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Sonochemical degradation of endocrine disruptor propylparaben in pure water, natural water, and seawater

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ABSTRACT

In this work, the sonolytic degradation of an endocrine disrupting chemical, propylparaben (PPB), was carried out at 352 kHz and 80 W. The effects of initial substrate concentration and initial solution pH on the ultrasonic degradation of PPB were examined. Additionally, sonochemical degradation of substrate was investigated in natural water and seawater. The best performances were achieved in the pH range of 3–8, whereas the degradation rate decreased with increasing solution pH from 8 to 10.5. The obtained results showed an interesting effect of real water matrices. At a low concentration of PPB (5 mg/L), an improvement in the degradation process was observed in natural matrices, while at higher concentrations of PPB (25–100 mg/L), degradation was slightly inhibited, particularly in natural water. At a medium concentration of PPB (10 mg/L), similar degradation rates were observed for all the tested media. The Langmuir-type kinetic models fit well the substrate sonolytic degradation. A perfect representation of the experimental data of PPB sonochemical degradation at different initial concentrations in pure water was obtained using the Serpone et al.'s model. In real water matrices, an adequate description of the sonolytic destruction of PPB was attained by the Okitsu et al.'s equation. These results indicate that PPB undergoes degradation predominantly at the bubble/solution interface in natural water and seawater, whereas the sonolytic destruction of substrate in pure water is mainly achieved both at bubble/solution interface and in the bulk solution.

Keywords: Endocrine disrupting compound; Propylparaben; Sonolytic degradation; Natural water matrices

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This article is dedicated to Prof Christian Pétrier on the occasion of his retirement.

1. Introduction

In recent years, development of society modernization leads to the extensive use of pharmaceuticals and personal care products (PCPs), which has been documented and reported as an emerging environmental issue [1]. Most of the preservatives may be harmful to the consumers due to their potency to induce allergic contact dermatitis [2]. Parabens, alkyl esters of 4-hydroxybenzoic acid, are widely used preservatives and bactericides in the PCPs (e.g. deodorants, hair gels, shampoos, creams, and toothpastes), foods and pharmaceuticals industries [3,4]. These compounds are considered endocrine disrupting chemicals, because they possess an estrogenic activity [5]. Furthermore, parabens are continually introduced into the environment and, despite being considerably removed during conventional sewage treatments, they have been detected in sewage effluents [6–9], surface and ground water [8–11], and even drinking water [8,12]. Consequently, the US Environmental Protection Agency (USEPA) has classified parabens as emerging environmental contaminants [13]. Therefore, it is of great importance to develop efficient and cost-effective treatment technologies for the removal of such compounds.

Advanced oxidation processes (AOPs), which are based on the formation and use of the extremely oxidant hydroxyl radical, offer promising solutions to the elimination of emergent pollutants in water. Ultrasonic treatment has been extensively used as an efficient AOP for the breakdown of contaminants in water and wastewater [14–19]. Sonochemical techniques involve the use of ultrasonic waves to generate an oxidative environment via cavitation. Under the influence of an acoustic field, bubbles are produced from existing gas nuclei in liquids. Acoustic cavitation refers to the cyclical formation, rapid growth and implosive collapse of bubbles in a liquid resulting in an unusual reaction environment within and in the vicinity of bubbles [20]. The rapid collapse of the bubbles adiabatically compresses gas and entrapped vapor, producing small local hot spots [21,22]. At the final step of the violent collapse of bubble, localized pressures of around hundreds of atmospheres and temperatures as high as 5,200 K are reached within these collapsing bubbles and the interfacial region would reach about 2,000 K [23–26]. Under these extreme conditions, a wide range of homolysis/pyrolysis reactions of the gaseous contents occur, resulting in highly reactive radical formation. In aqueous solutions, the thermal dissociation of water vapor into reactive hydroxyl radicals and hydrogen atoms, and with other species present, various other radicals may form. The main reactions occurring during collapse of a bubble are shown below [27]:

$$H_2O \rightarrow H^{\cdot} + {}^{\cdot}OH \quad (1)$$

$$O_2 \rightarrow 2\,O \quad (2)$$

$$H^{\cdot} + O_2 \rightarrow {}^{\cdot}OOH \quad (3)$$

$$O + H_2O \rightarrow 2{}^{\cdot}OH \quad (4)$$

$$H^{\cdot} + O_2 \rightarrow {}^{\cdot}OH + O \quad (5)$$

These primary radicals of sonolysis can react in the gas phase, recombine at the cavitation bubble interface and ejected to the solution bulk to form hydrogen peroxide (reactions (6) and (7)) and/or to initiate oxidation reactions:

$$2{}^{\cdot}OH \rightarrow H_2O_2 \quad (6)$$

$$2{}^{\cdot}OOH \rightarrow H_2O_2 + O_2 \quad (7)$$

According to hot spot theory, three different regions have been suggested for sonochemical reactions. The gaseous interior of the collapsing bubbles, the interfacial region being the thin shell of fluid surrounding the collapsing cavitation bubble and the bulk of the solution [28]. The chemistry involved in the degradation of organic pollutants is not identical for all organic pollutants. Volatile and hydrophobic molecules are degraded via pyrolytic and combustive reactions inside the collapsing cavities. Non-polar compounds with low volatility will be destructed at the interfacial liquid region between cavitation bubbles where the hydroxyl radical reactions are predominant and the bulk solution, and, to a lesser extent, hydrophilic chemicals will react with hydroxyl radicals that migrate from the bubble–liquid interface into the bulk solution region.

The advanced oxidation kinetics and mechanisms of methylparaben and PPB have been investigated using photocatalysis as an AOPs model [29,30]. In a recent work [31], the potential of a photosonolysis process for the degradation of butylparaben was examined. To the best of our knowledge, data on the ultrasonic removal of PPB from contaminated water have not been reported previously. Additionally, it is of considerable practical interest to examine the sonochemical degradation of PPB in complex matrices such as natural water and seawater. Thus, the aim of this work was to evaluate PPB elimination under sonochemical conditions. It is of special and practical interest to study this process in complex matrices, as various matrix components may considerably affect the sonochemical kinetics and therefore the overall treatment efficiency. Hence, the degradation of PPB in natural water and seawater was investigated. Additionally, the effect of initial solution pH on the sonolytic destruction of the pollutant was examined.

2. Materials and methods

2.1. Materials

Analytically pure PPB ($C_{10}H_{12}O_3$, Propyl 4-hydroxybenzoate) was obtained from Sigma–Aldrich. Table 1 lists relevant data for PPB. Deionized water was obtained with activated carbon and ion exchange resins from Fisher Bioblock Scientific (Illkirch, France). The solutions of PPB were prepared by dissolving the corresponding amount of substrate into pure water, mineral water, or seawater. Pure water was used as a component of the mobile phase in analysis by high performance liquid chromatography (HPLC).

2.2. Ultrasonic reactor

Sonolysis experiments were performed at 352 kHz using a Sea & Sun Technology USW 51–52 ultrasonic flat plate transducer with an active area of 25 cm^2. The used frequency was reputed to be the best for the degradation of non-volatile organic pollutants [33,34]. A double-walled glass thermostated vessel containing 300 mL of PPB solution was directly coupled to the transducer. The transducer was powered by a T&C Power Conversion, Inc. Amplifier (AG series). The temperature of the system was maintained at 25℃ by circulating water through a double-walled jacketed reaction cell. The acoustic power dissipated into the solution volume was determined using a standard calorimetric technique [35,36].

Each experiment was repeated at least three times in order to verify the reproducibility.

2.3. Analyzes

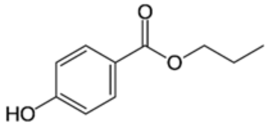
Quantitative analysis of the pollutant was performed by HPLC using a Waters Associates 590 instrument equipped with a Supelcosil LC-18 column (ID = 4.6 mm, length = 250 mm). Sample injections were achieved with a Rheodyne injection system equipped with a 20 μL sample loop for PPB concentrations above 1 mg/L and a 200 μL loop for the lowest concentrations. Detection was realized with a UV detector (model 440) set at 254 or 190 nm. The mobile phase, water/acetonitrile (50/50, v/v), was run in an isocratic mode.

3. Results and discussion

3.1. Degradation of PPB in pure water

Aqueous solutions of PPB at different initial concentrations in the range of 10–400 mg/L were irradiated by 352 kHz and 80 W ultrasonic wave. The obtained results are presented in Fig. 1. From this figure, it was observed that the initial concentration of substrate decreased exponentially with sonication time. The extent of degradation is found to be inversely proportional to the initial concentration of PPB. The removal of PPB was completely accomplished after 60 min of sonication for initial substrate concentration of 10 mg/L, but the elimination percentage decreased to 99% for 25 mg/L PPB, 78% for 50 mg/L

Table 1
Physico-chemical properties of PPB [32]

Molecule	PPB
CAS number	94-13-3
Molecular formula	$C_{10}H_{12}O_3$
Chemical structure	
Molecular weight (g/mol)	180.20
Solubility (mg/L) at 25℃	4.63×10^2
pK_a	8.24
log K_{OW}	3.04
Vapor pressure (mm Hg at 25℃)	5.55×10^{-4}
Henry’s law constant at 25℃ (atm m^3/mol)	6.37×10^{-9}
·OH reaction rate constant (M^{-1} s^{-1})	8.49×10^9

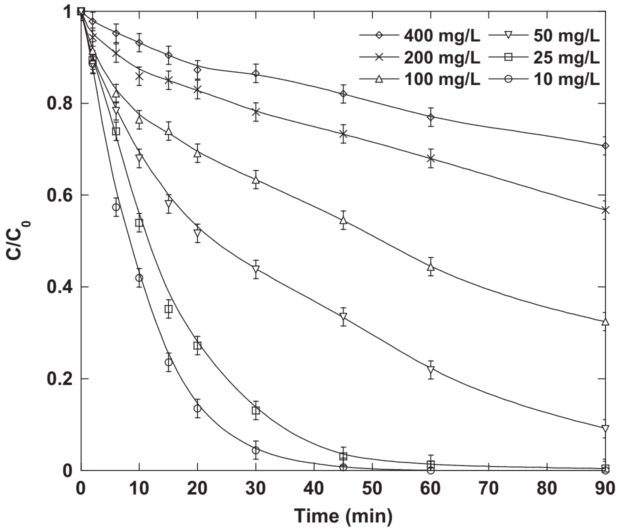


Fig. 1. Sonochemical degradation of PPB at different initial concentrations in pure water (conditions: solution volume: 300 mL, initial PPB concentration: 10–400 mg/L, temperature: 25℃, natural pH (~6), frequency: 352 kHz, ultrasonic power: 80 W).

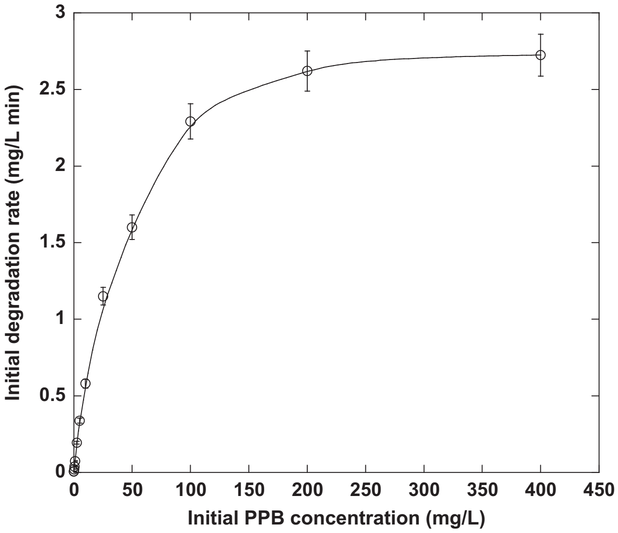


Fig. 2. Evolution of initial degradation rate of PPB as a function of initial substrate concentrations (conditions: solution volume: 300 mL, initial PPB concentration: 0.05–400 mg/L, temperature: 25℃, natural pH (~6), frequency: 352 kHz, ultrasonic power: 80 W).

PPB, 56% for 100 mg/L PPB, 32% for 200 mg/L PPB and 23% for 400 mg/L PPB. At high PPB concentrations, the low elimination percentage was attributed to the competition between various PPB molecules and/or the intermediate products formed during the oxidation process. Both PPB and its transformation products can compete for hydroxyl radical generated from the cavitation bubbles. Thus, the PPB removal percentage was decreased due to increasing competition for the hydroxyl radical when initial substrate concentration was higher.

The initial degradation rates of PPB were obtained over the first minutes of sonication from the results showing the evolution of solute concentration vs. sonication time. In Fig. 2, initial degradation rate of PPB is plotted as a function of initial substrate concentrations of 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25, 50, 100, 200, and 400 mg/L. Initial degradation rate increased with an increase in the initial concentration up to 200 mg/L, followed by almost constant sonolytic degradation rate (within experimental error) for higher concentration. However, a linear relationship was not observed, as expected, for a first-order kinetic law. Consequently, it is clear that sonochemical degradation does not follow a first-order kinetics and then cannot be characterized by a single rate constant expressed in 1/time (min^{-1}). The degradation rate is dependent on the concentration of ·OH radicals produced and the concentration of the substrate at the interface of the cavitation bubble. Although about 80% of the ·OH radicals generated in sonolysis recombine to form H_2O_2, ·OH radicals can react with solute molecules adsorbed at the bubble/solution interface, and thus are in competition with radical recombination reactions. At low concentrations of PPB, the combination of ·OH radical to produce H_2O_2 would dominate. With an increase in the solution concentration of solute, the probability of ·OH radical attack on PPB molecules would increase, leading to an increase in the degradation rate. However, if the solute molecules at high concentration reach a saturation limit at the bubble surface during the persistence time of the bubble, an almost constant degradation rate would be achieved.

The properties of organic pollutants, such as octanol-water partition coefficient, vapor pressure, Henry's law constant, second-order rate constant with ·OH and solubility, have been shown to affect degradation rates by ultrasound [37]. The two main pathways for the sonochemical degradation of organic compounds in aqueous solution are: (i) thermal decomposition of volatile pollutant molecules entrapped inside the bubble and (ii) the reaction of ·OH radicals with the nonvolatile solute at the bubble interface and in the bulk solution [25,26]. With low Henry's law constant (6.37×10^{-9} atm m^3/mol at 25℃), suggesting low fugacity, relative high solubility in water (4.63×10^2 mg/L at 25℃), indicating hydrophilic nature of the molecules, and low vapor pressure (5.55×10^{-4} mm Hg at 25℃), PPB cannot be degraded by pyrolysis inside the cavitational bubble. Furthermore, due to its relative high octanol-water partition coefficient ($\log K_{OW} = 3.04$), the main mechanism of PPB degradation by ultrasound is most likely its oxidation by free radicals both at the cavitation bubble interface and in the aqueous phase, rather than by pyrolysis inside the bubble. Thus, the $^{\cdot}$OH radicals generated by ultrasound are the principal responsible for the degradation of the pollutant.

3.2. Effect of initial pH on PPB degradation

The solution pH is generally a paramount factor influencing the efficiency of the sonochemical degradation of organic pollutants [38–41]. The effect of pH on the sonolytic degradation of PPB was examined in the pH range of 3–10.5 at initial substrate concentration of 10 mg/L. The obtained results are presented in Fig. 3. From this figure, it can be seen that the initial degradation rate of PPB was not markedly affected in the pH interval of 3–8, but decreased with increasing pH for the pH range of 8–10.5. The lower degradation is observed at pH 10.5. As previously reported [42], solution initial pH in the interval 3–10.5 has no significant effect on the sonochemical production of hydrogen peroxide in the absence of substrate. Therefore, the influence of pH on the sonolytic degradation of PPB is possibly due to the chemical structure of PPB. As a phenolic compound with pK_a value of 8.24 [29], PPB mainly existed as a neutral molecule at low pH value under pK_a, while it mainly existed as a negative species when pH value was higher than pK_a. Thus, the reaction of PPB with $^{\cdot}$OH was expected to be significantly affected by pH value because pH may determine radical reaction mechanisms of $^{\cdot}$OH with PPB. That is, in the pH range of 3–8, PPB is mostly found in its molecular neutral form and it is accumulated at the bubble/solution interface, where $^{\cdot}$OH radical concentration is remarkably high. Thus, in these conditions, PPB is more readily subjected to the $^{\cdot}$OH radical attack. As the pH increases higher than the pK_a of PPB, where the compound is in its deprotonated ionic form because of the ionization of the hydroxyl group, its hydrophilicity is increased. In these circumstances, PPB degradation takes place in the bulk solution where a lower proportion of $^{\cdot}$OH radicals are available [43]. Thus, high pH solutions undergo sonochemical degradation at a much slower rate.

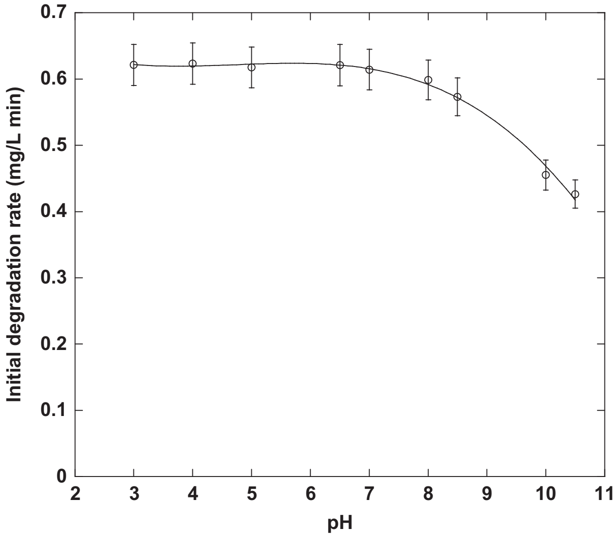


Fig. 3. Effect of pH on sonochemical degradation of PPB (conditions: solution volume: 300 mL, initial PPB concentration: 10 mg/L, temperature: 25˚C, frequency: 352 kHz, ultrasonic power: 80 W).

3.3. Degradation of PPB in natural water and seawater

Many works have been carried out on the ultrasonic degradation of pollutants but a limited number of them involve water matrices effects. Ultrasound presents important advantages compared to other advanced oxidation technologies, because some works have indicated that the rate of sonochemical degradation of organic pollutants in real water matrices was not affected or enhanced and few studies have shown inhibition effects [15,44–50]. Therefore, the evaluation of the effect of inorganic compounds and organic species present in natural water and seawater on the sonolytic degradation of pollutant is of special interest. In order to assess this and to evaluate the applicability of the sonochemical treatment to a real water treatment, PPB was dissolved in a natural mineral water and in seawater. The main characteristics of the natural mineral water are: Ca^{2+}: 468 mg/L, Mg^{2+}: 74.5 mg/L, Na^+: 9.4 mg/L, K^+: 2.8 mg/L, SO_4^{2-}: 1,121 mg/L, HCO_3^-: 372 mg/L, Cl^-: 7.6 mg/L, NO_3^-: 2.9 mg/L, F^-: 0.36 mg/L, pH 7.4, salinity: 2,078 mg/L. The seawater has a high salinity (~35 g/L), which is composed mainly of Na^+: 11 g/L, Mg^{2+}: 1.3 g/L, Ca^{2+}: 0.4 g/L, Cl^-: 20 g/L, SO_4^{2-}: 3 g/L. Figs. 4 and 5 show the comparative degradation of PPB in pure water, natural mineral water, and seawater at various initial substrate concentrations in the range of 5–100 mg/L. From Fig. 4(a), the matrices in natural water and seawater accelerate the degradation of PPB (5 mg/L) compared to that obtained in pure water. As noticed in Fig. 4(b), the degradation of 10 mg/L PPB was not affected in the three studied water media. However, as seen in Fig. 5(a) and (b), a slightly negative effect was observed at initial concentration of PPB of 25 and 100 mg/L, especially in natural mineral water. Thus,

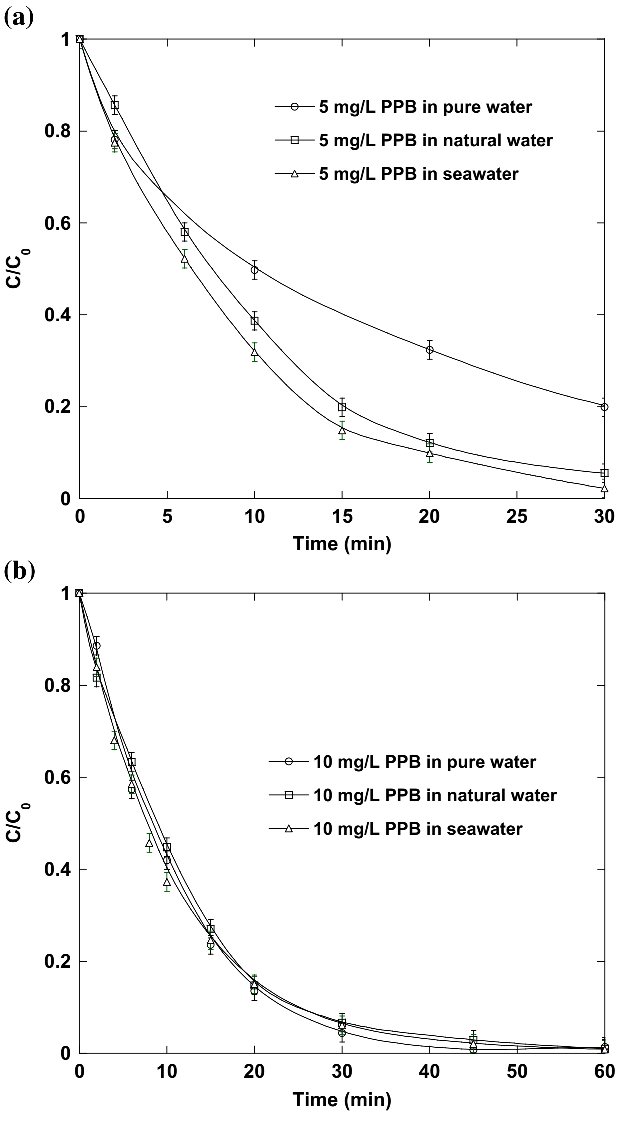


Fig. 4. Degradation of PPB in pure water, natural water, and seawater. (a) 5 mg/L of PPB and (b) 10 mg/L of PPB (conditions: solution volume: 300 mL, temperature: 25˚C, frequency: 352 kHz, ultrasonic power: 80 W).

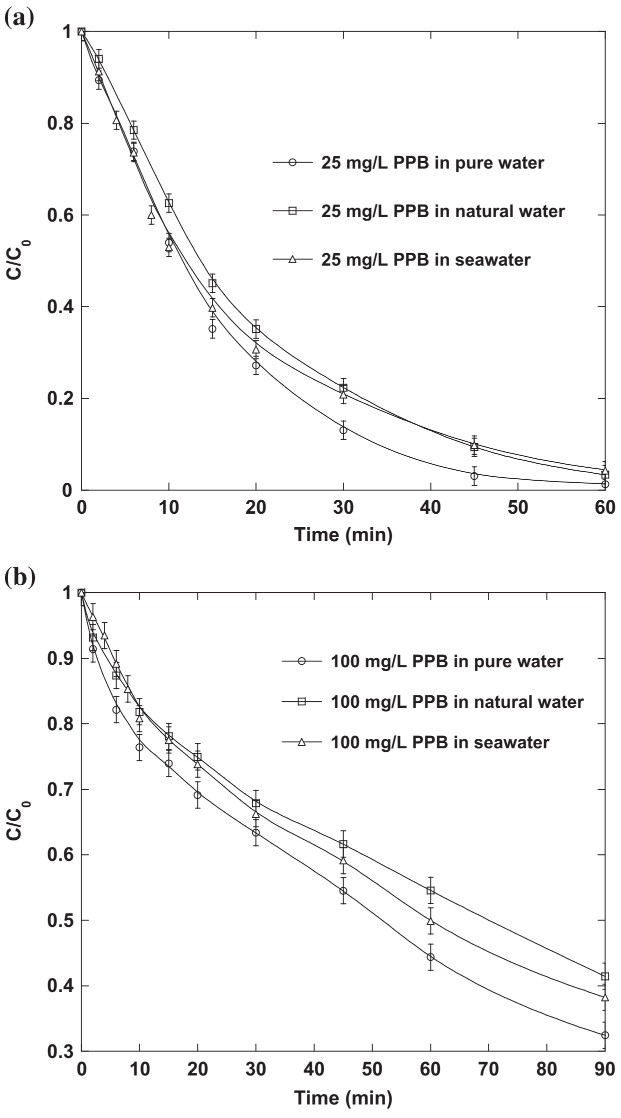


Fig. 5. Degradation of PPB in pure water, natural water, and seawater. (a) 25 mg/L of PPB and (b) 100 mg/L of PPB (conditions: solution volume: 300 mL, temperature: 25˚C, frequency: 352 kHz, ultrasonic power: 80 W).

the sonochemical degradation of PPB in natural mineral water and in seawater is depending on the substrate concentration. The sonolytic degradation of the pollutant is interestingly enhanced at low PPB concentration, but the removal is marginally affected when a highly concentrated solution of PPB is treated.

3.4. Determination of degradation mechanism

In order to determine the local reaction zone, the kinetic pattern of sonochemical degradation of non-volatile hydrophilic compounds was described by the models of Serpone et al. [51] and Okitsu et al. [52–54], which correlate the rate of reaction with the concentration regime.

Serpone et al. [51] have investigated sonochemical degradation of three chlorophenols in aqueous media and proposed the degradation rate model described by Eq. (8):

$$r = K_b + \frac{k_S K_S C_0}{1 + K_S C_0} \tag{8}$$

where r is the initial degradation rate (mg/L min), K_b is a constant representing the rate of decomposition in the bulk liquid (mg/L min), k_S is the pseudo-rate constant (mg/L min), K_S is the equilibrium constant of adsorption–desorption (L/mg) and C_0 (mg/L) is the pollutant initial concentration.

Expression (8) indicates that the rate of disappearance of the pollutant follows a concentration-independent path and a concentration-dependent course [51]. In this model, the overall rate of solute decomposition r is the sum of the rates in the bulk solution and the interfacial layer and can be estimated by the observed concentration reduction within short time intervals.

Okitsu et al. [52–54] have proposed a Langmuir type kinetic model based on a heterogeneous reaction system, and this model is applicable to the analysis of sonochemical degradation of PPB. In this model, the degradation rate (r) is represented as shown in Eq. (9):

$$r = \frac{k_O K_O C_0}{1 + K_O C_0} \tag{9}$$

where r is the initial degradation rate (mg/L min), k_O is the pseudo-rate constant (mg/L min), K_O is the equilibrium constant of adsorption–desorption (L/mg), and C_0 (mg/L) is the pollutant initial concentration.

The kinetics of the sonochemical degradation of PPB was monitored for a large initial concentration range of 0.05–400 mg/L in pure water and 0.05–100 mg/L in natural mineral water and seawater. Figs. 6–8 show the evolution of initial degradation rate of PPB vs. initial substrate concentration in pure water, natural water, and seawater, respectively. The results of Figs. 6–8 were modeled by the equations of Serpone et al. [51] and Okitsu et al. [52–54]. The parameters of the models were determined by non-linear regression method using KaleidaGraph© software and the curves were reconstituted using the determined values. This method was found to be the more appropriate technique to determine the parameters of the used models [55]. The obtained values of the parameters of both models, correlation coefficients (R) and average percentage errors (APE), calculated using Eq. (10), are regrouped in Table 2. Figs. 6–8 show the corresponding theoretical curves superposed on the experimental data points:

$$\mathrm{APE}(\%) = \frac{\sum_{i=1}^{N} \left| \frac{r_{\mathrm{experimental}} - r_{\mathrm{predicted}}}{r_{\mathrm{experimental}}} \right|}{N} \times 100 \tag{10}$$

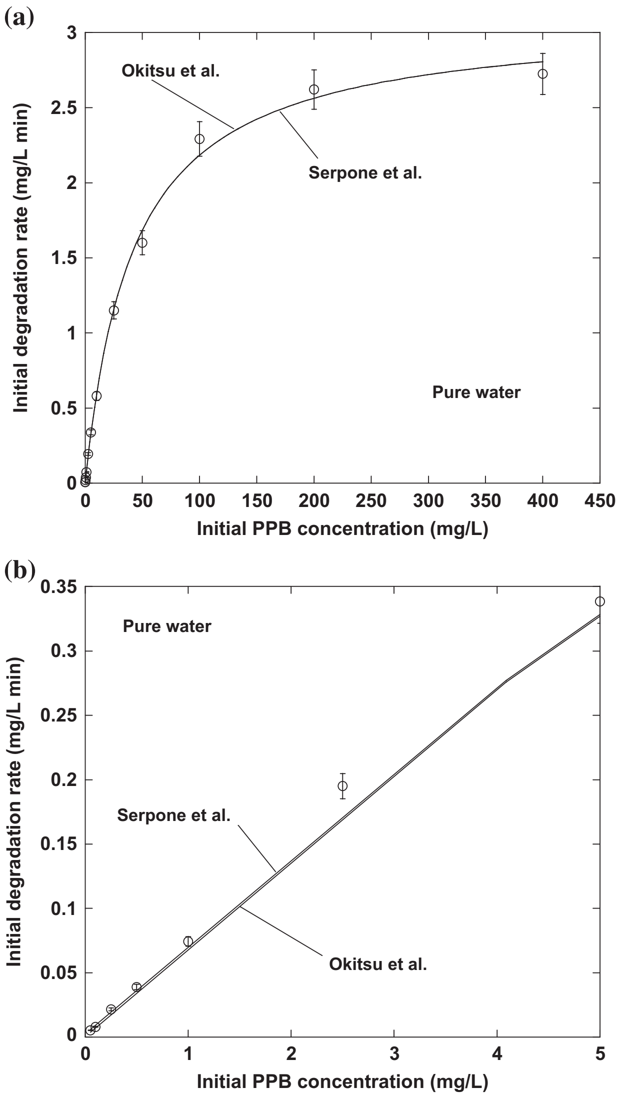


Fig. 6. Comparison of experimental and predicted initial degradation rate in pure water (a) at different initial concentrations of PPB and (b) at low initial concentrations of PPB.

where N is the number of experimental data.

From Fig. 6 and Table 2, it was clearly seen that the two models adequately described the sonolytic destruction of PPB in pure water, but the Serpone et al.'s equation was better because of the low value of APE. This indicates that the degradation of PPB mostly takes place at the bubble/solution interface by hydroxyl radical attack, whereas some radical reactions also occurred in the bulk of the solution as the Serpone's model showed the more perfected fitting of the experimental data at low substrate concentration (<5 mg/L). At high PPB concentration (≥5 mg/L),

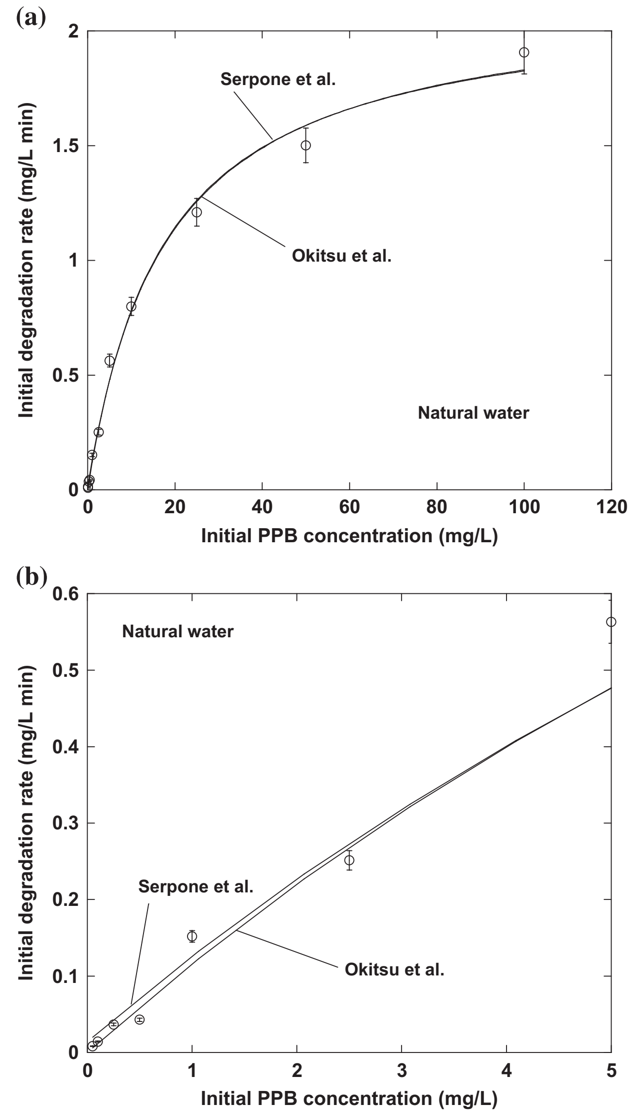


Fig. 7. Comparison of experimental and predicted initial degradation rate in natural water (a) at different initial concentrations of PPB and (b) at low initial concentrations of PPB.

both models perfectly fitted the experimental results with the same APE values (4.1%).

As seen in Fig. 7 and Table 2, it seems that the experimental data for the sonochemical degradation of PPB in natural water are well represented by the Okitsu et al.'s model. A worse fit of the sonolytic degradation results is obtained at low initial PPB concentration (<5 mg/L) using the Serpone et al.'s model because of the extremely high values of APE. At high substrate concentration (≥5 mg/L), it was clearly shown that the two tested equations satisfactorily fitted the ultrasonic destruction results in natural water.

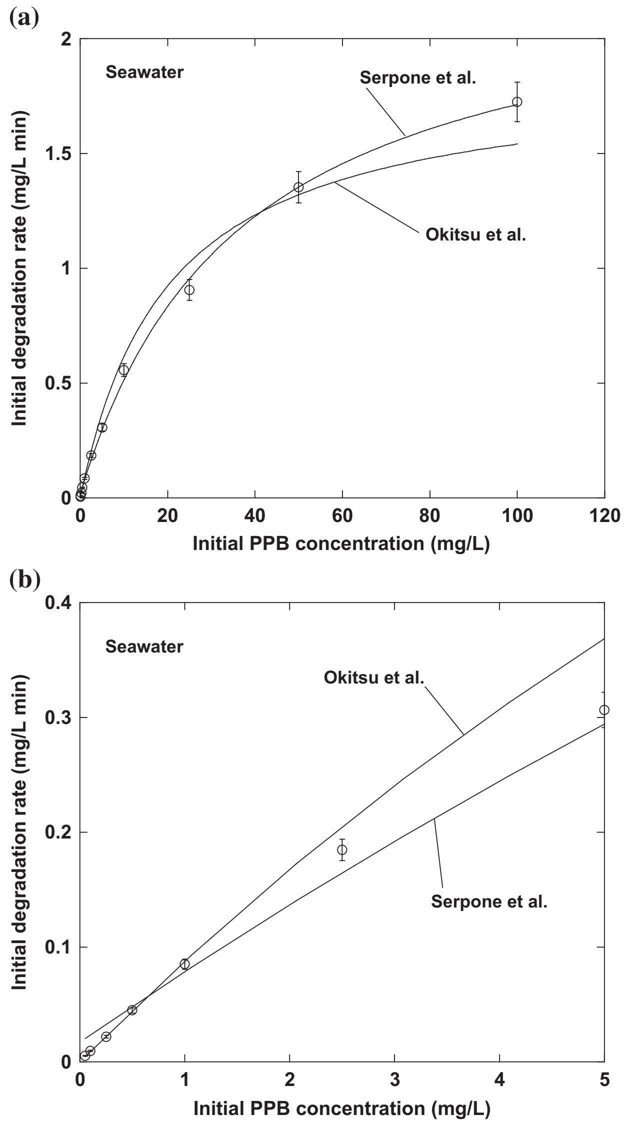


Fig. 8. Comparison of experimental and predicted initial degradation rate in seawater (a) at different initial concentrations of PPB and (b) at low initial concentrations of PPB.

The high values of APE obtained for the two tested models in natural water (Table 2) are due to a worse fit of the sonochemical degradation results at low initial PPB concentration (<5 mg/L).

From Fig. 8 and Table 2, it appears that the better and perfect representation of the experimental results of the ultrasonic degradation of PPB in seawater is obtained using the Okitsu et al.'s model for all the range of tested initial substrate concentration. At low initial substrate concentration (<5 mg/L), a worse fit of the experimental degradation data was observed using the Serpone et al.'s equation. The experimental

Table 2
Parameters of the models of Okitsu et al. and Serpone et al. obtained using the non-linear regression method

Model	Parameters	Pure water	Natural water	Seawater
Okitsu et al. $r = \frac{k_O K_O C}{1+K_O C}$	K_O (L/mg)	0.02387	0.05721	0.04978
	k_O (mg/L min)	3.0999	2.1445	1.8507
	R	0.9989	0.99705	0.99209
	APE (%)	7.9	32.3	10.7
Serpone et al. $r = K_b + \frac{k_S K_S C}{1+K_S C}$	K_S (L/mg)	0.02379	0.05492	0.02711
	k_S (mg/L min)	3.099	2.1467	2.3221
	K_b (mg/L min)	0.00222	0.01430	0.01737
	R	0.9989	0.99715	0.99922
	APE (%)	5.7	58.5	33.1

results of the sonochemical degradation was appropriately simulated by both models at high initial PPB concentration (≥5 mg/L), but the Okitsu et al.'s model was better because of the low values of APE.

The results of Figs. 6–8 and Table 2 indicate that a perfect representation of the experimental data of PPB sonochemical degradation in pure water was obtained using the Serpone et al.'s model. In real water matrices (natural water and seawater), an adequate description of the sonolytic destruction of PPB was attained by the Okitsu et al.'s equation. These results indicate that PPB undergoes degradation predominantly at the bubble/solution interface in natural water and seawater, whereas the sonolytic destruction of substrate in pure water is mainly achieved both at bubble/solution interface and in the bulk solution. It seems that the fraction of PPB reacting primarily on the bubble surface are minimally affected by real waters components but the portion of substrate reacting primarily in bulk solution are significantly affected by real water matrices components.

4. Conclusion

The results presented in this study illustrate the interesting potential of 352 kHz ultrasonic irradiation to treat water contaminated with endocrine disrupting compounds such as propylparaben, even in complex natural water matrices. Sonochemical degradation of PPB for a large range of initial concentrations in pure water, natural water, and seawater was investigated. The initial rates of pollutant degradation at different initial concentrations were determined. The obtained results show that the destruction rate increases with increasing initial substrate concentration up to a plateau. At a medium concentration of PPB (10 mg/L), similar degradation rates were observed for all the tested media. At a low concentration of PPB (5 mg/L), an improvement in the degradation process was observed in natural matrices, while at high concentrations of PPB (25–100 mg/L), degradation was slightly inhibited, particularly in natural water. PPB sonochemical degradation in water occurs mainly through reactions with hydroxyl radicals generated by ultrasound. Due to the acid–base properties of PPB, initial pH of the solution is fundamental for the sonochemical treatment. Best results were found in the pH range of 3–8, where the chemical structure of the substrate is in the molecular protonated form. Kinetic models based on a Langmuir-type mechanism were used to predict the sonochemical degradation of PPB. An adequate description of the ultrasonic destruction of PPB in natural water and seawater was obtained by the Okitsu et al.'s model. In pure water, a perfect representation of the experimental data of PPB sonolytic degradation was attained using the Serpone et al.'s equation. These results indicate that PPB undergoes degradation in pure water predominantly both at bubble/solution interface and in the bulk solution, whereas the sonolytic destruction of substrate in natural water and seawater is mainly achieved at the bubble/solution interface. Hence, ultrasonic treatment represents a very interesting advanced oxidation technique for the removal of PPB in complex matrices such as natural water and seawater.

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