# Ultrasonic degradation of 1-H-benzotriazole in water

Henry Zúñiga-Benítez, Jafar Soltan and Gustavo Peñuela

## ABSTRACT

This paper reports on the effect of different parameters of ultrasonic power, pollutant initial concentration, pH and the presence of co-existing chemical species (oxygen, nitrogen, ozone, and radical scavengers) on the ultrasonic degradation of the endocrine disruptor 1-H-benzotriazole. Increasing the 1-H-benzotriazole initial concentration from 41.97 to 167.88 μM increased the pollutant degradation rate by 40%. Likewise, a high applied ultrasonic power enhanced the extent of 1-H-benzotriazole removal and its initial degradation rate, which was accelerated in the presence of ozone and oxygen, but inhibited by nitrogen. The most favorable pH for the ultrasonic degradation was acidic media, reaching ~90% pollutant removal in 2 h. The hydroxyl free radical concentration in the reaction medium was proportional to the ultrasound power and the irradiation time. Kinetic models based on a Langmuir-type mechanism were used to predict the pollutant sonochemical degradation. It was concluded that degradation takes place at both the bubble–liquid interfacial region and in the bulk solution, and OH radicals were the main species responsible for the reaction. Hydroxyl free radicals were generated by water pyrolysis and then diffused into the interfacial region and the bulk solution where most of the solute molecules were present.

**Key words** | advanced oxidation process, benzotriazole, degradation, ultrasound, water treatment

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## INTRODUCTION

Emerging pollutants and endocrine disruptors (compounds that alter the hormonal balance) are present in various commercial products with wide use in industry and domestic applications (Bolong et al. 2009). 1-H-benzotriazole (BZ), a polar high production-volume chemical, has been regarded as an emerging pollutant (Xu et al. 2013). This compound and its derivatives are commonly used in several applications including corrosion inhibitor for metals, antifoggant in photography and UV stabilizer for plastics. Benzotriazoles are UV stable and resistant to biodegradation and oxidation under environmental conditions; as a result they can persist in the environment for a very long time. This kind of substance has the potential to cause damage to aquatic species, compromising their growth and reproduction, due to the disruption of the endocrine system. It can also induce toxic effects in plants such as tomato plants, cucumber seedlings and bush bean plants (Tangtian et al. 2012; Durjava et al. 2013).

BZ has been found in wastewaters and the subsequently impacted surface waters. This compound is resistant to removal by chlorination, conventional wastewater treatment processes, bank filtration, and biologically active filters. However, it can be degraded by ozone and advanced oxidation processes (Reemtsma et al. 2010; Mawhinney et al. 2012).

Ultrasound (US) irradiation is a novel advanced oxidation technology that has received considerable attention as a new alternative for removal of persistent organic pollutants (Méndez-Arriaga et al. 2008; Mahvi 2009; Chiha et al. 2011). The propagation of US through a liquid leads to the acoustic cavitation phenomenon. In the cavitation process, bubbles are generated from existing gas nuclei in liquids. They form, grow, and collapse through compression and rarefaction cycles. Temperature and pressure in collapsing bubbles can reach extreme levels (Mahvi 2009; Chiha et al. 2011). In aqueous systems, these conditions lead to the thermal dissociation of water vapor into reactive hydroxyl free radicals and hydrogen atoms (Equation (1)); but under different conditions, various other radicals may be present (Chiha et al. 2011).

$$H_2O + )))) \rightarrow H^\bullet + {}^\bullet OH \tag{1}$$

The chemistry involved in the destruction of organic pollutants by US is not the same for all substances and depends on volatility, hydrophobicity, and surface activity of the compound, causing a number of chemical processes. According to the hot spot theory, sonochemical reactions can occur in three different regions: (i) the interior of the collapsing bubbles; (ii) the bubble–liquid interfacial region where the hydroxyl free radical reactions are predominant; and (iii) the bulk of the solution region (Chiha *et al.* 2010, 2011). Taking into account this theory, a volatile and hydrophobic pollutant most probably will be decomposed inside the bubble of cavitation, while a non-volatile and hydrophilic compound will be oxidized by the radicals in the interfacial region or bulk solution.

Based on the literature and the fact that data on the sonochemical degradation of BZ have not been reported previously, the aim of this study was to evaluate the use of US for BZ degradation, studying the effect of operating parameters such as pH, pollutant initial concentration, applied power, and the presence of co-existing chemical species (dissolved gases: oxygen, nitrogen and ozone; and radical scavengers: alcohols). Additionally, the amount of hydroxyl free radicals generated in the process was determined and its impact on the reaction was analyzed.

## MATERIALS AND METHODS

### Materials

All the chemicals used were of analytical grade. Solutions were prepared using Millipore water (18.2 MΩ cm). BZ containing more than 99% of pure compound was purchased from Alfa-Aesar. Ultra-high purity grade oxygen, nitrogen, and air were supplied by Praxair. Ozone was produced from pure oxygen using a laboratory ozone generator (Azco Industries Ltd, VMUS-4S). High performance liquid chromatography (HPLC)-grade methanol and acetonitrile were obtained from Sigma-Aldrich. The pH adjustment was carried out with concentrated solutions of sodium hydroxide and nitric acid obtained from Alfa-Aesar.

### Ultrasonic reactor

Experiments were conducted in a cylindrical glass reactor. An Ultrasonic VCX-500 (Sonics and Materials, USA) was used as US generator. Ultrasonic waves (20 kHz) were emitted from the probe (tip diameter: 13 mm, length: 136 mm, material: titanium alloy) which was completely immersed in the solution (probe/horn system). The temperature of the solution was maintained at $25 \pm 2\,^{\circ}C$ using a cooling water bath. The amplitude of vibration at the probe tip was controlled at different levels (80, 90, and 100%), corresponding to three nominal powers – 87.50, 101.40, and 114.80 W. Ultrasonic energy dissipated in the reactor was estimated using the calorimetric method; for each system under study the initial temperature rise ($T$) was recorded against time ($t$) in different time intervals. In each sonication run 200 mL of solution were processed, and samples of 1 mL were withdrawn at different time intervals. In the experiments with ozone, samples were quenched using a sodium thiosulfate solution. All the runs were conducted at least three times, and the standard deviations and coefficients of variation of the data were below 5%.

### Analytical methods

BZ concentration in water was determined using an Agilent Technologies 1100 HPLC system, with a Phenomenex Luna C-8 column (250 mm × 4.6 mm) and a diode array detector set at 275 nm. The mobile phase was a mixture of methanol and Milli-Q water (30:70, v/v) at a constant flow rate of 1 mL min$^{-1}$. The column temperature was maintained at 30 $^{\circ}$C and the injection volume was 100 μL. The OH radical concentration was measured using dimethyl sulfoxide as a capture agent to generate formaldehyde. The formaldehyde was treated with 2,4-dinitrophenylhydrazine to produce formaldehyde-2,4-dinitrophenylhydrazone, which was quantified using HPLC with an Eclipse Plus C-18 column (150 mm × 4.6 mm) and a mixture of acetonitrile and Milli-Q water (45:55, v/v) as mobile phase. The dissolved organic carbon (DOC) was determined using a Shimadzu TOC-L CPH/CPN instrument.

## RESULTS AND DISCUSSION

### Effect of initial BZ concentration

The effect of BZ initial concentration was studied in the range of 5–20 mg L$^{-1}$ (41.97–167.88 μmol L$^{-1}$) and the concentration profiles are shown in Figure 1(a). It can be noticed that the extent of BZ degradation ($C/C_0$) is inversely proportional to the pollutant initial concentration, but the initial degradation rates (depicted in Figure 2), computed as $\Delta C/\Delta t$ over the first minutes of sonication, are higher for higher initial substrate concentrations. A linear relationship was not observed, as expected, for a first-order kinetic law.
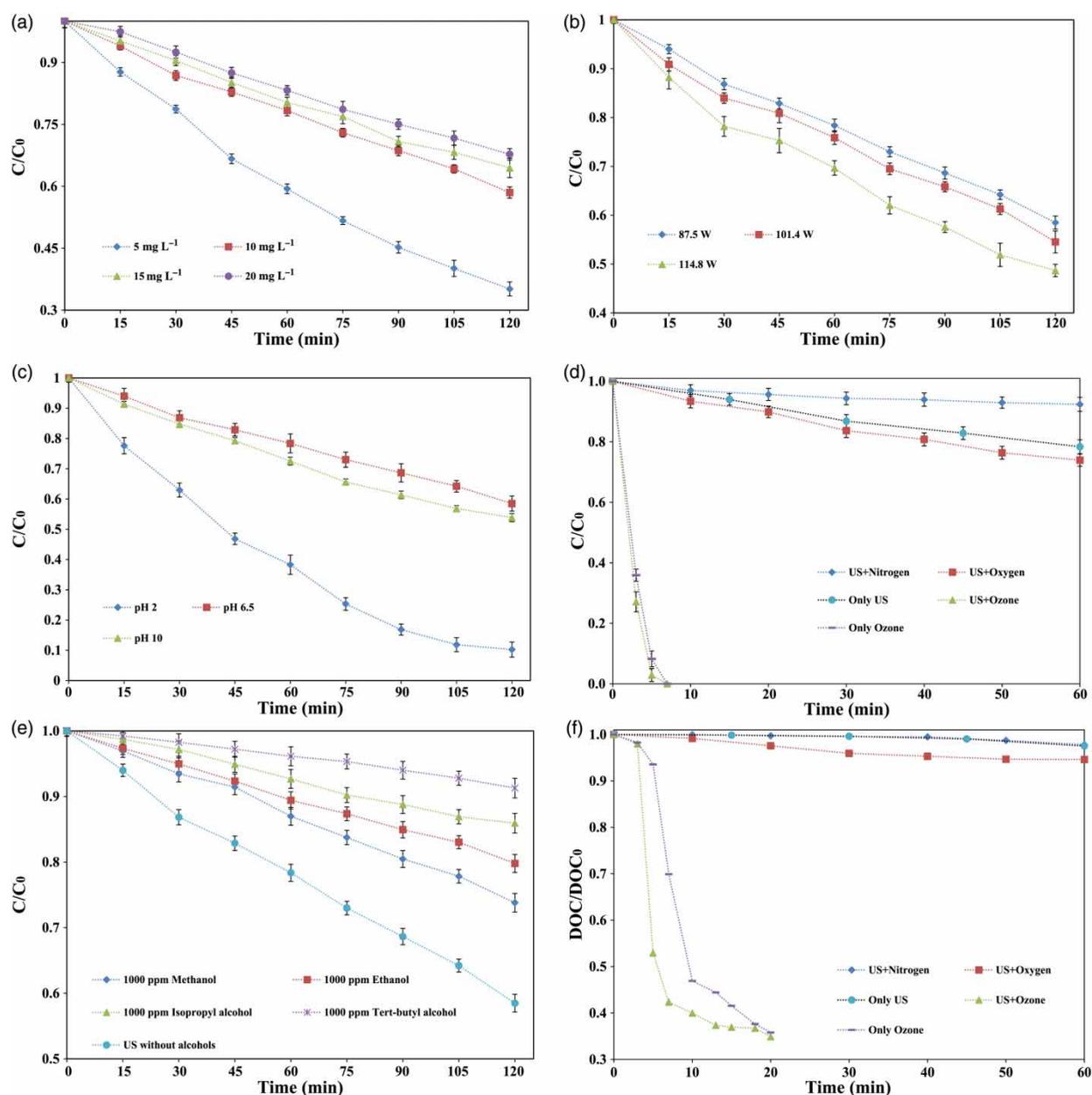
**Figure 1** │ Effect of different parameters on BZ ultrasonic degradation: (a) effect of BZ initial concentration (frequency: 20 kHz, temperature: $25 \pm 2$ °C, power: 87.5 W, pH: natural (6.5)); (b) effect of the applied power (frequency: 20 kHz, temperature: $25 \pm 2$ °C, BZ concentration: 10 mg $L^{-1}$, pH: natural (6.5)); (c) effect of the initial pH (frequency: 20 kHz, temperature: $25 \pm 2$ °C, BZ concentration: 10 mg $L^{-1}$, power: 87.5 W); (d) effect of the dissolved gas and (e) effects of different hydroxyl free radical scavengers (alcohols) on the BZ degradation (frequency: 20 kHz, temperature: $25 \pm 2$ °C, BZ initial concentration: 10 mg $L^{-1}$, power: 87.5 W, pH: 6.5); (f) effect of the dissolved gas on the solution DOC (frequency: 20 kHz, temperature: $25 + 2$ °C, BZ initial concentration: 10 mg $L^{-1}$, power: 87.5 W, pH: 6.5).

This observation is consistent with the results that other groups have reported for the sonolytic degradation of other emerging contaminants (Serpone *et al.* 1994; Méndez-Arriaga *et al.* 2008; Chiha *et al.* 2011). It is clear that the sonochemical degradation does not obey a first-order kinetics and cannot be characterized by a single rate constant (Chiha *et al.* 2010).

Table 1 shows some of the physicochemical properties of BZ. From the physical properties, it can be inferred that

this pollutant cannot be degraded by pyrolysis inside the cavitation bubbles (Henry's law constant is low). In addition, due to its high solubility in water and relatively high octanol/water partition coefficient, BZ preferentially distributes at the interfacial and bulk solution regions. Thus, the OH radicals generated by US are the main species responsible for the pollutant degradation, which most probably occurs not only in the bulk solution but also at the
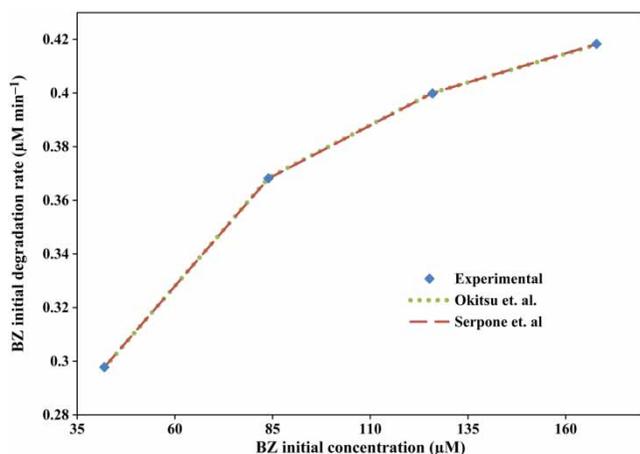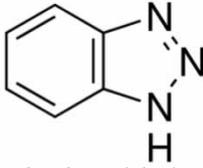
**Figure 2** │ Initial degradation rate as function of the initial concentration of BZ and comparison with predicted values (frequency: 20 kHz, temperature: 25 ± 2 °C, power: 87.5 W, pH: natural (6.5)).

**Table 1** │ Physicochemical properties of BZ (SRC PHYSPROP Database, 2013; http://www.srcinc.com/what-we-do/environmental/scientific-databases.html)



| | |
|---|---|
| Molecular weight (g gmole$^{-1}$) | 119.13 |
| Water solubility (mg L$^{-1}$), 25 °C | $1.98 \times 10^4$ |
| Henry's law constant (atm m$^3$ mol$^{-1}$), 25 °C | $1.47 \times 10^{-7}$ |
| Octanol/water partition coefficient (Log $K_{OW}$) | 1.44 |

bubble–liquid interfacial region where hydroxyl free radical concentration is higher (Méndez-Arriaga *et al.* 2008). The fact that the degradation rate increases with a higher solute initial concentration shows that the probability of a hydroxyl free radical attack on contaminant molecules increases with increase of substrate in solution, since a higher BZ concentration would imply that initially the hydroxyl attack on contaminant molecule predominates over other reactions such as OH recombination (Chiha *et al.* 2010, 2011; Gao *et al.* 2013). Additionally, the formation of byproducts could generate additional reactions that could compete with the BZ removal.

Models have been developed with the objective of describing the kinetic pattern of sonochemical degradation of non-volatile hydrophilic compounds. This is the case of the heterogeneous kinetic model based on a Langmuir-type mechanism proposed by Okitsu *et al.* (2005), in which

it is assumed that the rate of adsorption, $r_1$, of pollutant molecules from the bulk solution to the interfacial region of cavitation bubbles is proportional to the pollutant concentration in the bulk solution and $(1-\theta)$, where $\theta$ corresponds to the occupied ratio of the pollutant molecules in the effective reaction site; and the rate of desorption, $r_{-1}$, is proportional to $\theta$. Consequently, the rates of $r_1$ and $r_{-1}$ are expressed by use of the rate constants $k_1$ (min$^{-1}$) and $k_{-1}$ (μM min$^{-1}$) for adsorption and desorption, respectively; as follows (Equations (2) and (3)):

$$r = k_1 C_0 (1 - \theta) \tag{2}$$

$$r_{-1} = k_{-1}\theta \tag{3}$$

where $C_0$ is the initial concentration of pollutant in the bulk solution. When the steady state is reached

$$k_1 C_0 (1 - \theta) = k_{-1}\theta \tag{4}$$

Therefore, $\theta$ can be determined using Equation (5)

$$\theta = \frac{KC_0}{1 + KC_0} \tag{5}$$

where $K$ is $k_1/k_{-1}$. When pollutant molecules in the interfacial region of cavitation react with hydroxyl free radicals, the degradation rate, can be expressed by Equation (6)

$$r = \frac{kKC}{1 + KC} \tag{6}$$

where $r$ is the initial degradation rate (μM min$^{-1}$); $k$ is the pseudo-rate constant (μM min$^{-1}$); $C$ is the BZ initial concentration (μM) and $K$ is the equilibrium constant (μM$^{-1}$).

Serpone *et al.* (1994) also proposed a model in which $r$ is the sum of the rates in the bulk solution and the interfacial layer. They considered that the rate of disappearance of the pollutant follows a concentration-independent path and a concentration-dependent course (Chiha *et al.* 2010), as shown below (Equation (7)):

$$r = K_b + \frac{kKC}{1 + KC} \tag{7}$$

where $K_b$ is a constant representing the rate of decomposition in the bulk liquid (μM min$^{-1}$), $r$ is the initial degradation rate (μM min$^{-1}$), $k$ is the pseudo-rate constant

($\mu$M min$^{-1}$), $C$ is the BZ initial concentration ($\mu$M), and $K$ is the equilibrium constant ($\mu$M$^{-1}$).

Considering the above, the sonolytic degradation data were analyzed by the non-linear curve fitting analysis method, using Origin 9.0 software. The results of modeling are shown in Table 2 and Figure 2. An excellent fit between the experimental data and both models exists. However, comparing the coefficients of determination ($R^2$) of each model, it seems that the experimental initial rates for sonochemical degradation of BZ are described better by the Serpone et al. model ($R^2$ higher). This fact indicates that BZ degradation, at the initial concentration range studied, takes place at both the bubble–liquid interfacial region and in the bulk solution.

## Effect of the applied ultrasonic power

The effect of input power on the BZ degradation is shown in Figure 1(b). The percentages of BZ removal were 42, 46, and 51% under the ultrasonic powers of 87.5, 101.4, and 114.8 W, respectively. Additionally, with increasing power in this range, the initial degradation rate increased, reaching a maximum value around 0.61 $\mu$M min$^{-1}$ for 114.8 W applied power, which meant a 66% increase with respect to the initial rate at the lowest power.

It is believed that the number of active cavitation bubbles increases with the increase in the irradiation power. This in turn leads to an increase in the amount of hydroxyl free radical generated (Lim et al. 2007; Chiha et al. 2011; Gao et al. 2013). Experiments carried out to determine the concentration of OH radical based on the methods described by Tai et al. (2004) and Ji et al. (2012), showed that as the applied power increases, the amount of radical increases, as shown in Figure 3. The increase in the amount of radicals might be responsible for the enhancement in the BZ degradation rates. In addition, a high US
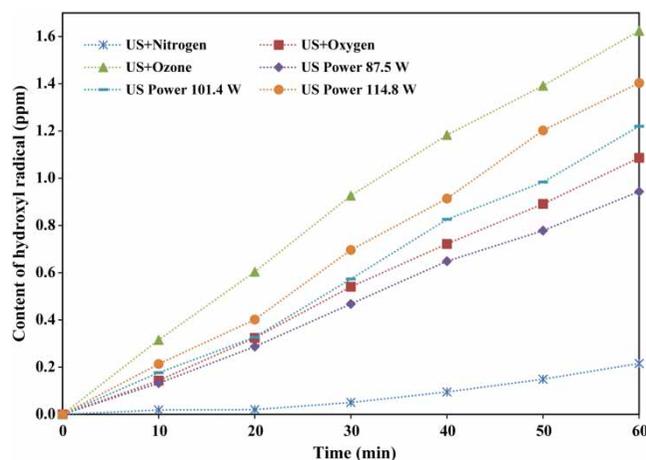


**Figure 3** | Hydroxyl free radical content with respect to time of US application, using different input powers (frequency: 20 kHz, temperature: 25 ± 2 °C, BZ concentration: 10 mg L$^{-1}$, pH: natural (6.5)) and dissolved gases (power 87.5 W).

power means an increase in the acoustic amplitude, leading to more violent cavitation bubble collapse.

## Effect of initial pH

The effect of solution pH on the sonolytic degradation of BZ was studied by varying the initial pH of the solution. BZ has two p$K_a$ values (logarithm of acid dissociation constant), one at 8.2 and the other at 0.4 (Vel Leitner & Roshani 2010), this means that in aqueous solution BZ can exist in three different conjugate acid–base forms depending on the solution pH. Thus, experiments were carried out at three pH values of 2, 6.5, and 10.

In Figure 1(c), the effect of initial solution pH on the BZ sonochemical degradation is depicted. The substrate conversion follows the order; pH 2 > pH 10 > pH 6.5. This behavior can be attributed to the presence of pollutant conjugate acid–base forms in the solution and the extent of dissociation of each case. The ionic fraction of BZ can be calculated using Equation (8) (Chiha et al. 2011).

$$\varphi_{ions} = \frac{1}{1 + 10^{(pK_a - pH)}} \qquad (8)$$

Consequently, at pH values of 2 and 6.5, the compound exists mainly in neutral form, whereas at pH of 10 it is almost completely in anionic form ($\varphi_{ions} = 0.98$), due to deprotonation occurring at the NH group in the five-membered heterocyclic ring of the BZ molecule. It is expected that the pollutant degradation mainly occurs at the exterior of the cavitation bubbles (interfacial and bulk

**Table 2** | Parameters of the models of Okitsu et al. (2005) and Serpone et al. (1994) in the BZ ultrasonic treatment

| Model | Parameters |
|---|---|
| Okitsu et al. | $k$ ($\mu$M min$^{-1}$) = 0.483 16 ± 5.343 03 × 10$^{-4}$ <br> $K$ ($\mu$M) = 0.038 23 ± 1.874 95 × 10$^{-4}$ <br> $R^2$ = 0.9970 |
| Serpone et al. | $K_b$ ($\mu$M min$^{-1}$) = 0.015 84 ± 0.008 18 <br> $k$ ($\mu$M min$^{-1}$) = 0.469 16 ± 0.007 18 <br> $K$ ($\mu$M) = 0.035 89 ± 0.001 22 <br> $R^2$ = 0.9999 |

solution regions). At pH 2 and 6.5, the molecular/neutral form of BZ has a stronger hydrophobic character, and it would distribute mainly in the interface of the cavitation bubbles, where the concentration of hydroxyl free radicals is higher, leading to a faster degradation of the compound. On the other hand, the anionic form of BZ at pH 10 is more reactive toward electrophilic radicals such as OH, enhancing the degradation with respect to the neutral media as has been indicated in the literature (Naik & Moorthy 1995; Vel Leitner & Roshani 2010).

## Effects of different dissolved gases

The presence of dissolved gases in the sonochemical treatment of organic substances in water is a parameter that can enhance or inhibit cavitation and may change the reaction efficiency, promoting radical species not only from sonolysis of the solvent but also from the dissolved gases involved (Méndez-Arriaga et al. 2008; Chiha et al. 2011). In order to study the influence of the dissolved gases on the degradation of BZ, experiments with ozone, oxygen, and nitrogen were carried out during the US irradiation. In the case of $O_2$ and $N_2$, the flow rate was 762 mL min$^{-1}$, while in the experiments with ozone, pure oxygen (762 mL min$^{-1}$) was used to generate 3.5 g h$^{-1}$ of $O_3$. Figure 1(d) shows the time dependence of BZ degradation under $O_3$, $O_2$, and $N_2$ atmospheres. It can be seen from the figure that the order of degradation ratio is US + $O_3$ > $O_3$ alone > US + $O_2$ > US alone > US + $N_2$.

In the presence of ozone, the coupling of ultrasonic irradiation with ozonation slightly improves the pollutant degradation compared to ozonation alone, which appears to be the main oxidizing agent in this case. In both cases the same dose of $O_3$ was employed, but combination of US and ozone leads to generation of more hydroxyl free radicals in comparison with the other gases as shown in Figure 3. In sonolysis, ozone is decomposed thermolytically in the vapor phase of the cavitation bubbles, generating additional hydroxyl radicals (Weavers et al. 1998). Although in terms of $C/C_0$ a significant difference between US+ $O_3$ and US alone is not evident, in terms of mineralization, as Figure 1(f) shows, the presence of US accelerates the DOC reduction.

On the other hand, under an oxygen atmosphere extra hydroxyl free radicals are generated by molecular oxygen dissociation inside the cavitation bubble (Equations (9) and (10)) (Pétrier et al. 2007).

$$O_2 \rightarrow 2O^\bullet \tag{9}$$

$$O^\bullet + H_2O \rightarrow 2^\bullet OH \tag{10}$$

These parameters can lead to faster degradation of BZ, mainly due to the greater availability of additional OH radicals.

In the case of $N_2$, there is a reduction in the extent of substrate degradation. This can be associated with the fact that dissolved nitrogen present in the aqueous solution can scavenge the free radicals and inhibit the free radical oxidation, as shown in Equations (11)–(16) (Chiha et al. 2011).

$$N_2 + {}^\bullet OH \rightarrow NO_2 + H^\bullet \tag{11}$$

$$N_2 + O \rightarrow NO^\bullet + N^\bullet \tag{12}$$

$$O_2 + N^\bullet \rightarrow NO^\bullet + O \tag{13}$$

$$NO^\bullet + O \rightarrow {}^\bullet NO_2 \tag{14}$$

$$NO^\bullet + {}^\bullet OH \rightarrow HNO_2 \tag{15}$$

$$NO_2 + {}^\bullet OH \rightarrow HNO_3 \tag{16}$$

Figure 3 also verifies that oxygen promotes the radical generation, while nitrogen reduces considerably the amount of OH radicals.

## Effects of hydroxyl radical scavengers

The effect of the presence of four alcohols (methanol, ethanol, isopropyl alcohol, and tert-butyl alcohol) in the sonolytic degradation of BZ was investigated. These alcohols, as well as other organic species of low molecular weight can act as quenchers in reactions with OH radicals (Behnajady et al. 2008). Figure 1(e) shows that all of them inhibit the degradation of BZ, which is evidence of the role of the hydroxyl radicals as the main contaminant oxidant.

The inhibition of the 1-H degradation is due to $^\bullet$OH competitive reactions with BZ and alcohols. The scavenging activity follows the order tert-butyl alcohol > isopropyl alcohol > ethanol > methanol, which can be attributed to the possible reaction of hydroxyl free radicals with hydrogens bonded to carbon in alcohol molecules (Behnajady et al. 2008). There are nine, seven, five, and three hydrogen atoms, in the tert-butyl alcohol, isopropyl alcohol, ethanol,

and methanol molecules, respectively. On the other hand, this scavenging activity order was in agreement with the order of alcohol specific heat capacities, which could indicate that an alcohol with larger specific heat exhibits a greater inhibition effect. This may be attributed to the fact that large specific heat capacities would reduce the maximum size of micro-bubbles and the interfacial temperatures achieved from bubble collapse, which could produce fewer OH radicals (Gao *et al.* 2013).

## Mineralization of BZ

The change in the DOC content of the solution under the different conditions evaluated is shown in Figure 1(f). It can be noted that there was not a significant reduction in this parameter. In most of the experiments, around 10% reduction in DOC was achieved. This indicates that BZ is being transformed into organic byproducts with low volatility and high hydrophilicity, and thermal decomposition inside the bubbles was insignificant. It has been reported that reactions of hydroxyl free radicals with BZ could give hydroxycyclohexadienyl radicals, by addition of OH radical in the benzene ring present in the BZ molecule (Naik & Moorthy 1995). Only in the presence of ozone did the percent of DOC reduction reach around 76% in just 20 min; it could indicate that organic solutes were mineralized due to the combined oxidation with ozone and US.

## CONCLUSIONS

Removal of the endocrine-disrupting BZ by 20 kHz ultrasonic irradiation was studied. Hydroxyl radicals generated by collapse of cavitation bubbles during the sonochemical treatment are responsible for the BZ degradation. Kinetic equations based on a Langmuir-type mechanism were used to model the sonochemical degradation of the BZ. The expression developed by Serpone *et al.* (1994) showed a better fit with the experimental data; in comparison with the Okitsu *et al.* (2005) model, indicating that pollutant degradation takes place at both the bubble–liquid interfacial region and in the bulk solution. The degradation rate increased with increasing ultrasonic power from 87.5 to 114.8 W due to increase in the amount of OH. Acidic media was the most favorable condition for the degradation of BZ. In addition, in the presence of $O_3$ and $O_2$, the degradation rate was higher since they promote the hydroxyl radical generation whereas $N_2$ acted as an OH scavenger and inhibited the BZ removal. It is very difficult to

mineralize BZ by ultrasonic treatment alone; however, in the presence of ozone a reduction of around 76% of the total organic carbon in the solution was achieved.

## ACKNOWLEDGEMENTS

## REFERENCES

Behnajady, M. A., Modirshahla, N., Shokri, M. & Vadhi, B. 2008 Effect of operational parameters on degradation of Malachite Green by ultrasonic irradiation. *Ultrasonics Sonochemistry* **15** (6), 1009–1014.

Bolong, N., Ismail, A. F., Salim, M. R. & Matsuura, T. 2009 A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination* **239** (1–3), 229–246.

Chiha, M., Merouani, S., Hamdaoui, O., Baup, S., Gondrexon, N. & Pétrier, C. 2010 Modeling of ultrasonic degradation of non-volatile organic compounds by Langmuir-type kinetics. *Ultrasonics Sonochemistry* **17** (5), 773–782.

Chiha, M., Hamdaoui, O., Baup, S. & Gondrexon, N. 2011 Sonolytic degradation of endocrine disrupting chemical 4-cumylphenol in water. *Ultrasonics Sonochemistry* **18** (5), 943–950.

Durjava, M. K., Kolar, B., Arnus, L., Papa, E., Kovarich, S., Sahlin, U. & Peijnenburg, W. 2013 Experimental assessment of the environmental fate and effects of triazoles and benzotriazole. *Alternatives to Laboratory Animals: ATLA* **41** (1), 65–75.

Gao, Y., Gao, N., Deng, Y., Gu, J., Gu, Y. & Zhang, D. 2013 Factor affecting sonolytic degradation of sulfamethazine in water. *Ultrasonics Sonochemistry* **20** (6), 1401–1407.

Ji, G., Zhang, B. & Wu, Y. 2012 Combined ultrasound/ozone degradation of carbazole in APG1214 surfactant solution. *Journal of Hazardous Materials* **225–226**, 1–7.

Lim, M. H., Kim, S. H., Kim, Y. U. & Khim, J. 2007 Sonolysis of chlorinated compounds in aqueous solution. *Ultrasonics Sonochemistry* **14** (2), 93–98.

Mahvi, A. H. 2009 Application of ultrasonic technology for water and wastewater treatment. *Iranian Journal of Public Health* **38** (2), 1–17.

Mawhinney, D. B., Vanderford, B. J. & Snyder, S. h. A. 2012 Transformation of 1H-benzotriazole by ozone in aqueous solution. *Environmental Science and Technology* **46** (13), 7102–7111.

Méndez-Arriaga, F., Torres-Palma, R., Pétrier, C., Esplugas, S., Gimenez, J. & Pulgarín, C. 2008 Ultrasonic treatment of

water contaminated with ibuprofen. *Water Research* **42** (16), 4243–4248.

Naik, D. B. & Moorthy, P. N. 1995 Studies on the transient species formed in the pulse radiolysis of benzotriazole. *Radiation Physics and Chemistry* **46** (3), 353–357.

Okitsu, K., Iwasaki, K., Yobiko, Y., Bandow, H., Nishimura, R. & Maeda, Y. 2005 Sonochemical degradation of azo dyes in aqueous solution: a new heterogeneous kinetics model taking into account the local concentration of OH radicals and azo dyes. *Ultrasonics Sonochemistry* **12** (4), 255–262.

Pétrier, C., Combet, E. & Mason, T. 2007 Oxygen-induced concurrent ultrasonic degradation of volatile and non-volatile aromatic compounds. *Ultrasonic Sonochemistry* **14** (2), 117–121.

Reemtsma, T. h., Miehe, U., Duennbier, U. & Jekel, M. 2010 Polar pollutants in municipal wastewater and the water cycle: occurrence and removal of benzotriazoles. *Water Research* **44** (2), 596–604.

Serpone, N., Terzian, R., Hidaka, H. & Pelizetti, E. 1994 Ultrasonic induced dehalogenation and oxidation of 2-, 3- and 4-CP in air-equilibrated aqueous media, similarities with irradiated semiconductor particles. *Journal of Physical Chemistry* **98**, 2634–2640.

Tai, C., Peng, J., Liu, J., Jiang, G. & Zou, H. 2004 Determination of hydroxyl radicals in advanced oxidation processes with dimethyl sulfoxide trapping and liquid chromatography. *Analytica Chimica Acta* **527** (1), 73–80.

Tangtian, H., Bo, L., Wenhua, L., Shin, P. K. & Wu, R. S. 2012 Estrogenic potential of benzotriazole on marine medaka (*Oryzias melastigma*). *Ecotoxicology and Environmental Safety* **80**, 327–332.

Vel Leitner, N. K. & Roshani, B. 2010 Kinetic of benzotriazole oxidation by ozone and hydroxyl radical. *Water Research* **44** (6), 2058–2066.

Weavers, L. K., Ling, F. H. & Hoffmann, M. R. 1998 Aromatic compound degradation in water using a combination of sonolysis and ozonolysis. *Environmental Science Technology* **32** (18), 2727–2733.

Xu, J., Li, L., Guo, C., Zhang, Y. & Wang, S. 2013 Removal of Benzotriazole from solution by BiOBr photocatalysis under simulated solar irradiation. *Chemical Engineering Journal* **221**, 230–237.