Sonolysis of levodopa and paracetamol in aqueous solutions

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A B S T R A C T

Pharmaceutical products are often present in wastewater treatment effluents, rivers, lakes and, more rarely, in groundwater. The advanced oxidation methods, like ultrasound, find a promising future in the area of wastewater treatment. The aim of this paper is to evaluate the influence of several parameters of the ultrasound process on the degradation of paracetamol, a widely used non-steroidal anti-inflammatory recalcitrant drug found in water and levodopa, the most frequently prescribed drug for the treatment of Parkinson disease. Experiments were carried out at 574, 860 and 1134 kHz of ultrasonic frequency with horn-type sonicator and actual power values of 9, 17, 22 and 32 W at 20 °C. Initial concentrations of 25, 50, 100 and 150 mg L^{-1} of both products were used. Treatment efficiency was assessed following changes in pharmaceuticals concentration and chemical oxygen demand.

The sonochemical degradation of both products follows a pseudo-first-order reaction kinetics. Complete removal of pharmaceuticals was achieved in some cases but some dissolved organic carbon remains in solution showing that long lived intermediates were recalcitrant to ultrasound irradiation. Pollutants conversion and COD removal were found to decrease with increasing the initial solute concentration and decreasing power. The best results were obtained with 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, although some differences were observed between both molecules. Addition of H_2O_2 had a positive effect on degradation rate, but the optimum concentration of hydrogen peroxide depends on the pollutant.

1. Introduction

The presence of drugs in waterways has been established for almost 30 years. However, there were few attempts to evaluate the occurrence, fate and effects of pharmaceutical residues on the environment until fairly recently, when more intensive efforts began to be made. A wide variety of drugs have been found in waterways of many countries, including analgesics, antibiotics, antiepileptics, β-blockers and lipid regulators [44,31,32,39,26,36].

Most drugs are designed so that they retain their chemical structure long enough to exert their therapeutic effect. This property, combined with their continuous input, may enable them to remain in the environment for extended periods of time. The possibility for continuous but undetectable or unnoticed effects of pharmaceuticals on aquatic organisms is particularly worrisome because the effects could accumulate so slowly that major change goes undetected until the cumulative level of these effects finally cascades to irreversible change [38].

Several research works 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 [44,19].

Considering the potential impacts of pharmaceutical products, it is highly important to remove them from wastewater before discharge. Alternative treatment technologies have to be considered. In recent years, considerable interest has been shown in the application of advanced oxidation processes for the treatment of pharmaceutical contaminants in water. Examples of these studies are the use of ozonation for the treatment of progesterone and amoxicillin [5,1], the study of photocatalytic degradation of carbamazepine, clofibric acid, iomeprol and iopromide [8,9], the use of Fenton oxidation to improve the biodegradability of a real pharmaceutical wastewater [37] and the paracetamol, diclofenac and clofibric acid oxidation by means of ozonation and H_2O_2 photolysis [2,3,45].

On the other hand, ultrasound has increasing potential use in the treatment of water, wastewater and sewage sludge. The

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sonochemical destruction of pollutants in aqueous phase generally occurs as the result of imploding cavitation bubbles and 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 [40]. The process was found to be effective for the removal of several target chemical compounds like phenol, chlorophenols, nitrophenols, polychlorinated biphenyls, chloroaromatics, pesticides, dyes, CFCs, polycyclic aromatic hydrocarbons and surfactants from relatively dilute (typically in the micro- to milli-molar range) solutions [20,43]. However, it is notable that only few studies have reported the use of ultrasound for the removal of pharmaceutical products which are typically found in waterways, as for the ibuprofen, diclofenac and some endocrine disrupting compounds oxidation [27,15,7,11].

Levodopa is the most frequently prescribed drug for the treatment of Parkinson disease [23] and although its occurrence in the environment was not reported yet, it has been identified in the effluents of a formulation plant in Cuba [35]. Levodopa effects on the cellular death by oxidative stress and its neurotoxicity on animals have been demonstrated [28]. On the other hand, paracetamol is one of the most frequently detected pharmaceutical products and its transformation into toxic compounds during chlorination in wastewater treatment plants is well described by Bedner and Maccrehan [6] .

The purpose of the present work was to examine the sonochemical degradation of model aqueous solutions of levodopa and paracetamol and to investigate the effects of various operating conditions on removal efficiency.

2. Experimental section

2.1. Chemicals

Levodopa and paracetamol for synthesis (Sigma–Aldrich) containing more than 99% of pure compounds were used for the preparation of solutions. Structural formula and solubility in water of both compounds are shown in Table 1. Acetonitrile (Merck) was HPLC quality, while orthophosphoric acid (85% purity) was purchased from Fluka. Ultrapure water, used for sample preparation, was obtained in a water purification system PURELAB Option (ELGA).

2.2. Sonochemical degradation experiments

An ultrasound multifrequency generator (MEINHARDT ULTRASCHALLTECHNIK) connected to a stainless steel-made transducer (E 805/T/M), operating in continuous mode at frequencies of 574, 860 and 1134 kHz and at variable electric power output, was used for the sonication experiments. Reactions were carried out in a 0.5 L cylindrical glass reaction vessel. Cooling of the reaction mixture was achieved by circulating water, so as to maintain an average temperature of 20 ± 2 °C. In all cases, 300 mL of the aqueous solution at initial concentrations of 25, 50, 100 and 150 mg L^{-1} were prepared and subjected to ultrasonic irradiation. The samples, periodically withdrawn from the reactor, were analyzed according to the procedures described below. The experimental set-up is depicted in Fig. 1.

2.3. Calorimetry

Thompson and Doraiswamy [40] pointed out the importance of reporting the acoustic power dissipated in the reaction systems for subsequent researchers to reproduce results or compare reaction conditions. In order to verify the actual ultrasonic power, the energy dissipated in the solution was determined by calorimetry [30,21], the results are shown in Table 2.

2.4. High performance liquid chromatography (HPLC)

A fully computer controlled HPLC system UV/Vis Varian ProStar 310 involving a two solvents delivery pump Prostar 230, and an autosampler Prostar 410 was used to follow the concentration-time profiles of levodopa and paracetamol. Both products were

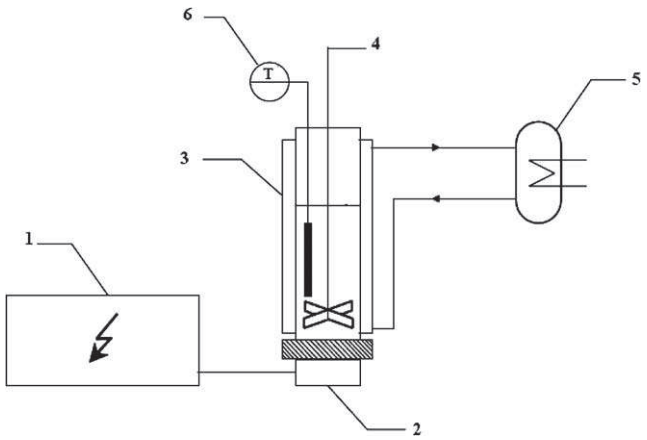
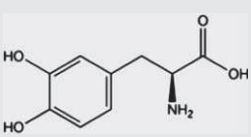
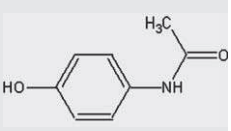


Fig. 1. Experimental set-up: 1 –ultrasonic generator, 2 – transducer, 3 – glass reactor, 4 – stirrer, 5 –thermostate, 6 – temperature measurement.

Table 2
Relationship between input and actual powers versus ultrasonic frequencies.

Frequency (kHz)	Input power (W)	Actual power (W)
1134	281	27
860	257	32
574	215	32
574	186	22
574	145	17
574	99	9

Table 1
Physical properties of levodopa and paracetamol.

Properties	Levodopa	Paracetamol
Structural formula		
Solubility in water (gL^{-1})	1.65 (20 °C)	14 (20 °C)
log P_{ow}	−2.9	0.89

separated on a Prontosil column, 120-5-C18-AQ, 250 mm, 2 mm, using 99:1 and 90:10 aqueous solutions of orthophosphoric acid (pH 2.2):acetonitrile as an isocratic mobile phase respectively, at 0.25 mL min^{-1} flow rate and ambient temperature. The injection volumes were 20 and 10 μL, respectively and detection was achieved with the diode array detector set at 278 and 254 nm. For quantification, the Varian Star Workstation chromatography data handling software was used. Linearity between absorbance and concentration was tested using external standards at various concentrations and the response was found to be linear (with a correlation coefficient r^2 = 0.999 in both cases) over the whole range of used concentrations. The dead time of the column was 2.6 min and the retention times of levodopa and paracetamol were 7 min and 6 min, respectively.

2.5. Chemical oxygen demand (COD)

The closed reflux colorimetric method was used to determine COD values. Each time the appropriate amount of sample was introduced into a commercially available digestion solution (Hach Europe) and the mixture was then incubated for 120 min at 150 °C in a COD reactor (Model DRB 200, Hach Company). COD concentration was measured colorimetrically using an Odyssey DR/2500 spectrophotometer (Hach Company).

3. Results and discussion

3.1. Effect of initial solute concentration

Fig. 2 shows the concentration–time profiles of levodopa and paracetamol during their sonochemical degradation at 574 kHz, 20 °C, 32 W of actual power and initial solute concentrations of 25, 50, 100 and 150 mg L^{-1}. It should be pointed out that the percentage of degradation decreases with increasing initial concentration, but the amount of substrate destroyed increases with an increase of initial concentration. 4 h sonication of a reaction mixture initially containing 25, 50, 100 and 150 mg L^{-1} of levodopa results in 91%, 70%, 54% and 46% of degradation respectively. However, the amount of levodopa degraded at 150 mg L^{-1} is as much as about 2.8 times higher than that degraded at 25 mg L^{-1}. For paracetamol, after 4 h of sonolysis, the extent of degradation was 95%, 82%, 70% and 56%, for the reaction mixture initially containing 25, 50, 100 and 150 mg L^{-1} respectively, but the amount of paracetamol degraded at 150 mg L^{-1} is as much as about 3.6 times greater than that degraded at 25 mg L^{-1}. Similar results have been obtained by other authors with different products and the explanation was that an increase in solute concentration would increase the probability of hydroxyl radical attack on pollutant molecules [4,25,42]. This behavior is characteristic of the OH chemistry at the air-water interface of the bubbles [33]. Because at the interface the steady-state OH concentration is very high and the OH–OH recombination would be the dominant process, an increase of substrate concentration would increase the fraction of OH that reacts with the substrate, and the degradation rate would be increased as a consequence. This fact is in accordance with the results obtained in Section 3.4 and with the well fitting to the pseudo first-order kinetics.

The degradation rate constants were determined assuming pseudo first-order reaction kinetics as follows:

$$-\frac{dC}{dt} = kC \iff \ln\frac{C_0}{C} = kt \quad (1)$$

where k is the pseudo first-order rate constant and C_0 and C are the product concentrations at time zero and t, respectively. If the results of Fig. 2 are plotted in the form of Eq. (1), k values can be computed from the slopes of the straight lines. These values are shown in Table 3. Similar results have been obtained in previous studies by Emery et al. [10] and Inoue et al. [17] where the sonochemical degradation of various products was found to obey a pseudo first-order reaction kinetics with k values decreasing when increasing initial concentration. But, as previously explained, the initial reaction rate ($=k \cdot C_0$) increases with substrate concentration. From Table 3, it is clear that the degradation rate of paracetamol is always larger than that of levodopa under the same sonication conditions and initial concentrations. These results are consistent with the previously

Table 3
Pseudo first-order rate constants of pharmaceuticals degradations.

Concentration	Levodopa		Paracetamol	
(mg L^{-1})	k(min^{-1})	r^2	k(min^{-1})	r^2
25	8.0×10^{-3}	0.98	1.25×10^{-3}	0.99
50	5.1×10^{-3}	0.99	7.1×10^{-3}	0.99
100	3.4×10^{-3}	0.99	5.4×10^{-3}	0.99
150	2.5×10^{-3}	0.98	3.6×10^{-3}	0.99

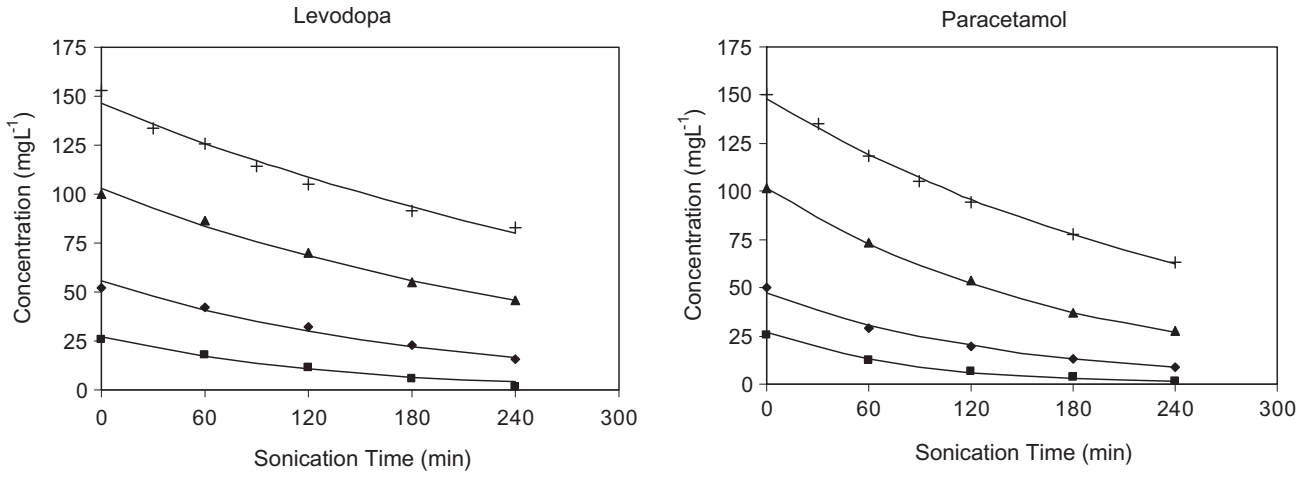


Fig. 2. Effect of initial concentration on sonochemical degradation of levodopa and paracetamol (frequency: 574 kHz, actual power: 32 W, temperature: 20 °C). (■) 25 mg L^{-1}, (♦) 50 mg L^{-1}, (▲)100 mg L^{-1}, (+) 150 mg L^{-1}, (–) calculated concentration from the pseudo first-order kinetic model.

Table 4
Degradation and mineralization percentages after 8 h ultrasonic irradiation (frequency: 574 kHz, actual power: 32 W, temperature: 20 °C).

Initial concentration ($mg\ L^{-1}$)	Levodopa		Paracetamol	
	Degradation (%)	Mineralization (%)	Degradation (%)	Mineralization (%)
25	100	31	100	39
50	97	26	98	33
100	80	17	96	27
150	61	13	73	18

reported finding that the more hydrophobic the solute is, the more effective its sonochemical degradation will be [18], hydrophobicity being characterized by log P_{OW} (log of partition coefficient octanol/water) as in Table 1.

Table 4 shows the substrate degradation and the COD removal percentages after 8 h of ultrasonic irradiation. The negative effect of an increase of pollutants initial concentration is evident on both the degradation and the COD removal. Although a complete degradation occurred in some cases, the conversion of all atoms of carbon to CO_2 was never achieved. These results suggest that organic carbon partially remains in the degradation products as recalcitrant organic acids. These results are in accordance with those of other authors who, after a long time of ultrasonic irradiation, observed only a small COD removal percentage. Inoue et al. [17] studied the sonochemical decomposition of Rhodamine B and Orange II. The best COD removal percentages for both products, after 10 h of reaction, at 41.5 W, were: 37.3% and 37.6%, respectively. Ku et al. [22] and Tiehm and Neis [41] studied other aromatic compounds such as phenol and chlorophenol and also reveal a low COD removal. These results show that the limiting step is the oxidation of organic intermediate products. So, the complete mineralization would be possible only with a much extended irradiation time and with a very high ultrasonic supplied energy.

3.2. Influence of ultrasonic frequency

It is well known that the rate of sonochemical destruction for an organic compound is frequency dependent. In addition, there is an optimum frequency that may depend on the physical and chemical properties of the organic compound.

In further experiments, the sonochemical degradation of levodopa and paracetamol at an initial concentration of 25 $mg\ L^{-1}$, 20 °C and 574, 860 and 1134 kHz was investigated (see Fig. 3). After 240 min of ultrasonic irradiation time, at frequencies of 574 kHz and 860 kHz, very similar results were obtained for both products. A possible explanation for these results is that levodopa and paracetamol oxidation takes place by reaction with OH radicals and hydrogen peroxide. Petrier and Casadonte [29] in an investigation carried out at 20, 200, 500 and 800 kHz with transducers having similar diameters and operating with the same power (30 W), demonstrated that the rates of hydrogen peroxide formation at 500 and 800 kHz are very similar. Although the collapse of the cavity is rapid and more violent at higher frequencies, resulting in an increase in the magnitude of pressure generated at the time of breakup and in an increased efficiency of the $OH^{\cdot}$ radical production, it is well known that there is an optimum frequency beyond which there are detrimental effects of frequency on the degradation rates [16,12]. At very high frequencies, the cavitational effect is reduced because either the rarefaction cycle of the sound wave produces a negative pressure which is insufficient in its duration and/or intensity to initiate cavitation or the compression cycle occurs faster than the time required for the microbubble to collapse [40]. In our case, although the results at 574 and 860 kHz are very similar, it is important to remember that lower frequencies are preferred due to the associated drawbacks of the high frequency operation. Frequencies below 574 kHz were not probed due to the limits of the equipment frequency range.

On the other hand, the ultrasonic frequency of 1134 kHz showed the lowest extent of degradation for both products. The effects of high frequency ultrasound in the megahertz range on the degradation of organic pollutants and sonochemical mechanisms are not clear because they are rarely studied [14]. Lifka et al. [24] affirm that at frequencies above 1 MHz, the degradation rate of low and high-volatile compounds decreases, but Hao et al. [14] have demonstrated that products like 4-chlorophenol are decomposed under high temperature pyrolysis at 1.7 MHz. It is necessary to notice that in this work, comparison of the results at 1134 KHz with those obtained at 574 and 860 KHz frequencies is difficult because the actual power dissipated in the reactor is not exactly the same (see Table 2).

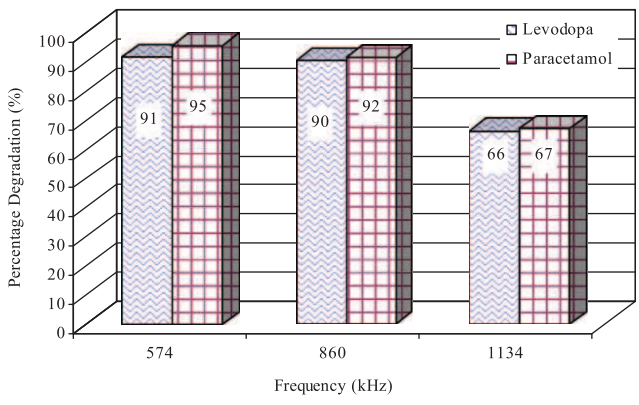


Fig. 3. Influence of ultrasonic frequency on levodopa and paracetamol degradation after 240 min of sonolysis (actual power: 32 W for 574 and 860 kHz and 27 W for 1134 kHz, pollutant initial concentration: 25 $mg\ L^{-1}$, temperature: 20 °C).

3.3. Influence of ultrasonic power

In order to evaluate the influence of ultrasonic power on levodopa and paracetamol degradation, the frequency of 574 kHz was selected, and actual powers of 9, 17, 22 and 32 W were tested. As showed in Fig. 4, above a threshold power of about 9 W, the initial degradation rates increase linearly with the actual power for both products (with correlation coefficients of 0.9939 for levodopa and 0.9967 for paracetamol). 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 (number of cavities multiplied by the collapse pressure due to a single cavity) will also increase. It is important to note that, although in this work the initial degradation rates increase linearly with the actual power for both products, it does not mean that this increase will be unbounded. It is well known that the enhancement of sonochemical effects with increasing power dissipation in the system is only obtained until an optimum power value, beyond which the rates of degradation decrease with increased power input.

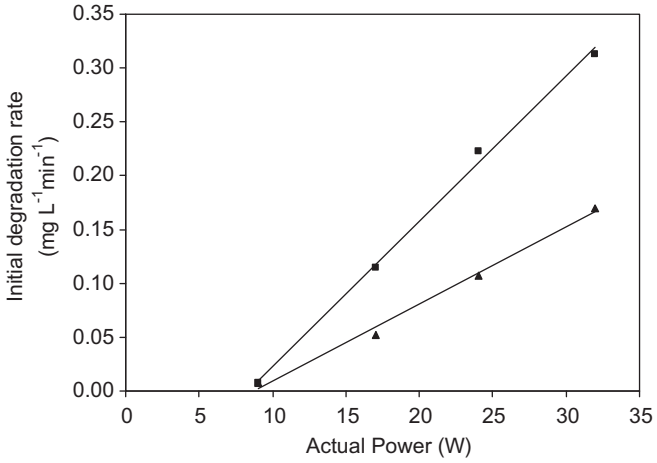


Fig. 4. Influence of ultrasonic actual power on levodopa (-▲-) and paracetamol (-■-) removal after 240 min of sonolysis (frequency: 574 kHz, pollutant initial concentration: 25 mg L^{-1} temperature: 20 °C).

3.4. Sonochemical degradation in the presence of radical scavengers or promoter

Sonolysis of organic compounds may occur by different mechanisms. Compounds may be degraded via thermal decomposition inside the bubble and/or in the interface, or by reactions with hydroxyl radicals and hydrogen peroxide at the interface and/or in the bulk liquid. The relative importance of these mechanisms depends on different factors such as the nature of the organic compounds, the ultrasonic frequency, and the presence of gases in the system, among others [42]. In our case, because both molecules are non volatile, the solutes do not pyrolyze in the cavitation bubbles.

It is possible to obtain information about the mechanism and the zones in which sonochemical reactions take place by adding radical scavengers to the system. When degradation rates of target contaminants are considerably reduced in the presence of scavengers, free radical chain reactions are involved. Alcohols such as 1-butanol are known to be effective OH radical scavengers for the gaseous region and/or interfacial region of the collapsing bubble [25]. A known scavenger for the liquid region is potassium bromide, a non volatile strong electrolyte that can be readily oxidized by free radicals.

Degradation experiments of levodopa and paracetamol have been carried out in the presence of 1-butanol (22-fold molar concentration of 1-butanol to levodopa and paracetamol). The results are shown in Fig. 5. As it can be seen, the addition of 1-butanol in the reaction mixture inhibits both products degradation, indicating that both pharmaceuticals are mainly decomposed by the attack of OH radicals at the interface of collapsing bubbles. However 5% of degradation was reached for paracetamol and 17% for levodopa, suggesting that some minor degradation can also take place in the bulk solution. Because paracetamol has a higher log P_{OW} than levodopa, one could expect that its degradation at the interface will reach a higher extend than levodopa and thus that the influence of 1-butanol will be also higher. For levodopa, due to its higher hydrophilicity (log P_{OW} = −2.92), the mechanism in the bulk solution is more important than for paracetamol. On the other hand, the thermal decomposition of levodopa at the gas–liquid interface cannot be neglected because in recent studies developed in our laboratory, the thermal decomposition of levodopa was observed for temperatures between 120 and 150 °C under inert atmosphere. Then, the differences observed in the degradation mechanisms of the two products could be linked to the difference in physical and chemical properties of the molecules (Table 1).

3.5. Sonochemical degradation with hydrogen peroxide

Additional experiments were carried out in order to study the benefits, if any, of using ultrasound in conjunction with an oxidant such as H_2O_2 at various initial concentrations. The reference H_2O_2 concentration corresponds to the stoichiometric amount of the oxidant needed for the complete oxidation of 25 mg L^{-1} of the pharmaceutical aqueous solution (95 mg L^{-1} for levodopa and 106 mg L^{-1} for paracetamol) according to the following reactions:

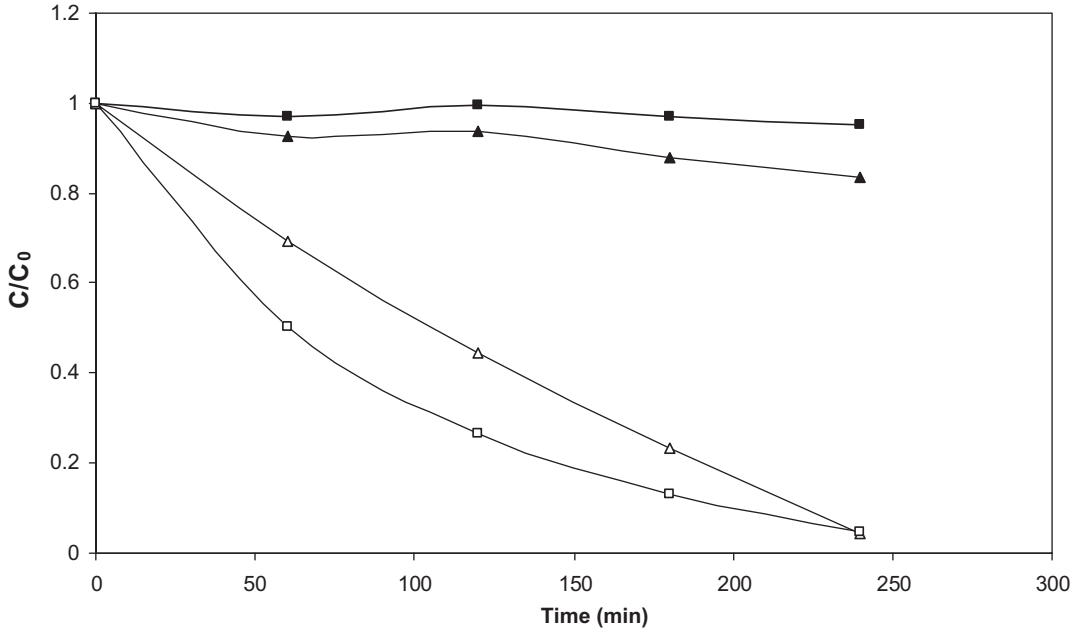


Fig. 5. Effect of *n*-butanol on levodopa and paracetamol sonochemical degradation. (frequency: 574 kHz, actual power: 32 W, pollutant initial concentration: 25 mg L^{-1}). (-△-) Levodopa without scavenger, (-▲-) Levodopa with *n*-butanol, (-⊟-) paracetamol without scavenger, (-■-) paracetamol with *n*-butanol.

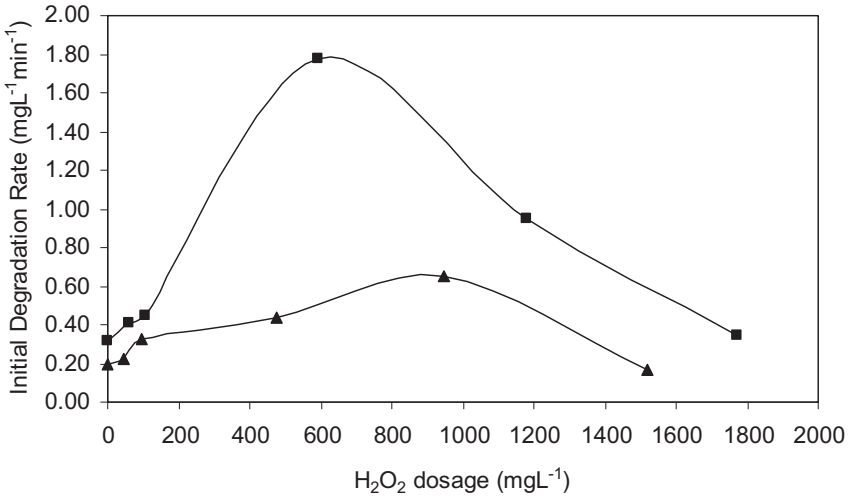


Fig. 6. Effect of H2O2 concentration on levodopa (-▲-) and paracetamol (-■-) sonochemical degradation (frequency: 574 kHz, actual power: 32 W, pollutant initial concentration: 25 mg L^{-1}).

$$C_9H_{11}NO_4 + 22H_2O_2 \rightarrow 9CO_2 + 27H_2O + HNO_3 \quad (2)$$

$$C_8H_9NO_2 + 21H_2O_2 \rightarrow 8CO_2 + 25H_2O + HNO_3 \quad (3)$$

For a better understanding of the H_2O_2 influence, smaller and higher concentrations than stoichiometry were used. The results of this study at 574 kHz, 20 °C, 32 W of actual power and initial solute concentrations of 25 mg L^{-1} are shown in Fig. 6. For comparison, the degradation of the two pharmaceuticals in identical conditions but without sonication, was also studied (data not shown). No pollutant degradation was observed in silent conditions.

In the case of levodopa, the initial degradation rate increases slightly up to an H_2O_2 concentration of 948 mg L^{-1} (10 fold stoichiometric), beyond which it decreases. Paracetamol shows a dramatic dependence on the hydrogen peroxide concentration present in the reaction medium (initial rate can be multiplied by 6). Similarly to levodopa, there is an optimum for the H_2O_2 concentration used. Initial degradation rate increases up to an H_2O_2 concentration of 590 mg L^{-1} (5 fold stoichiometric) beyond which it decreases. However, the position of these maxima is not very accurate, due to the low number of H_2O_2 concentration values.

In general, H_2O_2 is expected to promote degradation since it may be decomposed by ultrasound to reactive hydroxyl radicals, thus promoting pollutant degradation. Several authors published the positive influence of H_2O_2 in organic pollutants sonodegradation [34,42,10]. On the other hand, Manousaki et al. [25] found a detrimental effect of H_2O_2 on sodium dodecylbenzene sulfonate sonochemical degradation and Velegraki et al. [43], who studied the effect of H_2O_2 concentration (0–1050 mg L^{-1}) on acid orange 7 photocatalytic oxidation, found that degradation is impeded for the whole range of H_2O_2 concentration studied. They argued that, depending on the reaction conditions and on the system in question, there is an optimum H_2O_2 concentration, above which H_2O_2 acts as a radical scavenger, thus leading to reduced degradation. It is important to note that such an effect would probably be more marked in the solution bulk, where the reaction with the substrate is the main removal process for OH, than at the air–water interface where the recombination of OH + OH would strongly predominate. The difference in the optimum concentrations of H_2O_2 could be due to the difference in degradation sites (interface vs. bulk) of both products (see Section 3.4), but also to the presumably different reaction rate constants of the substrates.

Gogate [13] affirms that the effect of the combined ultrasound plus H_2O_2 process will be very much dependent on the utilization of free radicals by the pollutant molecules, which in turn is dependent on the efficiency of contact of the generated free radicals with the pollutant over a specified time period. Our results suggest that effectively levodopa and paracetamol degradation mechanisms are different, and thus optimum H_2O_2 concentration values depend on the nature of pollutants.

4. Conclusions

High frequency ultrasound can promote the oxidation of levodopa and paracetamol in relatively dilute synthetic solutions and the extent of degradation strongly depends on the operating conditions. Ultrasonic treatment alone may not be suitable for decontaminating completely levodopa and paracetamol solutions. However, process efficiency may be improved by coupling with biological treatment, which will carry on mineralization as far as possible.

Hydroxyl radical-mediated reactions occurring at the gas–liquid interface appear to be the prevailing degradation mechanism. The use of an extra oxidant like H_2O_2 for enhancing the extent of degradation is possible but the use of the adequate concentration is an important parameter because H_2O_2 can act as a radical promoter or scavenger, depending on the product and the conditions used.

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