Sonochemical degradation of 2chloro-5methyl phenol assisted by TiO_2 and H_2O_2

P. Nalini Vijaya Laxmi [a], P. Saritha [a], N. Rambabu [a], V. Himabindu [a,*], Y. Anjaneyulu [b]

[a] Center for Environment, Institute of Science and Technology, Jawaharlal Nehru Technological University, Kukatpally, Hyderabad 85, Andhra Pradesh, India
[b] Trent Lott Geospatial Visualization Research Center, Jackson State University, Jackson, MS, USA

ARTICLE INFO

ABSTRACT

The degradation of 2chloro-5methyl phenol (2C-5MP) in aqueous solution by ultrasonication (US) in the presence of TiO_2 and H_2O_2 has been studied. Maximum degradation rate of 2.66×10^{-2} was achieved by $US/TiO_2/H_2O_2$ process when compared to US/TiO_2 (1.01×10^{-2}) and US/H_2O_2 (5.5×10^{-3}) systems. The effect of inorganic ions on degradation rate of 2C-5MP were found to be in the order of $Cl^- > SO_4{}^{2-} > HPO_4{}^{2-} > HCO_3{}^-$. Further, the impact of synthetic additives like CCl_4 as hydrogen radical scavenger and CH_3OH as hydroxyl radical scavenger on US were studied which confirmed the involvement of hydroxyl radicals in the degradation of 2C-5MP. Kinetic studies revealed that the degradation process followed pseudo-first-order mechanism with the correlation coefficient (R^2) of 0.9913 under experimental conditions.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

2Chloro-5methyl phenol is extensively used in the manufacture of resins, herbicides, pharmaceuticals, tricresylic acid surfactants. Wastewater from these industries together with coal-conversion unit and petrochemicals [1] contain high concentration of cresol. Discharge of cresols into the environment poses significant health threat due to carcinogenic and refractory nature [2]. Furthermore, the high toxicity of these chemicals makes it difficult to decompose them by biological treatment [3]. With growing risk of environmental hazards associated with these chemicals, several methods have been developed to treat the wastewater. 2C-5MP is one such chemical which is found in very low concentrations in the ground water. However, even at such low concentrations, it cannot be ignored because of it's high toxicity. Sonication is the fast clean technology for lower concentrations of hazardous compounds, so we have selected this technology. Recently, the application of ultrasound in wastewater treatment has attracted great interest [4–7]. Ultrasonic irradiation of liquids gives rise to cavitation bubbles, which during compression/rarefaction cycles grow and expand by entrapping volatile vapors and gases in the medium. When the bubbles become too large to sustain themselves, they undergo violent implosions resulting in local hot spots with extreme temperatures and pressures. Organic compounds exposed to ultrasound may undergo degradation via thermal and/or chemical reactions depending on the degree of solute's partitioning between the gaseous bubble and the aqueous solution. The degradation of highly and moderately volatile compounds takes place in the gas phase by molecular fragmentation and at the interfacial sheath by oxidative destruction, respectively [8]. However, the complete mineralization of organic pollutants using only sonication is not economically attractive. Therefore, acoustic irradiation followed by other techniques, such as biological treatment or sonication coupled with other oxidation techniques is usually adopted in the wastewater treatment. Chemat et al. studied the degradation of humic substances in drinking water using a synergic combination of ultrasound and hydrogen peroxide [9]. Neppolian et al. observed that the coupled $US/Fe^{2+}/H_2O_2$ technique was effective in the mineralization of methyl-tert-butyl ether (MTBE) [10]. Nakajima et al. reported that TiO_2 is more effective for destruction of 1,4-dioxane in aqueous systems [11].

The main objective of the present study is to investigate for the first time the degradability of 2C-5MP a USEPA listed priority pollutant by ultrasonic irradiation coupled with H_2O_2 as oxidant and TiO_2 as catalyst. The rate of degradation of 2C-5MP is investigated as a function of H_2O_2 concentration, TiO_2 dosage, ultrasonic temperature and ultrasonic frequency. Besides this, the impact of inorganic ions, hydrogen and hydroxyl radical scavengers on the ultrasonication are also studied. Finally, kinetic constants are evaluated using pseudo-first-order equation.

2. Materials and methods

2.1. Materials

Degussa P_{25} titanium dioxide (80% anatase, 20% rutile) was obtained from Degussa corporation, Pune, India. 2C-5MP, hydrogen

* Corresponding author. Tel.: +91 040 23156133; fax: +91 040 23156133.
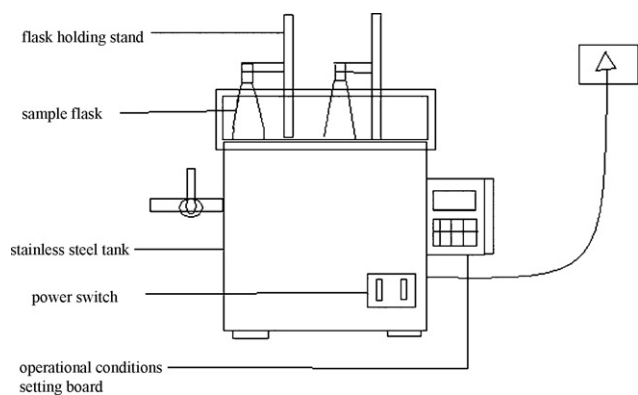E-mail address: vurimindihimabindu@yahoo.com (V. Himabindu).

Fig. 1. A schematic representation of ultrasonicator.

Fig. 2. Effect of pH on sonochemical degradation of 2C-5MP a kinetic representation.

peroxide (30%), NaHCO$_3$, Na$_2$HPO$_4$, Na$_2$SO$_4$, NaCl were of highest purity (Merck, 99%) and used as received. Aqueous stock solutions of 2C-5MP were prepared by dissolving 2C-5MP in ultrapure Milli-Q water.

2.2. Sonochemical reactor

The experimental setup consisted of a 3.3 L ultrasonic bath (Model No. EN-30-US, Enertech Electronics Pvt. Ltd., Bombay, India) with a high-frequency Mosfet based electronic ultrasound generator Fig. 1. The ultrasonic bath has a two piezo-ceramic transducers bonded to the bottom of a stainless steel tank, with the option of operating at 25 or 33 kHz in a continuous or pulse (5 s on and 1 s off) mode. The ultrasonicator could be operated at power outputs 1255 W (power calculated by calorimetric method).

2.3. Methodology

Ultrasonic degradation of 2C-5MP (5 mg/L) was carried out using a constant volume of 100 ml in batch mode. According to the experimental plan, initially the ultrasonic pulses (on/off) were used to initiate 2C-5MP degradation at a frequency of 33 kHz and the power in to the system of 1255 W, which was measured using calorimetry. The pH and temperature were varied from 3 to 11 and 25 to 45 °C. In peroxide mediated sonodegradation experiments the concentration of H$_2$O$_2$ was varied from 10 to 500 mg/L while in sonocatalytic experiments with TiO$_2$, the dosage of TiO$_2$ was varied from 15 to 60 mg given in Table 1. 5 to 10 ml samples were withdrawn from the reactor at regular intervals. Samples from sonocatalytic experiments were centrifuged and filtered using 0.25 μm MDI filters to remove the catalyst particles. The samples were then analysed using spectrophotometer. Through out the entire study, control samples were run for every experiment to validate the degradation and also check for any loss on volatalization. To study the effect of inorganic ions on the degradation of 2C-5MP using H$_2$O$_2$, predetermined amounts of (0.003 M) chlorides, sulphates, phosphates and bicarbonates were added to the aqueous solution of 2C-5MP. To verify the mechanism of degradation of 2C-5MP, 100 mg/L of CCl$_4$ as hydrogen radical scavenger and 1% of

CH$_3$OH as hydroxyl radical scavenger were added to the aqueous solution of 2C-5MP.

2.4. Analytical methods

Reduction in 2C-5MP concentration is measured by Systronics-1272 UV–vis spectrophotometer (wave length 320 nm) and further confirmed by reverse phase high performance liquid chromatography (HPLC, Aligent1100), which was equipped with a multiple wavelength UV detector. The determination wavelength was set at 360 nm the eluent used consisted of 70% methanol and 30% water [12] and the column temperature was maintained at room temperature.

3. Results and discussion

3.1. Effect of pH

The effect of pH on sonochemical degradation of 2C-5MP was investigated at 33 kHz with ultrasonic power of 1255 W and the temperature of aqueous media is 25 ± 1 °C. The pH was varied from 3 to 11 as illustrated in Fig. 2. The results revealed that the efficiency of 2C-5MP degradation at low pH is markedly higher compared to that at higher pH. At pH 3 the degradation rate was 1.1×10^{-3} where as at pH 11 the degradation rate decreased to 5×10^{-4}. At low pH, the contribution from pyrolysis increased as 2C-5MP species mainly exist in the neutral form and 2C-5MP molecules can penetrate into cavitation bubbles, which accounts for the increased degradation efficiency of 2C-5MP at low pH values. This result also implies that the degradation of 2C-5MP mainly results from the pyrolysis effect of sonotreatment. The sonodegradation of 2C-5MP fitted first-order kinetics irrespective of the change in the solution pH values, which indicates that the change in solution pH value does not lead to the change in the degradation kinetics. Lin et al. [13] studied the sonodecomposition of 2-chlorophenol and found that the degradation efficiency decreased with the increase of solution pH and ascribed the increased degradation efficiency of 2-chlorophenol to the pyrolysis effect, which resulted from the penetration of a larger amount of 2-chlorophenol into the cavitation bubbles at lower pH value. Similarly, Gultekin et al. [8] studied the ultrasonic destruction of bisphenol-A and found that the degradation efficiency decreased with the increase of solution pH.

3.2. Effect of temperature

Sonodegradation of 2C-5MP was carried out under different temperatures. With increasing temperature, the rate of degradation also increased. At 25 °C the degradation rate of reaction is 7×10^{-4} where as at 45 °C the degradation rate of reaction increased to 1.1×10^{-3}. This may be due to the hydrophilic property of 2C-5MP which is mostly degraded outside the cavitation process by the hydroxyl radicals produced by ultrasound. The increase of aqueous temperature certainly increases the number of cavitation bubbles on sonolysis and thus the rate of production of radicals (•OH and

Table 1
Showing parameters and operational conditions for the degradation of 2C-5MP.

S.No.	Parameters	Operational conditions
1	Frequency	33 kHz
2	Power	1255 W
3	Temperature	Varied from 25 to 45 °C
4	H$_2$O$_2$ dosage	Varied from 10 to 250 mg/L
5	TiO$_2$ dosage	Varied from 15 to 60 mg

Table 2
Rate constants of degradation under different temperatures.

|	Temperature (K)		
	298	308	318
Rate constant (k/min^{-1})	7×10^{-4}	9×10^{-4}	1.1×10^{-3}
k/k_{293}	1.0	1.28	1.57

$^\bullet$OOH) results in a lowering of the cavitation threshold. Additionally, at low temperature (<45 °C), the vapor pressure of water is lower, and the solubility of gas is higher, hence the cavitation bubbles exhibit a more gaseous nature. As a result, the reaction rates do not decrease with increase in solution temperature between 25 and 45 °C. Therefore, reactions in the bulk are facilitated by increasing the temperature due to the higher mass transfer of different species at higher temperatures and this leads to an enhancement on the rate of reaction of radicals with pollutant. Table 2 summarizes the rate constants at different temperatures. Jiang et al. [14] studied the effect of temperature on 4-chloro phenol and found that the degradation efficiency increased with increasing temperature from 10 to 40 °C.
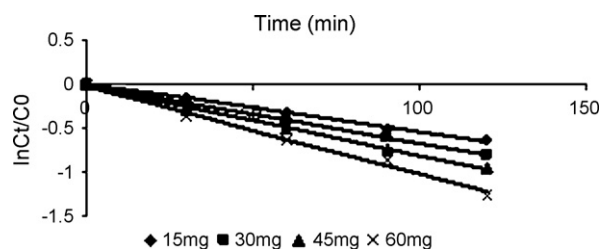
3.3. Degradation of 2C-5MP by US/H₂O₂

The degradation of aqueous 2C-5MP using sonooxidation was investigated in the presence of H_2O_2 with different concentrations and the results are shown in Fig. 3. The degradation of 2C-5MP fitted to first-order kinetics. With an increase in the concentration of H_2O_2 from 10 to 250 mg/L, there was an increase in degradation efficiency. The degradation rate increased from 4.1×10^{-3} to 6.8×10^{-3}. The maximum degradation rate was 6.8×10^{-3} observed at a peroxide concentration of 250 mg/L and this was used as optimum peroxide concentration for further experiments. However, addition of excess peroxide i.e., 500 mg/L did not increase the degradation rate. This may be because of the formation of peroxyl radicals. Drijvers et al. [15] investigated the degradation of 2-chlorophenol using ultrasonic irradiation and observed the increased degradation efficiency in the presence of H_2O_2.

3.4. Degradation of 2C-5MP by US/TiO₂

Sonocatalytic degradation of 2C-5MP solution was carried out in the presence of TiO_2 using different dosages ranging from 15 to 60 mg and the results are shown in Fig. 4. From the results, it can be inferred that with an increase in TiO_2 dosage, the degradation rate also increased. A maximum degradation rate of 1.01×10^{-2} was achieved with a TiO_2 dosage of 60 mg. The increase in degradation rate may be explained by the fragmentation of catalyst by the cavitation process which produces higher surface area. In this method, ultrasonic waves not only destroy the 2C-5MP through cavitation process but also it increases the adsorption process by increasing the surface area of the catalyst.
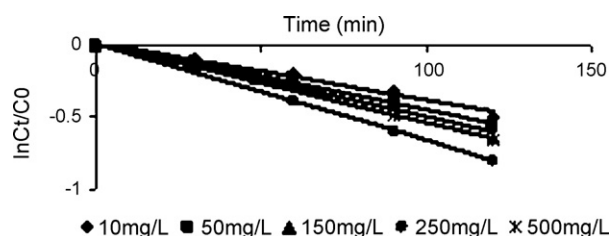
Fig. 3. Effect of H₂O₂ concentration on sonochemical degradation of 2C-5MP.

Fig. 4. Effect of TiO₂ concentration on sonochemical degradation of 2C-5MP.
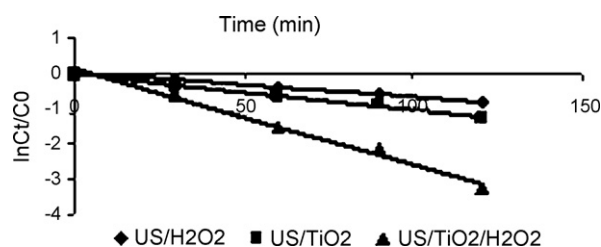
Fig. 5. Effect of different reaction systems on sonochemical degradation of 2C-5MP.

Table 3
Pseudo-first-order degradation rate constants of 2C-5MP in different reaction systems.
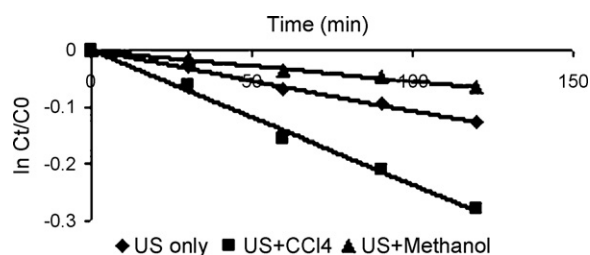
Reaction system	Rate constant, k (min^{-1})	Correlation coefficient, R^2
US/H₂O₂	0.0068	0.9978
US/TiO₂	0.0101	0.9912
US/TiO₂/H₂O₂	0.0266	0.9913

3.5. Degradation of 2C-5MP by US coupled with TiO₂/H₂O₂

Ultrasound coupled with TiO_2/H_2O_2 reactions may markedly accelerate the degradation. The degradation of 2C-5MP in US/H_2O_2, US/TiO_2 and US/TiO_2/H_2O_2 systems are compared in Fig. 5. The maximum removal of 2C-5MP i.e. 98% was observed in US/TiO_2/H_2O_2 system where as 55% removal was observed in US/H_2O_2 and 72% was observed in US/TiO_2 system after 2 h of ultrasonic irradiation. The highest removal was observed in US/TiO_2/H_2O_2 system compared to US/H_2O_2 and US/TiO_2 systems which was mainly attributed to the promotion of ultrasound on TiO_2-catalysed decomposition of H_2O_2 to form more active free radicals, such as $^\bullet$OH radicals and $HO_2^\bullet$/$^\bullet O_2^-$ radicals. In addition the degradation was followed by first-order kinetics. The reaction rates of 2C-5MP are given in Table 3.

3.6. Degradation of 2C-5MP by US/CCl₄ and US/CH₃OH

To study the impact of CCl_4 as hydrogen atom scavenger on the degradation of 2C-5MP, experiments were conducted in the presence of CCl_4 (100 mg/L) and the results are illustrated in Fig. 6. From the figure it can be inferred that CCl_4 had a significant effect

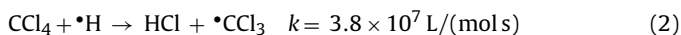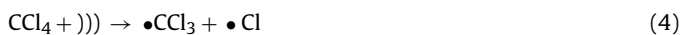Fig. 6. Effect of hydrogen and hydroxyl radical scavengers on sonochemical degradation of 2C-5MP.

Table 4
Pseudo-first-order degradation rate constants of 2C-5MP by US/H_2O_2 and different ions.

Reaction system	Rate constant, k (min^{-1})	Correlation coefficient, R^2
US/H_2O_2	0.0068	0.9978
US/H_2O_2/Cl^{-1}	0.0078	0.9976
US/H_2O_2/SO$_4^{2-}$	0.0072	0.9972
US/H_2O_2/HPO$_4^{2-}$	0.0056	0.9938
US/H_2O_2/HCO$_3^-$	0.0046	0.9919

Table 5
Percentage degradation of COD on different reactive systems.

S.No.	Reaction system	% Degradation of COD
1	US/H_2O_2	35%
2	US/TiO_2	52%
3	US/TiO_2/H_2O_2	70%

on the rate of degradation of 2C-5MP. The removal efficiency and the percentage degradation of 2C-5MP in US/CCl_4 processes were remarkably increased to 33% which compared to those in US process was 12%. This may be due to two distinct properties of CCl_4 in the first case, CCl_4 acts as a hydrogen atom scavenger according to the following reactions (1)–(3):

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

$$CCl_4 + {}^\bullet H \rightarrow HCl + {}^\bullet CCl_3 \quad k = 3.8 \times 10^7 \, L/(mol\,s) \tag{2}$$

$$CCl_4 + {}^\bullet OH \rightarrow no\ reaction \tag{3}$$

Consequently, CCl_4 inevitably restrained the recombination reaction between hydrogen atom and ${}^\bullet OH$ radicals in sonochemical degradation process. Considering that there was no reaction between CCl_4 and ${}^\bullet OH$ radicals an increase in ${}^\bullet OH$ radicals concentration and an enhancing effect in 2C-5MP degradation were achieved in the presence of CCl_4. Zheng et al. [16] studied that the effect of CCl_4 on the ultrasonic degradation of phenol. Secondly, CCl_4 is a hydrophobic organic compound, is prone to enter the cavitation bubbles, further undergoing degradation by pyrolytic cleavage. The C–Cl bond in CCl_4 was preferentially broken at high temperature to produce large amount of ${}^\bullet Cl$ radicals compared to the H–OH bond in H_2O due to the fact that the C–Cl bond energy in CCl_4 is 73 kcal/mol and the H–OH bond energy in H_2O is 119 kcal/mol. The formation of ${}^\bullet Cl$ radicals will lead to a series of reactions (4)–(7).

$$CCl_4 +))) \rightarrow {}^\bullet CCl_3 + {}^\bullet Cl \tag{4}$$

$$ {}^\bullet CCl_3 +))) \rightarrow CCl_2 + {}^\bullet Cl \tag{5}$$

$$ {}^\bullet Cl + {}^\bullet Cl \rightarrow Cl_2 \tag{6}$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \tag{7}$$

HClO and chlorine-containing radicals, such as ${}^\bullet Cl$, ${}^\bullet CCl_3$ and CCl_2, have strong oxidizing property. Methanol is a good hydroxyl radical scavenger. Addition of methanol is therefore expected to decrease 2C-5MP degradation rates. Methanol was added at 1% (v/v) since this concentration was found to be the major sink for hydroxyl radical [16]. From the figure it can be observed that 2C-5MP degradation was inhibited in the presence of methanol to 12–6%, the enhancement effect of CCl_4 is largely eliminated by addition of methanol. From both the above experiments i.e. US/CCl_4 and US/CH_3OH, it can be inferred that, hydroxyl radicals plays a very important role in degrading 2C-5MP.

3.7. Degradation of 2C-5MP by US/H_2O_2/ions

The effect of different anions on sonodegradation of 2C-5MP in US/H_2O_2 process, is shown in Table 4. The rate of the reaction was found to decrease in the following order Cl$^-$ > SO$_4^{2-}$ > HPO$_4^{2-}$ > HCO$_3^-$. The degradation of 2C-5MP was observed to be 7.8×10^{-3} min^{-1} in the presence of chlorine ion and 7.2×10^{-3} min^{-1} in the presence of sulphate ion. Bicarbonate and phosphate anions were found to delay the process of the 2C-5MP degradation. The degradation rate was observed as

4.6×10^{-3} min^{-1} in bicarbonates and in phosphates the degradation rate was observed as 5.6×10^{-3} min^{-1}, as they are efficient scavengers of hydroxyl radicals.

$$HO^\bullet + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O \tag{8}$$

$$HO^\bullet + HPO_4^{2-} \rightarrow HPO_4^{\bullet-} + H_2O \tag{9}$$

Adding salt to the reaction mixture results in reduced vapor pressure and increased surface tension, both of which tend to reduce the number of bubbles formed and consequently a decrease in reaction rate [17–18].

3.8. Degradation of COD%

The % degradation of COD on sonodegradation of 2C-5MP in US/H_2O_2, US/TiO_2 and US/TiO_2/H_2O_2 systems are given in Table 5. The maximum removal of 2C-5MP i.e.70% was observed in US/TiO_2/H_2O_2 system where as 35% removal was observed in US/H_2O_2 and 52% was observed in US/TiO_2 system after 2 h of ultrasonic irradiation. The highest removal was observed in US/TiO_2/H_2O_2 system compared to US/H_2O_2 and US/TiO_2 systems.

4. Conclusions

1. In the present study, using US with TiO_2 and H_2O_2 the degradation of 2C-5MP has been initiated by reaction with the ${}^\bullet OH$ radical.
2. 2C-5MP is hydrophilic and hence reacts with hydroxyl radicals in solution, rather than inside the bubble, since the bubble/liquid interface is hydrophobic.
3. The rate of degradation of 2C-5MP by US/H_2O_2/TiO_2 was greater than that which can be achieved by either ultrasound alone or in combination with any other chemical or reagent used in the present study.
4. Many advanced oxidation processes for water and wastewater decontamination undergo a variable level of inhibition by natural water components, particularly the anions, because of the scavenging of reactive species (replaced by less reactive radicals) or competitive adsorption on active surfaces.
5. Sonochemistry could therefore undergo lesser inhibition by the anions than other techniques. This work additionally shows that bicarbonate and phosphate anions were found to delay the process of the 2C-5MP degradation even more than Cl$^-$ and SO$_4^{2-}$, as they are efficient scavengers of hydroxyl radicals.

References

[1] N. Shivaraman, R.A. Pandey, Characterization and biodegradation of phenolic wastewater, J. Indian Assoc. Environ. Manage. 27 (2000) 12–15.
[2] M.A. Callahan, M. Slimark, N. Gbel, I. May, C. Fowler, R. Freed, P. Jennings, R. Dupree, F. Whitemore, B. Maestri, B. Holt, C. Gould, Water related environmental fate of 120 priority pollutants, Report no. EPA-44014-79-029a, b, United States Environmental Protection Agency, NTIS, Washington, DC.
[3] D. Sreekanth, D. Sivaramakrishna, V. Himabindu, Y. Anjaneyulu, Thermophilic degradation of phenolic compounds in lab scale hybrid up flow anaerobic sludge blanket reactors, J. Hazard. Mater. 164 (2009) 1532–1539.
[4] Y.G. Adewuyi, Sonochemistry in environmental remediation. 1. Combinative and hybrid sonophotochemical oxidation processes for the treatment of pollutants in water, Environ. Sci. Technol. 39 (2005) 3409–3420.
[5] M. Sivakumar, P.A. Tatake, A.B. Pandit, Kinetics of *p*-nitrophenol degradation: effect of reaction conditions and cavitational parameters for a multiple frequency system, Chem. Eng. J. 85 (2002) 327–338.

[6] Z.B. Guo, R. Feng, Y.F. Zheng, X.R. Fu, Improvement in properties of coal water slurry by combined use of new additive and ultrasonic irradiation, Ultrason. Sonochem. 14 (2007) 583–588.

[7] Z.B. Guo, C.H. Gu, Z. Zheng, R. Feng, G.Z. Gao, Y.F. Zheng, Sonodegradation of halomethane mixtures in the chlorinated drinking water, Ultrason. Sonochem. 13 (2006) 487–492.

[8] I. Gultekin, N.H. Ince, Ultrasonic destruction of bisphenol-A: the operating parameters, Ultrason. Sonochem. 15 (2008) 524–529.

[9] F. Chemat, P.G.M. Teunissen, S. Chemat, P.V. Baartels, Sono-oxidation treatment of humic substances in drinking water, Ultrason. Sonochem. 8 (2001) 247–250.

[10] B. Neppolian, H. Jung, H. Choi, Sonolytic degradation of methyl-tert-butyl ether: the role of coupled fenton process and persulphate ion, Water Res. 36 (2002) 4699–4708.

[11] Akira Nakajima, Hirokazu Sasaki, Yoshikazu Kameshima, Kiyoshi Okada, Hisashi Harada, Effect of TiO_2 powder addition on sonochemical destruction of 1,4-dioxane in aqueous systems, Ultrason. Sonochem. 14 (2007) 197–200.

[12] Zhaobing Guo, Ruo Feng, Jiuhai Li, Zheng Zheng, Youfei Zheng, Degradation of 2,4-dinitrophenol by combining sonolysis and different additives, J. Hazard. Mater. 158 (2008) 164–169.

[13] J.G. Lin, C.N. Chang, J.R. Wu, Decomposition of 2-chlorophenol in aqueous solution by ultrasound/H_2O_2 process, Water Sci. Technol. 33 (1996) 75–81.

[14] Yi Jiang, Christian Petrier, T. David Waite, Sonolysis of 4-chlorophenol in aqueous solution: effects of substrate concentration, aqueous temperature and ultrasonic frequency, Ultrason. Sonochem. 13 (2006) 415–422.

[15] D. Drijvers, H.V. Langenhove, M. Beckers, Decomposition of phenol and trichloroethylene by the ultrasound/H_2O_2/CuO process, Water Res. 33 (1999) 1187–1194.

[16] W. Zheng, M. Maurin, M.A. Tarr, Enhancement of sonochemical degradation of phenol using hydrogen atom scavengers, Ultrason. Sonochem. 12 (2005) 313–317.

[17] Y.C. Chen, P. Smirniotis, Ind. Eng. Chem. Res. 41 (2002) 5958.

[18] E. Psillakis, G. Goula, N. Kalogerakis, D. Mantzavinos, Degradation of polycyclic aromatic hydrocarbons in aqueous solutions by ultrasonic irradiation, J. Hazard. Mater. 108 (2004) 95–102.