



# Combined advanced oxidation processes for the synergistic degradation of ibuprofen in aqueous environments

Jagannathan Madhavan, Franz Grieser, Muthupandian Ashokkumar\*

Particulate Fluids Processing Centre, School of Chemistry, University of Melbourne, Grattan Street, Melbourne, 3010 VIC, Australia

## ARTICLE INFO

### Article history:

Received 14 December 2009

Received in revised form 11 January 2010

Accepted 12 January 2010

Available online 22 January 2010

### Keywords:

Sonolysis

Photocatalysis

Sono-Fenton

Sonophotocatalysis

Ibuprofen

## ABSTRACT

Ibuprofen (IBP) is a widely used analgesic and anti-inflammatory drug and has been found as a pollutant in aqueous environments. The sonolytic, photocatalytic and sonophotocatalytic degradations of IBP in the presence of homogeneous ( $\text{Fe}^{3+}$ ) and heterogeneous photocatalysts ( $\text{TiO}_2$ ) were studied. When compared with sonolysis and photocatalysis, a higher degradation rate was observed for sonophotocatalysis in the presence of  $\text{TiO}_2$  or  $\text{Fe}^{3+}$  and also a slight synergistic enhancement was found with a synergy index of 1.3 and 1.6, respectively. Even though  $\text{TiO}_2$  sonophotocatalysis showed an additive process effect in the mineralization, a significant synergy effect was observed for the sonophotocatalysis in the presence of  $\text{Fe}^{3+}$ . This might be due to the formation of photoactive complexes between  $\text{Fe}^{3+}$  and IBP degradation products, such as carboxylic acids. High performance liquid chromatography (HPLC) and electrospray ionisation mass spectrometry (ESMS) techniques were employed for the identification of the degradation intermediates. The sonication of IBP led to the formation of its mono- and di-hydroxylated intermediates. Apart from the hydroxylated intermediates, products formed due to the oxidation of propanoic acid and isobutyl substituents of IBP were also observed.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

The synthesis of a variety of drugs that have a pharmaceutical significance is important because they are useful for both mankind and animals. The major sources of environmental contamination are the continuous disposal of wastewaters released from the pharmaceutical industries, excretory products of medically treated humans and animals. Therefore, this has been increasingly recognized as an emerging environmental problem [1].

The compound 2-[3-(2-methylpropyl)phenyl] propanoic acid, commercially available as ibuprofen (IBP), is widely used as an anti-inflammatory and antipyretic drug especially prescribed for the treatment of fever, migraine, muscle aches, arthritis and tooth aches. Due to its widespread applications, several kilotons of ibuprofen has been synthesised world wide [2]. Industrial and domestic routes were identified as the major contamination pathways for IBP in aquatic environments [3]. Industrial pollution occurs because of the release of untreated effluents from the pharmaceutical companies whereas the domestic contamination is due to the use of IBP as a medicinal drug by human beings and animals. Therefore, IBP and its metabolized products enter into environmental water via sewage treatment plants. Sometimes,

the metabolites formed are more harmful than the parent organic compounds [4–6]. So, the treatment of these wastewaters is important before discharging them into the ecosystem. There are several advanced oxidation technologies available in the literature for the degradation of wastewater namely  $\text{TiO}_2$  photocatalysis, Fenton and photo-Fenton oxidation, electrolysis, sonolysis, ozonolysis, etc. [7,8].

Over the last few years, sonochemical treatment has been found to be one of the successful techniques for the degradation of organic pollutants [9–13]. Several studies have examined the sonochemical degradation of organic pollutants, such as pharmaceuticals, pesticides, dyes [1,11,14–17]. Although sonochemical degradation has been found to be efficient for environmental remediation purposes, complete mineralization of the organic material was not achieved in most of the cases [18,19] due to the hydrophilic nature of the degradation intermediates. Therefore, in order to overcome this problem, the sonochemical process is often combined with other advanced oxidation technologies like, ozonation,  $\text{TiO}_2$  photocatalysis and Fenton and photo-Fenton reactions [8].

The degradation of IBP by several oxidation processes has already been reported [20–25]. Mendez-Arriaga et al. [20] studied the  $\text{TiO}_2$  photocatalytic degradation of pharmaceutical compounds, such as diclofenac, naproxen and IBP. They have suggested that post-biological treatment was possible based on the biodegradability test of the treated IBP solutions. The same research group also studied the sonolytic degradation of IBP and showed that sonolysis

\* Corresponding author. Tel.: +61 3 93475180; fax: +61 3 83447090.  
E-mail address: [masho@unimelb.edu.au](mailto:masho@unimelb.edu.au) (M. Ashokkumar).

produced long-lived intermediates [21]. Although photocatalysis and sonolysis have been investigated separately for the degradation of IBP in aqueous medium, their combination in the presence of  $\text{TiO}_2$  or  $\text{Fe}^{3+}$  catalysts has become the main focus of current research. Hence, the homogeneous and heterogeneous sonophotocatalytic degradations of IBP using  $\text{Fe}^{3+}$  and  $\text{TiO}_2$  as photocatalyst, has been studied in the present investigation.

## 2. Experimental details

### 2.1. Experimental conditions

Sonolysis experiments were performed at an ultrasound frequency of 213 kHz in a continuous wave mode with a power output of 55 mW/mL. The ultrasound unit used was ELAC LVG-60 RF generator coupled with ELAC Allied signal transducer with a plate diameter of 54.5 mm. All reagents used were of AR grade and were used without further purification. Milli-Q water was used for the preparation of IBP (Sigma–Aldrich) solutions. Though IBP occurs at ng/L in surface water, we choose higher concentrations to check the feasibility of the sonolysis, photocatalysis and sonophotocatalysis systems. The sonolysis experiments were performed at natural solution pH (5.65).

During an hour of sonolysis, the pH of the solution changes from 5.65 to 4, this is lower than the pKa value of IBP (4.9). However, there was no significant change in the absorption spectra taken at pH 2.7, 4 and 5.65 and hence the pH was left uncontrolled during the reaction. Degussa P25  $\text{TiO}_2$  (surface area  $55 \text{ m}^2/\text{g}$ ) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (AR grade) were used as the photocatalysts. The temperature was maintained ( $20 \pm 2^\circ\text{C}$ ) by circulating cooling water through a jacket surrounding the cell. The volume of the solutions sonicated was 250 mL. Photo-irradiation was carried out by means of a Xenon arc lamp (450 W, Oriol).

All sonolytic, photocatalytic and sonophotocatalytic experiments were performed in the same experimental setup. The typical experimental procedure adopted for the heterogeneous photocatalytic degradation of IBP is described below. A desired concentration of IBP was prepared by dissolving an appropriate amount of IBP in 250 mL water and then a known amount of the  $\text{TiO}_2$  (1 g/L) was added to the IBP solution. The overnight dark adsorption experiments showed that there was a small change in the concentration due to dark equilibrium adsorption ( $\sim 9\%$  in 45 min) of IBP. In our previous study [26], a maximum photocatalytic degradation rate was observed at 1 g/L and hence experiments at very low catalyst loading were not carried out. Hence, 1 g/L photocatalyst amount was maintained for photocatalytic and sonophotocatalytic reactions. This aqueous suspension was mixed continuously in the dark for 45 min to ensure that adsorption equilibrium of IBP on the catalyst surface was reached. During irradiation, 3 mL aliquots were withdrawn at appropriate time intervals and the photocatalyst was removed immediately by filtration through a  $0.45 \mu\text{m}$  syringe filter (Pall Corporation).

The following order of addition was done for all experiments employing  $\text{Fe}^{3+}$  photocatalyst: IBP,  $\text{Fe}^{3+}$  and then the pH was adjusted to 2.7 using HCl. Then the irradiation was started and 3 mL aliquots were withdrawn at regular time intervals. The concentration of IBP was analyzed by HPLC.

### 2.2. Analytical determinations

The degradation products were analyzed using electrospray mass spectrometry (ESMS). The mass spectrometer used was a Micromass QUATTRO 11 coupled to a Hewlett Packard series 1100 degasser. The instrument was calibrated using the automatic tuning procedure with respect to the parent compound as the standard.

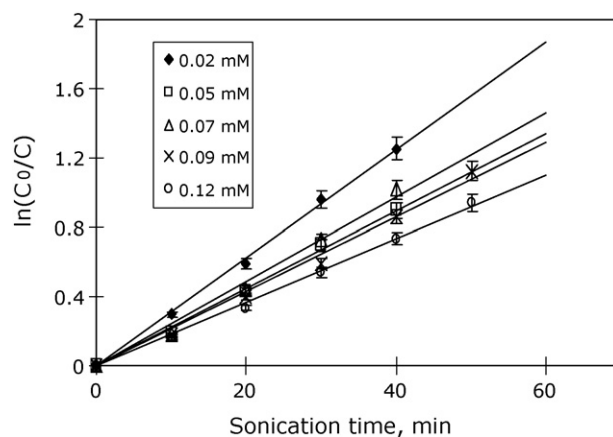


Fig. 1. Effect of IBP concentrations on its sonolytic degradation kinetics.

The mass range scanned was  $m/z$  50–1000 and several spectra were obtained across each chromatographic peak. The analysis was carried out in negative electrospray ionisation mode at cone voltages of 30, 50 and 80 V. The mobile phase consisted of 50/50 (acetonitrile/water). The flow rate of the solvent was  $0.03 \text{ mL min}^{-1}$  and the capillary voltage was set at 3.5 kV. The concentration of IBP was determined by a high-performance liquid chromatograph, Shimadzu LC-10 AT VP system with a Shimadzu SPD-M10 A VP photo diode array detector with a Phenomenex reversed phase column (Kromasil, C18,  $250 \text{ mm} \times 4.6 \text{ mm}$  inner diameter,  $5 \mu\text{m}$  beads). A mobile phase of acetonitrile/orthophosphoric acid (0.01 mM) = 60/40 with 0.2 mM sodium octyl sulphate was employed. The flow rate was maintained at  $0.8 \text{ mL min}^{-1}$  [27].

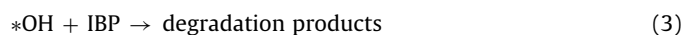
TOC was determined using a total organic carbon analyser TOC-V<sub>CSH</sub> (Shimadzu) programmed by TOC-Control V Software. The instrument was calibrated before each use with standardized TOC solutions of 100 mg/L. The absorption spectrum of IBP was recorded with a "Cary Varian 50 Bio" UV-vis spectrophotometer. The spectrophotometer was coupled to a computer, which measured the absorption spectrum using Scan 2 software. The samples were placed in a quartz cell and the spectra were recorded in the wavelength range, 200–600 nm.

## 3. Results and discussion

### 3.1. Sonolytic degradation of IBP

The degradation kinetics of IBP followed first order kinetics. The change in  $\ln(C_0/C)$  as a function of time ( $t$ ) [Fig. 1], showed a linear trend and the slope of this plot yielded the first order rate constants reported later. Fig. 2 shows the effect of IBP concentration on the sonolytic degradation rate at 213 kHz and 55 mW/mL power for the initial concentrations, 0.02, 0.05, 0.07, 0.09 and 0.09 mM. It should be pointed out that the relative percentage of degradation decreases with increasing initial concentration, but the degradation rate increases with an increase of initial concentration.

The observed first order kinetics and the dependence of the rate on the initial concentration can be explained by considering the following reactions (1)–(3) that take place during the sonolysis process.



Generally, in a sonochemical process, micro-sized bubbles readily form due to acoustic cavitation, and then grow and subsequently

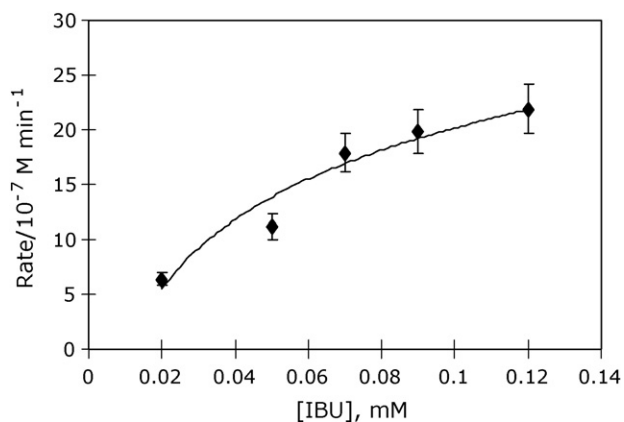


Fig. 2. Sonochemical degradation rates obtained as a function of [IBP].

collapse with the generation of extreme temperatures and pressures. This creates three regions for high energy chemical reaction: (i) the region inside the bubble cavity where the volatile and hydrophobic molecules are degraded via pyrolytic reactions; (ii) 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. [21] suggested that pyrolytic degradation of IBP is not possible due to its hydrophobic and low volatility character at pH less than its pKa (4.9) [21]. Hence, the degradation of IBP can occur by the hydroxyl radicals present in the bubble–liquid interface.

The degradation rate can be expected to be dependent on the concentration of  $\cdot\text{OH}$  produced by water thermolysis (Reaction (1)) and the concentration of the IBP molecules at the interface of the cavitation bubble. In the absence of IBP, the recombination of hydroxyl radicals predominate (Reaction (2)) and form hydrogen peroxide. However, in the presence of IBP, a fraction of hydroxyl radicals produced attack IBP molecules and initiate its degradation. As the concentration of IBP increases, Reaction (3) dominates leading to an increase in the rate. Recently, Mendez-Arriaga et al. [21] also observed similar results for the degradation of IBP in a 300 kHz batch reactor and observed a reduction in the amount of  $\text{H}_2\text{O}_2$  formation at higher IBP concentrations.

### 3.2. Effect of power

In order to evaluate the influence of ultrasonic power on IBP degradation, the acoustic power was varied (16, 35 and 55 mW/mL). As expected, the initial degradation rates increased linearly with an increase in the acoustic power. The degradation rates obtained for the actual US powers 16, 35 and 55 mW/mL were 1.04, 11.6 and  $29.8 \times 10^{-7}$  M min $^{-1}$ , respectively. It is known that the number of active cavitation bubbles increases with an increase in the acoustic power leading to an increase in the amount  $\cdot\text{OH}$  generated [28,29], which might be responsible for the observed enhancement in the degradation rates.

### 3.3. Photocatalytic and sonophotocatalytic degradations

In order to check the feasibility of sonophotocatalysis process for the degradation of IBP, the following control experiments were performed and the results are presented in Fig. 3; photo irradiation alone (UV – “control”), ultrasound alone (US), photocatalysis (UV +  $\text{TiO}_2$ ) and sonophotocatalysis (US + UV +  $\text{TiO}_2$ ) in the presence of  $\text{TiO}_2$ . It is evident from Fig. 3 that a relatively higher degradation

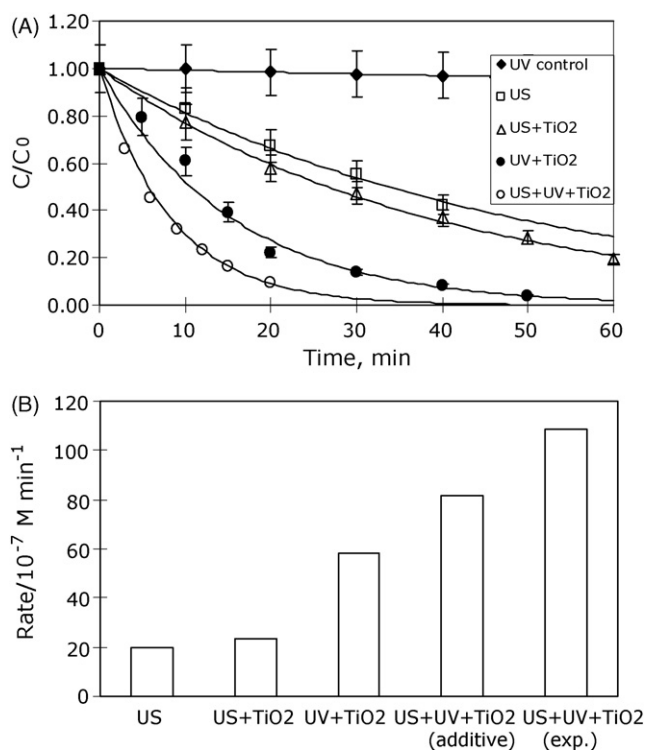


Fig. 3. (A) Degradation of IBP (0.09 mM; 18.5 mg/L) in the presence of  $\text{TiO}_2$  (1 g/L) using different processes. (B) Comparison of degradation rates of IBP (0.09 mM = 18.5 mg/L) in the presence of  $\text{TiO}_2$  (1 g/L) using different processes.

of IBP was achieved by combining sonolysis and photocatalysis than that observed during the individual processes.

The preliminary experiments revealed no significant degradation of IBP in the presence of UV alone. However, under the action of US with 55 mW/mL amplitude at the frequency of 213 kHz, about 18% degradation of IBP occurred within 10 min. An enhancement in the sonolytic reaction rate in the presence of semiconductor particles was recently reported by Pandit et al. [30,31] which is referred to as sonocatalysis. The suspended solids may also increase the extent of cavitation generated in solution and hence the sonochemical degradation rate by providing additional nuclei for bubble generation. Therefore, in order to study the effect of  $\text{TiO}_2$  on the sonolytic degradation of IBP in the absence of photoirradiation, the following experiment was conducted under the experimental conditions of  $[\text{IBP}] = 0.09$  mM and  $\text{TiO}_2$  amount of 1 g/L, and the results obtained are shown in Fig. 3A and B. It was noted that about 23% degradation in 10 min under the sonocatalytic conditions was observed. An approximately 5% increase in the degradation amount observed in the presence of  $\text{TiO}_2$  particles, during sonolysis. This increase might be due to additional cavitation activity, but it is within experimental error the same as the system in the absence of  $\text{TiO}_2$ .

In the case of photocatalytic degradation, about 61% degradation (Fig. 3) was achieved in 15 min and can be explained using the general degradation mechanism available in the literature [32–34]. The photoirradiation of the  $\text{TiO}_2$  forms an electron in the conduction band and a hole in the valence band. As a consequence of such photoinduced charge separation on the semiconductor surface, electron exchange reactions occur at the water–semiconductor interface. The superoxide radical anion  $\text{O}_2^{\cdot-}$  is formed by interaction of photo-generated conduction band electrons with adsorbed oxygen molecules, while  $\cdot\text{OH}$  are formed via valence band hole oxidation of adsorbed water or hydroxyl anions [33] to generate  $\cdot\text{OH}$  that subsequently oxidize the adsorbed pollutant molecules. Holes may also directly oxidize the adsorbed organic pollutant.

**Table 1**  
Degradation rates obtained at different processes for a [IBP] = 0.09 mM ( $\equiv 18.5$  mg/L) using  $\text{TiO}_2$  (1 g/L) or  $\text{Fe}^{3+}$  (0.05 mM).

Process	Rate, $10^{-7}$ M $\text{min}^{-1}$
US	19.9
US + $\text{TiO}_2$	23.5
UV + $\text{TiO}_2$	58.0
US + UV + $\text{TiO}_2$	108.4
US + $\text{Fe}^{3+}$	32.8
UV + $\text{Fe}^{3+}$	30.4
US + UV + $\text{Fe}^{3+}$	99.0

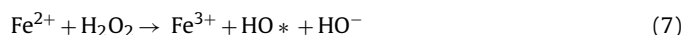
However, when both the US and UV are combined (sonophotocatalysis), a significant enhancement in the degradation (85% in 15 min, Fig. 3) of IBP was observed. About 24% increment in the degradation under the same processing time suggests that the hydroxyl radicals formed by both the advanced oxidation processes, viz., photocatalysis and sonolysis are involved in the sonophotocatalytic degradation of IBP. The synergy index (Eq. (4)) was calculated from the degradation rates of sonocatalysis  $R_{(\text{US}+\text{TiO}_2)}$ , photocatalysis  $R_{(\text{UV}+\text{TiO}_2)}$  and sonophotocatalysis  $R_{(\text{US}+\text{UV}+\text{TiO}_2)}$  (Table 1).

$$\text{Synergy index} = \frac{R_{(\text{US}+\text{UV}+\text{TiO}_2)}}{R_{(\text{US}+\text{TiO}_2)} + R_{(\text{UV}+\text{TiO}_2)}} \quad (4)$$

It was deduced based on the synergy index value ( $\sim 1.3$ ) that the combination of sonolysis and photocatalysis only resulted in the slight synergistic effect. The main effect of ultrasound is to contribute, together with photocatalysis, to the scission of  $\text{H}_2\text{O}_2$ , produced by both photocatalysis and sonolysis, with an increase of the reactive radical species inducing degradation of the substrate.

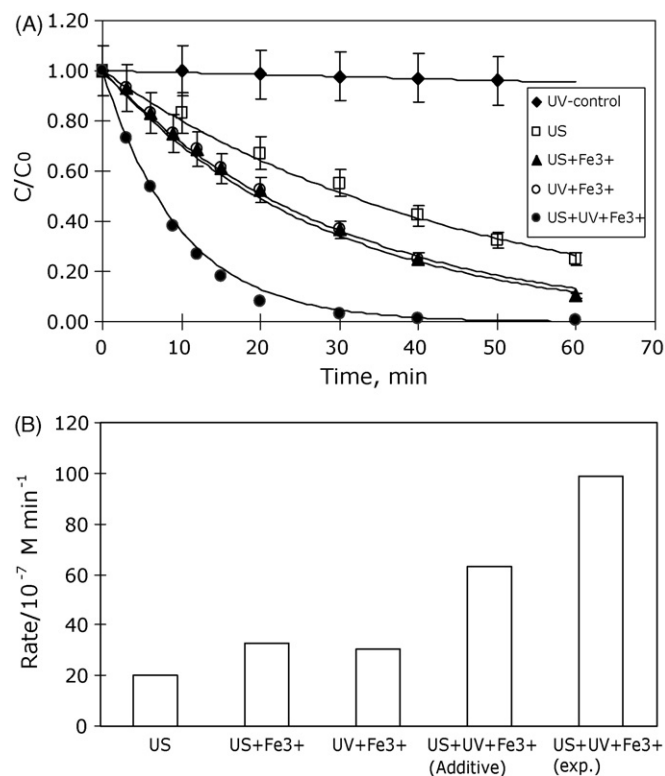
#### 3.4. Sonolytic, photocatalytic and sonophotocatalytic degradations of IBP in presence of $\text{Fe}^{3+}$

An oxidation process that utilizes the activation of  $\text{H}_2\text{O}_2$  by iron salts is known as Fenton's oxidation which is effective in the destruction of many hazardous organic pollutants in water. Since the sonolysis of water produces hydrogen peroxide, the addition of an iron salt during the sonolysis can initiate the Fenton's reaction for the degradation of any pollutant. The following major reactions (5)–(9) take place in the Fenton-like oxidation process [35].



The preliminary experiments carried out revealed that there was no change in the absorption spectrum of the IBP when  $\text{Fe}^{3+}$  was introduced into the IBP solution, indicating no complex formation occurred between IBP and the  $\text{Fe}^{3+}$ .

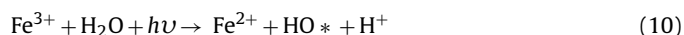
The degradation of IBP by sonolysis, photolysis and sonophotocatalysis in presence of  $\text{Fe}^{3+}$ , was performed under the following experimental conditions; [IBP] = 0.09 mM,  $[\text{Fe}^{3+}] = 0.045$  mM at pH 2.7 and the obtained degradation results are shown in Fig. 4A and B. The ratio of  $\text{Fe}^{3+}$ :IBP was maintained at 0.5:1 in the present investigation because the addition of higher concentrations of the catalyst may lead to the quenching of the reactive hydroxyl radicals [36]. It can be seen that the addition of  $\text{Fe}^{3+}$  significantly increased the sonolytic degradation of IBP. For example, about 45% degradation in 15 min due to the sonolysis in the presence of  $\text{Fe}^{3+}$  was observed whereas it took double the time to achieve the same degradation efficiency in the absence of  $\text{Fe}^{3+}$  (Fig. 4). About a 1.6-fold increment



**Fig. 4.** (A) Degradation of IBP (0.09 mM  $\equiv 18.5$  mg/L) in the presence of  $\text{Fe}^{3+}$  (0.05 mM  $\equiv 20$  mg/L) using different processes. (B) Comparison of degradation rates of IBP (0.09 mM  $\equiv 18.5$  mg/L) in the presence of  $\text{Fe}^{3+}$  (0.05 mM  $\equiv 20$  mg/L) using different processes.

in the degradation rate of IBP was observed by the addition of  $\text{Fe}^{3+}$  when compared with sonolysis on its own (Table 1). In sonolysis, the sonolytic cleavage of water is the main source of hydroxyl radicals whereas in the case of sonolysis in the presence of  $\text{Fe}^{3+}$ , hydroxyl radicals are also formed by the Fenton oxidation (sonofenton reactions: (2), (3), (5)–(9)) [37]. The additional generation of hydroxyl radicals due to the presence of  $\text{Fe}^{3+}$  are responsible for the observed enhancement in the degradation of IBP.

In the case of the photolytic degradation in the presence and absence of  $\text{Fe}^{3+}$  revealed that the rate significantly increased by the addition of  $\text{Fe}^{3+}$  during photolysis. This may be due to the photolysis of the iron aqua complex  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  (abbreviated as  $\text{Fe}(\text{OH})^{2+}$ ) formed by dissolving iron salt in water. During the excitation of  $\text{Fe}(\text{OH})^{2+}$  by light, an electron is transferred from the ligand to the metal center producing  $\text{Fe}^{2+}$  and a hydroxyl radical (Reaction (10)) [38]. Also, the regeneration of the catalyst with the formation of an additional hydroxyl radical can be achieved by irradiating the solution mixture containing  $\text{Fe}^{3+}$ . The degradation of IBP can be expected to cease after all the hydrogen peroxide (formed via Reaction (2)) is consumed by  $\text{Fe}^{2+}$ . However, in the case of IBP, we observed a gradual decrease in its concentration for extended irradiation times. The continued regeneration of  $\text{Fe}^{3+}$  from  $\text{Fe}^{2+}$  in the absence of  $\text{H}_2\text{O}_2$  may be due to formation of a radical intermediate ( $\text{P}^*$ ) which oxidizes  $\text{Fe}^{2+}$  (Reactions (11) and (12)). Recently, Mendez-Arriaga et al. [39] also observed the unexpected decrease in IBP concentration for the photolysis of  $\text{Fe}^{2+}$  without  $\text{H}_2\text{O}_2$ .



In the case of the sonophotocatalytic degradation in the presence of  $\text{Fe}^{3+}$ , an approximate 3-fold increase in the degradation

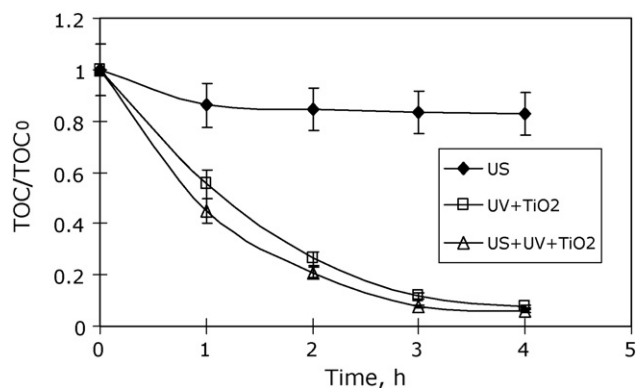


Fig. 5. Change in TOC as a function of time for different degradation processes in presence of  $\text{TiO}_2$ .

was observed when compared with the individual sonolytic and photocatalytic degradation rates. Apart from the sonolytic degradation of water and cleavage of sonochemically produced hydrogen peroxide, the following are the major pathways for the generation of hydroxyl radicals which are responsible for the observed enhancement in the sonophotocatalytic degradation rates: (i) the photo-Fenton oxidation (Reaction (10)) where photolysis of  $\text{Fe}^{3+}$  complex species form hydroxyl radicals and  $\text{Fe}^{2+}$  necessary to drive the Fenton reaction (Eq. (7)), (ii) the involvement of sonochemically produced hydrogen peroxide in the Fenton reaction along with added  $\text{Fe}^{3+}$  species (Eqs. (5), (6), (9)). From the degradation rates of these three processes in the presence of  $\text{Fe}^{3+}$  (Table 1), the synergy index was calculated to be 1.6.

### 3.5. Mineralization studies

It has been widely reported that some of the intermediate products of a degradation process are more toxic and carcinogenic than the parent organic compounds [40,41]. Hence, the complete degradation of the pollutants should be ensured before discharging them into the ecosystem. A comparison of total organic carbon (TOC) values was made from the experiments carried out under identical conditions, viz.  $[\text{IBP}] = 0.09 \text{ mM}$ ,  $\text{TiO}_2 = 1 \text{ g/L}$  for sonolysis, photocatalysis and sonophotocatalysis, and the obtained results are shown in Fig. 5. Based on the TOC data, the following conclusions can be made: (i) the TOC removal rate was much less than that of the degradation process under the same experimental conditions; (ii) sonochemical reactions were quite efficient for the degradation of IBP, but complete mineralization was not achieved over the time range examined which may be due to the high polarity of the intermediate products; (iii) photocatalysis showed higher selectivity for the mineralization of IBP as it showed about 74% mineralization in 2 h of light irradiation; and (iv) Sonophotocatalysis achieves higher TOC removal (~92% in 3 h) than the individual processes of sonolysis (~16% in 3 h) and photocatalysis (~88% in 3 h). Although a higher percentage of mineralization was observed for sonophotocatalysis, it is an additive effect for the entire processing time rather than a synergy effect.

The TOC values obtained for the sonolytic, photocatalytic and sonophotocatalytic degradation of IBP in presence of  $\text{Fe}^{3+}$  is shown in Fig. 6. It is clearly seen that there is no significant improvement in the TOC removal for the sonolytic and photocatalytic degradation in presence of  $\text{Fe}^{3+}$  for the first 2 h of reaction time. This may be due to the formation of more stable intermediates in the degradation process in the first 2 h. After 2 h, a marginal increase in the mineralization was observed for photolysis of IBP solution with  $\text{Fe}^{3+}$ . More interestingly, a synergistic mineralization was observed for the sonophotocatalytic degradation in presence of  $\text{Fe}^{3+}$ , i.e., a 73%

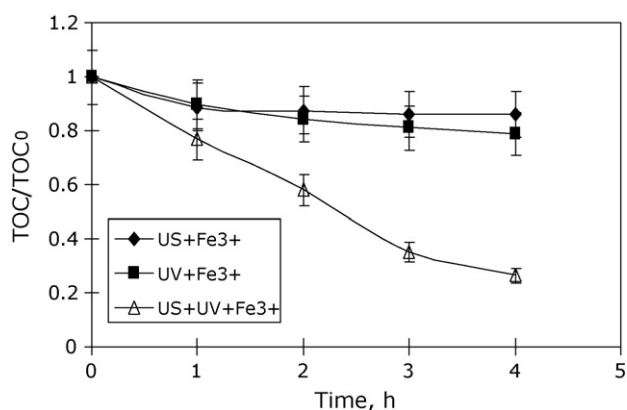


Fig. 6. Change in TOC as a function of time for different degradation processes in presence of  $\text{Fe}^{3+}$ .

mineralization in 4 h which is about four times higher than that observed with the sonolysis and photocatalysis in the presence of  $\text{Fe}^{3+}$ . Apart from the reasons mentioned in the above section for the formation of higher amounts of hydroxyl radicals, it is anticipated that the formation of carboxylated products which are capable of forming a photoactive complex with  $\text{Fe}^{3+}$  might facilitate faster decarboxylation. The formation of carboxylated products by these processes were also identified by the HPLC–MS analysis. These iron complexes underwent fast photodecarboxylation and resulted in the higher mineralization of IBP. But in the case of photolysis, the formation of carboxylated by-products is less rapid and did not undergo significant mineralization. Further HPLC runs were carried out using a prevail organic acid column (Alltech) with a 25 mM potassium phosphate (pH 2.5) mobile phase which was run at a flow rate of  $1 \text{ mL min}^{-1}$  at a detection wavelength of 220 nm. Particularly, the formation of oxalic acid was confirmed by deliberately injecting its standard solutions and matching its retention time with that of the treated solutions of IBP. Skoumal et al. [42] also reported that oxalic acid was the ultimate by-product of the photoelectron-Fenton degradation of IBP and observed higher oxidation rates under solar irradiation, due to the photodecarboxylation of iron complexes of oxalic acid. Hence, we propose that the formation of ferrioxalate complex might be responsible for the observed enhancement in the mineralization process. Also, many researchers have reported that the photocatalytic activity of ferrioxalate complexes are more efficient than other aqua complexes of iron because of their ability to absorb a wide range of light in the visible region ( $\lambda < 450 \text{ nm}$ ) [43,44].

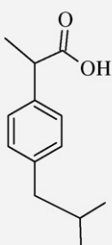
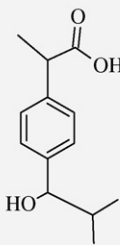
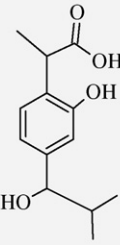
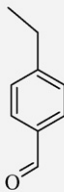
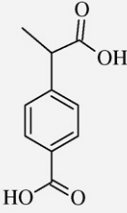
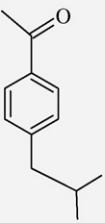
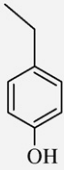
### 3.6. Possible degradation pathway

In order to identify reaction by-products of IBP degradation, samples collected at various time intervals were analyzed by means of HPLC and ESMS. The results indicate that sonolysis degrades the IBP and results in the formation of a number of products including substituted phenols, aromatic carboxylic acids, etc. (Table 2). It was observed that attack of hydroxyl radicals on both the propanoic acid and isobutyl substituents of the IBP structure results in the formation of products such as 2-[4-(1-hydroxyisobutyl)phenyl]propanoic acid (I), 2-[2-hydroxy-4-(1-hydroxy-2-methylpropyl)phenyl]propanoic acid (II), 4-ethylbenzaldehyde (III), 4-(1-carboxyethyl)benzoic acid (IV), 4-isobutylacetophenone (V) and 4-ethyl phenol (VI).

Sonolysis of IBP resulted in the degradation of IBP which was evidenced from the decrease in the peak intensity corresponding to IBP ( $m/z$  205) after an hour of sonication (data not shown). At the same time, the peaks that appear at  $m/z$  221 and 237

**Table 2**

Degradation products observed for IBP during sonolysis, photocatalysis and sonophotocatalysis.

			
Ibuprofen	I	II	
m/z. 205	m/z. 221	m/z. 237	
			
III	IV	V	VI
m/z. 133	m/z. 191	m/z. 176	m/z. 122

show the formation of mono- and dihydroxylated products of IBP such as 2-[4-(1-hydroxyisobutyl)phenyl]propionic acid (I) and 2-[2-hydroxy-4-(1-hydroxy-2-methylpropyl)phenyl]propanoic acid (II). However, the intensity of product I after 2 h of sonication was less compared with 1 h. It shows that the product I is converted into some other product following an extended sonication period. The formation of hydroxylated products (I) and (II) was seen in all the processes used—sonolysis, photocatalysis and sonophotocatalysis. Also, the products with the *m/z* values 133 and 191 may correspond to 4-ethylbenzaldehyde (III) and 4-(1-carboxyethyl) benzoic acid (IV). Mendez-Arriaga et al. [20] studied the photocatalytic degradation of IBP in presence of TiO<sub>2</sub> and reported the formation of products I and III and argued that the hydroxylation process can be the first step of the degradation, followed by a second step of demethylation or decarboxylation with other different by-products with smaller *m/z* values. Skoumal et al. [42] also reported the formation of 4-ethylbenzaldehyde by the photoelectron-Fenton degradation of IBP. Under our experimental conditions, the formation of product 4-(1-carboxyethyl) benzoic acid (IV) was also observed. In the case of the sonophotocatalysis with TiO<sub>2</sub>, *m/z* values of 176 and 122 were obtained which may correspond to 4-isobutyacetophenone (V) and 4-ethylphenol (VI). Caviglioli et al. [45] observed the formation of 4-isobutyacetophenone during the oxidative degradation of IBP using permanganate solution.

#### 4. Summary

The sonolytic, photocatalytic and sonophotocatalytic degradation of IBP in the presence of homogeneous (Fe<sup>3+</sup>) and heterogeneous photocatalysts (TiO<sub>2</sub>) were studied. The following observations can be made based on our experimental investigations

1) Sonolytic degradation followed first order dependence with respect to IBP.

- Both TiO<sub>2</sub> and Fe<sup>3+</sup> sonophotocatalysis showed a slight synergy in the degradation of IBP when compared with the individual sonolysis and photocatalysis.
- Mineralization using TiO<sub>2</sub> sonophotocatalysis was found to be an additive effect. However, a higher synergistic enhancement in the mineralization was obtained when Fe<sup>3+</sup> was used as a photocatalyst and this may be a result of the complex formation of photoactive complexes between Fe<sup>3+</sup> and carboxylic acid intermediates.
- HPLC–MS was employed for the identification of the degradation intermediates. Sonication of IBP leads to the formation of its mono and di-hydroxylated intermediates. Apart from the hydroxylated intermediates, products due to the oxidation of propanoic acid and isobutyl substituents of the IBP were also identified.

#### Acknowledgements

The authors thank DIISR, Australia and DST, New Delhi for the financial support of an India–Australian strategic research fund (INT/AUS/P-1/07 dated 19 September 2007).

#### References

- M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, *Environ. Int.* 35 (2009) 402–417.
- H.-R. Buser, T. Poiger, M.D. Muller, Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater, *Environ. Sci. Technol.* 33 (1999) 2529–2535.
- M.L. Richardson, J.M. Bowron, The fate of pharmaceutical chemicals in the aquatic environment, *J. Pharm. Pharmacol.* 37 (1985) 1–12.
- E. Idaka, T. Ogawa, H. Horitsu, Reductive metabolism of aminoazobenzenes by *Pseudomonas cepacia*, *Bull. Environ. Contam. Toxicol.* 39 (1987) 100–107.
- E.A. Sweeney, J.K. Chipman, S. Forsythe, Evidence for direct-acting oxidative genotoxicity by reduction products of azo dyes, *J. Environ. Health Perspect.* 102 (1994) 119–122.
- P.K. Wong, P.Y. Yuen, Decolorization and biodegradation of methyl red by *Klebsiella pneumoniae* RS-13, *Water Res.* 30 (1996) 1736–1744.

- [7] S. Esplugas, D.M. Bila, L.G.T. Krause, M. Dezotti, Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents, *J. Hazard. Mater.* 149 (2007) 631–642.
- [8] E. Selli, C.L. Bianchi, C. Pirola, G. Cappelletti, V. Ragaini, Efficiency of 1,4-dichlorobenzene degradation in water under photolysis, photocatalysis on TiO<sub>2</sub> and sonolysis, *J. Hazard. Mater.* 153 (2008) 1136–1141.
- [9] R. Singla, F. Grieser, M. Ashokkumar, Sonochemical degradation of martius yellow dye in aqueous solution, *Ultrason. Sonochem.* 16 (2009) 28–34.
- [10] Z. Ai, L. Lu, L. Zhang, J. Qiu, M. Wu, FeFe<sub>2</sub>O<sub>3</sub> core-shell nanowires as the iron reagent. 2. An efficient and reusable sono-Fenton system working at neutral pH, *J. Phys. Chem. C* 111 (2007) 7430–7436.
- [11] R.J. Emery, M. Papadaki, L.M. Freitas dos Santos, D. Mantzavinos, Extent of sonochemical degradation and change of toxicity of a pharmaceutical precursor (triphenylphosphine oxide) in water as a function of treatment conditions, *Environ. Int.* 31 (2005) 207–211.
- [12] Q.P. Isariebel, J.L. Carine, J.H. Ulises-Javier, W. Anne-Marie, D. Henri, Sonolysis of levodopa and paracetamol in aqueous solutions, *Ultrason. Sonochem.* 16 (2009) 610–616.
- [13] J. Hartmann, P. Bartels, U. Mau, M. Witter, W.V. Tumpling, J. Hofmann, E. Nietzsche, Degradation of the drug diclofenac in water by sonolysis in presence of catalysts, *Chemosphere* 70 (2008) 453–461.
- [14] Y.C. Chen, A.V. Vorontsov, P.G. Smirniotis, Enhanced photocatalytic degradation of dimethyl methylphosphonate in the presence of low-frequency ultrasound, *Photochem. Photobiol. Sci.* 2 (2003) 694–698.
- [15] V. Naddeo, S. Meric, D. Kassinos, V. Belgiorno, M. Guida, Fate of pharmaceuticals in contaminated urban wastewater effluent under ultrasonic irradiation, *Water Res.* 43 (2009) 4019–4027.
- [16] V. Neddeo, V. Belgiorno, D. Kassinos, D. Mantzavinos, S. Meric, Ultrasonic degradation, mineralization and detoxification of diclofenac in water: optimization of operating parameters, *Ultrason. Sonochem.* 17 (2010) 179–185.
- [17] J.M. Joseph, H. Destaillets, H.M. Hung, M.R. Hoffmann, The sonochemical degradation of azobenzene and related azo dyes: rate enhancements via Fenton's reactions, *J. Phys. Chem. A* 104 (2000) 301–307.
- [18] J. Peller, O. Wiest, P.V. Kamat, Synergy of combining sonolysis and photocatalysis in the degradation and mineralization of chlorinated aromatic compounds, *Environ. Sci. Technol.* 37 (2003) 1926–1932.
- [19] K. Hirano, H. Nitta, K. Sawada, Effect of sonication on the photo-catalytic mineralization of some chlorinated organic compounds, *Ultrason. Sonochem.* 12 (2005) 271–276.
- [20] F. Mendez-Arriaga, S. Esplugas, J. Gimenez, Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO<sub>2</sub> and simulated solar irradiation, *Water Res.* 42 (2008) 585–594.
- [21] F. Mendez-Arriaga, R.A. Torres-Palmaa, C. Petrier, S. Esplugas, J. Gimenez, C. Pulgarin, Ultrasonic treatment of water contaminated with ibuprofen, *Water Res.* 42 (2008) 243–248.
- [22] V.K. Sharma, S.K. Mishra, Ferrate(VI) oxidation of ibuprofen: a kinetic study, *Environ. Chem. Lett.* 3 (2006) 182–185.
- [23] C. Zwierner, F.H. Frimmel, Oxidative treatment of pharmaceuticals in water, *Water Res.* 34 (2000) 1881–1885.
- [24] J.L. Packer, J.J. Werner, D.E. Latch, K. McNeill, W.A. Arnold, Photochemical fate of pharmaceuticals in the environment: Naproxen, diclofenac, clofibrac acid, and ibuprofen, *Aquat. Sci.* 65 (2003) 342–351.
- [25] R. Molinari, F. Pirillo, V. Loddò, L. Palmisano, Heterogeneous photocatalytic degradation of pharmaceuticals in water by using polycrystalline TiO<sub>2</sub> and a nanofiltration membrane reactor, *Catal. Today* 118 (2006) 205–213.
- [26] Y. Hua, Ph.D. Thesis. University of Melbourne.
- [27] R.G. Chayeh, M.B. Salah, R. Chemli, A validation of an HPLC method for the determination of ibuprofen in presence of its degradation products, *Orient. J. Chem.* 23 (2007) 793–800.
- [28] R. Emery, M. Papadaki, L.M. Freitas dos Santos, D. Mantzavinos, Extent of sonochemical degradation and change of toxicity of a pharmaceutical precursor (triphenylphosphine oxide) in water as a function of treatment conditions, *Environ. Int.* 31 (2005) 207–211.
- [29] M.H. Lim, S.H. Kim, Y.U. Kim, J. Khim, Sonolysis of chlorinated compounds in aqueous solution, *Ultrason. Sonochem.* 14 (2007) 93–98.
- [30] A.B. Pandit, P.R. Gogate, S. Mujumdar, Ultrasonic degradation of 2:4:6 trichlorophenol in presence of TiO<sub>2</sub> catalyst, *Ultrason. Sonochem.* 8 (2001) 227–231.
- [31] I.Z. Shirgaonkar, A.B. Pandit, Sonophotocatalytic destruction of aqueous solution of 2,4,6-trichlorophenol, *Ultrason. Sonochem.* 5 (1998) 53–61.
- [32] T.N. Rao, D.A. Tryk, A. Fujishima, in: A.J. Bard, M. Martin, S. Licht (Eds.), *Encyclopedia of electrochemistry, semiconductor electrodes and photoelectrochemistry*, 6, Wiley-VCH, 2002, p. 540.
- [33] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.* 32 (2004) 33–177.
- [34] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation for environmental applications—a review, *J. Chem. Technol. Biotechnol.* 77 (2002) 102–116.
- [35] J. Liang, S. Komarov, N. Hayashi, E. Kasai, Recent trends in the decomposition of chlorinated aromatic hydrocarbons by ultrasound irradiation and Fenton's reagent, *J. Mater. Cycles Waste Manage.* 9 (2007) 47–55.
- [36] J. Madhavan, F. Grieser, M. Ashokkumar, Kinetics of the sonophotocatalytic degradation of orange G in presence of Fe<sup>3+</sup>, *Water Sci. Technol.* 60 (8) (2009) 2195–2202.
- [37] C. Berberidou, I. Poulios, N.P. Xekoukoulotakis, D. Mantzavinos, Sonolytic, photocatalytic and sonophotocatalytic degradation of malachite green in aqueous solutions, *Appl. Catal. B: Environ.* 74 (2007) 63–72.
- [38] J. Kiwi, A. Lopez, V. Nadtochenko, Mechanism and kinetics of the OH-radical intervention during Fenton oxidation in the presence of a significant amount of radical scavenger (Cl<sup>-</sup>), *Environ. Sci. Technol.* 34 (2000) 2162–2168.
- [39] F. Mendez-Arriaga, S. Esplugas, J. Gimenez, Degradation of the emerging contaminant ibuprofen in water by photo-Fenton, *Water Res.* in press, doi:10.1016/j.watres.2009.07.009.
- [40] J.H. Weisburger, Comments on the history and importance of aromatic and heterocyclic amines in public health, *Mutat. Res.* 506–507 (2002) 9–20.
- [41] C. Jakopitsch, G. Regelsberger, P.G. Furtmuller, F. Ruker, G.A. Peschek, C. Obinger, Catalase-peroxidase from *Synechocystis* is capable of chlorination and bromination reactions, *Biochem. Biophys. Res. Commun.* 287 (2001) 682–687.
- [42] M. Skoumal, R.M. Rodríguez, P.L. Cabot, F. Centellas, J.A. Garrido, C. Arias, E. Brillas, Electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton degradation of the drug ibuprofen in acid aqueous medium using platinum and boron-doped diamond anodes, *Electrochim. Acta* 54 (2009) 2077–2085.
- [43] M.E. Balmer, B. Sulzberger, Atrazine degradation in irradiated iron/oxalate systems: effects of pH and oxalate, *Environ. Sci. Technol.* 33 (1999) 2418–2424.
- [44] K.A. Hislop, J.R. Bolton, The photochemical generation of hydroxyl radicals in the UV-vis/ferrioxalate/H<sub>2</sub>O<sub>2</sub> system, *Environ. Sci. Technol.* 33 (1999) 3119–3126.
- [45] G. Caviglioli, P. Valeria, P. Brunella, C. Sergio, A. Attilia, B. Gaetano, Identification of degradation products of ibuprofen arising from oxidative and thermal treatments, *Pharm. Biomed. Anal.* 30 (2002) 499–509.