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Sonochemical and photochemical elimination of ibuprofen in aqueous solution

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ABSTRACT

Ibuprofen (IBP) is a widely used analgesic and anti-inflammatory drug, found as a pollutant in aqueous environments. Sonochemistry offers a new alternative against persistent water organic-pollutants. The aim of this paper is to evaluate the influence of several parameters on degradation of IBP in water solutions (in air saturated): the power of the ultrasonic process, the pH of the solution, the initial concentration of the pollutant. Moreover, the effects of photo irradiation and the combination of both treatments (UV+US) were studied. A higher degradation was observed in lower initial concentration of IBP, while a higher power increased the initial rate of IBP degradation. When sonophotolysis was applied (at a wavelength of 254 nm and ultrasonic power of 80 W), a significant enhancement in the degradation of IBP (99.6 % in 10 min) was observed. Otherwise, elimination of total organic carbon (TOC) was investigated.

1. Introduction

The presence of drugs in water constitutes a serious environmental problem. This is because many of them are highly toxic and may accumulate in living organisms, causing severe disorders and diseases [1]. Indeed, municipal wastewater treatment plants (WWTPs) are generally not equipped to deal with complex pharmaceuticals, as they were built and upgraded with the principal aim of removing easily or moderately biodegradable carbon, nitrogen and phosphorus compounds and microbiological organisms [2]. Part of the drugs present in water, the 2-[3-(2-methylpropyl) phenyl] propanoic acid, commercially available as ibuprofen (IBP), is a nonsteroidal anti-inflammatory drug belonging to the group of propionic acid derivatives. It is widely used for painful and inflammatory conditions and is available for over-the-counter (OTC) sale. The usual dose, from 200 to 1200 mg daily, can be increased for prescription use to 3200 mg in divided portions. For instance, Miege et al [3] reported that concentrations of 0.002 and 24.6 µg/L of IBP are present in waterdischarged from water treatment plants.As classical wastewater treatments do not completely eliminate drugs, alternative processes have been studied in recent years. Advanced oxidation processes (AOPs) generate highly reactive and unstable hydroxyl radicals with a high oxidation potential that can also oxidize drugs [1,4]. Among them, sonochemical treatment has been found to be one of the mostsuccessful techniques for degradation of recalcitrant organic pollutants, in the case of organic dyes and pesticides [5, 6]. Particular attention has been paid to the remediation of substances present in the health domain [7] or to pharmaceutical compounds [8-17]. Nevertheless, sonochemical degradation has been found to be efficient for environmental remediation purposes, although complete mineralization of the organic material was not achieved in most cases [18, 19] due to the hydrophilic nature of the degradation intermediates. Therefore, ultrasound is often combined with other processes such as Fenton [5], or recently to electrochemistry [20].

Fang et al. have shown that treatment by photolysis may lead to a degradation of IBP by a direct UV excitation (λ<300 nm). During the treatment, pollutants may exhibit strong absorption of the excitation light and a sufficient quantum yield. Then, compounds oxidized by initial photoexcitation (Eq 01) react with the dissolved oxygen in the water before being converted into products (equations 2 and 3) [21].

$$R + h\nu \rightarrow R^{*} \quad (1)$$
$$R^{*} + O_2 \rightarrow R^{+\cdot} + O_2^{-\cdot} \quad (2)$$
$$R^{+\cdot} \rightarrow \text{products} \quad (3)$$

Jagannathan Madhavan et al. [22] studied a combined advanced oxidation processes for synergistic degradation of ibuprofen in aqueous environments (US, US+TiO_2, UV+TiO_2, US+UV+TiO_2). While the presence of titanium oxide particles is always difficult to manage, the combination of ultrasound and additional processes is promising.

The aim of the present research concerns the study of degradation of ibuprofen (IBP) using sonochemistry as well as UV, and the combination of both techniques (UV+US). On the one hand, the effect of initial concentration of IBP, pH, and applied ultrasonic power were investigated, while on the other, mineralization studies were carried out to contribute tothe knowledge of the IBP degradation mechanism.

2.Experimental

2.1. *Chemicals*

Ibuprofen was purchased from Sigma, 4-ethylphenol 97%, 4-ethylbenzaldehyde 97% and 4-isobutylacetophenone 97% from Alfa Aesar, while 1- hydroxyibuprofen 99.6 % is from Fluka. pH was adjusted with solutions of sulfuric acid obtained from Fluka. Water for preparation of the solutions was purelab UHQ ELGA quality.

2.2. *Ultrasonic and photolysis systems*

Sonolysis experiments were conducted at an ultrasound frequency of 500 kHz in a continuous wave mode. The ultrasound unit used was an UNDATIM ULTRASONICS generator coupled with a transducer by impedance with a 55 mm plate diameter; the transducer consists of a piezoelectric disk affixed to a PZT plate protective glass. Power output on the generator for all experiments varies between 10 and 80 W. To verify actual ultrasonic power, the energy dissipated by the apparatus was determined by calorimetry [23]. Actual transmitted power corresponding to an output of 80 W is 49.8W.

The UV irradiation source was a 25 W low pressure mercury vapor lamp (maximum emission at 254 nm) encased in a quartz tube.

The Fricke dosimetry method allows quantification of free radicals production and hydrogen peroxide produced by homolytic scission of water molecules due to inertial cavitation collapse [24, 25]. Its principle is based on determination of Fe^{3+} by spectrophotometry UV from oxidation of Fe^{2+} by free radicals (equations 4 and5) and hydrogen peroxide (equation 6) [26]:

$$HO\bullet + Fe^{2+} + H^{+} \rightarrow H_2O + Fe^{3+} \quad (4)$$
$$HO\bullet_2 + Fe^{2+} + H^{+} \rightarrow H_2O_2 + Fe^{+3} \quad (5)$$
$$H_2O_2 + Fe^{2+} + H^{+} \rightarrow H_2O + Fe^{3+} + HO\bullet \quad (6)$$

The Fricke solution consists of $Fe(SO_4)_2(NH_4)_2,6H_2O$ (0.25 mM), H_2SO_4 (0.4 M) and NaCl (1mM). Sampling absorbance (304nm) is measured by UV spectrometer (HITACHI U-2001®), and the Fe^{3+} concentration in solution is determined as a function of absorbance. The sonochemical yield (G) has been calculated according to the Iida equation $G(Fe^{3+}) = [Fe^{3+}].V_T.E_a^{-1}$, where E_a is the acoustic energy (J) and V_T the volume of solution (dm^3) [25].

2.3. *Analytical methods*

Chemical oxygen demand (COD) was measured according to the method presented by (Thomas 1986), using a sulphuric acid-potassium dichromate solution in the presence of silver sulphate as a catalyst (from HACH LANGE (LCK 314)). Test solution (2 mL) are mixed with dichromate reagent and digested at 148°C in the thermostat (HT 200 S) in standard program HT for 15 min. Optical density for the color change of dichromate solution was determined at 445 nm with a DR 2800 photometer.

TOC was determined using a total organic carbon analyzer, which uses oxidative combustion followed by infrared detection. The instrument used was a Shimadzu TOC-LCSH. H_2O_2 was analytically determined by spectrophotometric method.

Water/acetonitrile (50/50 v/v) was the mobile phase for quantification of IBP in HPLC UltiMate 3000 with a column C18 _ 3µm, at 25°C, 20µL of volume injection, and recorded at 220 nm. This system is connected to an acquisition and data processing unit using the analysis software Chromeleon.

3. Results and discussion

3.1 *Effect of the applied ultrasonic power*

The most crucial parameters for application of sonolysis are power and frequency. In this study, a frequency of 500 kHz was applied. Thus, the effects of 10, 30, 50 and 80 W of applied ultrasonic power were investigated on degradation of 20 mg.L^{-1} of IBP under aerated conditions. Control experiments assessed the power dissipated in the reactor by the calorimetric method. 49.8% of power is transmitted to the reactor, while the rest is lost mainly as heat. Figure 1 depicts the effect of applied ultrasonic power on IBP degradation.

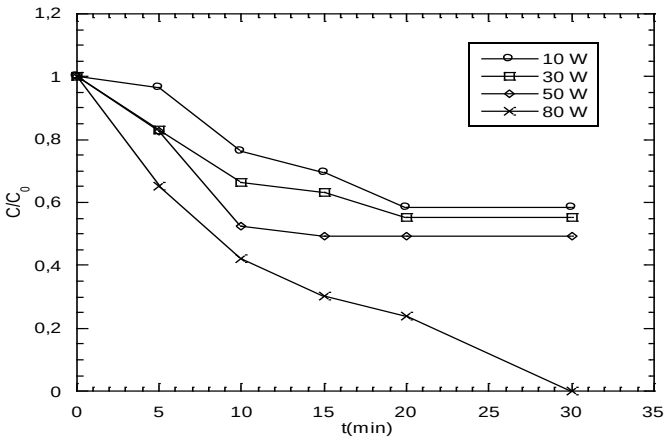


Figure 1: Effect of ultrasonic power in sonochemical IBP degradation ([IBP] =20mg.L^{-1}, T=25°C, pH=5.2, ultrasonic frequency=500kHz)

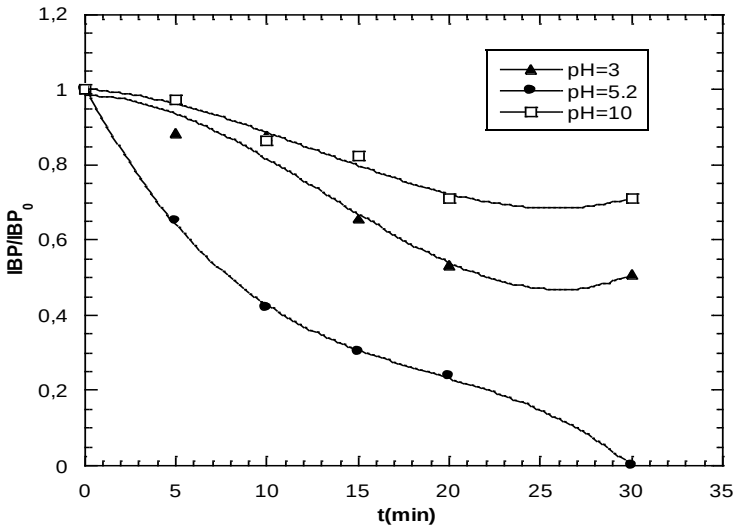
The results show that IBP degradation is highly dependent on the applied power of ultrasound. A higher initial degradation rate was reached around 4.6 µmol.$L^{-1}min^{-1}$ for 80W of applied power, whereas it was 2.99 µmol.$L^{-1}min^{-1}$ only for 50W, 1.92µmol.$L^{-1}min^{-1}$ for 30W and 1.65µmol.$L^{-1}min^{-1}$ for 10W , 100% of degradation of IBP was obtained after 30min of treatment under 80W.

Propagation of ultrasound irradiation in liquid promotes a series of compression and rarefaction waves. Bubbles grow in successive cycles forming cavitation bubbles which, at sufficiently high power, reach an unstable size and collapse violently. The concomitant heat release follows formation of the so-called "hotspots" attaining temperature and pressure limits of 2000°C and 200 atm. When water vapor, dissolved gas and/or organic substances are exposed to these extreme conditions, bond rupture may occur [27]. Moreover, sonolysis generates hydroxyl radicals from water dissociation. In the presence of oxygen, the perhydroxyl radical is also formed. The radicals formed are then diffused in the solution, simultaneously with the hydrogen peroxide released from the combination of ·OH and ·OOH radicals. During the process, three clearly determined zones can be described: the cavitation bubble, the supercritical interface, and the bulk of the solution. For instance, degradation of volatile compounds takes place in the gas phase of the cavitational bubble and/or in the interface of the hotspot. On the contrary, hydrophilic and non-volatile compounds are mainly degraded once the reactive radical species attain sufficient diffusion mass transfer in the aqueous phase. [28].

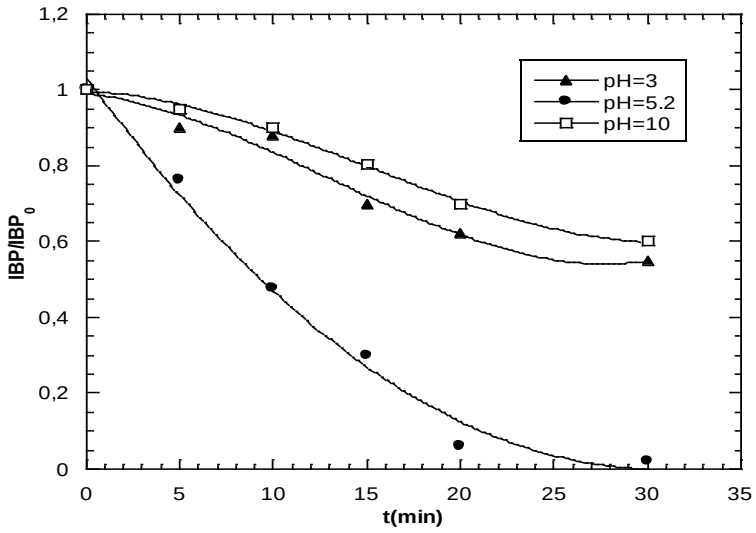
Enhancement of IBP degradation with increase in ultrasonic power can be explained by the increase in the number of active cavitation bubbles. When power increases, transmittance of ultrasonic energy into the reactor increases. Due to this energy, bubble pulsation and collapse are quicker and the number of cavitation bubbles increases leading to a higher concentration of •OH radicals in the IBP aqueous solution [29, 30]. Thus, an increase in ultrasonic power results an increase in acoustic amplitude, promoting more violent cavitation bubble collapse because bubble collapse time, transient temperature and internal pressure in the cavitation bubble during collapse all depend on acoustic amplitude [31]. In other words, an increase in sound power leads to sonochemical effects, resulting in quicker and higher IBP degradation rates. It is noteworthy that degradation rates increase with ultrasonic power in the 20–80 W range, because continual increase in power does not necessarily imply continual increase in sonochemical degradation. It is very common that, at very high power, the degradation rate may slow down. Moreover, operation at an ultrasonic power of 100 W is not recommended, since this could damage the piezoelectric disk of the ultrasonic instrument.

3.2 *Effect of pH*

The pH of the solution is an important parameter to study since IBP is a weak acid, with aIBP pKa value of 4.9. To study sonochemical action on the different IBP structures, i.e. ionic and neutral forms, experiments were carried out at pH =3, 5.2 and 10. pH 3 and 10 constitute extreme values for sonolytic and photolytic degradation of IBP. The result is shown in Figure 2.



(a)



(b)

Figure 2: Effect of initial pH on IBP degradation ([IBP] =20mg.L^{-1}, T=25°C, Ultrasonic frequency = 500 kHz, Pc=49.8W, UV (254nmn, 25W)), (a) Sonolytic degradation, (b) Photolytic degradation

The results show that the degradation rate of IBP is a function of pH, the lowest degradation rate of IBP was observed at pH 10, whereas the highest occurred at pH 5.2. Otherwise pH 3 present similar trends at pH 10. At pH 5.2, the slope of the curve is the highest of all, and IBP degradation is observed to be total after 30 minutes of sonolytic and photolytic treatments. A comparison of both treatments shows that ultrasound leads to higher initial degradation rates.

The degradation rate decreases at pH 10 due to the fact that a higher number of $^{\cdot}OH$ recombine to H_2O_2 and do not interact with IBP (Table1).

Table 1: Effect of pH on the sonolytic and photolytic IBP degradation rate

pH	Initial Sonolytic IBP degradation rate ($\mu mol.L^{-1}min^{-1}$)	Initial Photolytic IBP degradation rate ($\mu mol.L^{-1}min^{-1}$)
3.0	2.9	2.1
5.2	4.6	2.9
10.0	1.6	0.8

3.3 *Effect of initial concentration of IBP*

Figure 3 shows the effect of IBP concentration on the sonolytic degradation rate at 500 kHz and 80 W power for initial concentrations of 5, 10 and 20 $mg.L^{-1}$. The results show an increase in the degradation rate as initial concentration increases.

The observed first-order kinetics and the dependence of rate on the initial concentration can be accounted for by the following reactions (8), (9), (10), which take place during the sonolytic process.

H_2O))) $\rightarrow$ $^{\cdot}H + {}^{\cdot}OH$ (8)

$2\ {}^{\cdot}OH \rightarrow H_2O_2$ (9)

${}^{\cdot}OH$ + IBP $\rightarrow$ degradation products (10)

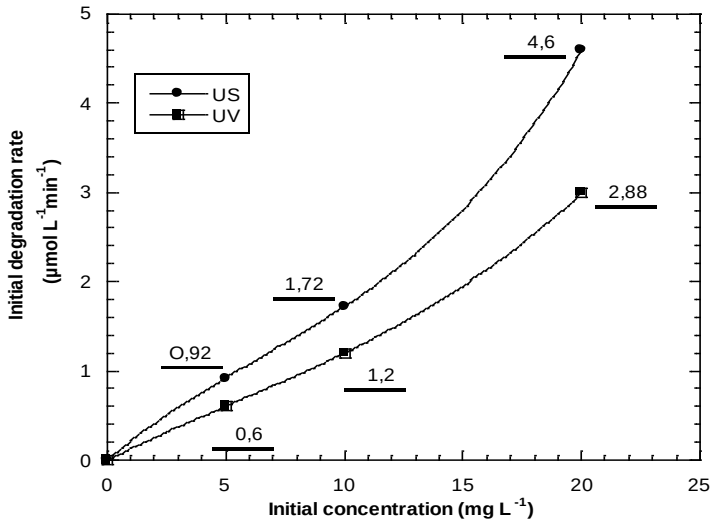


Figure 3: Initial degradation rate as a function of the initial concentration of IBP. (T=25°C, pH=5.2, ultrasonic frequency=500 kHz, Pc = 80 W, UV (254nm, 25W)

Generally, in a sonochemical process, micro-sized bubbles readily form due to acoustic cavitation. Then they grow and subsequently collapse with the generation of extreme temperatures and pressures.

This creates three regions for high energy chemical reactions: (i) the region inside the bubble cavity where the volatile and hydrophobic molecules are degraded via pyrolytic reactions; (ii) the bubble–liquid interfacial region where the hydroxyl radical reactions are predominant; (iii) the liquid bulk region where the free radicals that migrate from the bubble–liquid interface into the liquid, create secondary sonochemical reactions. In the case of IBP, Mendez-Arriaga et al. [33] suggested that pyrolytic degradation of IBP is not possible due to its hydrophobic and low volatility character at a pH lower than its pKa (4.9) [32]. Hence, degradation of

IBP can occur as a result of the hydroxyl radicals present in the bubble–liquid interface. The degradation rate is expected to be dependent on the concentration of ${}^{\cdot}OH$ produced by water thermolysis (Reaction (8)) and the concentration of IBP molecules at the interface of the cavitation bubble. In the absence of IBP, the recombination of hydroxyl radicals predominate (Reaction (9)) and form hydrogen peroxide. However, in the presence of IBP, a fraction of the hydroxyl radicals produced attack IBP molecules and initiate its degradation.

As IBP concentration increases, Reaction (10) dominates leading to an increase in IBP degradation rate. Recently, Mendez-Arriaga et al. [32] also observed similar results for degradation of IBP in a 500 kHz batch reactor, and observed a reduction in the amount of H_2O_2 formation at higher IBP concentrations.

3.4 *IBP degradation and hydrogen peroxide formation*

Taking into account the above results, the IBP degradation kinetics complied with first-order kinetics [32] and to compare different physical treatments, degradation of IBP by photo irradiation only (UV−"control"), ultrasound only (US), and a combination of both (UV+US) took place under the following experimental conditions: [IBP] = 20mg.L^{-1}, pH =5.2, V=300mL . The results of the different experiments are shown in Figure 4. This figure reveals the formation of hydrogen peroxide.

For photo-irradiation treatment, total degradation of IBP was obtained after 60 min. Then, with sonicated systems, IBP was totally eliminated after 30 min. When the ultrasound and UV treatments were combined, a significant enhancement of IBP degradation was observed: 99.65 %after 10 minutes of treatment as shown in Figure 4. Sonophotolysis dramatically increases IBP degradation rate.

Furthermore, the formation of hydrogen peroxide was observed within the first minutes of the experiment with the different treatments.

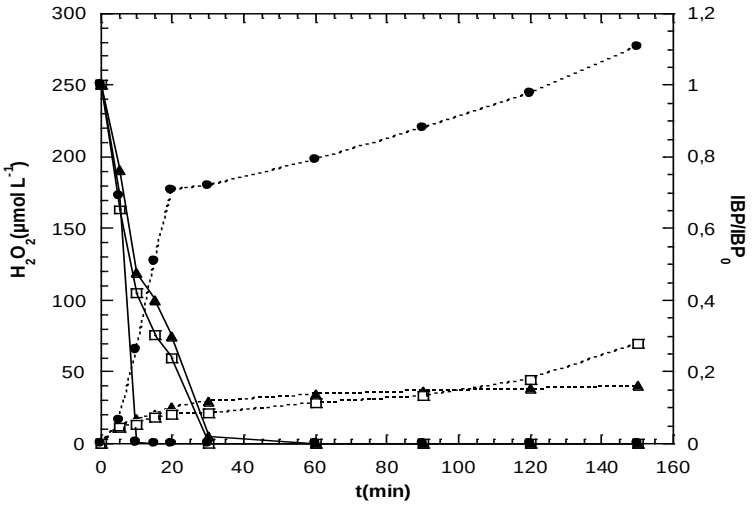


Figure 4: Comparative IBP degradation and evolution of hydrogen peroxide (H_2O_2) concentration (µM) when applying various advanced oxidation processes (UV, US, US/UV). ([IBP] =20mg.L^{-1}, pH=5.2, T=25°C, Pc =49.8 W, ultrasonic frequency=500 kHz, UV (254nm, 25W)), (▲) UV, (□) US, (●) UV+US

It should be noted that during the first five minutes of experiments, hydrogen peroxide concentrations were quite similar whatever the treatment. Then, the rate of hydrogen peroxide formation in the sonophotochemical process was 0.04 µM min^{-1} (Figure 4), whereas with the sonolytic process alone the rate was only 0.014µM min^{-1}, and0.0016 µM min^{-1} with the photolysis process alone. After elimination of IBP, a decrease in hydrogen peroxide formation was noticed.

In the combined system, the net rate of hydrogen peroxide formation reached a steady state after 150 min. This matches the results of Wu et al. [33] and Kidak and Ince [34], who also reported that significant IBP degradation was observed in the presence of excess hydroxyl radicals. The presence of this oxidant leads to a major degradation of ibuprofen.

3.5 *Frick dosimetry*

The results confirmed the presence of oxidizing agents: HO•, HO•$_2$ .Their formation is greater during sonolytic treatment than photolytic treatment. Moreover, the amount of formed radicals is highest when UV+US treatments were combined (Figure 5).

The presence of radicals contributes to elimination of IBP. With respect to peroxide hydrogen, their increased formation during sonophotolysis may account for the higher IBP degradation rate.

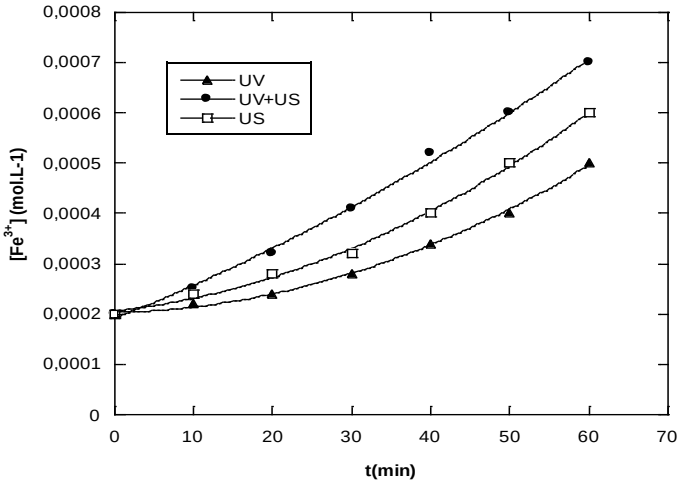


Figure 5: Development of the [Fe^{3+}] formed for each process studied

A quantification by sonochemical yield determination is shown in table 2 for each process studied.

Table2: Evolution of sonochemical yield for each process studied.

	$G(Fe^{3+})$ (mol/j)
UV	$3.30\ 10^{-6}$
US	$1.10\ 10^{-5}$
UV+US	$1.64\ 10^{-5}$

3.6. *Mineralization studies*

It has been widely reported that some intermediate products of a degradation process are more toxic and carcinogenic than the parent organic compounds [35, 36]. Hence, complete degradation of the pollutants should be guaranteed before discharging them into the ecosystem. A comparison of total organic carbon (TOC) was conducted from the experiments carried out under identical conditions, [IBP] = 20mg.$L^{-1}$and pH of 5.2, for sonolysis, photolysis and (UV/US), the results obtained are shown in Figure 6.

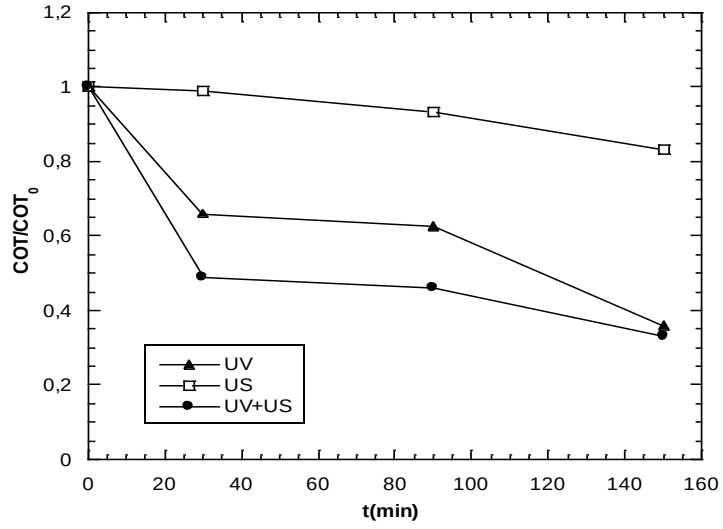


Figure 6: Total organic carbon (TOC) ratio content of IBP during sonolysis, photolysis and (UV+US)

Based on TOC data, the following conclusions can be drawn: UV/US achieves higher TOC elimination (67% in 150 min) than sonolysis (16.8% in 150 minutes) and photolysis UV (63.8% in 150 minutes).

It is known that complete degradation of IBP does not mean that the pollutant is completely degraded, and so the degradation of this pollutant in terms of COD removal was investigated. Figure 7 depicts the evolution of COD/COD_0 during sonication of $20mgL^{-1}$of IBP at 500 kHz and 49,8W.

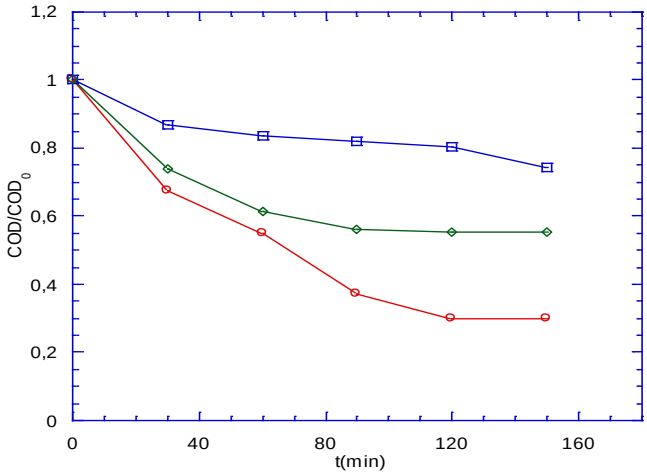
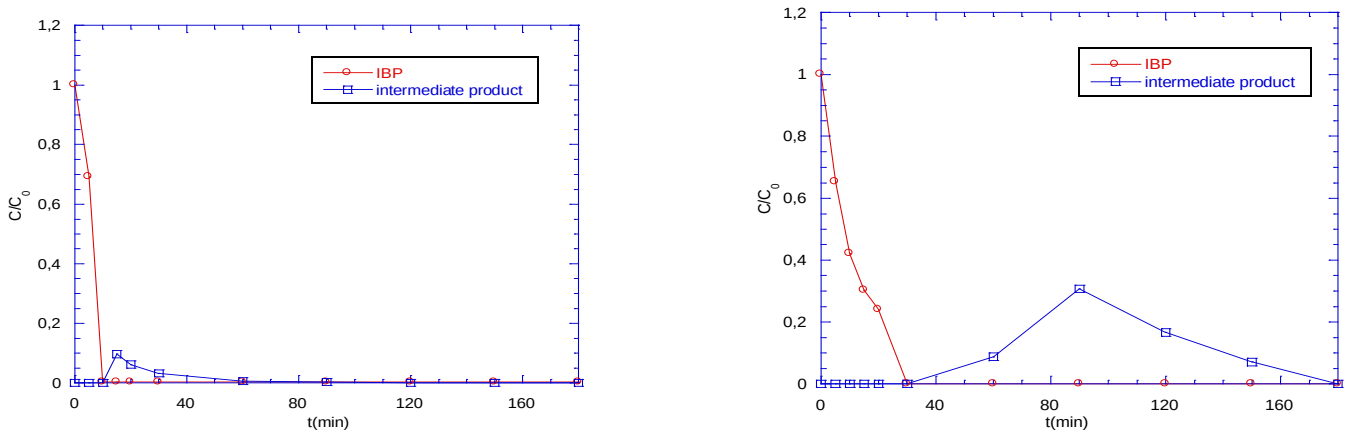


Figure 7: Chemical oxygen demand of IBP during 150min of US, UV irradiations and UV+US (pH=5.2, $20mg.L^{-1}$, Pc=49.8 W and 500kHz, UV (25W and 254nm))(◊) UV, (□) US, (●) UV+US

The COD removal was higher in combined process than sonolysis and photolysis. The maximum COD removal of 70, 2 % was observed for UV+US process.

The formation of more hydrophilic substrates explains the low efficiency of the ultrasonic action for COD removal. Several works have clearly indicated that in water sonochemistry, the efficiency of the HO• radical scavenging of an organic compound is related to its hydrophobicity.

In both cases (UV + US and US only), it is interesting to note that after complete degradation of IBP, a new intermediate products appear, with different retention times close to IBP ones (15.4 min). Figure 8 shows that degradation of IBP leads to the formation of other intermediate products that has not been identified, before leading to degradation for both processes (US figure 8.a) and (UV/US figure 8.b).



(a) **(b)**

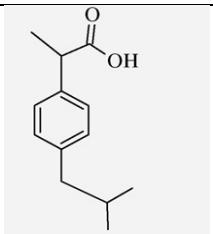
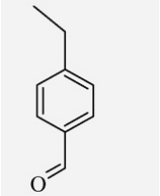
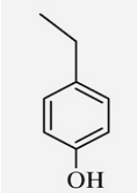
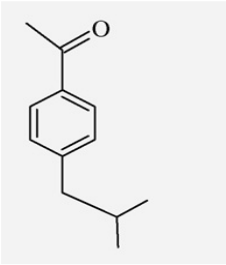
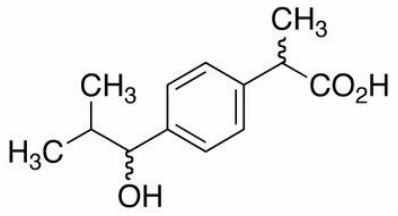
Figure 8: a) Sonolysis US: 500kHz, ultrasonic power=80W and b) sonophotolysis US: 500kHz, ultrasonic power=80W + UV= 25W of IBP (formation of intermediate products) ([IBP]=$20mg.L^{-1}$, T=25°C, pH=5.2)

Quantification and complete mass balance of all degradations are very difficult to analyze, whatever the operating conditions. Some information is missing, e.g. identification of some intermediate products. Thus, the

decision was taken to propose an original evaluation method, formulating the degradation product concentrations in an "equivalent COD". On this basis, the following facts were set forth:

- Each compound can be quoted in a COD value. This value was measured by a calibration prior to the degradation tests. It will be measured for all compounds identified by their retention times: IB, 4-Ethylbenzaldehyde, 4-Ethylphenol, 1-Hydroxyibuprofen, 4-Isobutylacetophenone. Values obtained by experimental measurements on a synthetic solution were compared in the theoretical COD.
- The global amount of COD is the sum of all the compounds, whether or not they are identified. Therefore, the residue consists of the COD of all unknown compounds, hereinafter referred to as "others".

Table 3: Degradation products identified for IBP during sonolysis.

	Products	Retention time (min)
	 Ibuprofen	15.6
1	 4-ethylbenzaldehyde	8.1
2	 4-ethyl phenol	5.8
3	 4-isobuthylacetophenone	2.1
4	 1-hydroxy Ibuprofen	3.2

A final experimental degradation of IBP at 20 mg.l^{-1}was carried out by 500 kHz ultrasound at 49.8 W and pH=5.2. Then, degradation of Ibuprofen took place, with samples taken every 30 min for 2 hours. For each sample, the following measurements were taken:

- global Chemical Oxygen Demand (COD)
- Analysis by HPLC, giving the concentration of the degradation product identified at various retention times: IB, 4-Ethylbenzaldehyde, 4-Ethylphenol, 1-Hydroxyibuprofen, 4-Isobutylacetophenone.

Then, all concentrations are converted into their equivalent COD, and the difference between the sum of the COD from the identified compounds and the global COD measured at a given time is used to calculate the COD of the "others". The results give the histogram shown in figure 9. After 30 min of sonication, it is interesting to note that, nearly all of IBP has been removed, degradation is not complete and the 4 main degradation products are present: 4-Ethylbenzaldehyde, 4-Ethylphenol, 1-Hydroxyibuprofen, 4-Isobutylacetophenone, with a preponderant percentage of 4-Ethylbenzaldehyde. These compounds are representative of organic content after 30 min. After this time, the presence of 4-Isobutylacetophenone is constant, 4-Ethylbenzaldehyde continues to decrease, while 4-Ethylphenol and 1-Hydroxyibuprofen disappear. Except in rare cases, organic content will consist of non-identified compounds, which seem to undergo a lower degradation rate.

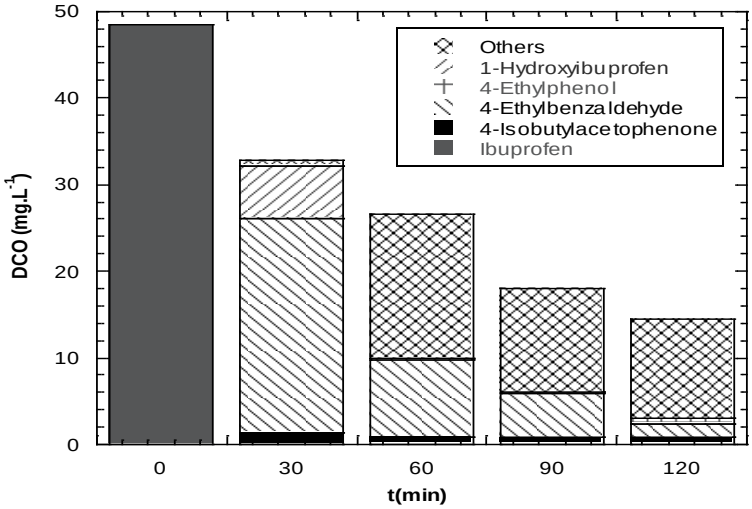


Figure 9: Chemical oxygen demand of IBP and intermediate products during sonolytic treatment (pH=5.2, 20mg.L^{-1}, Pc=80 W and 500kHz)

Conclusion

Degradation of ibuprofen in water by ultrasonic irradiation was investigated and compared with a treatment by UV irradiation and a sonophotolytic process.

The study has shown that IBP is effectively eliminated under ultrasonic irradiation (500 kHz) and was more efficient than photolytic treatment. The degradation rate increased proportionally as ultrasonic power increased from 10 to 80 W. The extent of degradation was inversely proportional to the initial concentration of substrate. The initial sonolytic degradation rate of IBP at different concentrations shows that, the higher the substrate concentration, the higher the initial decomposition rate. IBP sonochemical degradation in water occurs mainly through reactions with hydroxyl radicals at the bubble/solution interface.

A combination of UV and ultrasonic treatments leads to a significant enhancement of the IBP degradation rate. In this case, the higher rate of hydrogen peroxide formation may account for the results. The most favorable condition for degradation was observed at pH 5.2.

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