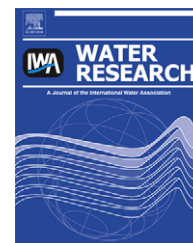


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Mineralization enhancement of a recalcitrant pharmaceutical pollutant in water by advanced oxidation hybrid processes

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ARTICLE INFO

Article history:

Received 5 February 2009

Received in revised form

18 June 2009

Accepted 22 June 2009

Published online 4 July 2009

Keywords:

Ibuprofen

TiO₂

Photo-Fenton

Sonolysis

Advanced oxidation process
hybrid systems

ABSTRACT

Degradation of the biorecalcitrant pharmaceutical micropollutant ibuprofen (IBP) was carried out by means of several advanced oxidation hybrid configurations. TiO₂ photocatalysis, photo-Fenton and sonolysis – all of them under solar simulated illumination – were tested in the hybrid systems: sonophoto-Fenton (FS), sonophotocatalysis (TS) and TiO₂/Fe²⁺/sonolysis (TFS). In the case of the sonophoto-Fenton process, the IBP degradation (95%) and mineralization (60%) were attained with photo-Fenton (FH). The presence of ultrasonic irradiation slightly improves the iron catalytic activity. On the other hand, total removal of IBP and elimination of more than 50% of dissolved organic carbon (DOC) were observed by photocatalysis with TiO₂ in the presence of ultrasound irradiation (TS). In contrast only 26% of mineralization was observed by photocatalysis with H₂O₂ (TH) in the absence of ultrasound irradiation. Additional results showed that, in the TFS system, 92% of DOC removal and complete degradation of IBP were obtained within 240 min of treatment. The advanced oxidation hybrid systems seems to be a promising alternative for full elimination/mineralization for the recalcitrant micro-contaminant IBP.

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1. Introduction

Several pharmaceutical compounds have been recently found in surface waters (rivers, lakes, sea, etc.), as a consequence of the high amount present and incomplete removal in wastewater treatment plants (WWTP) (Klaviaroti et al., 2009). The non-steroidal anti-inflammatory drug (NSAID) ibuprofen (IBP) is a pharmaceutical pollutant found in effluents of WWTPs. IBP is partially removed in the WWTP and its main metabolite forms – carboxy and/or hydroxyl IBP – remain after biological

treatment as toxic by-products affecting the aquatic environment (Weigel et al., 2004; Richards and Cole, 2006). Generally in WWTP the isolation, separation and conventional transformation processes are carried out consecutively in order to diminish the concentration of the contaminants progressively. The NSAIDs are only partially degraded in WWTP by oxidants such as O₃, H₂O₂, permanganate, etc. However the application of those oxidants has been shown to produce by-products more toxic than the original compounds such as chlorinated by-products of diclofenac, from treatment

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doi:10.1016/j.watres.2009.06.059

with ClO_2 (POSEIDON project, <http://poseidon.bafg.de/servlet/is/2884/>). On the other hand, several reports of ozonation treatment for NSAID have been successful with results in removal (more than 90%), however only slight increases have been observed in systems like $\text{O}_3\text{-H}_2\text{O}_2$ (Zwiener and Frimmel, 2000; Ternes, 2003; Huber, 2003). The application of physico-chemical steps, like filtration, flotation, coagulation, has shown only limited removal of NSAIDs due to the high solubility of most of the pharmaceutical compounds. By flotation, 20–45%, 10–25% and 10–30% of diclofenac, IBP and naproxen have been eliminated, respectively; and, by use of coagulants only the separation of 50–70% of diclofenac has been possible. In general coagulants like Ag_2SO_4 or FeCl_3 have shown a poor efficiency in removal. IBP has been not eliminated under any condition of additive or temperature as reported recently (Suarez, 2008). On the other hand, the separation by active carbon has showed to be a good option for separation, especially if this process is combined with membranes in the named Cristal[®] process, successfully probed in the USA (Sydner, 2005). Moreover, even though nano-filtration and reverse osmosis have been shown to eliminate 100% of the presence of pharmaceutical compounds, those techniques require a post-destructive process increasing the operation costs. The application of activated sludge is able to treat considerable amounts of contaminated water, however the presence of recalcitrant pharmaceutical compounds has resulted in the inactivation of several microbiologic processes in the activated sludge, reducing the effectiveness of the WWTPs. Pharmaceutical compounds are not a carbon source, but also are present as inhibitors of biological activity. Moreover, in the case of NSAIDs, it has been demonstrated that biological degradation produces the hydroxyl and carboxy-metabolites. Therefore the risk always exists of releasing more toxic compounds into surface waters such as lakes or rivers. On the last basis, due to the NSAIDs being compounds that are recalcitrant to biological oxidation, it is imperative that new ways for the degradation of these compounds be found to diminish the concentration of those compounds with novel techniques, reaching the highest levels of mineralization and/or promoting less toxic by-products than the parent compounds. The advanced oxidation processes (AOPs) appear as non-conventional techniques able to strengthen the oxidation ability of recalcitrant compounds. The AOPs are oxidative processes applied for the treatment of contaminants in water, soils and air, based on the presence and reactivity of the hydroxyl radical ($\cdot\text{OH}$) generated in atmospheric or subcritical conditions of temperature and pressure with or without a catalyst and/or reactive energy (electrochemical, UV-vis or ultrasounds) (Méndez-Arriaga, 2009). AOPs have been shown to be efficient for the degradation of several organic compounds by hydroxyl radical ($\cdot\text{OH}$) attack. However, even if the application of AOPs can be effective in the treatment of pharmaceutical pollutants in water, some dissolved organic carbon (DOC) removal is observed and the toxicity of the by-products increases after treatment (Méndez-Arriaga et al., 2008a).

In previous studies, we showed that IBP has been completely removed by using several AOPs: TiO_2 photocatalysis (Méndez-Arriaga et al., 2008b), photo-Fenton (Méndez-Arriaga et al., 2007) and sonolysis (Méndez-Arriaga et al., 2008c). It seems that

hydroxylation is the principal mechanism in IBP degradation by electrophilic addition of the $\cdot\text{OH}$ in the isobutyl or propionic moieties of IBP. The hydroxylation process of IBP implies its ability to react with hydroxyl radicals (Aruoma and Halliwell, 1988; Hamburger and McCay, 1990; Bilodeau et al., 1995; Halliwell et al., 1995; Patricio et al., 1999) but poor mineralization is concomitantly also observed. Thus the application of ultrasonic irradiation to 0.087 mM IBP solution finished with a slight 8% of DOC removal after 240 min of treatment (Méndez-Arriaga et al., 2008c). In the case of heterogeneous photocatalysis the maximum DOC removal was 17% for an initial IBP concentration of 0.87 mM employing 1 mg L^{-1} of TiO_2 irradiated during 240 min (Méndez-Arriaga et al., 2008b). Alternatively the photo-Fenton reaction applied to 0.87 mM of IBP leads a DOC removal between 30 and 40% depending on the H_2O_2 concentration (Méndez-Arriaga et al., 2007).

On the other hand, the AOP treatment can improve the mineralization of recalcitrant compounds by the use of sequential or simultaneous AOP hybrid configurations, for example, the solar O_3/TiO_2 systems against anionic surfactants (Oyama et al., 2009), TiO_2 and iron with artificial UV-vis irradiation against citric acid (Quici et al., 2005), etc. Regarding sonophotocatalysis, there exists large information on the treatment of contaminants such as BPA (Torres-Palma et al., 2008a), formic acid (Gogate et al., 2002) and dyes (Kritikos et al., 2007; Berberidou et al., 2007). The hybrid system formed by sonolysis and iron, in dark or illuminated processes (sonofenton or sonophoto-Fenton respectively), has also been reported for the treatment for phenols (Nagata et al., 2000), dyes (Joseph et al., 2000) or BPA (Torres-Palma et al., 2008b). The increase in the removal of organic compounds corresponds to the higher amount of reactive species promoted by the combination of AOPs than that generated with individual techniques. In addition, an increase in the overall mineralization efficiency is observed.

The objective of this investigation was to evaluate the removal efficiency of IBP through three AOP hybrid systems (sonophotocatalysis with TiO_2 , sonophoto-Fenton and sonophotocatalysis with $\text{TiO}_2 + \text{Fe}^{2+}$). The combination of AOPs appears to be a good strategy to improve the mineralization degree of the recalcitrant pharmaceutical micropollutants.

2. Reagents, experimental devices and analytical procedures

IBP (2-[3-(2-methylpropyl) phenyl] propanoic acid), in its sodium salt form, was purchased from Sigma and used as received. Initial concentrations of IBP were under its solubility limit between 0.016 and 0.039 mM. TiO_2 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 were Degussa P-25, Sigma and Panreac brand respectively. Potassium iodide and ammonium molybdate salts, for spectrophotometric determination of H_2O_2 (Torres-Palma et al., 2008c), were both Panreac brand and employed without previous treatment. Water for the preparation of the solutions was Millipore quality. Oxygen purge was Carbagas. The pH adjustment, to pH 3, was carried out with concentrated solutions of sulfuric acid and sodium hydroxide (obtained from Fluka and Merck respectively).

Fig. 1 shows the Suntest (for UV–vis irradiation) and the cavitation-producer tank (for ultrasonic irradiation). Six hundred milliliters of initial concentration of IBP were placed in the ultrasonic tank together with the corresponding catalyst (TiO_2 , Fe^{2+} or both) and reflowed to the Suntest. In the Suntest, a xenon arc lamp was employed, as source of UV–vis emission, for irradiation of three Pyrex photoreactors (150 mL of total irradiated volume), placed perpendicularly to the lamp. The dissolution was recycled to the ultrasonic tank in batch operation mode. Temperature was controlled through its cooling jacket at 25 °C. The source of ultrasound irradiation was a piezoelectric disc (diameter 4 cm) fixed at the bottom of the tank. Ultrasonic power was adjusted to 80 W while the frequency was fixed to 300 kHz. The ultrasound energy dissipated in the reactor in the form of heat was 41%, estimated by the calorimetric method (Mason et al., 1992). In the absence of ultrasonic irradiation, the H_2O_2 was injected by an external automatic syringe. The dosage of added hydrogen peroxide was $2.15 \mu\text{mol L}^{-1} \text{min}^{-1}$, equivalent to the amount produced with the ultrasound device in the aerated substrate free water. In order to keep saturated solutions with oxygen, the purging gas started 20 min before the experiments began. In the case of sonophotocatalysis, TiO_2 was added 30 min after gas purging. Simultaneous starting of UV–vis irradiation and ultrasound or H_2O_2 addition was considered as the initial time of the reaction.

The samples were withdrawn at different time intervals, and IBP concentration, DOC and H_2O_2 were followed during the degradation process. An isocratic flow of acetonitrile (Fisher Chemicals)/acetic acid 1% (Fluka) (60/40, v/v) was the mobile phase for the quantification of IBP in HPLC (Shimadzu LC-2010A) with a column SunFire TM C18 3.5 μm , at 25 °C, 50 μL injection and recorded at 220 nm. After filtration of samples, DOC measurements were obtained from a Shimadzu TOC-VCSN instrument operated in NPOC mode. H_2O_2 was analytically determined by the spectrophotometric method

with KI (0.1 mol L^{-1}) and ammonium molybdate salt as catalyst (0.01 mol L^{-1}). Aliquots taken from the reactor were immediately added in the sample quartz cell of the spectrophotometer (Shimadzu UV-1601) containing the reagents and absorbance at 350 nm was recorded after 120 s. All experiments were carried out at least three times.

3. Results and discussion

Table 1 summarizes the experimental conditions and results obtained (initial IBP degradation rates, DOC removal and residual H_2O_2 concentration). The nomenclature employed was as follow: T, presence of TiO_2 ; F, presence of iron ion from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ salt; S, under ultrasonic irradiation; H, external source of H_2O_2 , L, UV–vis illumination. All of the above processes mentioned were carried out under UV–vis irradiated conditions. The system SH was not considered because of the possible detrimental effect of excess H_2O_2 .

As in the previous test, photolysis and H_2O_2 did not show changes in the initial concentration or DOC. On the other hand, negligible dark adsorption of the IBP on TiO_2 was observed at pH 3, due to the unfavourable charge attraction between the TiO_2 and the molecular form of IBP.

3.1. Photo-Fenton vs. sonophoto-Fenton processes

A few reports are available regarding the treatment of pharmaceutical compounds by the combination of iron salt together with ultrasonic systems under UV–vis irradiated conditions. The major advantage of this hybrid system is the synergism between processes, sonolysis and photo-Fenton, promoting the photo-Fenton process by reaction of the H_2O_2 yielded by ultrasound. H_2O_2 comes from the recombination of radical species $\cdot\text{OH}$ and $\cdot\text{OOH}$ (Eqs. (1) and (2)), generated from homolysis of water after implosion of the acoustic cavitation

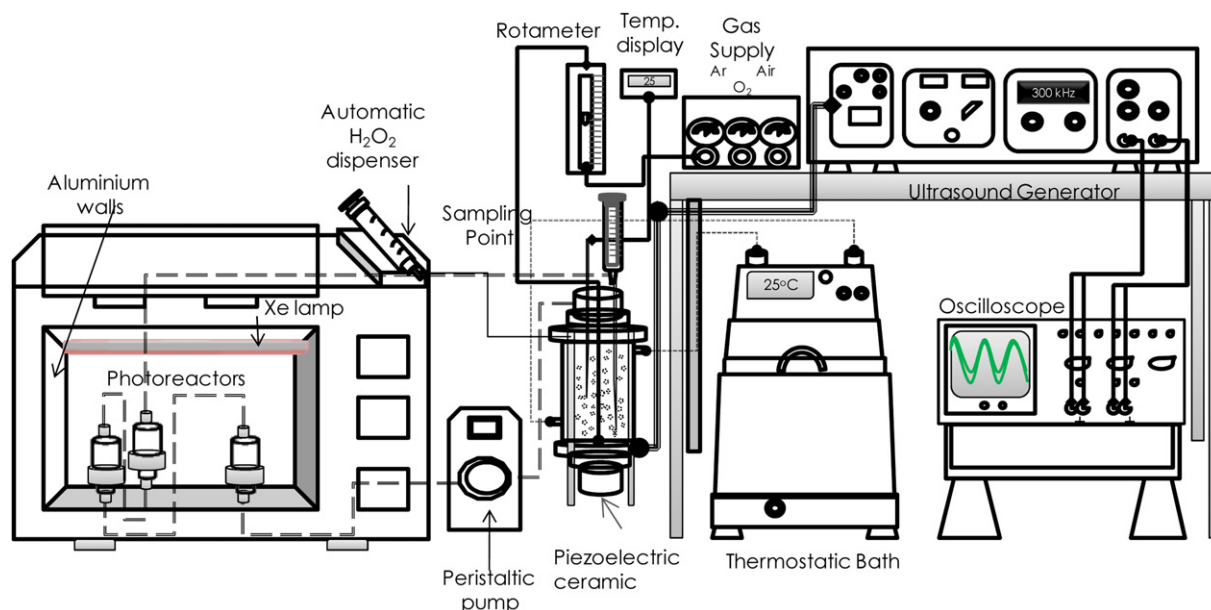


Fig. 1 – Experimental equipment and devices (SunTest for UV–vis irradiation, left, and sonolysis tank for ultrasound energy, right).

Table 1 – Initial IBP degradation rate, DOC removal and H₂O₂ residual for degradation at 240 min by advanced oxidation processes.

ID process	H ₂ O ₂ injected (μM min ⁻¹)	Fe(II) (mg L ⁻¹)	TiO ₂ (mg L ⁻¹)	Sonolysis frequency (kHz)/power (W)	Initial IBP (mM)	Initial IBP degradation rate (mM min ⁻¹)	DOC removal (%) (at 240 min)	H ₂ O ₂ residual (μM)
FS	–	100	–	300/80	0.039	4.46 × 10 ⁻³	55	30.01
FH	2.1	100	–	–	0.033	4.48 × 10 ⁻³	60	19.40
TS	–	–	10	300/80	0.032	1.84 × 10 ⁻³	55	92
TH	2.1	–	10	–	0.037	1.72 × 10 ⁻³	26	320
TFS	–	100	10	300/80	0.019	3.50 × 10 ⁻³	50, 76, 92 ^a	0
TFH	2.1	100	10	–	0.023	4.10 × 10 ⁻³	31, 79, 98 ^a	0
TF	–	100	10	–	0.016	0.69 × 10 ⁻³	18	–

All experiments at O₂ saturated conditions, pH 3, 25 °C and under UV–vis irradiative conditions. IBP initial concentration between 0.016 and 0.039 mM. T, presence of TiO₂; F, presence of iron ion from FeSO₄·7H₂O salt; S, under ultrasonic irradiation; H, external source of H₂O₂.

a Evaluated at 120,180 and 240 min of reaction respectively.

bubble. Thus, the accumulated H₂O₂ from water sonolysis is a new source of ·OH if iron is present by means of the Fenton reaction (Eqs. (3) and (4)).

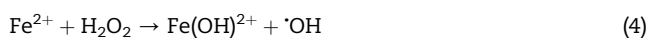
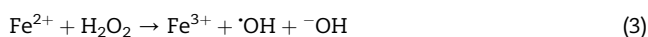


Fig. 2 shows the IBP degradation and the remained H₂O₂ in photo-Fenton (FH) compared with the sonophoto-Fenton (FS) processes. Fig. 3 shows the DOC degradation for the cases studied. From Fig. 2, it is possible to observe a strong similarity in the initial degradation rate in both processes. A marginal increase in the initial degradation rate is observed in FH. Other authors have reported similar behaviour in the degradation of phenol (Nagata et al., 2000) or BPA (Torres-Palma et al., 2008b) in analogous FS and FH experiments or major efficiencies in Fenton and sonolysis

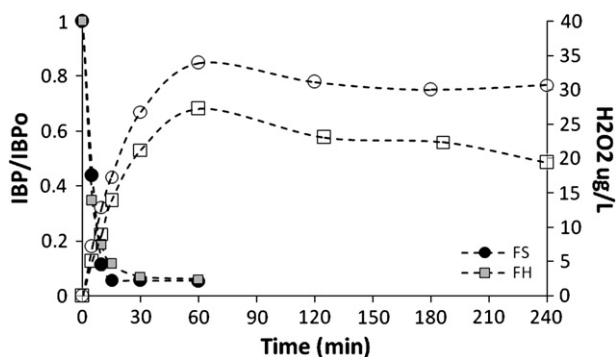
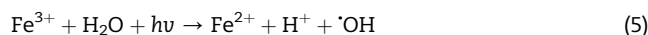


Fig. 2 – IBP degradation (filled symbols) and remaining H₂O₂ (empty dots) in photo-Fenton (FH) and sonophoto-Fenton (FS) processes.

individual processes. Moreover, Nagata et al. (2000) and Joseph et al. (2000) reported a high degradation rate increase depending on the iron concentration in both analogous FH and FS cases. Above an optimum concentration of reactant, a detrimental effect on the overall process is observed (Nagata et al., 2000; Joseph et al., 2000).

On the other hand, the DOC removal in both cases is favourable (around 67.5%) regarding the S and F individual processes (6 and 43% respectively) with a slight increase of 5% in the FH system as can be observed in Fig. 3. The removal was in relation to the final H₂O₂ remaining in the solution: an extra amount of 10 μmol/L of final H₂O₂ remains in FS compared with FH. Lesser reactivity of the FS system and higher consumption of H₂O₂ in the FH system were not expected. Although equal initial degradation rates of IBP were observed (4.46 and 4.48 mmol L⁻¹ min⁻¹ for FS and FH respectively), it is possible to ensure that the FS reaction does not contribute to increase in the DOC removal and FS is a less reactive process than FH. A possible formation of complex between iron and IBP by coordinate bond, which hinders the catalytic iron condition and decreases the DOC removal, cannot be suggested below the pK_a of IBP (4.9), because, under these conditions, IBP is present in a molecular form and no complex formation could be proposed. In FH the principal contribution of ·OH species comes from Eq. (3) and, under light, species of Fe³⁺ (Eq. (5)) or Fe(OH)²⁺ aquacomplex (Eq. (6)) also contribute to the generation of radical species.



On the other hand, during the sonolysis process three well-defined zones can be described: the cavitation bubble, the supercritical interface and the bulk of the solution. The reaction will take place in one of these zones according to the properties of the target compound, in particular the volatility and hydrophilic or hydrophobic characters. Volatile compounds are degraded mainly by pyrolysis inside the cavitation bubble and non-volatile substances are eliminated by ·OH in the interface bulk–cavitation bubble or in the solution

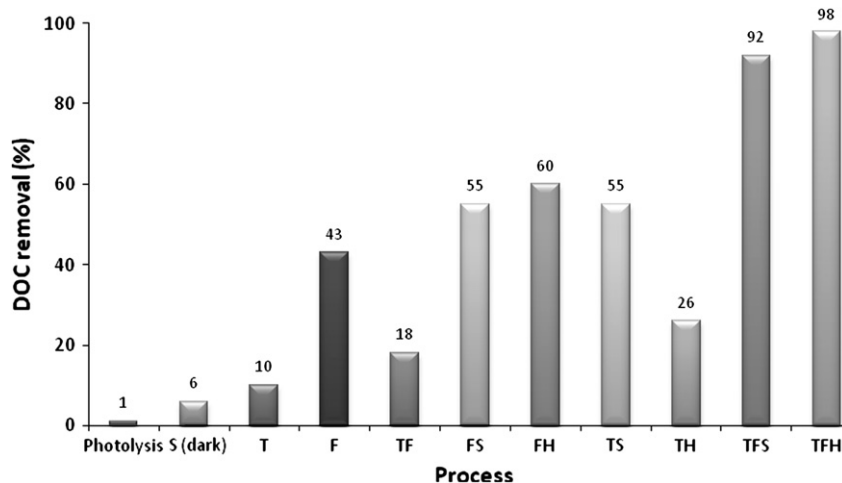
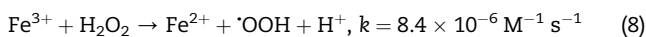
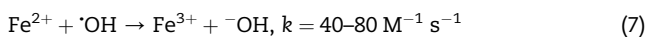


Fig. 3 – DOC removal at 240 min for systems tested.

bulk. IBP is a non-volatile compound and any degradation process by pyrolysis can occur (Méndez-Arriaga et al., 2008c). The IBP transformation will be in the gas–liquid interface and in the bulk of the solution, principally by free radical attack. However, in the FS process a detrimental reaction between Fe^{2+} and the $\cdot\text{OH}$ (rejected from the cavitation before $\cdot\text{OH}$ recombination) can take place and dominates the oxidation state of the metal. Interaction between the sonochemically thrower $\cdot\text{OH}$ and iron in solution could reduce the efficiency of sonolysis and, furthermore, promotes the formation of Fe^{3+} (Eq. (7)) and like Fenton controls the overall process.



The like Fenton reaction is several orders of magnitude slower than Fenton (De Laat and Gallard, 1999; Pignatello et al., 2006; Sires, 2006), and reaction (8) can become the rate-limiting step. Thus, the acoustic cavitation promotes the formation of Fe^{3+} and a deceleration in the DOC removal is observed. In turn, reaction (7) reduces the sonolysis efficiency. In FS, the loss of $\cdot\text{OH}$ by reaction with Fe^{2+} , previous recombination or attack against remaining DOC, produces similar mineralization as in the FH system. Moreover, FS promotes an accumulation of H_2O_2 with its further slow catalytic decomposition.

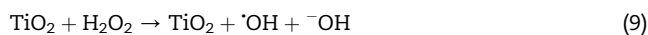
As before mentioned, Nagata et al. (2000) and Joseph et al. (2000) address the effect of the iron present on ultrasonic degradation of organic material. Moreover, an optimal concentration of iron is proposed and detrimental effects are reported if the amount of iron is higher than the optimal, due to precipitation of iron hydroxides. We suggest that parallel interactions between the $\cdot\text{OH}$, from bubble collapse and iron ion (previous recombination to yield H_2O_2), change the catalytic action of iron, without further radical formation and therefore FS does not promote a significant enhancement of the IBP degradation compared with FH.

3.2. Photocatalysis vs. the sonophotocatalytic process

The combination of heterogeneous photocatalysis (TiO_2 + UV-vis) and sonolysis (TS) showed a positive synergism in the degradation of organics as BPA, trichlorophenol, cuprophenyl yellow, phenyltrifluoromethyl-ketone, phenol, several azo dyes, dye wastewater, propane, ethanol, chlorophenol, formic acid, etc. (Gogate and Pandit, 2004; Torres-Palma et al., 2008a). However, under our knowledge, the hybrid system TS has not been applied for treatment of pharmaceuticals.

The advantages of the cavitation bubble on the heterogeneous photocatalysis and vice versa have been well explained by Torres-Palma et al. (2008a). The factors explaining the performance of the coupled system can be separated into two groups as follows:

1. Action of ultrasound toward photocatalysis
 - Increases the catalyst surface area due to the de-aggregation action of ultrasound.
 - Improves mass transfer of organic compounds between the liquid phase and the TiO_2 surface.
 - Reduces the charge recombination and promotes the production of additional $\cdot\text{OH}$ due to the residual H_2O_2 generated.
2. Action of photocatalysis toward ultrasound
 - Increases organic degradation due to the TiO_2 particles, providing extra nuclei for bubble formation.



In order to compare photocatalysis and sonophotocatalytic processes, H_2O_2 was introduced in the absence of ultrasound irradiation, at the same rate as it is generated by sonolysis. Fig. 4 shows the IBP degradation and the remaining H_2O_2 in enhanced photocatalytic (TH) and sonophotocatalytic processes (TS). Degradation of IBP (0.032 and 0.037 mM initial concentration) in both processes follows similar decay (degradation rate 1.84×10^{-3} and 1.72×10^{-3} for TS and TH

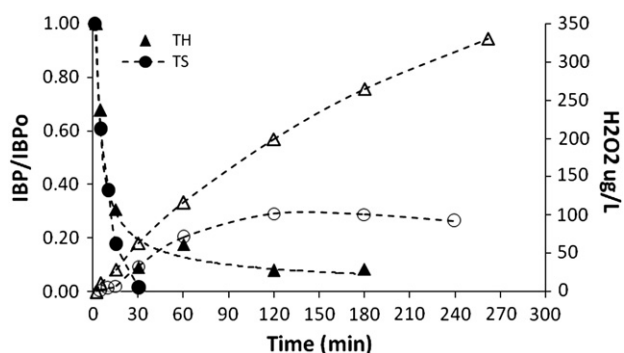


Fig. 4 – IBP degradation (filled symbols) and remained H₂O₂ (empty dots) in enhanced-photocatalysis (TH) and sonophotocatalysis processes (TS).

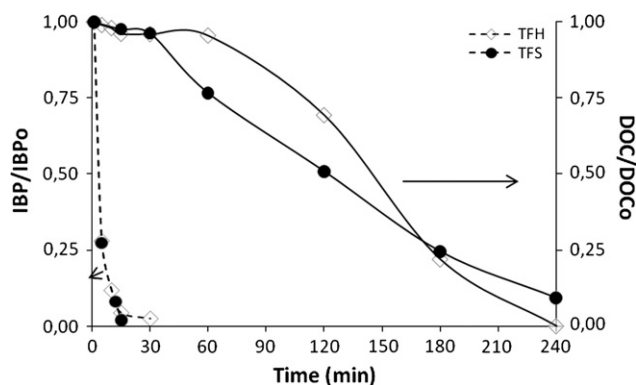


Fig. 5 – IBP degradation and DOC removal in presence of TiO₂ and Fe(II) as catalysts under illuminated conditions with (●) and without (◆) ultrasonic irradiation.

systems respectively). DOC removals for both systems are also included in Table 1. Almost twice DOC removal was observed in TS (55%) compared with the TH system (26%) and good correlation with the residual H₂O₂ is reached. Final H₂O₂ was measured at 4-fold lower in the TS system than in the TH process (Table 1). The sonolysis increases the mass transfer of the H₂O₂ to the catalyst and reaction (9) is highly favoured.

The TS improvement in the degradation of IBP is explained due to positive action on the catalyst of ultrasound irradiation and vice versa. Their relative contributions lead to more than 50% of IBP mineralization. As shown in Fig. 3 the individual processes reach only 6 and 10% of mineralization in S and T processes respectively. In an earlier report (Méndez-Arriaga et al., 2008b) it was explained that heterogeneous photocatalysis removed between 17 and 80% of IBP with 100 mg/L of catalyst. In the TS system, by using an amount of catalyst 10 times lower, total elimination of IBP and 55% of mineralization was reached in 240 min. Under TS systems the principal disadvantage of photocatalysis – the TiO₂ separation by filtration after treatment – could be avoided by using low amounts of catalyst, due to the innocuous properties of TiO₂ on bioreceptors.

3.3. TiO₂/Fe²⁺/H₂O₂ vs TiO₂/Fe²⁺/ultrasound processes

Sophisticated combined systems employing two catalysts (in homogeneous and heterogeneous forms) under ultrasonic and UV-vis for the degradation of pharmaceutical pollutants have not been reported in the open literature. Fig. 5 shows the IBP degradation and the remaining H₂O₂ in the sonobiphotocatalytic system (TFS) and the analogous ones TFH. In this case, the degradation of IBP, in both processes, increases with respect to the previous process tested. The initial degradation rate of IBP is much lower in the TFS system than that observed in TFH (3.5×10^{-3} and 4.1×10^{-3} for TFS and TFH respectively). The latter is related to that observed in Section 3.1. The like Fenton decelerates the photo-Fenton process. However 38% of extra DOC removal (see Fig. 5) is observed in TFS compared with TFH after 120 min of reaction. The final amount of residual H₂O₂ observed in both cases was zero (see Fig. 6), due to the presence of iron and TiO₂. Nevertheless the concentrations of DOC and H₂O₂ follow a different evolution as

shown in Figs. 5 and 6. In TFH a decrease in the overall efficiency of the DOC removal is observed specially within the 120 min of the reaction and the evolution of peroxide corresponds to the mineralization observed.

An evident accumulation of H₂O₂ is reached in the initial 90 min. However due to the gradual formation of the acid by-products, highly hydrophilic, taking place in the homogeneous phase, H₂O₂ is consumed after 120 min by photo-Fenton reaction and in heterogeneous phase this acid by-product suffers photo-decarboxylation on the catalyst surface by the photo-Kolbe reaction (Sato, 1983; Sanchez et al., 2004). In the case of TFS the amount of peroxide is always low due to constant consumption as an electron acceptor of the heterogeneous catalyst and as 'OH source in the photo-Fenton reaction. DOC removal is similar at 3 and 4 h of reaction, but for TFS, the 25% is reached in 60 min whereas similar DOC removal in TFH was observed within 120 min.

The hydrogen peroxide, as the source of the main radical reactive species in the AOPs tested, represents the key method of mineralization of IBP. This was confirmed by additional experiments in total absence of H₂O₂. The TF system showed a degradation rate of IBP ($0.69 \times 10^{-3} \text{ mM min}^{-1}$) and the scarce DOC removal of only 18%.

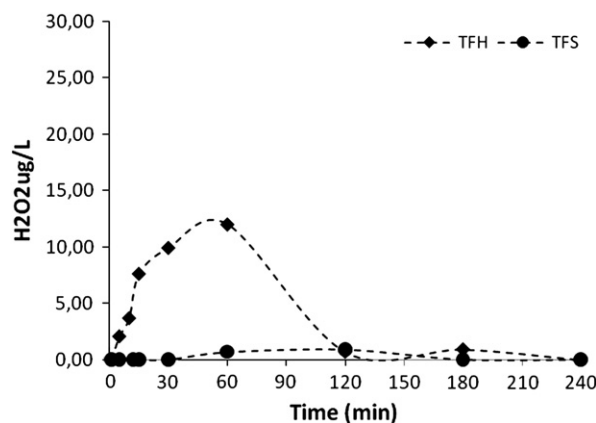


Fig. 6 – H₂O₂ concentration for TFS (●) and TFH (◆) hybrid configurations.

Table 2 – Initial IBP degradation rate, % DOC removal for degradation at 240 min by F, S and T processes

Individual process (initial IBP degradation rate, mM min ⁻¹), %DOC removal	Hybrid system (initial IBP degradation rate, mM min ⁻¹), %DOC removal	IBP removal qualitative effect	Mineralization qualitative outcome	Justification
F (1.72 × 10 ⁻³), 43	FS (4.46 × 10 ⁻³), 55	Synergic	Synergic	Promotion of Fenton reaction
S (2.00 × 10 ⁻³), 6	TS (1.84 × 10 ⁻³), 55	Non-synergic	Synergic	Photocatalytic reactivity enhance plus S improvement conditions
T (0.85 × 10 ⁻³), 10	TFS (3.50 × 10 ⁻³), 98	Non-synergic	Synergic	Strengthen of AOP by the useful presence of ·OH
All experiments at O ₂ saturated conditions, pH 3, 25 °C and under UV-vis irradiative conditions. IBP initial concentration between 0.024 and 0.044 mM.				

3.4. Cumulative or synergic effect of hybrid processes

In order to evaluate the qualitative cumulative/synergic effect of hybrid processes, the degradation of IBP by F, S and T individual processes were developed. Fig. 3 compares the percentage of DOC removed between each stand-alone process and the hybrid configurations, and Table 2 shows the initial IBP degradation rate, % DOC removal for degradation at 240 min by F, S and T processes. As can be observed in the case of FS, a synergic effect on IBP degradation is observed and also in mineralization due to the beneficial use of the H₂O₂ from S in the presence of iron in dissolution. The S alone process leads to non-reactive 269 μM residual H₂O₂ which is effectively reacted in the FS configuration. On the other hand, the system TS shows a non-synergic effect on the degradation of IBP (1.8 × 10⁻³ mM min⁻¹ for TS vs 2.00 × 10⁻³ and 0.85 × 10⁻³ mM min⁻¹ for S and T respectively). However, the final mineralization is highly synergic due to the eventual formation of hydrophilic by-compounds (such as carboxylic acids) following the reaction on the surface of the catalyst under enhanced photoreactivity in the presence of H₂O₂ from S.

Finally, in the TFS system the major beneficial application of the hybrid system is observed. Even a non-synergic effect on IBP elimination is observed, the highest mineralization of the compound is reached (98%) due to the increase of ·OH in all the phases of the suspension (hydrophilic and hydrophobic areas). Full degradation of IBP as well as the DOC in solution is the main character of the final treated water. The application of hybrid configurations is a real promising alternative not only to eliminate the concentration of recalcitrant pharmaceutical compounds but also their metabolites and subsequent by-products until well acceptable mineralization levels.

4. Conclusion

The presence of H₂O₂ plays an important role during the degradation of IBP in the hybrid systems tested. FH and FS degradation proceed at similar rates to that observed for IBP degradation and DOC removal. The FS does not enhance the IBP degradation because like Fenton is probably favoured over the photo-Fenton reaction.

Similar degradation was observed for IBP and TH by sonophotocatalysis. Moreover, DOC removal is higher in TS

and the residual H₂O₂ remained lower than in the TH case. Thus, the TS system has a positive synergic effect on the degradation of IBP. The presence of homogeneous and heterogeneous catalysts, under illuminated and ultrasonic irradiation, promotes the highest DOC removal (>90%). The TFS hybrid system has shown faster degradation of DOC and more efficient consumption of H₂O₂ than observed for the TFH system. Sonolysis increases the removal efficiency of IBP principally due to the tendency to concentrate in the interface of the cavitation where the highest amount of ·OH is reached.

Thus, hybrid systems seem to be a promising alternative to improve the mineralization of micro-contaminants.

Acknowledgments

Financial support from Spanish Ministry of Education and Science (CICYT Projects CTQ2004-02311/PPQ, CTQ2005-0446/PPQ and Consolider-Ingenio 2010 CSD2007-00055) is acknowledged. The authors thank University of Barcelona and École Polytechnique Fédérale de Lausanne for the grant given to accomplish this work.

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