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Sonolysis and sono-Fenton oxidation for removal of ibuprofen in (waste) water

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A B S T R A C T

Two sonochemical processes were compared for the removal of ibuprofen in different water matrixes (distilled water and effluent from wastewater treatment plant). The effect of various operating parameters, such as pH (2.6–8.0), ultrasound power density (25–100 W/L), sonication frequency (12–862 kHz), addition of radical promoters (H₂O₂ and Fenton's reagent) or scavengers (*n*-butanol and acetic acid), was evaluated.

Sono-degradation of ibuprofen followed a first-order kinetic trend, whose rate constant increased with ultrasound density and frequency. For this hydrophobic and low volatile molecule, a free-radical mechanism at the bubble interface was established. Coupling ultrasound with Fenton reaction showed a positive synergy, especially in terms of mineralization yield, while adding H₂O₂ alone had no significant beneficial effect. Dedicated experiments proved this synergy to be due to the enhanced regeneration of ferrous ions by ultrasound.

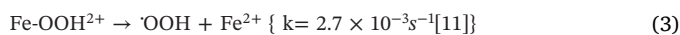
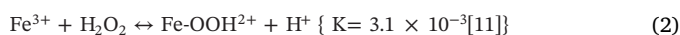
Efficacy of the sonolysis process was hampered in wastewater matrix, mainly as the consequence of higher pH increasing the molecule solubility. However, after convenient acidification, sono-Fenton oxidation results remained almost unchanged, indicating no significant radical scavenging effects from the effluent compounds.

1. Introduction

Ibuprofen (IBP) (2-[4-(2-methylpropyl)phenyl]propanoic acid) is a common drug used to treat fever, pain, inflammation or minor injury, its annual consumption being about 200 tons/year [1]. IBP can enter the environment through domestic, farming (intensive livestock production and aquaculture) and industry routes [2]. Several studies reported the presence of IBP in effluents from wastewater treatment plants (0.002–95 µg/L), in surface water (0.01–0.4 µg/L) and in drinking water (0.0002–0.0013 µg/L) [3,4], proving the inability of actual treatment processes to completely remove this compound, as well as its persistence in the environment. Notwithstanding its medicinal use, IBP was shown to significantly affect the growth of several fishes, microorganisms, algae, bacterial and fungal species [5,6]. Furthermore, partial degradation of IBP might be dangerous since its transformation products can be more toxic [7]. Therefore, the development of water treatment processes for the conversion of IBP into innocuous compounds (small organic acids and/or CO₂ and H₂O) is needed.

To date, advanced oxidation processes (AOPs) are among the most efficient treatments for the elimination of pharmaceutical contaminants

in water [2]. AOPs are characterized by the formation of highly reactive and non-selective hydroxyl radicals ([•]OH) which are able to mineralize almost all organic compounds. Among these, Fenton oxidation is very appealing due to its simplicity in generating [•]OH. Homogeneous Fenton oxidation (Eq. (1)) is based on the reaction between ferrous ions (Fe²⁺) and hydrogen peroxide (H₂O₂) under acidic condition [8]. This reaction is characterized by a rapid degradation of organic compounds in the early stage of the process involving ferrous ions, followed by a much slower oxidation by Fe³⁺/H₂O₂ [9].



Its main limitation is indeed due to the uneasy regeneration of Fe²⁺ (Eqs. (2) and (3)) that may cause wastage of expensive H₂O₂ reagent [12]. Furthermore, high iron salt concentrations (10–500 mg/L) – well above discharge limit (2 mg/L) – are normally needed to gain appreciable conversion and mineralization [10,13]. Such high concentrations can lead to techno-economic issues related to the formation of excessive Fe(III) hydroxide sludge and continuous loss of iron especially in large

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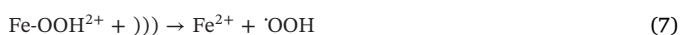
scale operation.

Ultrasound (US) is another promising AOP because it does not require any chemical addition and it is able to degrade organic pollutants through direct thermolysis (Eq. (4), in case of volatile compound) and/or $\cdot\text{OH}$ attack (Eqs. (5) and (6)). Sonication generates compression and rarefaction cycles, thus cavitation bubbles are formed from nuclei and then collapse violently producing localized shock waves (temperature of around 5000 °C and pressure of 500 atmospheres during a few microseconds) [14,15]. Such phenomenon gives rise to a pyrolytic cleavage of the molecules (including water) inside the bubble and to chemical reactions with the generated radicals at the bubble interface and/or in the liquid bulk.



where)) refers to the ultrasound irradiation

However, a low mineralization efficiency and a high energy consumption are the main drawbacks when US is used as single treatment [16]. Thus, it is more interesting to combine US with another AOP, for instance Fenton reaction [13]. Theoretically, coupling US irradiation and Fenton oxidation (in the so-called sono-Fenton or US/Fenton process) can promote faster pollutant conversion/mineralization due to (i) higher generation of $\cdot\text{OH}$ (Eqs. (1) and (5)) [17], (ii) improved mixing and contact between $\cdot\text{OH}$ and pollutant [13,16], and (iii) enhanced regeneration of ferrous ions (Eq. (7)) [18].



Several works have investigated the coupling of ultrasound and Fenton oxidation for the elimination of various organic compounds such as dyes, phenolic compounds and pesticides [13,19,20], and more recently pharmaceuticals [21–23]. However, to our knowledge, this latter mechanism (Eq. (7)) was not fully established.

The aim of this work is to investigate IBP removal by sonolysis, Fenton oxidation and coupled ultrasound/Fenton oxidation process. The effects of sonication parameters and Fenton's reagent dosage are also addressed, as well as the influence of real water matrix.

2. Material and methods

2.1. Chemicals and solvents

IBP ($\text{C}_{13}\text{H}_{18}\text{O}_2$, purity 99.99%) was purchased from BASF Corporation and used as received. The physicochemical properties of IBP are listed in Table 1. Hydrogen peroxide (H_2O_2) solution 30% w/w, monopotassium phosphate (KH_2PO_4), sodium phosphate dibasic dehydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$), potassium iodide (KI), titanium tetrachloride (TiCl_4), sodium sulfite (Na_2SO_3) and iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were obtained from Sigma-Aldrich.

2.2. Experimental set-up

Experiments were performed in a 1 L glass reactor, whose jacket

Table 1
Physicochemical properties of ibuprofen.

Properties	
Molecular weight	206.29 g/mol
Molecular size	1.3 nm × 0.6 nm [24]
Log Kow	3.97 [1]
pKa	4.9 (carboxylic group) [25]
Solubility in water	21 mg/L at 25 °C [26]
Henry's law constant	1.5×10^{-7} atm.m ³ /mol [27]
Vapor pressure	1.18×10^{-8} atm at 25 °C [28]

Table 2
Characteristics of sonication equipment.

Properties	Equipment		
	1	2	3
Supplier	Sonics & Materials, Inc.	SinapTec	Meinhardt Ultraschalltechnik
Model	VCX750	NexTgen Inside 500	E/805/T/M
Frequency (kHz)	20	12	580–862
Max nominal power (W) ^a	180	200	250
Max calorimetric power (W) ^b	131	156	32
Applied power (W) ^c	25, 50, 100	50	12.5
Liquid volume (mL)	1000	1000	250
Applied D_{US} (W/ L) ^d	25, 50, 100	50	50
Probe diameter (mm)	51	35	40
Applied I_{US} (W/ cm ²) ^e	1.2, 2.5, 4.9	5.2	1

^a Nominal power displayed on generator.

^b Dissipated power measured by calorimetry[29].

^c Power used in experiments.

^d Ultrasound density: applied power/liquid volume[14].

^e Ultrasound intensity: applied power/probe surface area[14].

was connected to a cooling thermostat in order to maintain the temperature (25 ± 2 °C). The reactor was stirred by a pitched-blade impeller. US probe was mounted at the bottom of the reactor (cup horn type) and direct continuous sonication of the solution was applied. Several ultrasonic devices were used in this study (Table 2). However, as shown in literature, calorimetric power can be used as reference for comparison of their results [16,29,30]. In addition, most of the experiments were carried out with equipment 1 since 20 kHz is a most common US frequency, which had already been successfully applied for such purpose [10,13]. It is also worth mentioning that a preliminary study indicated same sonochemical performance with various probe diameters (51 mm vs 35 mm).

20 mg/L IBP aqueous solution was prepared by dissolving IBP under vigorous stirring for 10 h in either distilled water or effluent from a municipal wastewater treatment plant (cf. Section 3.3). As above-mentioned, concentration of IBP in water bodies of the environment is usually of tens of ng/L to tens of µg/L. However considering that application of AOPs is more economical for high contaminant loadings [31,32], as well as to achieve enough analytical precision, 20 mg/L of IBP (just below the molecule solubility) was used as initial concentration. For the Fenton-related experiments, the pH of the solution was adjusted to 2.6 with H_2SO_4 (1 M solution), prior to the simultaneous addition of iron salt and H_2O_2 to start the reaction. For the US-related experiments, sonication was applied from the starting of the reaction. During the experiments several samples were withdrawn (of 1 and 8 mL for HPLC and TOC analyses, respectively) and were immediately treated by 1 mL of phosphate buffer (mixture of KH_2PO_4 0.05 M and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ 0.05 M) before HPLC analysis or 3 mL of quenching solution (mixture of phosphate buffer, KI 0.1 M and Na_2SO_3 0.1 M) before TOC analysis to stop the reaction by precipitating dissolved iron (buffer) and/or reducing remaining oxidant (KI/ Na_2O_3 mixture) [33]. The iron precipitate was removed on a 0.45 µm RC syringe filter prior to analyses of pollutant concentration.

Several experimental runs were duplicated to check for the reproducibility of concentration-time profiles of IBP and Total Organic Carbon (TOC) and the experimental errors were estimated by pooled standard deviations. The observed deviation was less than 5% for IBP and TOC concentration.

2.3. Analysis

IBP concentration was measured by liquid phase chromatography with UV detection at $\lambda = 222$ nm (PDA detector, Thermo Finnigan). Separation was performed on a C18 reverse phase column (ProntoSIL C18 AQ 5 μm , 250 \times 4 mm) maintained at 40 $^{\circ}\text{C}$. The mobile phase consisted in a mixture of acetonitrile and water (acidified with phosphoric acid at 0.1% v/v) fed in isocratic mode (60/40) at 1 mL/min. Samples were readily injected in the chromatograph after buffer treatment and filtration. Injection volume was set to 20 μL .

Total organic carbon (TOC) concentration was obtained from the difference between total carbon (TC) and inorganic carbon (IC) measured by a TOC analyzer (TOC-L, Shimadzu Corp.). In this case, samples were diluted by twofold with ultrapure water after addition of the quenching solution and filtrated. Injection volume was set to 50 μL and 400 μL for TC and IC, respectively.

Residual concentration of H_2O_2 was determined by titanium tetra-chloride method [34].

3. Results and discussion

The first series of experiments, described in Section 3.1 and 3.2, were performed using IBP solutions prepared in distilled water (DW). The matrix effect is addressed in Section 3.3.

3.1. Sonolysis (US)

3.1.1. Mechanism of IBP degradation under sonication

Under ultrasound irradiation (sonolysis), organic compounds can be degraded in three different zones, *i.e.* inside cavitation bubbles by thermolysis (Eq. (4)) and/or in the bubble interface and/or in the bulk solution by free radical attack (Eqs. (5) and (6)), depending on the volatility and the hydrophobicity of the molecule [29,35]. According to its low volatility and low water solubility (see Table 1), IBP degradation mechanism may correspond to a radical attack at the bubble surface. In order to confirm this hypothesis, two types of radical scavengers, namely *n*-butanol and acetic acid, were added to the IBP solution before 20 kHz sonolysis: *n*-butanol is a short chain alcohol with only partial solubility in water ($\log K_{ow} = 0.88$) known to be an effective $\cdot\text{OH}$ scavenger for the gaseous region and/or the interfacial region of the collapsing bubble [22,36], while fully miscible acetic acid ($\log K_{ow} = -0.17$) reacts with $\cdot\text{OH}$ in the solution bulk [37]. As shown in Fig. 1, addition of *n*-butanol and acetic acid (at 50 mM or 500 times the molar concentration of IBP) reduced the pollutant conversion from 48% after 3 h to 8% and 40%, respectively. Therefore, sono-degradation of IBP is mainly due to $\cdot\text{OH}$ attack at the liquid-bubble interface.

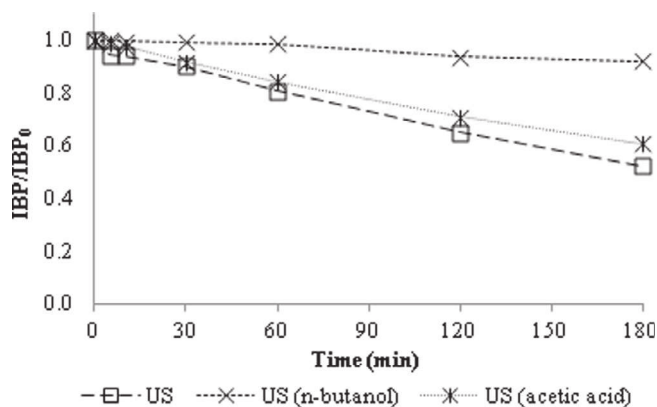


Fig. 1. Effect of radical scavenger on IBP sonolysis. ($[\text{IBP}]_0 = 20$ mg/L in DW, $\text{pH}_0 = 4.3$ (natural), $T = 25$ $^{\circ}\text{C}$, $f_{US} = 20$ kHz, $D_{US} = 50$ W/L, $[\text{scavenger}]_0 = 50$ mM).

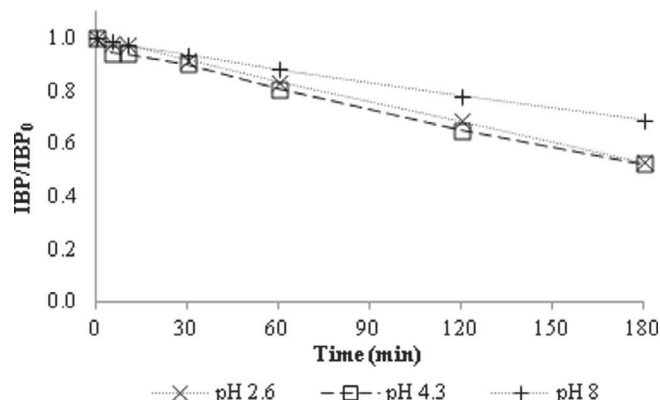


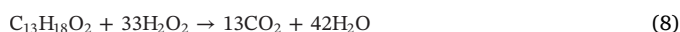
Fig. 2. Effect of the solution pH on IBP sonolysis. ($[\text{IBP}]_0 = 20$ mg/L in DW, $\text{pH}_0 = 2.6-8$, $T = 25$ $^{\circ}\text{C}$, $f_{US} = 20$ kHz, $D_{US} = 50$ W/L).

3.1.2. pH effect

The pH of IBP solution, initially at 4.3, was also adjusted before sonolysis to 2.6 and 8.0 with H_2SO_4 and NaOH (1 M solution), respectively. The aim was to mimic pH condition of the Fenton reaction on the one hand, and pH of the wastewater effluent on the other hand. Lowering the pH did not modify IBP degradation rate, but a significant reduction (from 0.0035 min^{-1} to 0.0020 min^{-1}) was observed at the alkaline value (Fig. 2). It can be explained by the different forms of IBP at a given pH. As the pK_a of its carboxyl group is 4.9, IBP is in molecular form at pH 2.6 and 4.3, but fully deprotonated at pH 8.0. In ionic form, IBP should be less accumulated at the surface of the cavitation bubbles, where radical attacks mainly occurred. This result is also in agreement with previous studies on the sonolysis of ibuprofen [27], diclofenac [38], dicloxacilin [39], paracetamol [21,40] and sulfadiazine [22] conducted at high sonication frequency (300–862 kHz), that showed a reduction of the degradation rate at a pH value higher than the pK_a of the molecule.

3.1.3. Effect of H_2O_2 addition on sonolysis

The stoichiometric amount of H_2O_2 required for IBP mineralization was calculated according to Eq. (8):



Under silent conditions, addition of two times (2 \times) the stoichiometric amount of H_2O_2 did not result in any measurable IBP and H_2O_2 conversion within 3 h at pH 4.3 or 8.0 and did not modify pH.

However, H_2O_2 is expected to be decomposed by US and/or to react with $\cdot\text{H}$ generated by water sonolysis (Eq. (5)) thus generating additional $\cdot\text{OH}$ (Eqs. (9) and (10)) [41,42].



Formed $\cdot\text{OH}$ can degrade organic compounds (Eq. (6)), but also react with H_2O_2 (especially when in large excess) (Eq. (11)) [22,34,41] or recombine with different radicals (Eqs. (12)–(16)) [23,27,43].



At natural pH, addition of two times the stoichiometric amount of H_2O_2 (6.4 mM) did not modify IBP sono-oxidation rate, while a slight decrease was observed at seven times (7 \times) the stoichiometric amount

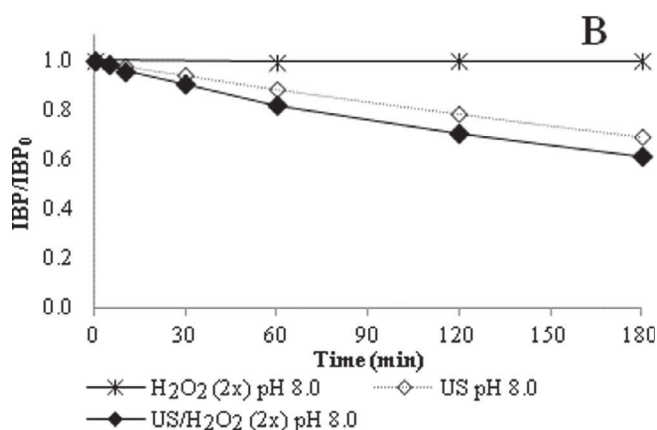
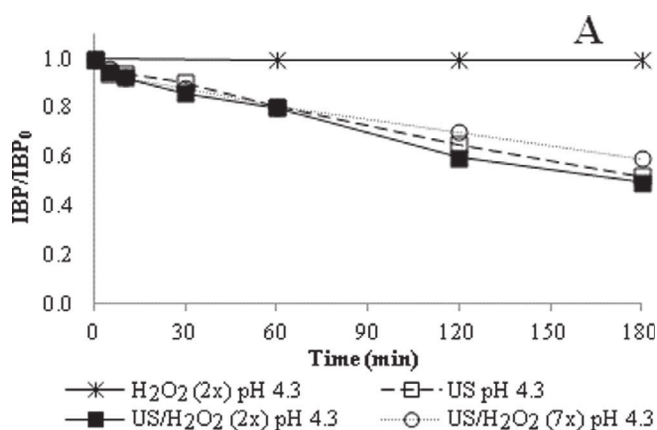


Fig. 3. Effect of H_2O_2 addition on IBP removal under US irradiation: (A) $\text{pH}_0 = 4.3$ and (B) $\text{pH}_0 = 8.0$ ($[\text{IBP}]_0 = 20 \text{ mg/L}$ in DW, $T = 25^\circ\text{C}$, $f_{\text{US}} = 20 \text{ kHz}$ with $D_{\text{US}} = 50 \text{ W/L}$ under sonication, $[\text{H}_2\text{O}_2]_0 = 0\text{--}22.4 \text{ mM}$).

of H_2O_2 (22.4 mM) of oxidant (Fig. 3A). These results confirmed those of some previous studies reporting no effect [34] or even a detrimental effect of H_2O_2 [44] for hydrophobic compounds and low frequency US.

The existence of different reaction zones for IBP (bubble surface) and H_2O_2 (bulk solution) could be hypothesized to explain why H_2O_2 did not help the pollutant degradation under US irradiation [44], while its scavenging effect at high concentration (Eq. (11)) could explain the results observed at 22.4 mM. However, no decomposition of H_2O_2 was measured at the lowest concentration, excluding the first mechanism.

On the other hand, at alkaline pH, H_2O_2 sonolysis did occur (5% conversion) and accelerated the pollutant oxidation (Fig. 3B), although not reaching the degradation yield observed at pH 4.3.

3.1.4. Effect of ultrasound operating parameters

3.1.4.1. Effect of ultrasound power density (D_{US}). Three levels of ultrasound power density (D_{US}) – 25, 50 and 100 W/L – were tested during 180 min, corresponding to a specific energy (E_{US}) of 270, 540 and 1080 kJ/kg, respectively. As shown in Fig. 4A, the degradation rate of IBP increased with increasing D_{US} in the investigated range. This is the consequence of higher number of collapsing bubbles that enhanced the formation of $\cdot\text{OH}$. An optimum value of D_{US} should be expected, due to bubble cloud formation on the emitter surface absorbing or scattering the sound waves above a critical value [45], but due to the limitation of our ultrasonic equipment it could not be attained. Calculated first-order rate constants were as follows: $k_{25\text{W/L}} = 0.0024 \text{ min}^{-1}$ ($R^2 = 0.992$), $k_{50\text{W/L}} = 0.0035 \text{ min}^{-1}$ ($R^2 = 0.996$), $k_{100\text{W/L}} = 0.0048 \text{ min}^{-1}$ ($R^2 = 0.994$), showing however that the positive effect of D_{US} already levelled off (Fig. 4B).

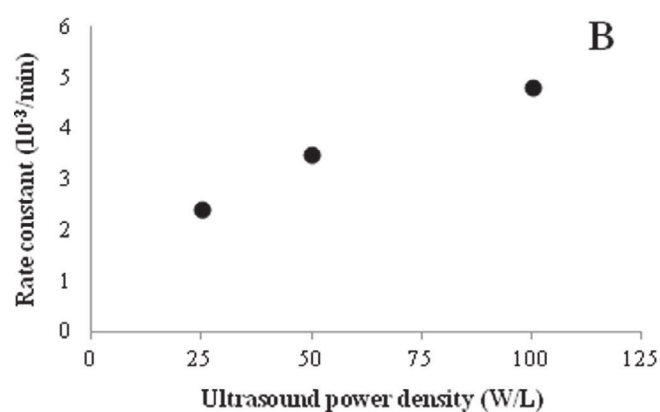
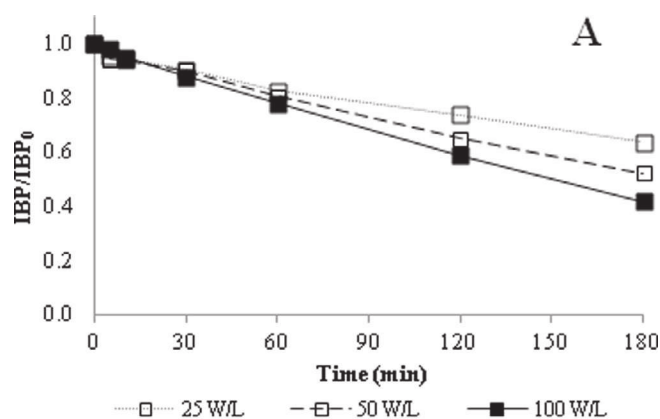


Fig. 4. Effect of ultrasound density on IBP sonolysis: (A) concentration-time profile and (B) first-order rate constant ($[\text{IBP}]_0 = 20 \text{ mg/L}$ in DW, $\text{pH}_0 = 4.3$, $T = 25^\circ\text{C}$, $f_{\text{US}} = 20 \text{ kHz}$, $D_{\text{US}} = 25\text{--}100 \text{ W/L}$).

3.1.4.2. Effect of sonication frequency (f_{US}). The influence of frequency on sonochemistry is complex. Cavitation threshold increases and cavities appear to release less energy upon collapse at high frequency ($> 100 \text{ kHz}$), but fewer acoustic cycles are required for the bubbles to reach their resonant size (which means more cavitation events) [46]. Moreover, more radicals should escape before being recombined due to a more rapid collapse [47]. Therefore, high frequency is usually preferred for sonochemistry applications. Indeed, according to Fig. 5, IBP removal after 180 min was increased from 48% to 87% when increasing f_{US} in the 20–862 kHz range. Degradation rates followed a first-order kinetic trend with: $k_{20\text{kHz}} = 0.0035 \text{ min}^{-1}$ ($R^2 = 0.996$), $k_{580\text{kHz}} = 0.0084 \text{ min}^{-1}$ ($R^2 = 0.984$) and $k_{862\text{kHz}} = 0.0102 \text{ min}^{-1}$ ($R^2 = 0.959$). Close values obtained at 580 and 862 kHz could be explained by similar $\cdot\text{OH}$ effective production rate (evaluated from H_2O_2 concentration monitoring), as reported by Güyer and Ince with analogous equipment [38]. An optimal frequency for radical-mediated sonolysis was also observed by these authors as a consequence of abovementioned antagonist effects at high frequency.

Interestingly, audible frequency (12 kHz) was also able to slightly degrade IBP (16% after 3 h, $k_{12\text{kHz}} = 0.0008 \text{ min}^{-1}$, $R^2 = 0.968$). Corresponding H_2O_2 generation rate was $0.18 \mu\text{M/min}$ ($R^2 = 0.928$) with respect to $0.45 \mu\text{M/min}$ ($R^2 = 0.940$) for 20 kHz irradiation, confirming the similar evolution of H_2O_2 generation and IBP degradation rates.

In all cases, TOC removal was low: 2%, 7%, 10% and 11% under 12, 20, 580 and 862 kHz irradiation, respectively. It could indicate that more hydrophilic degradation products were formed during sonication, as for instance *n*-hydroxyl-ibuprofen ($\log K_{\text{ow}} = 2.25$) [48,49].

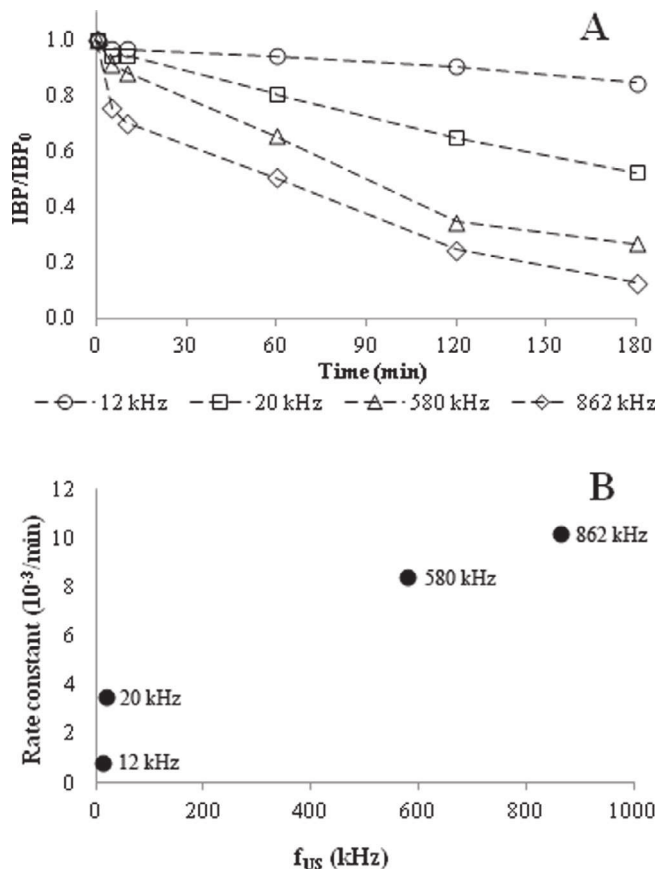


Fig. 5. Effect of sonication frequency on IBP sonolysis: (A) concentration-time profile and (B) first-order rate constant ($[IBP]_0 = 20$ mg/L in DW, $pH_0 = 4.3$, $T = 25$ °C, $f_{US} = 12$ –862 kHz, $D_{US} = 50$ W/L).

3.2. Homogeneous sono-Fenton oxidation process

3.2.1. Effect of Fenton's reagent concentration and 20 kHz US

In order to evaluate the effect of ultrasound irradiation on homogeneous Fenton oxidation, Fenton experiments were first conducted under silent conditions. Two concentration levels of Fenton's reagent were applied with molar ratio of H_2O_2/Fe set to 48: $[H_2O_2] = 3.2$ mM and $[Fe^{2+}] = 0.067$ mM (referred to as F(-)), $[H_2O_2] = 6.4$ mM and $[Fe^{2+}] = 0.134$ mM (F(+)). It is worth noting that iron concentrations used in this study (3.75–7.5 mg/L) were below the classical range (between 10 and 500 mg/L) [10,13].

Under silent conditions, the Fenton reaction (F) proceeded in two distinct steps (Fig. 6A): first a fast oxidation yielding up to 60% conversion of IBP within 5 min; then, a much slower degradation rate until the end of the reaction, which cannot be fitted either with first or second order kinetics. This behavior is consistent with that reported in previous studies on homogeneous Fenton oxidation of IBP [50,51]. At higher iron concentration (0.5–1 mM Fe), the authors observed 90% of IBP degradation in the first 5 min. The initial reaction stage corresponded to the fast $\cdot OH$ generation from reaction between ferrous ions and H_2O_2 (Eq. (1)). Then, formation of stable ferric complexes, such as $Fe-OOH^{2+}$ (Eqs. (2) and (3)), hindered Fe^{2+} regeneration and further radical generation. In the low concentration range investigated, increasing Fenton's reagent was found beneficial (no scavenging effect from H_2O_2 or Fe^{2+}).

Coupling Fenton reaction with 20 kHz ultrasound (US/F) led to a clear enhancement of IBP degradation rate after the first 5 min of reaction (Fig. 6A). At low reagent concentration, full abatement of IBP was observed in US/F(-) process after 3 h vs. only 62% in F(-). At high reagent concentration, application of US reduced the time needed for 95% IBP degradation from 180 to 60 min.

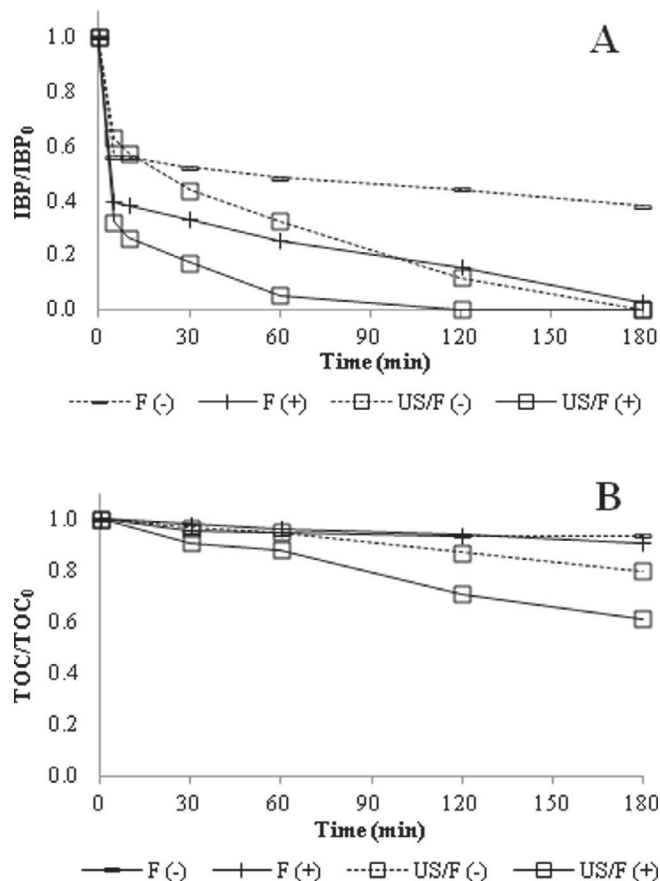


Fig. 6. Fenton (F) and sono-Fenton oxidation (US/F) of IBP: evolution of (A) pollutant and (B) TOC concentration ($[IBP]_0 = 20$ mg/L in DW, $pH_0 = 2.6$, $T = 25$ °C, $f_{US} = 20$ kHz with $D_{US} = 50$ W/L under sonication, (-): $[H_2O_2] = 3.2$ mM and $[Fe^{2+}] = 0.067$ mM, (+): $[H_2O_2] = 6.4$ mM and $[Fe^{2+}] = 0.134$ mM).

TOC removal was also significantly improved by the process coupling, but a much slower reaction rate indicated that more refractory degradation products were formed during the oxidation (Fig. 6B). At best conditions, US/F(+) achieved 40% TOC conversion within 180 min, vs. 10% or less for each of the separate process (cf. Section 3.1.4 for sonolysis).

Moreover, H_2O_2 consumption at the end of Fenton (F(+)) and sono-Fenton (US/F(+)) oxidation was 13% and 44%, respectively. Higher amount of residual oxidant confirmed a lower overall activity of the Fenton catalytic system under silent conditions. Indeed, beyond additional radicals generated from water sonolysis (Eq. (5)), positive synergistic effect observed in the combined process could be ascribed to the sono-regeneration of ferrous ions, as illustrated by Eq. (7) [18].

In order to confirm such effect, a complementary experiment was conducted. Same amounts of H_2O_2 and ferrous salt as in F(+) experiment were mixed into 100 mL of acidic distilled water (pH 2.6) during 60 min to pre-form the expected $Fe-OOH^{2+}$ complex. Fenton oxidation was then started by addition of this solution into 900 mL of IBP solution. The system was let under stirring for 180 min (silent Fenton oxidation), then sonication was applied for another 180 min period (sono-Fenton oxidation). In this case, only 4% of IBP was converted within 5 min (Fig. 7) vs. 60% for the standard Fenton oxidation procedure (Fig. 6A). The time-concentration profile of the pollutant also exhibited two different stages, with an IBP removal yield almost plateauing at 20–25% after 90 min. Ultrasound application at $t = 240$ min immediately accelerated IBP oxidation, the first-order rate constant ($k = 0.0102$ min⁻¹, $R^2 = 0.978$) being three times higher than for the sole sonolysis (cf. Section 3.1.4, $k = 0.0035$ min⁻¹).

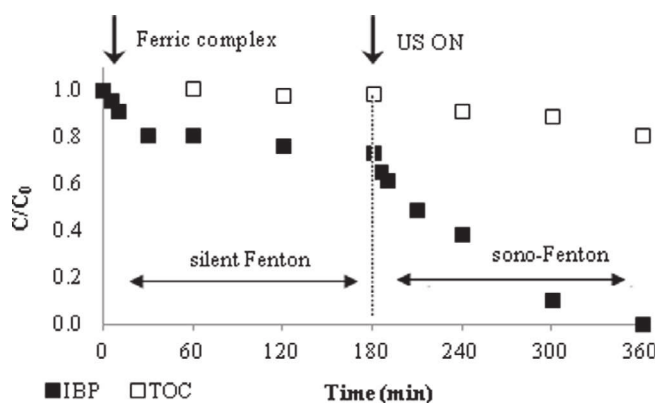


Fig. 7. Effect of sonication on Fenton catalyst regeneration. ($[IBP]_0 = 20$ mg/L in DW, $pH_0 = 2.6$, $T = 25$ °C, $f_{US} = 20$ kHz with $D_{US} = 50$ W/L under US, $[H_2O_2] = 6.4$ mM and $[Fe^{2+}] = 0.134$ mM).

3.2.2. Effect of ultrasound operating parameters

To achieve appreciable TOC removal, the highest concentration of Fenton's reagent was applied for the study of ultrasonic parameters: $[H_2O_2] = 6.4$ mM (twice the stoichiometric amount) and $[Fe^{2+}] = 0.134$ mM.

3.2.2.1. Effect of ultrasound power density (D_{US}). As abovementioned, high ultrasound power density (D_{US}) promotes higher formation of $\cdot OH$ and thus improves degradation rate and efficiency of sonolysis process (Section 3.1.4). Nonetheless, the effect of D_{US} on sono-Fenton oxidation process has been scarcely investigated. Siddique and coworkers [19] reported that degradation of dye by homogeneous sono-Fenton oxidation increased from 60% to 75% with increasing ultrasonic intensity from 4 W/cm² (40 W/L) to 8 W/cm² (80 W/L). In the present study, the effect of ultrasound power density on sono-Fenton oxidation process was evaluated at 25 W/L, 50 W/L and 100 W/L (figure not shown). Time-concentration profiles of IBP were found similar on the whole D_{US} range. Conversely, varying D_{US} from 25 to 50 W/L improved TOC removal from 29% to 39%, but further increase to 100 W/L did not show additional benefit. This observation suggests the existence of optimum D_{US} for sono-Fenton process.

3.2.2.2. Effect of ultrasound frequency (f_{US}). Despite growing interest for sono-Fenton process in the literature, information about optimum US frequency is still scarce, because previous studies [10,13,23] usually operated at a single value (in the 20–40 kHz range). Sonochemical effects being suspected in the enhanced ferrous iron regeneration, two high US frequencies (580 and 862 kHz) were investigated. An audible frequency (12 kHz) was also applied since this frequency is rarely used

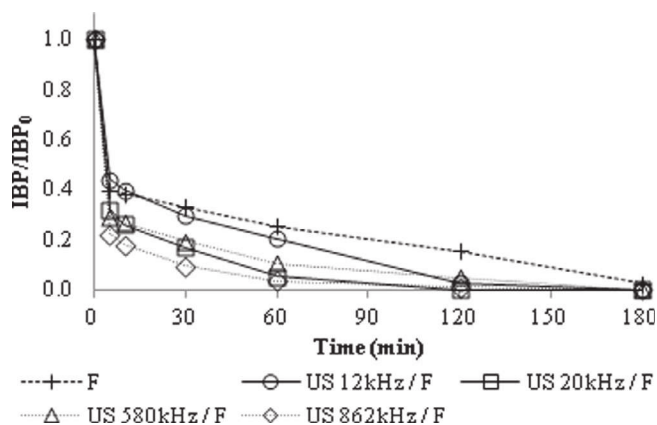


Fig. 8. Effect of sonication frequency on sono-Fenton oxidation of IBP: evolution of pollutant concentration ($[IBP]_0 = 20$ mg/L, $pH_0 = 2.6$, $T = 25$ °C, $f_{US} = 12$ –862 kHz with $D_{US} = 50$ W/L under sonication, $[H_2O_2] = 6.4$ mM and $[Fe^{2+}] = 0.134$ mM).

in sono-Fenton process. Experimental operating conditions were set to 20 mg/L IBP, 6.4 mM H_2O_2 , 0.134 mM Fe, pH 2.6 and temperature 25 °C.

Fig. 8 revealed that degradation rate of IBP increased with increasing sonication frequency, but the differences were mostly marked between 12 and 20 kHz. Likewise, TOC abatement was also favored at high frequency: 25% at 12 kHz vs. 48% at 862 kHz (after 3 h of reaction). The mineralization results are comparable to that obtained in previous studies on sono-Fenton oxidation of IBP (55% in 240 min) performed with high frequency ultrasound (300 kHz) and low molar ratio of H_2O_2/Fe (0.3) [52], and on sono-enzymatic degradation of IBP (37% in 60 min) using low frequency ultrasound (37 kHz) and horseradish peroxidase enzyme [53].

3.3. Effect of real water matrix

Sonolysis and homogeneous sono-Fenton oxidation processes were shown to be promising methods for the removal of IBP in water. However, all the experiments that have been done so far were conducted in distilled water (DW). In order to investigate the efficiency in real application, some experiments with a real wastewater matrix (WW) were performed. Wastewater consists in a complex mixture of organic and inorganic compounds, such as nutrients, salts and many substances that could influence the outcome of advanced oxidation processes [54]. For instance, the presence of organic (humic acid, fulvic acid, etc.) and inorganic compounds (chloride, carbonate, bicarbonate, and phosphate ions) in WW may hamper Fenton reaction by scavenging $\cdot OH$ and/or forming iron complex [26,55]. On the other hand, phenolic compounds that WW may contain could reduce ferric ion to ferrous ion and thus enhance Fenton reaction [55].

According to recent reviews on hybrid processes [56,57], AOPs are recommended in combination with membrane filtration as post-treatment of biological process for destruction of refractory organics in concentrate stream. Such hybridization allows the AOPs to reach appreciable mineralization level in relatively short oxidation time, and to save chemicals and energy.

In this study, water samples taken after biological treatment of a municipal wastewater treatment plant located in Nailloux village (France) were used to prepare the IBP solution (at 20 mg/L). Table 3 shows the physicochemical characteristics of this effluent. After addition of IBP, TOC concentration increased to 25 mg/L, IBP being the major organic compound in this matrix. The amount of carbonate and bicarbonate was evaluated from inorganic carbon (IC) analysis and the measured concentration level (29.4 mg/L) could be high enough to scavenge $\cdot OH$ at neutral and alkaline pH [58]. On the other hand, the initial iron concentration (< 0.05 mg/L) appeared too low to effectively contribute to Fenton oxidation mechanism.

Matrix effect is evaluated for sonolysis (US), homogeneous Fenton (F) and sono-Fenton (US/F) oxidation in Fig. 9. The treatment efficiency in distilled water (DW) was also recalled for comparison purpose. As usual, the initial pH of DW and WW was set to 2.6 (using H_2SO_4) for the Fenton and sono-Fenton oxidation runs, while the pH of WW was not

Table 3
Physicochemical properties of the WW.

Parameters	
pH	8
Turbidity (NFU)	1
BOD (mg/L)	< 2
COD (mg/L)	< 30
TC (mg/L)	39.2
IC (mg/L)	29.4
TOC (mg/L)	9.8 (25 ^a)
Total Fe (mg/L)	< 0.05

^a After the addition of IBP.

processes for pharmaceutical containing wastewaters.

4. Conclusion

The objective of this work was to study ibuprofen removal by sonolysis and sono-Fenton process. $\cdot\text{OH}$ -mediated oxidation at the bubble surface was proved as the main degradation mechanism in the pollutant sonolysis. Combination of homogeneous Fenton oxidation with US irradiation was found to be more effective than the sum of individual processes, especially in terms of mineralization yield. The sono-regeneration of ferrous ions from ferric complex could explain this positive synergy, which yielded up to 50% of TOC removal in 3 h with a low concentration of Fenton's reagent (especially an iron concentration below 10 mg/L). In real wastewater effluent, sonolysis was hampered mainly due to alkaline pH conditions increasing the pollutant solubility. Preliminary acidification could maintain the efficiency of Fenton and sono-Fenton oxidation.

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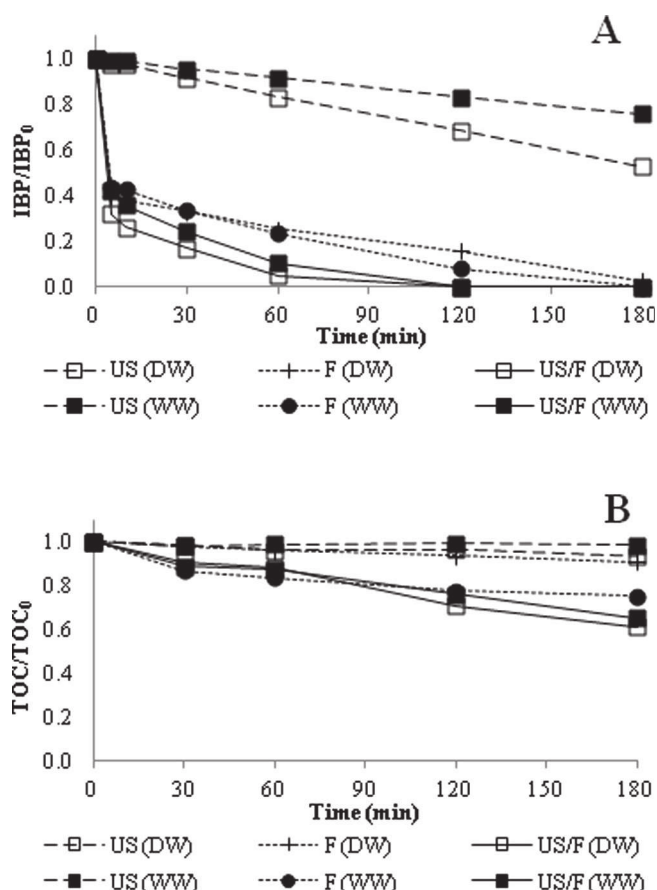


Fig. 9. Effect of water matrix (DW: distilled water, WW: wastewater effluent) on sonolysis (US), Fenton (F) and sono-Fenton (US/F) oxidation of IBP: evolution of (A) pollutant and (B) TOC concentration ($[\text{IBP}]_0 = 20 \text{ mg/L}$, $\text{pH}_0 = 2.6$ except for US in WW ($\text{pH}_0 = 8.0$), $T = 25 \text{ }^\circ\text{C}$, $f_{\text{US}} = 20 \text{ kHz}$ with $D_{\text{US}} = 50 \text{ W/L}$ under US, $[\text{H}_2\text{O}_2]_0 = 6.4 \text{ mM}$ and $[\text{Fe}^{2+}] = 0.134 \text{ mM}$ for F and US/F).

adjusted for sonolysis.

Degradation of both IBP and TOC by ultrasound was significantly hampered in WW. Lower IBP removal in WW (24% vs. 48% in DW after 180 min) could be mainly explained by a pH effect, the initial pH of the IBP solution varying from 4.3 to 8.0 whether prepared with DW or WW, respectively. As abovementioned (see Section 3.1.2.), pH value of 8.0 indeed reduced the sono-degradation of IBP to 31% in DW by increasing the molecule solubility. Competition or scavenging effects from organic and/or inorganic compounds of WW thus seemed to have only a minor effect.

After preliminary acidification to 2.6, time-concentration profiles of IBP during Fenton oxidation were almost superimposed for the two matrixes, while a slight decrease was observed for sono-Fenton process when in WW (Fig. 9A). Therefore, it seems to confirm that IBP didn't strongly compete for radicals with the organic molecules present in WW, and that iron complexation and free-radical scavenging were not significantly increased in this matrix. In particular, inorganic carbon content was almost totally converted into carbonic acid and CO_2 .

Moreover, overall TOC removal by Fenton oxidation was improved in WW (25% vs. 9%, Fig. 9B). Fenton oxidation test without IBP proved this result to be mainly the consequence of more readily oxidized organic compounds in WW (50% TOC removal). However, similar behavior was not observed in sono-Fenton oxidation. This might be due to selective effect of acoustic cavitation towards specific organic molecules [59] and complex interplay between iron and WW compounds (and/or their oxidation intermediates) somewhat hampering sono-regeneration of Fe^{2+} .

All these results showed Fenton and sono-Fenton oxidation as

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