Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.846234

53 (2015) 462–468
January

Taylor & Francis
Taylor & Francis Group

Effects of operating parameters and additives on degradation of phenol in water by the combination of H_2O_2 and hydrodynamic cavitation

C.D. Wu[a,b,*], Z.L. Zhang[a,b], Y. Wu[a,b], L. Wang[a], L.J. Chen[a]

[a]*School of Environment and Energy, South China University of Technology, Guangzhou 510006, P.R. China*
Tel. +86 20 39380569; Fax: +86 20 39380508; email: ppchdwu@scut.edu.cn
[b]*The Key Laboratory of Pollution Control and Ecosystem Restoration, Industry Clusters of Ministry of Education, Guangzhou 510006, P.R. China*

Received 28 April 2013; Accepted 14 September 2013

ABSTRACT

The combination of H_2O_2 and hydrodynamic cavitation has been used to degrade phenol in water. The effects of parameters including inlet pressure (P1), orifice geometries of hydrodynamic reactor, initial concentration of H_2O_2, the presence of dissolved gases and catalysts (CuO, Fe, and TiO_2) have been discussed. It revealed that increased P1, more number of holes on plates, optimum initial H_2O_2 concentration, the higher flow rate of oxygen, and the presence of Fe or CuO are more favorable in phenol degradation. Nitrogen has different effect on cavitation from oxygen. Furthermore, the identification of primary intermediates of the reaction (hydroquinone, catechol, benzoquinone, and resorcin) indicated that hydroxyl radicals are involved in phenol degradation mechanisms.

Keywords: Hydrodynamic cavitation; H_2O_2; Phenol; Water treatment; Mechanism

1. Introduction

Phenol and other aromatic compounds are ubiquitous contaminants in wastewater, which exhibit high toxicity and non-biodegradability and are difficult to be treated. With the greater attention and more strict environmental regulations, there is a huge demand for developing novel water treatment techniques. Many studies on degradation/oxidation of phenol and substituted phenols have been reported. Among those studies, H_2O_2 was often used for degradation/oxidation reaction. It is known that H_2O_2 in combination with other conventional methods such as ultrasound/Fe [1], microwave and UV [2], ozone [3], photocatalysis [4], electrocoagulation process [5], and UV/Fe^{2+} [6] have obtained better results than conventional method alone. Moreover, phenol mineralization by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing was also reported [7]. Lu et al. [8] have achieved by assessing phenol degradation combined cavitation water jet and H_2O_2. However, few reports are available about H_2O_2 combined with hydrodynamic cavitation in the presence of different additives [9,10].

Cavitation promises an efficient alternative to degrade complex organic substances [11]. It can be described as formation, growth, and subsequent collapse of cavities releasing large magnitudes of energy locally, creating conditions similar to hot spots,

---

*Corresponding author.

and also generating strong oxidizing conditions by way of production of OH radicals [12]. Acoustic cavitation has been proved to be able to generate suitable conditions for the degradation or oxidation in the presence of various chemicals [13]. Over the past few decades, the sonochemical dynamics and the reactors have been extensively studied both theoretically and experimentally. Considerable work has indeed focused concentration on the application of sonochemical reactors for wastewater treatment [14–16]. However, these still cannot be applied on an industrial scale usually due to comparatively higher costs of the treatment [17].

Considerable researches including numerical simulation [18,19] and experiment [10,20] have concluded that hydrodynamic cavitation generates the cavitate conditions similar to that of acoustic cavitation and is an advanced oxidation process [21]. Moreover, there are several advantages on hydrodynamic cavitation: large handling capacity, low energy consumption, easy design of reactor, etc. So far, there are some illustrations about the operating and geometry parameters of hydrodynamic cavitation [22,23].

In this study, the combination of hydrodynamic cavitation and H_2O_2 for phenol degradation has been investigated. CuO, Fe, or TiO_2, which was used as the heterogeneous catalyst, were, respectively added into the reaction system. It is well known that hydrodynamic cavitation can generate high temperature and pressure conditions, in which the dissolved O_2, H_2O, and H_2O_2 in the system can be cracked into free radicals. Those free radicals and supercritical water oxidation reaction are responsible for the degradation of organic compounds in water. Therefore, the combination of hydrodynamic cavitations and H_2O_2 could create a faster and more effective way to degrade phenol. In addition, a predominant pathway of the degradation process will be suggested by measuring the primary intermediates of the reaction.

2. Materials and methods

2.1. Materials

Phenol and H_2O_2 (30% w/v) were analytically pure. CuO (99% wt.) was prepared as Yang et al. [24]. Its average particle size was about 63 nm. TiO_2 was purchased from Degussa AG. The ratio of anatase to rutile in TiO_2 was 3:1. The average particle size was about 30 nm, and the surface area measured by BET was 50 m^2/g. Fe was synthesized as Sun et al. reported [25], and the bare iron particles had a median size of 59.4 nm. All other chemicals were of at least 99% purity and were used without further purification. Bubbling gases (air, oxygen, and nitrogen) of five-nine grades were purchased from Guangzhou gas factory. Distilled water was used for preparing all aqueous solutions.

2.2. Hydrodynamic cavitation reactor

The experimental setup is shown in Fig. 1. The setup consists of a holding tank of 70 L volume, a coil of copper pipe (length 30 m, diameter 10 mm), a centrifugal pump (2,900 rpm, 2.2 kW, China), pressure meters (P1 and P2), control valves (V1, V2, and V3), flanges to accommodate the orifice plate, a mainline, and a bypass line. The copper pipe acts as the cooling tube to control the temperature of the reactive system. The temperature ranged from 26 to 30°C. The mainline consists of a flange which houses the orifice plate. The bypass line is provided to control the liquid flow through the mainline and the inlet pressure (P1). Both the mainline and the bypass line terminate well inside the tank below the liquid level in order to avoid any induction of air into the liquid. The control valves are provided to control the flow rate through the mainline. The mainline and the bypass line terminate were both well inside the tank below the liquid level in order to avoid any induction of air into the liquid. The inside diameter of the import and the export of the centrifugal pump is 50 and 40 mm, respectively. Four multiple-hole orifice plates (with different diameter and number of holes) were prepared in order to study the navigational effect. The diameter of each plate is 40 mm. Detailed information on the plates and the arrangement of the holes on the plates is presented in Fig. 2. In the setup, the holding tank was made of PVC, whereas all the pipe and multi-holes orifice plates were made of stainless steel. The setup is a close cycle system designed to draw the phenol

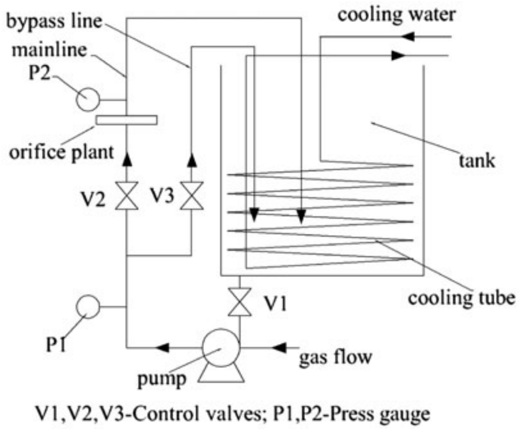


Fig. 1. Hydrodynamic cavitation setup.

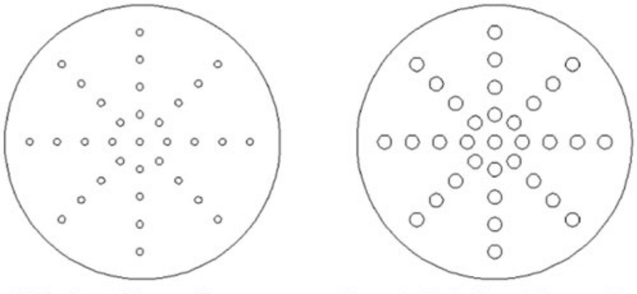


Plate 1. 33 holes of 1mm diamter Plate 2. 33 holes of 2mm diameter

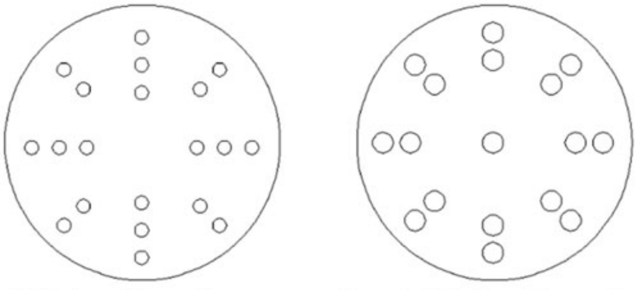


Plate 3. 20 holes of 2mm diameter Plate 4. 17 holes of 3mm diameter

Fig. 2. Arrangement of holes on orifice plates.

solution from a holding tank, then taking it into the cavitation region, and finally discharging the treated solution again back to the tank.

2.3. Methods

Twenty-five litres of different concentrations of phenol and H_2O_2 solutions was prepared by using distilled water and transferred to the holding tank. In all the process, the concentrations of phenol and H_2O_2 were 10 and 100 mg/L, respectively, and the multi-hole orifice plate 2 was used throughout the experiment, unless especially indicated. The temperature was maintained at 28 ± 2°C. During the experiment, V1 and V2 were always kept fully open, while V3 changed. A sample of the solution collected and the pump started. Then, the experiment condition was accommodated by controlling V3. The samples were withdrawn at intervals of 15 min. Each of the texts lasted 90 min. All the samples were filtrated by the filter membrane in order to remove the suspended solids. The concentrations of phenol were analyzed quantitatively using 4-aminoantipyring method and UV–vis spectrophotometer. The concentrations of H_2O_2 were determined by audiometric titration with sodium hyposulfite. The primary intermediates of phenol degradation were monitored using a high-performance liquid chromatography (HPLC) (Agilent 1100, USA). A Hypersil 5 μm C18 ODS column (5.0 mm × 250 mm) was used, and the detection wavelength was fixed at 220 nm for hydroquinone, catechol, resorcin, and at 254 nm for benzoquinone. Eluent consisted of a water/methanol mixture containing acetic acid (1%). Total organic carbon (TOC) was analyzed with TOC analyzer (USA, Phoenix-8000).

3. Results and discussion

3.1. Effect of P1

The effects of different initial pressures of hydrodynamic cavitation on phenol degradation for plate 2 were investigated over the range of 0.1–0.35 MPa, and the results are shown in Fig. 3. It can be seen clearly that the higher P1, the more effective in the rapid degradation of phenol. The degradation ratio was only 17.6% at 0.1 MPa while 46% at 0.35 MPa. These trends can be attributed to the enhancement of the OH radical production which was a result of the intensification of cavitational activity at higher pressures [26]. On the one hand, the increase of the P1 will lead to an increase of the collapse pressure of the cavity. On the other hand, the increase of the passed liquid through the cavitational zone can lead to the increase of cavitation yield. Superior degradation with higher P1 was consistent with other literature reports [12,27].

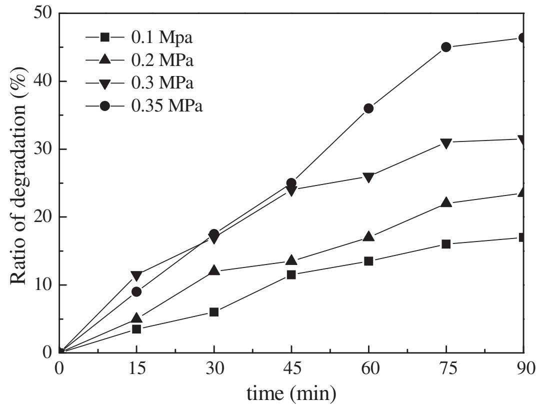


Fig. 3. Effect of P1 on phenol degradation for plate 2.

3.2. *Effect of multi-holes orifice plate*

The multi-holes orifice plate installed in the mainline would change the hydrodynamic performance and even induce cavitation. Different multi-holes orifice plates result in different intensities of cavitation and hence in different magnitude of pressures generated due to collapse of cavities. The holes on the orifice plates and their percentage flow area determine the magnitude of collapse pressure. In order to evaluate the effect of multi-holes orifice plate, oxidation/degradation of phenol using H_2O_2 with or without hydrodynamic cavitation generated was studied. It can be seen from Fig. 4 that there was significant degradation of phenol (8.2%) without the orifice plate mainline. During another static experiment before, it has been found that only 6.2% of 10 mg/L phenol was degraded after 90 min of oxidation with 100 mg/L H_2O_2. The cavitation generated by pump was responsible for the additional ratio of phenol degradation. It can also be observed from Fig. 4 that the degradation ratio on plate 2 is 31.8%, whereas only 28.4% on plate 3. It is suggested that the increased quantity of orifices on plate can generate more cavities. Compared plate 2 with plate 4, which has the similar flow areas, the degradation of phenol on plate 2 which has smaller diameter was faster than that on plate 4. The results indicate that the presence of orifice is favorable to enhance the degradation and the more holes, the higher efficiency of degradation at the same diameter of holes. The possible reason is that the smaller holes can provide the larger turbulence or turbulence intensity and the larger shear layer area [20,22]. With the same number of holes, the hole with larger diameter is more favorable than the smaller one, that is, the plate 2 (31.4%) is more available than the plate 1 (27.2%) at the oxidation time of 75 min. This can be attributed to the fact that this multiple orifices resulted in a greater number of cavitation events and caused greater overall cavitational intensity and enhanced degradation.

3.3. *Effect of initial H_2O_2 concentration*

The initial concentration of H_2O_2 plays a crucial role on determining the efficiency of the degradation process. The effect of H_2O_2 concentration within the range of 50–150 mg/L was shown in Fig. 5. The maximum degradation ratio reached 32% at the concentration of 100 mg/L at the time of 90 min. The H_2O_2 was formed by the recombination of OH radicals produced by reactive system. More OH radicals were produced, and then, phenol was oxidized more efficiently. However, the degradation ratio did not increase with the increase of H_2O_2 concentration, and higher concentration was not recommended because H_2O_2 is also a scavenger for free radicals [28]. In Fig. 5, there is another case that the total quantity of 100 mg/L H_2O_2 was added into the reactive system twice equally.

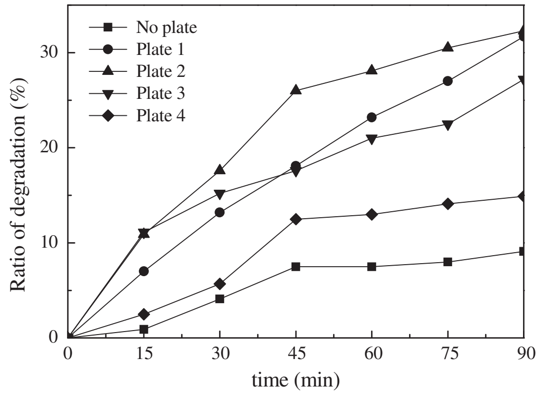


Fig. 4. Effect of orifice plates on phenol degradation at 0.3 MPa.

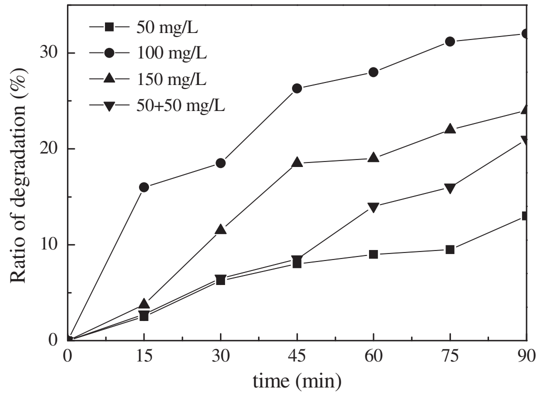


Fig. 5. Effect of concentrations of hydrogen peroxide on phenol degradation at 0.3 MPa.

After a treatment time of 45 min, the rest 50 mg/L H_2O_2 was added into the holding tank. The efficiency was low in the first 45 min but increased after adding H_2O_2. The result reveals that the lower initial H_2O_2 concentration, the worse the efficiency. It has been established that the extent of increase in the phenol removal percentage does not decrease with an increasing H_2O_2 concentration over the range investigated in the present work. An optimum hydrogen peroxide ratio is necessary. Fig. 6 shows the change of the H_2O_2 concentration and the phenol degradation ratio with respect to time. It can be seen that the concentration of H_2O_2 decreased nearly 80% after an hour. Correspondingly, the ratio of the phenol degradation goes unchanged evidently (remained 30 ~ 32%) after an hour. It accounts for that the concentration of H_2O_2 is crucial to the cavitation, which plays an important role in the occurrence of free radicals. The result indicates that the free radicals attack is the dominating reactive mechanism for degradating phenol.

3.4. Effect of dissolved gases

The dissolved gas is another key parameter which affects the intensity of hydrodynamic cavitation as well as the efficiency of phenol degradation. Fig. 7 shows the effect of different flow rate and varieties of dissolved gases on phenol degradation. The percentage of phenol degradation at low flow rate 0.05 L/min was less than that of high flow rate 0.27 L/min. This is because that the presence of dissolved gases increased the number of cavities, which contributed to the inception of cavitation. When adding nitrogen at 0.27 L/min, the degradation rate was higher than that without gases in the initial one hour, but after that, the rate is lower. It can be explained that too much gas has a negative effect on cavitation. Besides, when the flow rate of nitrogen is lower, the extent of degradation is worse, because the energy content of these cavities can be orders of magnitude lower, compared to the vaporous cavities [24]. In terms of the oxygen, the degradation rate at high flow rate was higher than that without gas, which was different from nitrogen. It showed the different reactive mechanism between oxygen and nitrogen. Nitrogen can only provide cavities, but oxygen can also take part in the free radical reaction with intermediates species produced by cavitation. This might explain why the yield of OH radical formation might be larger under O_2 than that under N_2. Serpone et al. [29] also reported that the presence of dissolved oxygen in aqueous solution plays a very important role on the generation of OH free radicals.

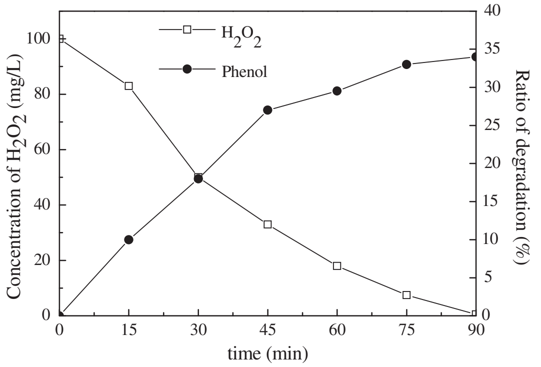


Fig. 6. Formation of hydrogen peroxide and degradation ration of phenol versus time at 0.3 MPa.

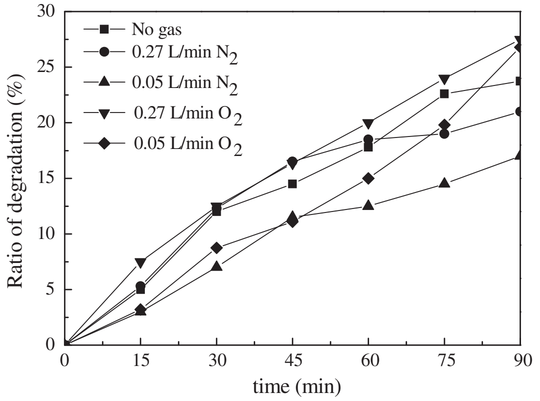


Fig. 7. Effect of dissolve gases on phenol degradation at 0.2 MPa.

3.5. Effect of catalysts

The extents of phenol degradation with the existence of different catalyst (CuO, Fe, and TiO_2) are shown in Fig. 8. It described that the order of degradation rate for 60 min treatment time was as follows: Fe > CuO > TiO_2 > particles. About 44 and 36.5% of phenol was removed in the presence of Fe and

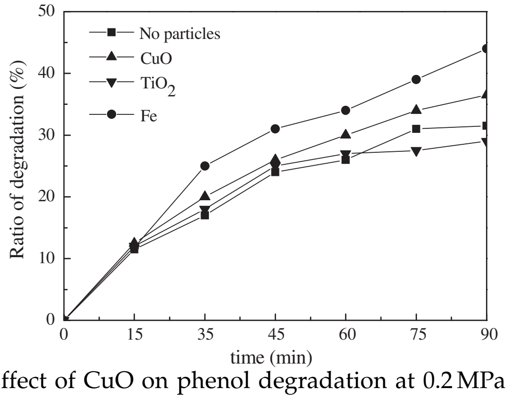
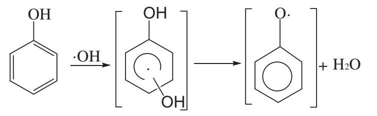


Fig. 8. Effect of CuO on phenol degradation at 0.2 MPa.

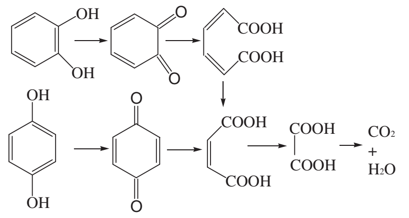
CuO after 90 min, respectively, compared to 28.8% without catalyst and 27.2% in the presence of TiO_2. It is founded that the addition of metal catalyst (Fe or CuO) has a positive impact on the degradation of phenol in water. This can be explained that the metal catalyst (Fe or CuO) exhibited an excellent catalytic activity, and it could generate more radicals to degrade phenol. Fe would form Fe^{2+} in aqueous solution and generate OH radicals by Fenton reaction with H_2O_2. Wu et al. [30] examined the effect of Fe^{2+} (as a catalyst) on the photosonochemical degradation of phenol and founded the presence of Fe^{2+} enhanced TOC removal of phenol solutions. Besides, it was previously reported that CuO shows the high activities in the oxidation and has the ability to activate H_2O_2 [31]. However, TiO_2 belongs to photocatalyst and is promoting to the generation of OH radicals in the case of UV. While this experiment was not under the UV condition, TiO_2 was used as a cavitation core and did not play a larger role in degradation of phenol. The difference of overall complicated degradation process was not exactly understood yet and further research is needed.

3.6. The primary intermediates and mechanism of phenol degradation

During the experiments, the reactive solution went pale red after 10 min. Then, the color became deeper. It can infer that benzoquinone was generated. In order to gain a deeper insight into the mechanism of phenol degradation by H_2O_2 and hydrodynamic cavitation, HPLC was used to analyze the primary intermediates of the degradation process. Hydroquinone, benzoquinone, catechol, and resorcin were detected (Fig. 9). It can be seen that the concentration of all the primary intermediates firstly increased and then decreased with run-time, and the concentration of resorcin was the lowest. It can be also observed from Fig. 9 that the TOC was removed slower than phenol and 41.8% of TOC was removed within 90 min. The formation of the primary intermediates and the low efficiency of TOC removal described above demonstrated that the main pathway of phenol degradation was through OH radical attack. The reaction of phenol with OH radicals leaded to the formation of dihydroxyl cyclohexadienyl radicals (Eq. (1)). These compounds were further degraded into biodegradable products such as carboxylic acids (Eq. (2)) [32]. Furthermore, the reaction products for all the catalysts were CO_2 (mainly), diphenols, quinones, and organic acids as could be observed in the equations, which showed a simplified reaction pathway for the phenol oxidation reaction. In addition, it can found that the primary intermediates in this study were consistent with our former report [30]. This result also revealed that OH radicals oxidation is one of the main degradation mechanisms. However, the overall complicated degradation process is not yet exactly understood and further special research is in progress.



(1)



(2)

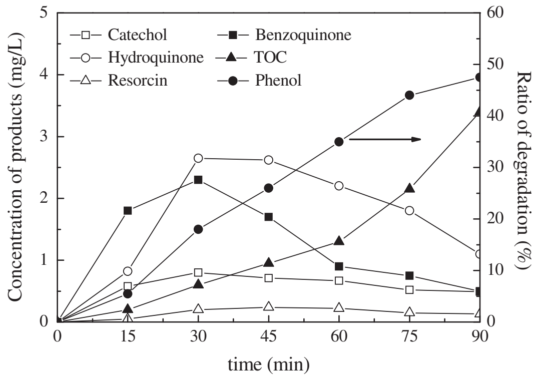


Fig. 9. Concentrations of intermediates, TOC, and phenol removal with respect to time at 0.35 MPa.

4. Conclusion

Based on the experiments reported here, it can be concluded:

(1) The operating and geometer parameters of hydrodynamic cavitation reactor have an important effect on the degradation of phenol. The higher P1 is in favor of the treatment. Different arrangements of orifice plates would achieve different intensities of cavitation. Thus, hydrodynamic cavitation setup can offer flexible cavitational conditions to adjust the needs of reactions.

(2) The degradation of phenol has an optimum initial H_2O_2 concentration. For 100 mg/L H_2O_2, the degradation was more efficient. Too high or too low initial concentration will decrease the efficiency of phenol degradation.

(3) Different kinds of dissolved gases have different effect on cavitation. Oxygen not only can take

part in reaction of free radicals, but also can increase the number of cavities, while the nitrogen can just increase the number of cavities. The efficiency of oxygen is higher than that of nitrogen at the same flow rate. And by adding Fe or CuO particles, the degradation rate would also be enhanced.

(4) The free radicals attack may play a considerable role in the degradation of phenol. Further work is in progress for better understanding of the degradation mechanisms.

Acknowledgments

This study was financially supported by the National Nature Science Foundation of China (No. 51078148 and No. 41173103).

References

[1] Y. Segura, F. Martínez, J.A. Melero, R. Molina, R. Chand, D.H. Bremner, Enhancement of the advanced Fenton process (Fe-0/H_2O_2) by ultrasound for the mineralization of phenol, Appl. Catal. B-Environ. 113 (2012) 100–106.

[2] D.H. Han, S.Y. Cha, H.Y. Yang, Improvement of oxidative decomposition of aqueous phenol by microwave irradiation in UV/H_2O_2 process and kinetic study, Water Res. 38 (2012) 2782–2790.

[3] C.H. Wu, H.Y. Ng, Degradation of CI reactive red 2 (RR2) using ozone-based systems: Comparisons of decolorization efficiency and power consumption, J. Hazard. Mater. 152 (2008) 120–127.

[4] J. Arana, J.M. Dona-Rodriguez, D. Portillo-Carrizo, C. Fernandez-Rodriguez, J. Perez-Pena, O.G. Diaz, J.A. Navío, M. Macías, Photocatalytic degradation of phenolic compounds with new TiO_2 catalysts, Appl. Catal. B-Environ. 100 (2010) 346–354.

[5] M. Kobya, E. Demirbas, O. Sahin, Effect of operational parameters on the removal of phenol from aqueous solutions by electrocoagulation using Fe and Al electrodes, Desalin. Water Treat. 46 (2012) 366–374.

[6] K.M. Parida, A.C. Pradhan, Fe/meso-Al_2O_3: An efficient photo-fenton catalyst for the adsorptive degradation of phenol, Ind. Eng. Chem. Res. 49 (2010) 8310–8318.

[7] A.G. Chakinala, D.H. Bremner, P.R. Gogate, K.C. Namkung, A.E. Burgess, Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing, Appl. Catal. B-Environ. 78 (2008) 1–2.

[8] Y.Y. Lu, Y. Liu, B.W. Xia, W.Q. Zuo, Phenol oxidation by combined cavitation water jet and hydrogen peroxide, Chin. J. Chem. Eng. 20 (2012) 760–767.

[9] G.V. Ambulgekar, S.D. Samant, A.B. Pandit, Oxidation of alkylarenes to the corresponding acids using aqueous potassium permanganate by hydrodynamic cavitation, Ultrason. Sonochem. 11 (2004) 191–196.

[10] K.P. Mishra, P.R. Gogate, Intensification of degradation of Rhodamine B using hydrodynamic cavitation in the presence of additives, Sep. Purif. Technol. 75 (2010) 385–391.

[11] P.R. Gogate, Treatment of wastewater streams containing phenolic compounds using hybrid techniques based on cavitation: A review of the current status and the way forward, Ultrason. Sonochem. 15 (2008) 1–15.

[12] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced Fenton processing, Chem. Eng. J. 152 (2009) 498–502.

[13] S.I. Nikitenko, L. Venault, R. Pflieger, T. Chave, I. Bisel, P. Moisy, Potential applications of sonochemistry in spent nuclear fuel reprocessing: A short review, Ultrason. Sonochem. 17 (2010) 1033–1040.

[14] Y. Jiang, C. Petrier, T.D. Waite, Kinetics and mechanisms of ultrasonic degradation of volatile chlorinated aromatics in aqueous solutions, Ultrason. Sonochem. 9 (2002) 317–323.

[15] K. Okitsu, K. Iwasaki, Y. Yobiko, H. Bandow, R. Nishimura, Y. Maeda, 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, Ultrason. Sonochem. 12 (2005) 255–262.

[16] N. Golash, P.R. Gogate, Degradation of dichlorvos containing wastewaters using sonochemical reactors, Ultrason. Sonochem. 19 (2012) 1051–1060.

[17] T.J. Mason, Large scale sonochemical processing: Aspiration and actuality, Ultrason. Sonochem. 7 (2000) 145–149.

[18] V.S. Moholkar, A.B. Pandit, Modeling of hydrodynamic cavitation reactors: A unified approach, Chem. Eng. J. 56 (2001) 1411–1418.

[19] A. Sharma, P.R. Gogate, A. Mahulkar, A.B. Pandit, Modeling of hydrodynamic cavitation reactors based on orifice plates considering hydrodynamics and chemical reactions occurring in bubble, Chem. Eng. J. 143 (2008) 201–209.

[20] M. Sivakumar, A.B. Pandit, Wastewater treatment: A novel energy efficient hydrodynamic cavitational technique, Ultrason. Sonochem. 9 (2002) 123–131.

[21] M. Capocelli, M. Prisciandaro, A. Lancia, D. Musmarra, Modeling of cavitation as an advanced wastewater treatment, Desalin. Water Treat. 51 (2013) 1609–1614.

[22] N.P. Vichare, P.R. Gogate, A.B. Pnadit, Optimization of hydrodynamic cavitation using a model reaction, Chem. Eng. Technol. 23 (2000) 683–690.

[23] P. Braeutigam, M. Franke, Z.L. Wu, B. Ondruschka, Role of different parameters in the optimization of hydrodynamic cavitation, Chem. Eng. Technol. 33 (2010) 932–940.

[24] C. Yang, X.T. Su, F. Xiao, J.K. Jian, J.D. Wang, Gas sensing properties of CuO nanorods synthesized by a microwave-assisted hydrothermal method, Sens. Actuators B-Chem. 158 (2011) 299–303.

[25] Y.P. Sun, X.Q. Li, W.X. Zhang, H.P. Wang, A method for the preparation of stable dispersion of zero-valent iron nanoparticles, Colloid Surf. A. 308 (2007) 1–3.

[26] P.R. Gogate, A.B. Pandit, Hydrodynamic cavitation reactors: A state of the art review, Rev. Chem. Eng. 17 (2001) 1–85.

[27] A.G. Chakinala, D.H. Bremner, P.R. Gogate, K.C. Namkung, A.E. Burgess, Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced Fenton processing, Appl. Catal. B-Environ. 78 (2008) 11–18.

[28] P.R. Gogate, A.B. Pandit, Sonophotocatalytic reactors for wastewater treatment: A critical review, AIChE J. 50 (2004) 1051–1079.

[29] N.R. Serpone, T.H. Hidaka, E.J. Pelizzetti, Ultrasonic induced dehalogenation and oxidation of 2-,3-,4-chlorophenol in air-equilibrated and aqueous media. Similarities with irradiated semiconductor particulates, J. Phys. Chem. 98 (1994) 2634–2640.

[30] C.D. Wu, X.H. Liu, D.B. Wei, J.C. Fan, L.S. Wang, Photosonochemical degradation of phenol in water, Water Res. 35 (2001) 3927–3933.

[31] F. Ji, C.L. Li, L. Deng, Performance of CuO/Oxone system: Heterogeneous catalytic oxidation of phenol at ambient conditions, Chem. Eng. J. 178 (2011) 239–243.

[32] N.R. Serpone, P. Terzan, P. Colarusso, C. Minerco, E. Pelizzetti, H. Hidaka, Sonochemical oxidation of phenol and three of its intermediate products in aqueous media: Catechol, hydroquinone, and benzoquinone, kinetic and mechanistic aspects, Res. Chem. Intermed. 18 (1992) 183.