

# Catalysis of advanced oxidation reactions by ultrasound: A case study with phenol

R. Kidak, N.H. Ince\*

*Bogazici University, Institute of Environmental Sciences, Bebek, 34342, Istanbul, Turkey*

Available online 4 May 2007

## Abstract

The present study is about the enhancement in ozone-mediated degradation and UV (254 nm) photolysis of phenol in aqueous solutions by 300 kHz acoustic cavitation and the selection of operating parameters for optimum phenol removal efficiency. The method was based on monitoring of the concentration of phenol during 90 min exposure to ozonation, sonication, UV photolysis, O<sub>3</sub>/ultrasound, UV/ultrasound and O<sub>3</sub>/UV/ultrasound operations. It was found that ozonation at alkaline pH was an effective method of phenol destruction, but it was considerably more effective when applied simultaneously with ultrasonic irradiation. The observed synergy particularly at alkaline pH was attributed to combined effects of: (i) increased ozone mass transfer (upon hydrodynamic shear forces created by ultrasonic bubbles) and (ii) excess hydroxyl radical formation (upon thermal decomposition of ozone in the gaseous cavity bubbles). Degradation of phenol by photolysis alone was negligible, while combination of UV-irradiation and ultrasound rendered considerable degrees of decay. The synergy here was explained by excess hydroxyl radicals that are formed by photolysis of ultrasound-generated H<sub>2</sub>O<sub>2</sub>. Maximum rate of phenol degradation was observed in case of combined application of ozone, UV and ultrasound at basic pH.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Ultrasound; Advanced oxidation; Ozone; UV-irradiation; Hydroxyl radicals

## 1. Introduction

Phenolic compounds are common contaminants in wastewater, where they appear as a result of imperfect manufacturing and/or inadequate treatment operations in petroleum, petrochemical, coal, and phenol producing industries [1]. Methods of destroying phenolic wastes and phenol residuals in water environment have been widely studied and advanced oxidation processes (AOPs) have been reported in the last decade as excellent alternatives, owing to their unique potential for in situ generation of hydroxyl radicals in solution [2–5]. Among many tools of producing hydroxyl radicals in AOPs (e.g., UV irradiation, ozonation, Fenton's process and combinations thereof) ultrasound is a novel method, by which water molecules undergo molecular fragmentation to release hydroxyl and hydrogen radicals [6]. The phenomenon is based on the formation, growth and implosive collapse of acoustic cavity bubbles that entrap molecules of gases and water vapor from the surrounding liquid. During collapse, gas molecules are thermally fragmented to

generate a variety of reactive species, including hydroxyl radicals [7]. The radicals either react and recombine in the gas and gas-liquid interface or escape into the aqueous phase, where they readily attack organic molecules for oxidative destruction. In addition to such chemical effects, ultrasonic cavitation also induces very unique mechanical effects in liquids upon hydraulic shear forces and jet streams that enhance mass transfer, dispersion and solubility of existing solutes.

The purpose of this study was to investigate the effect of ultrasonic cavitation at 300 kHz on the enhancement of ozone and UV-mediated decomposition of phenol and to select the operating parameters of optimum effectiveness. Control processes of singly operated ozonation, UV irradiation (254 nm) and sonolysis were run in parallel with combined processes to evaluate the contribution of ultrasound on the employed combination.

## 2. Material and equipments

Phenol was purchased from Riedel Haen (97% pure) in solid form, and was dissolved in deionized water. Potassium ferrocyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>), 4-aminoantipyrine, ammonium potassium hydrogen phthalate (KHP) and all other reagents were obtained from Fluka and used as received.

\* Corresponding author. Tel.: +90 212 3597038; fax: +90 212 2575033.  
E-mail address: [ince@boun.edu.tr](mailto:ince@boun.edu.tr) (N.H. Ince).

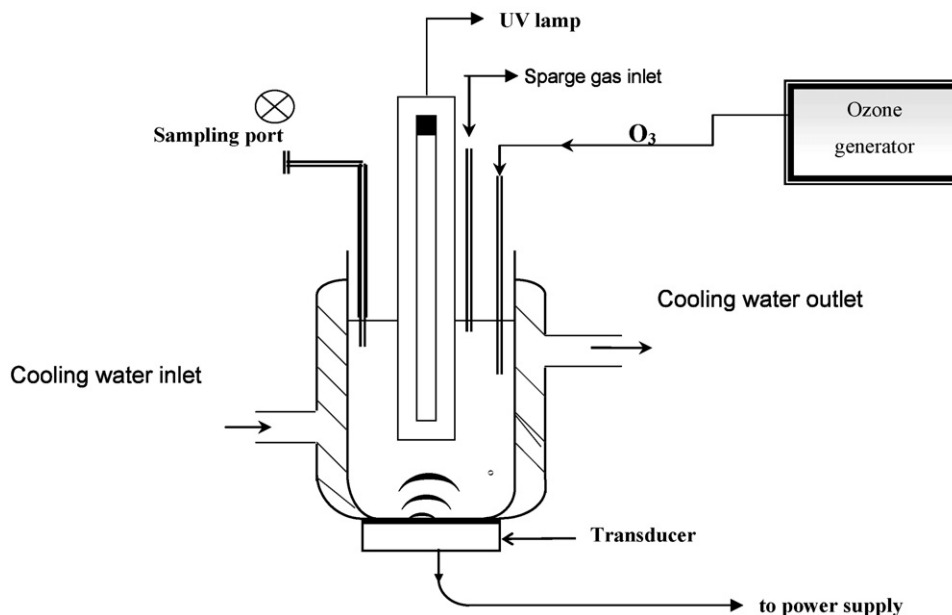
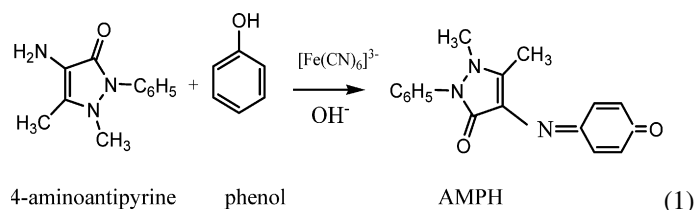


Fig. 1. The experimental set-up.

The experimental set up consisted of a 150 ml ultrasonic reactor equipped with a piezo-electric transducer (emitting ultrasonic pressure waves at 300 kHz and connected to a 25 W generator (Undatim Ultrasonics), a low pressure Hg lamp (108 kW) emitting UV light at 254 nm and an onsite ozone generator that produced ozone from dry pure O<sub>2</sub> (Ozonelab 100 Model-Ozone Service). The ultrasonic power intensity in solution was 0.86 W cm<sup>2</sup> as determined by calorimetry. The system is schematically presented in Fig. 1.

### 2.1. Analysis

Phenol was monitored spectrophotometrically by the aminoantipyrine method [8]. The method is based on the reaction of phenol with 4-aminoantipyrine in the presence of potassium ferrocyanide at pH 7.9 to form a colored complex (AMPH) as shown:



Concentration of phenol in AMPH was estimated from the absorbance of the solution at 501 nm using a UNICAM-Helios, Alpha/Beta double beam spectrophotometer with an optical pathlength of 1 cm. Hydrogen peroxide was monitored by the analytic procedure described by Klassen et al. 1994 [9]. The concentration of dissolved ozone in solution was analyzed by the Indigo colorimetric method [8].

### 2.2. Procedure

A stock phenol solution of 0.5 M was made in deionized water and stored at 4 °C in the dark. Test samples of 100 mL at 2.5 mM were prepared from the stock using deionized water. The samples were adjusted to pH 2 or 10 with 6 M HCl or NaOH, respectively. Samples used for ultrasound control runs and UV/ultrasound combination were pre-treated for 30 min to enhance cavitation events. Air was sparged continually at 1.5 l min<sup>-1</sup> during all experiments that were run in the absence of ozone. The contact time for each test was 90 min. Samples were withdrawn from the reactors every 10 min for duplicate analysis of the antipyrine complex by spectrophotometry.

## 3. Results and discussion

### 3.1. Single operations (controls)

Comparison of single operations with an initial phenol concentration of 2.5 mM showed that ozonation at alkaline pH provided complete phenol removal, while sonication (most effective at acidic pH) and UV irradiation (at both pH levels) rendered 60% and nearly no removal at all, respectively.

#### 3.1.1. Impact of pH and dissolved ozone concentration

The crucial operating parameter in all single and combined operations (O<sub>3</sub>/US, UV/US and US/UV/O<sub>3</sub>) was pH, which rendered opposing effects on the efficiency of phenol removal by ozonation and sonication. In the former, maximum efficiency was accomplished at highly alkaline pH, owing to the fact that at such ozone is decomposed to peroxide and hydroxyl radicals, which are far more reactive with phenol than ozone itself. The variation of phenol removal rate on pH during ozonation

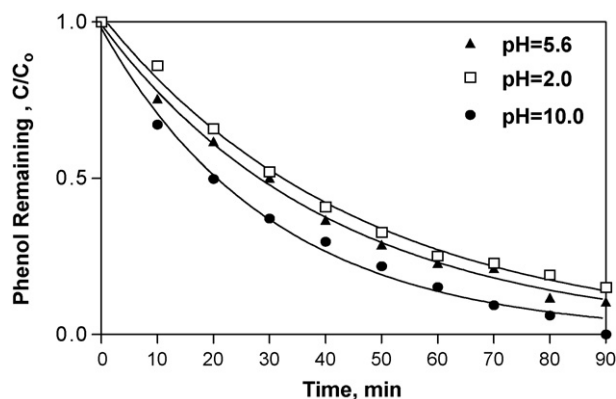


Fig. 2. The impact of pH on the rate of phenol ( $C_0 = 2.5$  mM) removal by 90 min ozonation.

is presented in Fig. 2 for three pH levels. It was found that in all cases the rate was pseudo-first order with rate constants of 0.021, 0.024 and 0.033  $\text{min}^{-1}$  at pH 2.0, 5.6 and 10.0, respectively.

During sonication, however, maximum rate of phenol removal was accomplished at highly acidic pH due to the fact phenol exists mainly in molecular form at this condition, which has a much higher liability to approach the cavity bubbles (or the interfacial area), where OH radical concentration is very high, than the disassociation product- phenolate ion that forms at alkaline pH [10].

To select the optimum ozone input, we tested three different ozone flow rates and monitored the residual phenol concentration in solution at each level. It was found that the rate of decay increased with increasing concentrations of dissolved ozone, as presented in Fig. 3. Estimated rate coefficients at 2, 4 and 6 mg/L ozone in solution (corresponding to flow rates of 0.75, 1.50 and 2.25  $\text{L min}^{-1}$ ) were 0.028, 0.033, and 0.041  $\text{min}^{-1}$ , respectively. The lowest rate of decay occurring at 2 mg/L ozone was found to be much higher than the highest rate accomplished at acidic pH by sonolysis alone (0.01  $\text{min}^{-1}$ ). Thus, 2 mg/L was selected as the operating ozone concentration to employ in combined operations.

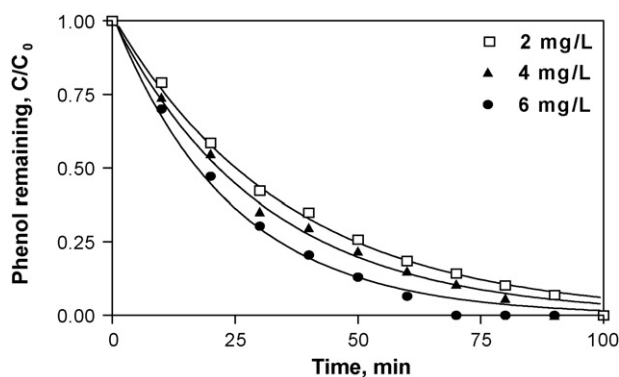
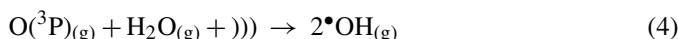
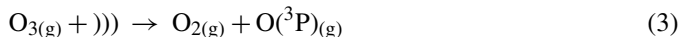


Fig. 3. The impact of ozone flow (or concentration) on the degradation of phenol during 90 min ozonation of 2.5 mM phenol at pH 10.

### 3.2. Combined processes

#### 3.2.1. Ultrasound/ozone

When ozone is injected into water simultaneously with ultrasonic irradiation, an additional pathway of hydroxyl radical generation arises upon the decomposition of ozone in the gaseous bubbles during implosive collapse. A brief summary of the reactions that occur in such a system is given in Eqs. (2)–(4) [11,12].



Since phenol is a hydrophilic solute, the destruction pattern during combined ozonation and sonolysis is expected to be governed by  $\bullet\text{OH}$ - mediated oxidation in the bulk liquid, although it may also react directly with molecular ozone and hydrogen peroxide. The probability of thermal and radical decomposition in the bubble-liquid interface is low, but likely to occur at high concentrations [6,13]. In any case, the rate-limiting step is the mass transfer of ozone in solution and the diffusion of OH radicals into the bulk liquid.

Comparison of phenol destruction in single and combined operations of ozonation and sonolysis at three pH levels is presented in Fig. 4. The negligible rate of decay by US at pH 10 is due to the relatively high distribution of phenolate ion at this condition, which remains far away from the bubble-liquid interface (due to extreme hydrophobicity), where hydroxyl radicals are at a maximum. Different degrees of enhancement in phenol degradation at different pH is evaluated in more detail in the following:

- pH 2: the rate of degradation ( $k_{\text{US/O}_3} = 2.21 \times 10^{-2} \text{ min}^{-1}$ ) is larger than those of single  $\text{O}_3$  and US operations, but less than their sum ( $k_{\text{sum}} = 3.21 \times 10^{-2} \text{ min}^{-1}$ ). The advantage over single operation of ozone is due to enhanced  $\text{O}_3$  transfer to solution (by mechanical effects of ultrasound). However, the improvement is limited by: i) the reactivity of molecular ozone (with phenol and its oxidation by-products) and ii) the gas-phase decomposition of ozone to more reactive radical species.
- pH 10: the rate of degradation ( $k_{\text{US/O}_3} = 3.26 \times 10^{-2} \text{ min}^{-1}$ ) is much larger than the sum of individual rates ( $k_{\text{sum}} = 2.85 \times 10^{-2} \text{ min}^{-1}$ ), showing that the combination induced a synergy of reactions, upon: i) enhanced rate of  $\text{O}_3$  transfer that results in larger degrees of molecular reactions and ii) larger degrees of aqueous and gas-phase decomposition of ozone to peroxy and hydroxyl radicals. In addition, a part of the synergy must be due to indirect chemical reactions in the bulk solution between aqueous ozone and US-generated  $\text{H}_2\text{O}_2$  to yield  $\text{HO}_3^-$  radicals, which was shown to enhance the reactivity of solutions undergoing simple ozonolysis [14]:



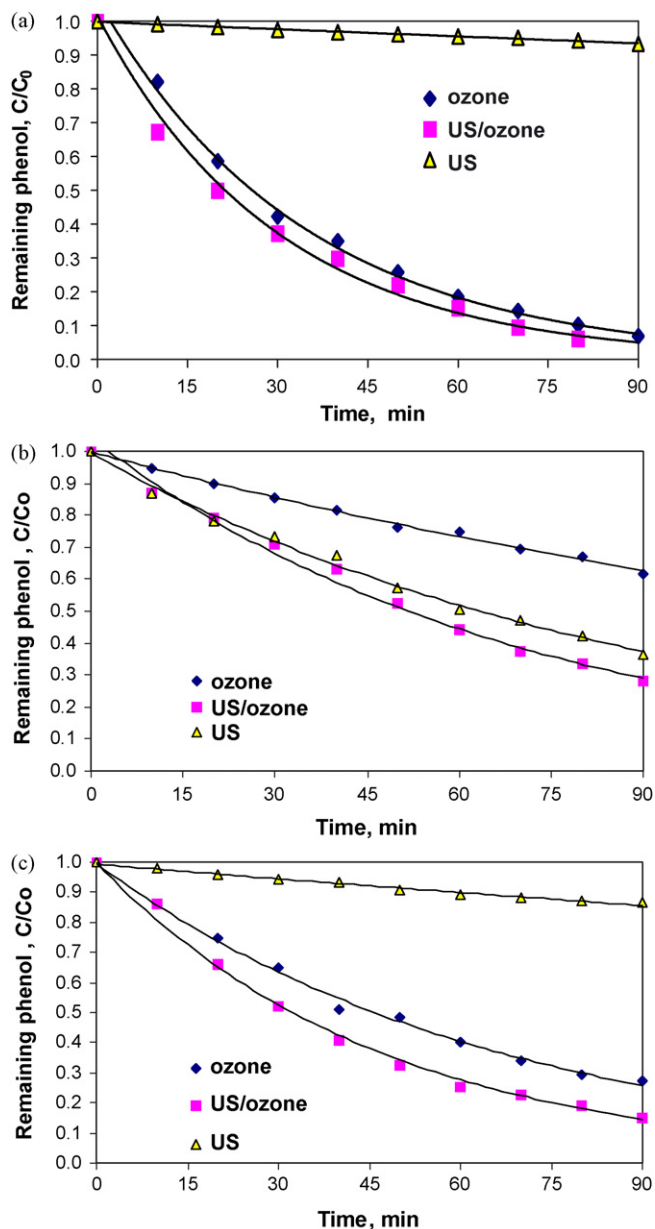


Fig. 4. Comparative rates of phenol ( $C_0=2.5$  mM) decay by US, ozone and US/ozone operations at three different pH values. (a) pH 10.0, (b) pH 2.0, (c) pH 5.6.



- pH 5.6: the effect is additive ( $k_{\text{US/O}_3} = 2.90 \times 10^{-2} \text{ min}^{-1}$ ), and the rate is nearly equal to the average of the rates observed at pH 10 and 2.

### 3.2.2. Ultrasound/UV combination

Integration of ultrasound with UV irradiation was found to provide a considerable advantage over single operations (of either UV or US) by the formation of excess OH radicals upon photolysis of US-induced hydrogen peroxide. Profiles of phenol decomposition during single UV, US and combined UV/US applications are presented in Fig. 5.

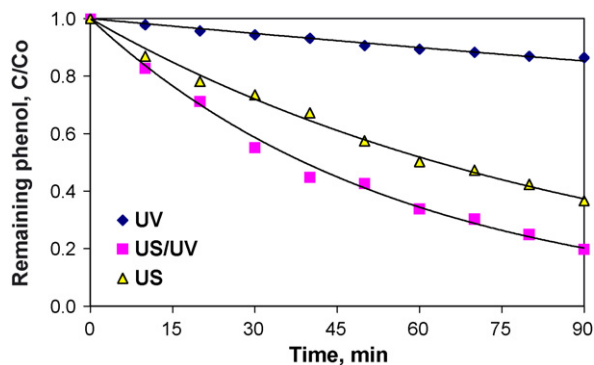


Fig. 5. Comparative rates of phenol ( $C_0=2.5$  mM) decay in 90 min by UV irradiation (254 nm), sonolysis (300 kHz) and US/UV operation, at pH 2.

Although UV irradiation alone induced negligible phenol decomposition, its combination with ultrasound nearly doubled the rate observed by ultrasound alone ( $k_{\text{US}} = 1.0 \times 10^{-2} \text{ min}^{-1}$ ;  $k_{\text{US/UV}} = 1.8 \times 10^{-2} \text{ min}^{-1}$ ). Monitoring of the  $\text{H}_2\text{O}_2$  concentration during 90 min sonolysis of deionized water in the presence and absence of UV irradiation showed that during sonolysis alone,  $\text{H}_2\text{O}_2$  tended to accumulate while in the presence of UV irradiation, the net rate of  $\text{H}_2\text{O}_2$  formation reached a steady state within 30 min due to photolysis. The data are presented in Fig. 6. A less significant factor in the enhancement of decomposition by combined UV/US operation may be the possibility of some ozone generation above the surface of the solution by the UV lamp.

The effect of pH was investigated by running the operation at four different pH levels and comparing the pseudo-first order rate coefficients. The results are presented in Fig. 7. Similar to what we observed in sonolysis alone, the rate in combined US/UV operation was decelerated by pH elevations. However, the effect was found less significant in the presence of UV light than in its absence, as presented in a comparative bar chart in Fig. 8. Note that the very low rate of phenol decay by ultrasound at pH 10 is accelerated by a factor of 7 when it is applied together with UV irradiation. At pH 5.6 and 4.0, UV light doubled the rate of sonochemical decay reactions, and at pH 2.0, where ultrasound is most effective, UV induced only 61% enhancement in the overall rate of decomposition.

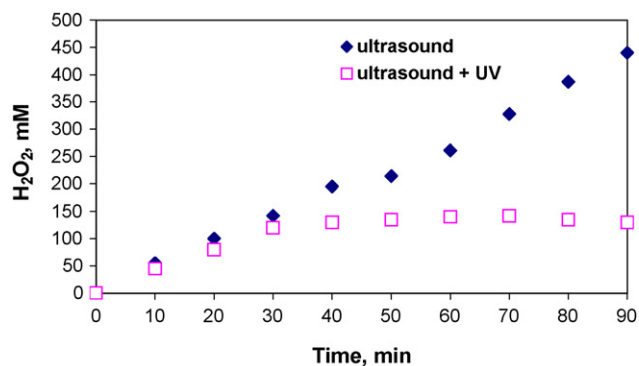


Fig. 6. Net rate of  $\text{H}_2\text{O}_2$  formation in sonolysis of deionized water in the presence and absence of UV irradiation during aeration.

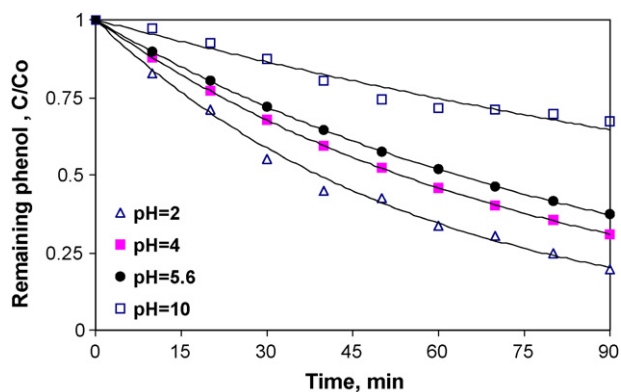


Fig. 7. Impact of pH on the rate of phenol decay by UV/US combination.

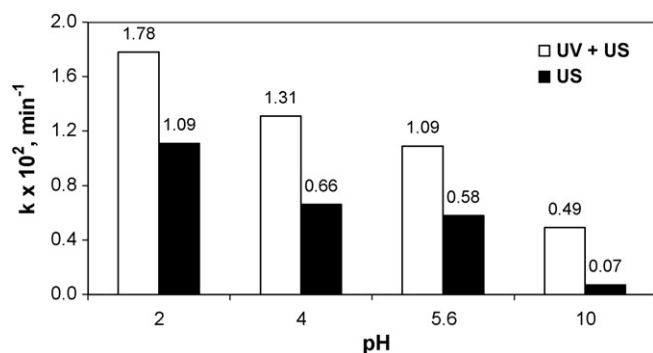
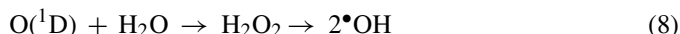


Fig. 8. Comparative response of the pseudo-1st order phenol decay coefficient ( $k$ ) to pH raises in 90 min US and US/UV operations.

### 3.2.3. Ultrasound/ozone/UV combination and comparison of all systems

Combined operation of ultrasound, ozone and UV light was the most effective method of phenol decay at all pH test levels. The advantage over both of the dual combinations ( $O_3$ /US and US/UV) arises from the reaction of ozone in the presence of UV irradiation (irrespective of the applied pH) to yield singlet state oxygen, which is readily converted to hydrogen peroxide and OH radicals as shown [15]:



The overall assessment of all systems in terms of phenol decay rate (for  $C_0 = 2.5$  mM) during 90 min operation at pH 2 and 10 is presented in Table 1.

## 4. Conclusions

The study showed that ozonation required highly alkaline pH for effective phenol removal, while in the presence of ultrasonic cavitation, the effectivity was improved via: i) enhanced peroxy and hydroxyl radical production (at high pH) upon increased mass transfer rate of ozone in solution; and ii) thermal decomposition of  $O_3$  in the gas phase (regardless of the pH level) during bubble collapse. Photolytic decay of phenol by UV irradiation at 254 nm was insignificant, while the operation in the presence of ultrasound was extremely effective due to the formation of

Table 1

Systems comparison for phenol ( $C_0 = 2.5$  mM) decay rate coefficients at two extreme pH levels

SYSTEM	Rate coefficient $\times 10^2$ min <sup>-1</sup>	
	pH 2.0	pH 10.0
UV irradiation (254 nm)	0.00 $\pm$ 0.00	0.21 $\pm$ 0.00
US (300 kHz)	1.07 $\pm$ 0.03	0.08 $\pm$ 0.00
$O_3$ (2 mg/L)	1.52 $\pm$ 0.04	2.79 $\pm$ 0.08
US/UV	1.79 $\pm$ 0.05	0.50 $\pm$ 0.03
US/ $O_3$	2.21 $\pm$ 0.06	3.26 $\pm$ 0.14
UV/ $O_3$	2.88 $\pm$ 0.19	8.69 $\pm$ 0.54
US/UV/ $O_3$	8.65 $\pm$ 0.32	17.93 $\pm$ 0.84

excess hydroxyl radicals by photolysis of ultrasound-generated  $H_2O_2$ . Combination of ozone, UV irradiation and sonolysis provided maximum rate of phenol decay at all test pH owing to the effects discussed above in dual combinations plus that of UV photolysis of ozone to generate excess  $H_2O_2$  and OH radicals. Hence in the triplet combination, limitations of both mass transfer and decomposition (pH-dependent) of  $O_3$  are minimized.

Finally, a comparison of single and combined operations with respect to the pseudo-first order phenol decay rates at acidic and alkaline pH is as follows:

pH 2.0: US/UV/ $O_3$  >  $O_3$ /UV > US/ $O_3$  > US/UV >  $O_3$  > US > UV.

pH 10.0: US/UV/ $O_3$  >  $O_3$ /UV >  $O_3$  > US/ $O_3$  > US/UV > UV > US.

## Acknowledgements

The authors appreciate the financial support of Bogazici University Research Projects Fund through the project BAP01Y104.

## References

- [1] H.H.P. Fang, O.C. Chan, Toxicity of phenol towards anaerobic biogranules, *Water Res.* 31 (1997) 2229–2242.
- [2] P.R. Gogate, S. Mujumbar, J. Thampi, A.M. Wilhelm, A.B. Pandit, Destruction of phenol using sonochemical reactors: scale-up aspects and comparison of novel configuration with conventional reactors, *Sep. Purif. Tech.* 34 (2004) 25–34.
- [3] A. Kotronarou, G. Mills, M.R. Hoffmann, Ultrasonic irradiation of *p*-Nitrophenol in Aqueous Solution, *J. Phys. Chem.* 95 (1991) 3630–3638.
- [4] M. Sivakumar, P.A. Tatake, A.B. Pandit, Kinetics of *p*-Nitrophenol degradation: effect of reaction conditions and cavitation parameters for a multiple frequency system, *Chem. Eng. J.* 85 (2002) 327–338.
- [5] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez, Comparison of different advanced oxidation processes for phenol degradation, *Water Res.* 36 (2002) 1034–1042.
- [6] N.H. Ince, G. Tezcanli, R.K. Belen, I.G. Apikyan, Ultrasound as a catalyst of aqueous reaction systems: the state of the art and environmental applications, *Appl. Catal. B: Environ.* 29 (2001) 167–176.
- [7] T.J. Mason (Ed.), *Chemistry with ultrasound: critical reports on applied chemistry* 28, society for chemical industry, Elsevier, London, 1990.
- [8] APHA/AWWA/WPCP, Standard methods for the examination of water and wastewater, 17th Edition, American Public Health Association, Washington DC, 1992.
- [9] N.V. Klassen, D. Marchington, H.C.E. McGowan,  $H_2O_2$  determination by the I3-method and by the  $KMnO_4$  Titration, *Anal. Chem.* 66 (1994) 2921–2925.



- [10] R. Kidak, N.H. Ince, Effects of operating conditions on sonochemical decomposition of phenol, *J. Haz. Mat. B* 137 (2006) 1453–1457.
- [11] L.K. Weavers, F.H. Ling, M.R. Hoffmann, Aromatic compound degradation in water using a combination of sonolysis and ozonolysis, *Environ. Sci. Technol.* 32 (1998) 2727–2733.
- [12] H. Destailats, A.J. Collusi, J.M. Joseph, M.R. Hoffmann, Synergistic effects of sonolysis combined with ozonolysis for the oxidation of azobenzene and methyl orange, *J. Phys. Chem.* 104 (2000) 8930–8935.
- [13] N. Serpone, R. Terzian, H. Hidaka, E. Pelizzetti, Ultrasonic induced dehalogenation and oxidation of 2-, 3-, and 4-chlorophenol in air-equilibrated aqueous media, similarities with irradiated semiconductor particulates, *J. Phys. Chem.* 98 (1994) 2634–2640.
- [14] T. Lesko, A.J. Colussi, M. Hoffman, Sonochemical decomposition of phenol: evidence for a synergistic effect of ozone and ultrasound for the elimination of total organic carbon from water, *Environ. Sci. Technol.* 40 (2006) 6818–6823.
- [15] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671–698.