molecules to O_2 and H_2O. On the other hand, other authors found a positive influence of H_2O_2 on sonodegradation when used at a five-fold H_2O_2: pollutant stoichiometric ratio [15, 37]. Therefore, the effect of hydrogen peroxide on sonolysis and the existence of an optimum H_2O_2 concentration seem to depend strongly on the particular pollutant, as well as the operating frequency and power and reactor configuration [11].

3.4. Intensification of Paracetamol Degradation by Sono-Fenton Process

Another possible way to increase the generation of free radicals in the ultrasonic system is to use it in combination with Fenton chemistry. Due to the recombination of hydroxyl radicals, amounts of H_2O_2 may form during ultrasonic treatment. Therefore, the addition of an iron salt can initiate the Fenton reaction in the presence of hydrogen peroxide during the sonolysis. Nevertheless, the H_2O_2 generated during sonolysis process is not sufficient to react with iron salts. For this reason, additional H_2O_2 is required to enhance the Fenton process in addition to ultrasound irradiation [9]. Table 1 shows the results of ultrasonic degradation of paracetamol ([Paracetamol]$_0$=100 mg L^{-1}, 862 kHz, 30.6 W, 30°C, pH 2.6) using different concentrations of Fe^{2+} and different concentrations of H_2O_2 following a factorial 3^2 experimental design (rows 4-12). The addition of Fe^{2+}/H_2O_2 resulted in high paracetamol degradation within the first 15 min of treatment if compare with the results obtained when not oxidant is added in the system (row 1) and when only hydrogen peroxide is used (row 2 and 3). In all cases, at 30 min degradation values higher than 90 % were observed.

During sono-Fenton process, Fe^{2+} ions are converted to Fe^{3+} in the presence of H_2O_2 and regenerated from Fe^{3+} by reacting with peroxyl radicals according to the mechanism proposed by Mohajerani *et al.* [9] and Velegraki *et al.* [38]. The enhancement of degradation by Fe(II)/H_2O_2 addition is due to H_2O_2 decomposition and hydroxyl radical generation during sono-Fenton process. It can be observed that at the same power and frequency of ultrasound and keeping constant the H_2O_2 concentration, the paracetamol degradation increases with an increase in applied Fe^{2+} concentration of Fenton reagent. In principle, Fe(II)/H_2O_2 system may enhance degradation providing additional nuclei for bubble formation [39]. After 60 min of ultrasonic treatment more than 95% of paracetamol is removed completely from the system for all the experimental conditions.

Table 1. Effect of Fe^{2+}/H_2O_2 on Paracetamol Sonochemical Degradation and Mineralization (F= 862 kHz, P = 30.6 W, [Paracetamol]$_0$ = 100 mg L^{-1}, T = 30°C, pH$_0$= 2.6)

	Concentration of H_2O_2 (mmol L^{-1})	Concentration of Fe^{2+} ($FeSO_4*7H_2O$) (mmo L^{-1})	Degradation, % (Mineralization, %)		
			15 min	30 min	60 min
1	0	0	11.6±0.8 (0.9±0.1)	22.7±1.7 (6.4±0.5)	40.4±2.1 (7.3±0.5)
2	3.45	0	15.8 (n.a.)	26.1 (n.a.)	44.9 (11.3)
3	6.9	0	2.14 (n.a.)	2.56 (n.a.)	27.3 (6.5)
4		0.7	70.8 (23.5)	85.3 (33.1)	96.8 (42.5)
5	6.9	1.2	73.3 (27.7)	92 (40.2)	97.8 (46.5)
6		3.5	95.7 (26.9)	96.4 (38.8)	97.5 (44.9)
7		1.4	91.5 (33.1)	96.3 (45.9)	99.8 (51.8)
8	13.9	2.3	98.9 ± 0.9 (38.4±1.9)	99.9 ± 0.1 (54.1±2.4)	99.9 ± 0.2 (58.3±1.0)
9		7.0	99.6 (36.4)	99.9 (50.8)	100 (55.6)
10		2.8	91.5 (30.8)	99.3 (42.6)	99.8 (45.8)
11	27.8	4.6	99.7 (35.8)	99.9 (50.6)	99.9 (56.8)
12		13.8	98.8 ± 0.6 (49.9±3.2)	99.9 ± 0.1 (50.1±2.8)	99.9 ± 0.1 (54.1±4.6)
Fenton	13.9	2.3	92.6 ± 1.2 (28.4±1.3)	97.8 ± 0.4 (39.6±3.5)	99.8 ± 0.2 (43.7±2.4)

3.5. Mineralization of Paracetamol with Sonochemical Degradation and Fe^{2+}/H_2O_2 Reagents

The mineralization was calculated from TOC values. In all cases, the mineralization for sono-Fenton process was higher than for single ultrasonic reaction (row 1 in Table 1) and for sonolysis with hydrogen peroxide (rows 2 and 3 in Table 1). The best mineralization was obtained when 13.9 mmol L^{-1} of H_2O_2 and 2.3 mmol L^{-1} of [Fe^{2+}] (row 8 in Table 1) were used. A mathematical model which describes the behavior of mineralization at 60 min as function of hydrogen peroxide and Fe^{2+} concentrations, is as follows:

$$\text{Mineralization}, \% = 24.63 + 3.48[H_2O_2] + 0.16[Fe^{2+}] + 0.42[H_2O_2][Fe^{2+}]$$
$$-0.14[H_2O_2]^2 - 0.67[Fe^{2+}]^2 .$$

$$4$$

The above model describes adequately the experiment with R^2 = 95.3%, a standard error of estimation of 1.87% and a mean absolute error of 1.04%. From statistical model the optimal experimental conditions for sono-Fenton process were determined and verified at 14.4 mmol L^{-1} of H_2O_2 and 4.7 mmol L^{-1} of [Fe^{2+}], which represents a [H_2O_2]/[Fe^{2+}] ratio of 3.06, with mineralization of 61.4% at 30 min. This value is better than the mineralization of paracetamol by several AOPs [12-15, 17-21, 27] and it is in the same order of mineralization reported by Quesada e*t al.* [16] and Im *et al.* [22] for paracetamol degradation by CWAO and ultrasonic degradation with single wall carbon nanotubes, respectively.

An additional experiment was carried out at the same conditions of row 8 (Table 1) without ultrasound (Fenton reaction). It can be seen, that at 15 min the degradation of sono-Fenton process is in 6.8 % (98.9 vs. 92.6) higher than for Fenton process, and mineralization at 60 min is in 15.4 % (58.3 vs. 43.7) higher for sono-Fenton if compared with Fenton process. This result shows that ultrasonic radiation enhances paracetamol degradation when it is combined with Fenton reagent.

4. Conclusions

According to our results, the paracetamol degradation was strongly affected by the ultrasonic power and frequency, pH and the initial concentrations of Fe^{2+}/H_2O_2. The degradation of paracetamol increases with increasing ultrasonic power at optimal value of frequency of 862 kHz. The intensification of paracetamol degradation is possible by sono-Fenton process.

In this study, practically the total degradation of pharmaceutical is obtained at 60 min for all studied concentrations of hydrogen peroxide and ferrum salt. The optimal conditions of sono-Fenton process that guarantee a mineralization higher than 60 % are 4.7 mmol L^{-1} of Fe^{2+} and 14.4 mmol L^{-1} H_2O_2.

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