



## Sonochemical destruction of nonylphenol: Effects of pH and hydroxyl radical scavengers

Nilsun H. Ince<sup>a,\*</sup>, Isil Gültekin<sup>a</sup>, Gökce Tezcanlı-Güyer<sup>b</sup>

<sup>a</sup> Bogazici University, Institute of Environmental Sciences, 34342, Istanbul, Turkey

<sup>b</sup> Fatih University, Department of Environmental Engineering, 34500, Istanbul, Turkey

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### ABSTRACT

Nonylphenols are water-stable endocrine disrupting compounds that inhibit the growth of sewage bacteria in biological processes. The study describes the decomposition of 4-n-nonylphenol (NP) in water by 20 kHz ultrasound with emphasis on the impacts of pH, concentration and OH<sup>•</sup> scavengers. It was found that the rate of degradation was accelerated by alkalization, but more so by the addition of hydroxide alkalinity than carbonate. The addition of low doses of CO<sub>3</sub><sup>2-</sup> and t-butyl alcohol as strong scavengers of OH<sup>•</sup> was also found to accelerate the decomposition of NP. The observation was attributed to the generation of reactive CO<sub>3</sub><sup>2-•</sup> and CH<sub>3</sub><sup>•</sup> via pyrolysis of the additives in the cavity bubbles. The results also revealed that NP did not compete with OH<sup>•</sup> scavenging agents when their relative concentration was low. In case of high frequency sonication (861 kHz) the competition was slightly effective (slowed down degradation) at an identical dose of t-butyl alcohol. The difference was attributed to shorter bubble life time at high frequencies leading to less violent/less energetic bubble collapse and lower yield of CH<sub>3</sub><sup>•</sup>.

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### 1. Introduction

Increasing evidence of endocrine system disruption in wildlife has raised public concern on the presence of endocrine disrupting chemicals in the environment. Alkylphenols (AP) comprise one of the most important groups of such chemicals and are of particular interest due to their widespread occurrence in the environment [1–3]. The majority of research on AP destruction in water is on nonylphenols, which enter the environment directly through wastewater streams or indirectly with nonylphenol polyethoxylates (NPEOs). Under anaerobic conditions such as those found in sewers, sediments and bio-treatment operations, NPEO is rapidly oxidized to nonylphenol, which is quite stable in water and exhibits aquatic toxicity and estrogenic activity [4–6].

Advanced Oxidation Processes (AOPs) are recognized with their potential to in situ generate hydroxyl radicals (OH<sup>•</sup>), which unselectively react with a wide range of organic chemicals in water. Among many different methods of AOP, those involving ultrasonic irradiation are of particular interest owing to the unique properties of ultrasound to enhance chemical reaction rates and surface properties [7]. Current research on nonylphenol elimination from water by classical AOP's covers indirect photolysis, photocatalytic oxidation, ozonation and others [8–11].

The use of ultrasound to destroy nonylphenols is not common, and the literature is limited to a couple of studies describing the degradation of alkyl phenols by 220 kHz ultrasound [12] and that of nonylphenol by a hybrid process involving oxidation by sono-Fenton reaction followed by fungal biosorption [13].

Sonochemistry is based on the formation, growth and implosive collapse of acoustic cavity bubbles that end up with very extreme temperatures and pressures at “local hot spots” in the liquid [14]. When the liquid is water, ultrasound acts as an advanced oxidation tool upon generation of hydroxyl radicals via water pyrolysis. While most of these radicals combine to form water and hydrogen peroxide, some are transported to the bulk solution to oxidize water contaminants. Water decontamination may also occur by thermal destruction of the pollutants in collapsing bubbles and/or by oxidation at the gas-liquid interface [7]. The degree of remediation depends on the composition of the water, chemical/physical properties of the contaminants and the type of ultrasonic equipment.

The purpose of this study was to investigate the degradability of 4-n-nonylphenol (NP) in water by short frequency ultrasound to select the operating conditions and to assess the potential reaction pathways, as OH<sup>•</sup>-mediated oxidation and/or thermal decomposition in the gas phase. The assessment was based on the degradation of NP in the presence of low doses of carbonates and t-butyl alcohol, both of which are strongly reactive with OH<sup>•</sup> in the bulk solution and the bubble-liquid interface, respectively.

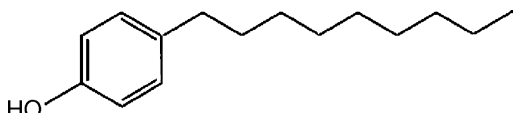
\* Corresponding author. Tel.: +90 2123597038; fax: +90 2122575033.

E-mail address: [ince@boun.edu.tr](mailto:ince@boun.edu.tr) (N.H. Ince).

## 2. Experimental

### 2.1. Materials

4-n-Nonylphenol (the chemical structure as given) was purchased from Riedel-de-Haën (Germany) in 99.9% purity and used as received. The chemical structure and physical properties of the compound are as given:



MW = 220.4 g mol<sup>-1</sup>, pKa = 10.7,  $p_i = 7.1 \times 10^{-7}$  atm, sol. = 5.43 mg l<sup>-1</sup>, log  $K_{ow} = 4.48$  [15–17].

The reagents H<sub>2</sub>SO<sub>4</sub>, NaOH, t-butyl alcohol and Na<sub>2</sub>CO<sub>3</sub> were all supplied from Merck (Turkey) in reagent grade. HPLC-grade (Merck) methanol and acetonitrile were used for preparing stock solutions of NP and for the mobile phase in HPLC analysis, respectively. Ultra pure milli-Q water (Millipore Gradient System) was used in all solutions.

### 2.2. Apparatus

The experimental set-up referred to as “Reactor 1” consisted of a 100 ml glass cell surrounded by a water-cooling jacket to keep the solution at 25 ± 0.5 °C, a probe type transducer (tip area = 1.13 cm<sup>2</sup>) emitting at 20 kHz, and a 180 W generator operated at 30% of its capacity (Bandelin/Sonoplus, Germany). The horn was immersed 3 cm into the solution, where the deposited power was 0.46 W ml<sup>-1</sup>, as determined by calorimetry [18]. Some of the tests were run in a high frequency system referred to as “Reactor 2”, which consisted of a 250 mL glass cell cooled to 25 °C, a plate type transducer (surface area = 22 cm<sup>2</sup>) emitting at 861 kHz, and a 120 W generator operated at 90% of its capacity (Ultraschall/Meinhardt, Germany). The power density in this reactor was 0.23 W ml<sup>-1</sup>.

### 2.3. Analytical

NP was analyzed by a Shimadzu LC-20AT HPLC using a SPD-20A UV-vis detector set at 220 nm and an Inertsil ODS-3V column. A mixture of acetonitrile–Milli-Q water solution (80:20 by volume) at 2 ml min<sup>-1</sup> was used as the mobile phase throughout the analysis. The analysis of potential phenolic intermediates was carried out in selected samples using an Agilent 6890N gas chromatograph equipped with a flame ionization detector and a HP5 capillary column (30 m × 250 μm, 0.25 μm).

### 2.4. Procedure

A stock NP solution of 0.0087 M was prepared in 100 ml methanol and stored in the dark at 4 °C. Test samples of 100 μM were made by dilution of the stock with Milli-Q water (1:435 by volume) and allowed for saturation with dry pure oxygen. The pH of all samples after saturation was 6.0, and no adjustment was made unless the effect of pH was investigated. Gas-saturated test samples were sonicated for 45 min in Reactor 1 (unless declared otherwise) during continuous O<sub>2</sub> bubbling at 0.25 L min<sup>-1</sup> to compensate for gas loss by cavitation. The effect of pH and aqueous phase OH• scavenging was tested by 45-min sonication of acid/base (pH 3 – with 1 M H<sub>2</sub>SO<sub>4</sub>; pH 10.8 – with 1N NaOH) and Na<sub>2</sub>CO<sub>3</sub> (5 mM) spiked test solutions (C<sub>0</sub> = 100 μM), respectively in Reactor 1. The impact of interfacial OH• scavenging was assessed by sonication of the test solutions (C<sub>0</sub> = 100 μM) in both reactors using 1 mM t-butyl alcohol. The concentration of NP in all experiments was monitored by HPLC analysis using the samples collected at 5-min intervals from the

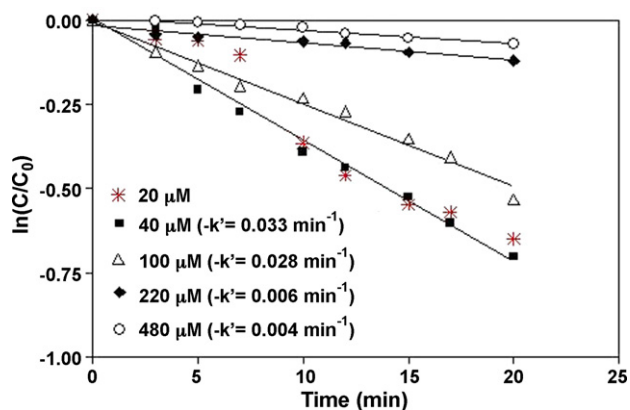


Fig. 1. Impact of concentration on the degradation of NP in Reactor 1 during O<sub>2</sub> bubbling.

reactors. Some of the samples (acidic and alkaline) were also analyzed by GC to evaluate the relative formation and disappearance of phenolic intermediates.

## 3. Results and discussion

### 3.1. Impact of concentration

O<sub>2</sub>-saturated test solutions of 20, 40, 100, 220 and 480 μM were sonicated in Reactor 1 for 45 min and samples were collected at every 5 min for analysis by HPLC. The time rate of NP degradation followed pseudo-first order kinetics (except at C<sub>0</sub> = 20 μM) and the rate constants were estimated using the integrated form of the 1st order rate equation ( $\ln(C/C_0) = k't$ , where  $k'$  is the apparent rate constant (min<sup>-1</sup>),  $t$  is the sonication time (min), and C<sub>0</sub> and C are the concentrations of NP at time zero and  $t$ , respectively). The data and the estimated rate constants are presented in Fig. 1.

The exponential character of the rate at C<sub>0</sub> > 20 μM implies that pyrolysis is part of the degradation process, as also pointed out in the literature for the sonolytic destruction of NPEO and other organic compounds [19,20]. The data in Fig. 1 further indicate that the rate of reaction is relatively rapid at low-to-medium concentrations (20–100 μM), but much slower at high concentrations of the compound (220–480 μM). To explain this profile, we monitored the initial variation of the reaction rate ( $t \leq 2$  min) with the initial concentration of NP and found that the relation was curvilinear, i.e. the rate increased to a maximum (at C<sub>0</sub> ≈ 100 μM) and declined to a plateau, as depicted in Fig. 2. The shape of the curve implies adsorption type of reaction kinetics, as supported by the hypoth-

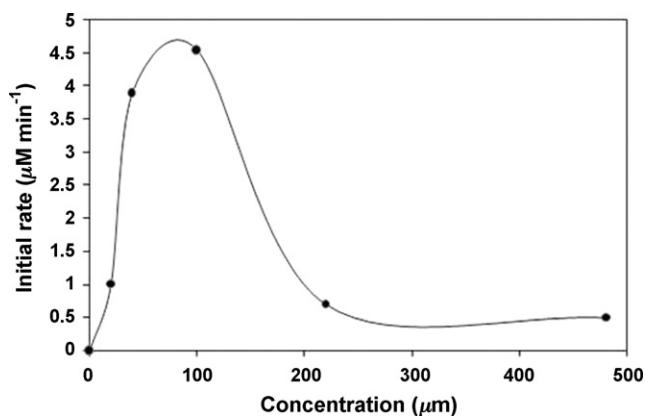


Fig. 2. Variation of the initial rate of NP decay in Reactor 1 with the initial concentration.

esis that the bubble-liquid interface in sonicated water is a highly potential adsorption site [21]. If we assume that the formation and destruction of acoustic bubbles in the reactor is at steady state and the number of free adsorption sites is practically constant at all times, then the up-slope of the line in Fig. 2 can be explained by enhanced adsorption of the solutes at the interfacial area, where the quantity of  $\text{OH}^\bullet$  is a maximum [22]. The decline and subsequent stabilization of the rate at larger concentrations is therefore due to the relative insufficiency of adsorption sites and the competition of excess solutes at the interface. It is also possible that at high concentrations of NP, bubbles are enriched in organic content (due to increased quantity of volatile byproducts) and they collapse less violently with lower collapse temperatures and lower yield of  $\text{OH}^\bullet$ . A similar rate pattern has been reported for the sonochemical degradation of NPEO surfactants at 363 kHz, at which the rate was a maximum at the critical micelle concentration [19].

### 3.2. Effect of pH

The degradation of NP at acidic and alkaline pH is presented in Fig. 3 together with a “control” representing the data at the natural pH of the solution. It was found that the reaction was extremely slow in the control (pH 6), 2.2 times faster at pH 3.0 and 4 times faster at pH 10.8. Acceleration by acidification must be due to enriched hydrophobicity of the molecule by protonation of the phenolic moiety [23]. Further acceleration by alkalization, however, is a more complex phenomenon that may be related to structural properties of the compound and more cautiously to its potential hydrolysis, which occurs frequently during its metabolic and enzymatic cleavage by wheat cells and by some aquatic organisms [24,25].

Regarding the structure, NP is characterized by covalent bonding between a hydrophobic alkyl chain ( $\log K_{ow} = 5.65$ ) and a hydrophilic phenol moiety ( $\log K_{ow} = 1.46$ ). At pH 10.8 ( $\text{p}K_{a\text{-NP}} = 10.7$ ), the phenolic part dissociates to the anionic form, which due to the negative charge is more hydrophilic than the uncharged state. Consequently, as the molecule approaches the bubble-liquid interface the two moieties pull against one another: one end leans towards the bulk solution, the other bends towards the interface. Such a profile reminds of surfactant properties although NP is poorly soluble and not subject to micelle formation [26]. Nevertheless, it is obvious that the presence of two moieties with significantly different  $K_{ow}$  simulates surfactant properties at alkaline pH. As such, the opposing tendencies of the moieties (to escape and to approach the gas bubbles) facilitate the cleavage of the covalent bond between them and accelerate the decomposition of the nonyl tail at the bubble-liquid interface.

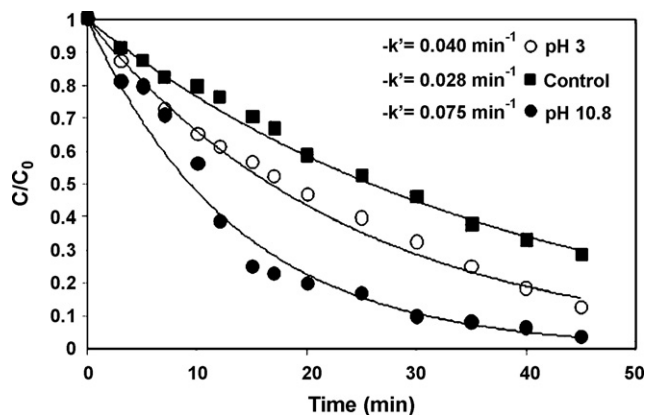


Fig. 3. The effect of pH on the rate of NP decay ( $C_0 = 100 \mu\text{M}$ ) in Reactor 1.

Table 1

pH-related distribution of p-BQ after 10, 30 and 45 min sonication in Reactor 1.

Sonication time (min)	% Benzoquinone	
	pH 3.0	pH 10.8
10	100	100
30	50	45
45	28	12

To verify this hypothesis, samples from acidic and alkaline solutions were collected at various time intervals for analysis by GC. The resulting chromatograms were too complex to identify any phenolic intermediates, except for the peak detected at a retention time of 14.54 min in both solutions. The compound was identified as p-benzoquinone (p-BQ), which was found to disappear more rapidly in the alkaline sample. The formation of BQ is a strong evidence of  $\text{OH}^\bullet$  addition to the phenolic group following the cleavage of the alkyl chain and the production of hydroxyhydroquinone. Percent distribution of p-BQ in samples collected at 10, 30 and 45 min is given in Table 1. Faster decline of p-BQ after 30 min sonication at pH 10.8 verifies the above hypothesis that all or a large fraction of the alkyl moiety has been decomposed by that time so that more  $\text{OH}^\bullet$  (and other reactive species) was available for the remaining components. (Note that pH remained nearly constant throughout the sonication time in both solutions.)

Acceleration of NP decay at elevated pH may also be explained by the formation of a supercritical region and the potential existence of a sphere between this and the interfacial area, where the temperature is higher than that in the bulk solution [27,28]. Accordingly, the enhancement in the rate of NP elimination at alkaline pH can be related to the dissipation of heat in the vicinity of collapsing bubbles that may lead to a variety of unexpected reactions, including hydrolysis.

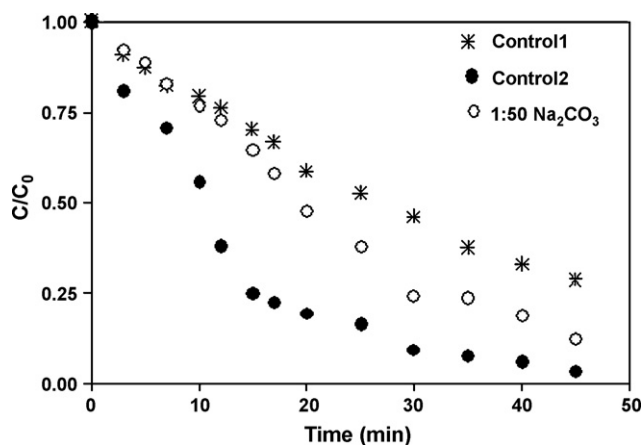
### 3.3. Assessment of the reaction sites

To assess the degradation pathway of NP and the potential reaction sites, the rate of reaction was monitored in the presence of: (i) an effective sink of hydroxyl radicals in the bulk solution (carbonate ion); and (ii) an effective sink of hydroxyl radicals at the hot interfacial sheath (t-butyl alcohol).

#### 3.3.1. The bulk solution

Keeping all other conditions identical as in the previous experiments; the rate of NP elimination in Reactor 1 was monitored in the presence of 5 mM  $\text{Na}_2\text{CO}_3$ . The data are presented in Fig. 4 together with two control sets that practically contained no carbonates (Control 1: pH 6.0, Control 2: pH 10.8-adjusted with NaOH). It was found that despite the strong reactivity of  $\text{CO}_3^{2-}$  with  $\text{OH}^\bullet$  ( $k = 3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [29]), the addition of sodium carbonate did not retard the rate of NP decay during the first 10 min, but accelerated it after longer contact. Unaffected rate at early sonication can be explained by the counterbalance between rate inhibitors and rate accelerators, i.e.  $\text{OH}^\bullet$  scavenging and alkalization, respectively. The enhancement at longer exposure must be the outcome of reduced rate of  $\text{OH}^\bullet$  scavenging (upon complete conversion of  $\text{CO}_3^{2-}$ ) and increased quantity of reactive  $\text{CO}_3^{2-}$ . Acceleration of sonolytic decay of organic compounds (e.g. dyes) by  $\text{CO}_3^{2-}$  has also been reported in the literature [30].

In our earlier study with bisphenol-A sonicated at 300 kHz, we found that the apparent reaction rate constant was lowered by 50% at an equivalent concentration of  $\text{CO}_3^{2-}$  [31]. The opposing trend observed here is the result of chemical properties (that affect the reactivity of the solutes in the bulk solution) and frequency. Bisphenol-A is very soluble and therefore reacts primarily in the



**Fig. 4.** The effect of carbonate addition (dose = 50:1 by M; pH 10.8) on the rate of NP degradation ( $C_0 = 100 \mu\text{M}$ ) in Reactor 1. "Control 1" and "Control 2" are additive free (pH 6.0) and NaOH-added solutions (pH 10.8), respectively.

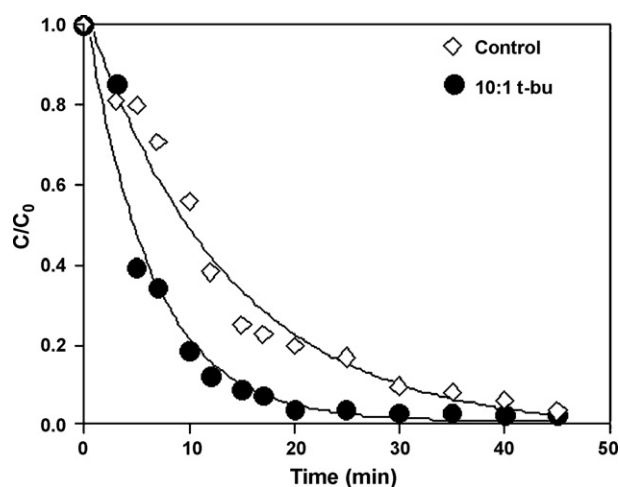
bulk solution, whereas NP is poorly soluble and prefers the gas-liquid interface for reaction. As such, bisphenol-A is largely affected by  $\text{OH}^\bullet$  scavenging in the bulk solution, but NP is not. Regarding frequency differences, bubble life time at 20 kHz is at least two orders of magnitude longer than that at larger frequencies, so that a significant fraction of hydroxyl radicals react or recombine in the cavity bubbles or at the surface before they escape to the bulk solution [7]. Hence,  $\text{OH}^\bullet$  scavenging in solution at 20 kHz (by  $\text{CO}_3^{2-}$ ) is not a significant source of rate inhibition for hydrophobic solutes like NP. Finally, acceleration of the rate of NP destruction at prolonged contact with  $\text{CO}_3^{2-}$  is due to their rapid conversion (to  $\text{CO}_3^{2-\bullet}$ ) in the vicinity of long-lived cavity bubbles via oxidation (by  $\text{OH}^\bullet$ ) or pyrolysis pathways.

The data in Fig. 4 also show that the rate of reaction in  $\text{Na}_2\text{CO}_3$ -added sample is more than 50% slower than that in NaOH-spiked sample despite identical pH levels. The difference can be explained by temperature variations, as some researchers proposed that the collapse temperature in solutions of  $\text{Na}_2\text{CO}_3$  is lower than in those of NaOH due to lower solubility of the former, which further decreases with increasing temperatures and reaches zero at the supercritical level [28]. At such, the vapor pressure of water is 220 atm whereas that in the presence of NaOH is only 100 atm. If we assume the presence of a sphere between the interfacial and the supercritical regions as suggested in the literature [27], then we would expect more water vapor inside the cavities in a solution containing  $\text{Na}_2\text{CO}_3$  than that with NaOH, and less energy available at collapse (through a cushion effect).

### 3.3.2. The interface

The effect of interfacial  $\text{OH}^\bullet$  scavenging by t-butyl alcohol at pH 10.8 (adjusted with NaOH) is demonstrated in Fig. 5, where "Control" refers to the absence of t-butyl alcohol. Because no literature is available on the decomposition of NP by short frequency ultrasound in the presence or absence of t-butyl alcohol, it was not possible to compare our results with those of others. Hence, we attributed the observed enhancement to: (i) the potential of power ultrasound to lower mass transfer limitations and to enhance thermal reactions; (ii) the relatively low dose of t-butyl alcohol (10:1 by M), at which competition for  $\text{OH}^\bullet$  is unlikely; and (iii) the rapid decomposition of the additive to produce reactive methyl radicals, which are the main products of high-temperature pyrolysis of the additive [32]. Note that it was not possible to test the effect of larger doses due to excessive foaming of the solution at such.

The only related literature source is the work of Yim et al. [12], which, however, reports suppression of NP decomposition rate at



**Fig. 5.** The effect of t-butyl alcohol (10:1 by M) on the rate of NP decay ( $C_0 = 100 \mu\text{M}$ ) in Reactor 1 at pH 10.8-adjusted with 1 N NaOH.

**Table 2**

Interactive effect of frequency and t-butyl alcohol on the rate of NP degradation at pH 10.8 ( $C_0 = 100 \mu\text{M}$ ).

Reactor/power	t-bu/NP=0 $k'$ ( $\text{min}^{-1}$ )	t-bu/NP=10 $k'$ ( $\text{min}^{-1}$ )
1. 20 kHz/0.46 $\text{W ml}^{-1}$	$7.54 \times 10^{-2}$	$16.20 \times 10^{-2}$
2. 861 kHz/0.23 $\text{W ml}^{-1}$	$3.64 \times 10^{-2}$	$3.18 \times 10^{-2}$

high frequency ultrasound (220 kHz) by 100:1 and 500:1 (M t-butyl alcohol:M NP). However, the data are not comparable with ours because of the vital difference between the dose of the additive and the applied frequency. To check if frequency is the critical parameter, we repeated the experiments in Reactor 2 (861 kHz) keeping the dose of the reagent identical. We found that at high frequency the presence of t-butyl alcohol led to a slight deceleration of the degradation reaction, implying that pyrolytic cleavage of the additive (that exists inside or just near a cavity) is less effective. This is consistent with the fact that at high frequency irradiation bubble life times and bubble collapse durations are much shorter than at low frequency. At such, less methyl radicals – the active species in Reactor 1 – are produced, and the competition for  $\text{OH}^\bullet$  at the interfacial area becomes effective. Relative impact of t-butyl alcohol in the two reactors is given in Table 2 for pH 10.8.

## 4. Conclusions

The study has shown that a non-biodegradable alkylphenol such as 4-n-nonylphenol (NP) can be effectively removed from water by irradiation with short frequency ultrasound. It was found that the rate of reaction increased with increasing concentrations of the solute up to a critical value, above which it declined and stabilized. In addition, the rate was significantly enhanced by alkalization, particularly by the presence of hydroxide alkalinity.

The addition of low doses of  $\text{OH}^\bullet$  scavengers in the bulk solution ( $\text{CO}_3^{2-}$ ) or the gas-water interface (t-butyl alcohol) did not inhibit the rate of reaction, but even accelerated it. A slight rate inhibition observed in the presence of an equivalent dose of t-butyl alcohol at high frequency irradiation was related to lower bubble density, shorter bubble life time and shorter collapse duration. However, more important than frequency is the applied chemical dose to keep scavenging effects at a minimum and to allow excess reactions of the solute with pyrolysis products of the scavengers.

## Acknowledgements

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