Korean J. Chem. Eng., **25**(1), 112-117 (2008)

Degradation of 2,4-dichlorophenol in aqueous solution by sono-Fenton method

Praveena Juliya Dorathi. Ranjit*, Kandasany Palanivelu*, and Chang-Soo Lee**,***,†**

*Centre for Environmental Studies, Anna University, Chennai-600 025, India
**BK21 E2M Program, ***Department of Chemical Engineering,
Chungnam National University, Yuseong-gu, Daejeon 305-764, Korea
(*Received 20 February 2007 • accepted 23 May 2007*)

Abstract−This study presents the results of the Sono-Fenton process for the degradation of 2,4-dichlorophenol (DCP). The influential parameters such as H_2O_2, Fe^{2+} and pH for the Sono-Fenton process were investigated. Sono-Fenton method was found to be the best one for degradation efficiency of DCP when compared with that of the Fenton process. The optimum concentrations for the degradation of DCP using conventional Fenton's method were found to be 20 mg/L of Fe^{2+} and 580 mg/L of H_2O_2 at pH 2.5. In the case of Sono-Fenton, the optimal concentrations were found to be 10 mg/L of Fe^{2+} and 400 mg/L of H_2O_2 at pH 2.5. Sono-Fenton method resulted in the reduction of required Fe^{2+} concentration (50%) and H_2O_2 concentration (31%). In addition, this method could be applicable even at pH 5.0 and a degradation efficiency of DCP was 77.6%. Kinetic studies for the degradation of DCP proved that the degradation of DCP tends to follow pseudo first order reaction and the rate constant was found to be 7×10^{-4} min^{-1}.

Key words: 2,4-Dichlorophenol, Degradation, Sono-Fenton Method

INTRODUCTION

Chlorophenols are toxic chemicals which are used in many industrial applications such as petrochemicals, pesticide, dye and dye intermediates, and paint [1]. Especially, 2,4-dichlorophenol (DCP) is an important chemical precursor for manufacture of a widely used herbicide, 2,4-dichlorophenoxy acetic acid (2,4-D) [2]. However, DCP may cause some pathological symptoms and changes to human endocrine systems. Their mode of exposure is through the skin and gastrointestinal tract.

Several treatment methods have been investigated for the degradation of chlorophenols including biological methods and physical-chemical methods [3,4] but they are found to be ineffective for the degradation of DCP. Simple physical methods including adsorption [5] and liquid membrane [6] are not effective in reducing the toxicity of chlorophenols since it merely transfers the chemical from one form to the other. On the other hand, chemical methods [7] such as chlorination, permanganate oxidation etc. lead to formation of toxic intermediate due to incomplete degradation. Hence, research for finding a more efficient way of destroying these chlorophenols has become necessary. Advanced oxidation processes (AOPs) are advanced wastewater treatment processes, which are used to oxidize organic compounds that are resistant to the conventional methods of treatment. This method involves generation of free hydroxyl radical, which acts as a strong oxidizing agent. Many studies have been done on the degradation of chlorophenols by different types of AOPs, namely, electrochemical oxidation [8], ozonation [9,10], photo-Fenton [11] and sonochemical method [12]. Application of ultrasound in the frequency range of 30-1,000 KHz leads to the generation of hydroxyl radicals from water [13]. Organic compounds could be degraded by sonolytic process because the generation of hydroxyl radicals, acoustic cavitation bubbles, and ultrasonic power induces splitting of water molecules [14,15]. Therefore, a sonolytic process combined with other techniques can be a promising way for the degradation of DCP [16]. The classical Fenton process has been used for the treatment of wide range of aromatics such as chlorobenzene [17], phenols [18], aromatic amines [19] and chlorophenol [20]. Environmentally benign and easily handlable, Fenton's reagents as well as lower cost compared to other techniques are the main advantages of this method. Combination of Fenton with sonolysis, Sono-Fenton process, can be applied to increase the mineralization efficiency of the organic compounds.

Thus, this study was to investigate the beneficial effect of ultrasonic waves on the degradation of 2,4-dichlorophenol (DCP) by Fenton's method (Sono-Fenton method). The influential factors for the degradation of DCP in Sono-Fenton method were evaluated.

MATERIALS AND METHODS

1. Chemicals

2,4-Dichlorophenol, hydrogen peroxide, and ferrous sulphate heptahydrate were of analytical grade. All the solutions were prepared with high purity water. The initial pH of the solution was adjusted with analytical grade sulphuric acid.

2. Experimental Setup for Fenton Processes

2-1. Fenton Process

Experiments were conducted in batch mode. The reactor was a 600 mL beaker with a reactant volume of 500 mL. Concentration of simulated wastewater (200 mg/L of DCP) was used. The experiments were carried out at room conditions. The addition of hydrogen peroxide to the reaction mixture marked the beginning of the reaction. The solution was well mixed with a magnetic stirrer. Samples were periodically collected at specified intervals and the reaction was stopped immediately by adding 0.1 M sodium hydroxide. Analytical samples were stored in plastic bottles at 4 °C.

†To whom correspondence should be addressed.
E-mail: rhadum@cnu.ac.kr

2-2. Sono-Fenton Process

Experimental condition was identical to the Fenton process. The reactor was immersed into the ultrasonic bath (Sonorex; Type-RK 52, Germany) where the ultrasonic wave frequency was 35 kHz.

3. Analytical Methods

The DCP concentration was determined spectrophotometrically by 4-amino antipyrine method [21] (Method No. 5530D, APHA 1998). The absorbance was measured at 500 nm in a Spectronic 20 Genesys spectrophotometer. The concentration of hydrogen peroxide was quantitatively assessed by iodometric titration method [22]. COD for the samples were measured to determine the degradation efficiency. An open reflux dichromate titrimetric method as standard procedure [21] (Method No. 5220B, APHA 1998) was employed for COD measurements. Mineralization efficiency was calculated by using the TOC values of the sample. The TOC analyzer used was micro C model 1997 (Analytica Jena, Germany) with auto sampler liquid injector ALS-C-104. Samples were pretreated by adjusting the pH to 2.0 with 10% H_3PO_4 solution to remove any inorganic carbon formed during oxidation reaction and were analyzed immediately without storage.

4. Degradation Efficiency (DE) and Mineralization Efficiency (ME)

The measured results of the degradation and mineralization efficiency in the process were calculated as follows

$$DE = \frac{(A-B)}{A} \times 100 \quad (1)$$

A=Initial concentration of DCP/ Initial COD in mg/L.
B=Final concentration of DCP/ Final COD in mg/L.

$$ME\,(\%) = \frac{(\text{Initial TOC value in mg/L} - \text{Final TOC value in mg/L})}{\text{Initial TOC value in mg/L}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

The addition of Fenton's reagent mixture generates hydroxyl radical, which degrades the organic compound

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + HO + Fe^{3+} \quad (3)$$

Eq. (3) indicates that reaction with one mole of H_2O_2 and Fe^{2+} generates 1 mole of hydroxyl radical theoretically as per Fenton. The generation of hydroxyl radical depends not only on the concentration of H_2O_2, but also concentration of Fe^{2+} as well as pH. When this reaction is coupled with an ultrasonic wave, it is called Sono-Fenton process. The degradation studies on DCP were investigated by Sono-Fenton method. The efficiency of thismethod was compared with the degradation efficiency of Fenton. Detailed studies on the Sono-Fenton method were carried out for the optimization of ferrous and hydrogen peroxide concentrations in Fenton's reagent and the pH of the process.

1. Comparison of Sono-Fenton and Fenton on the Degradation of DCP

The influence of an ultrasonic wave on Fenton's process (Sono-Fenton) for the degradation of DCP was compared with the degradation efficiency of the Fenton method with respect to the decrease of the DCP concentration. Both of the experiments were carried out simultaneously as described earlier. The optimum conditions for the comparative study were chosen based on the earlier studies conducted on the degradation of DCP using Fenton's method [23]. The optimized conditions were H_2O_2 (580 mg/L), Fe^{2+} (20 mg/L), and pH 2.5 when DCP (200 mg/L) was treated in 2 h. While ferrous ion and hydrogen peroxide were added to the reaction mixture containing DCP, the color of the solution rapidly changed from colorless to turbid yellow. Within half an hour of the reaction time, the color of the solution changed to yellow and then a clear solution was obtained.

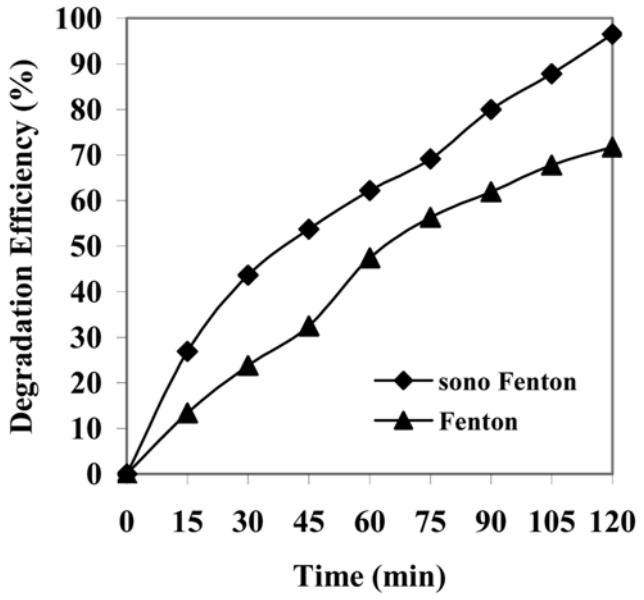

Fig. 1. Comparison of degradation efficiencies of DCP by Sono-Fenton and Fenton (Condition: DCP=200 mg/L, Fe^{2+}=20 mg/L, H_2O_2=580 mg/L, pH=2.5).

Fig. 1 shows the degradation efficiencies of both the processes. Sono-Fenton was found to be efficient in comparison with Fenton. This sonolytic degradation enhancement may be attributed to the following reactions.

a) Direct pyrolytic degradation of solute molecules occurs due to the enormous changes in both temperature and pressure during the collapse of the cavitation bubble. The potential energy of the liquid surrounding the bubble is transformed both into the kinetic energy of the moving liquid and into the internal energy of the bubble contents. At this time the internal energy as well as local temperature and pressure will be very high and likely to increase the reaction rates. The fragmentation of the solute results in generation of reactive free radicals, which further causes the degradation of other solute molecules [24].

b) Pyrolysis of water vapor yields hydroxyl and hydrogen radicals (Eq. (4)). The hydrogen free radical reacts with oxygen molecule to form hydroperoxyl free radical (Eq. (5))[13].

$$H_2O \xrightarrow{)))))} {}^{\bullet}OH + H^{\bullet} \quad (4)$$

$$H_2O \longrightarrow H^{\bullet} + O_2 \quad (5)$$

The hydroperoxyl and hydroxyl radical combine to form hydrogen

peroxide [17]. It is shown in Eq. (6) and (7).

$$2^{\cdot}OH \longrightarrow H_2O_2 \quad (6)$$

$$HO_2^{\cdot} \longrightarrow H_2O_2 \quad (7)$$

Hence, more hydrogen peroxide is generated in the system internally, which will ultimately increase the efficiency of Fenton's process and reduce the amount of hydrogen peroxide needed from outside the system.

a) The oxygen formed in Equation 8 leads to the formation of hydroxyl radical in the presence of ultrasonic waves [25].

$$O_2 \xrightarrow{)))))} 2O \quad (8)$$

$$O + H_2O \longrightarrow 2^{\cdot}OH \quad (9)$$

b) Super critical water oxidation: During sonolysis, it was proposed that super critical water is present in a small thin shell around the bubble. According to the previous result, this mode of destruction is expected to be secondary in importance because the fraction of water in the super critical water state is estimated to be on the order of 0.0015 parts out of 100 parts of water [26].

The final degradation efficiency of DCP showed 91% and 71% by Sono-Fenton and Fenton methods, respectively. The enhancement of the degradation efficiency resulted from sonolysis, which is well matched with the result of the Sonoelectrochemical Fenton method for the degradation of 2,4-D and DCP [27].

2. The Effect of Operating Parameters on the Degradation of DCP by Sono-Fenton Method

Hence, further experiments were conducted to find the effects of operating parameters such as H_2O_2, Fe^{2+}, and pH of the solution.

2-1. Effect of Hydrogen Peroxide Concentration

The effect of hydrogen peroxide was studied with a focus on the reduction of its required concentration in the Sono-Fenton method. The internal production of hydrogen peroxide (Eqs. (4) and (9)) makes it possible to operate even at the reduced concentration of initial hydrogen peroxide. The same experiments were also performed for Fenton's method as a control.

The influence of peroxide concentration was also examined by the decreasing concentration of H_2O_2 from 580 mg/L to 300 mg/L. Three sets of experiments were performed for Fenton and Sono-Fenton. In each set, the peroxide concentration was varied. The concentration of Fe^{2+} was maintained constant within the set but was different in all the three sets (10, 15, 20 mg/L).

The degradation and mineralization efficiencies at different peroxide concentrations are presented in Table 1, 2, and 3. As expected, the degradation efficiency decreases as the peroxide concentration decreases. In the first set of experiments, the Fe^{2+} concentration was maintained at 20 mg/L and initial H_2O_2 concentration was varied. For the Sono-Fenton method, the degradation efficiencies for H_2O_2 concentrations at 580 and 300 mg/L were found to be 88.7% and 82.8%, respectively. The decrease in the degradation efficiency was just 5.9%.

In the second set of experiments, the Fe^{2+} concentration was maintained at 15 mg/L and the degradation efficiencies were found to be 86.7 and 80.0% for 580 and 300 mg/L of H_2O_2, respectively, with the difference in the efficiency being 6.7%. 10 mg/L of Fe^{2+} was kept constant for the third set. The corresponding degradation

Table 1. Effect of hydrogen peroxide concentration on the degradation and mineralization efficiency of DCP at 20 mg/L of Fe^{2+} by Sono-Fenton (S.F) and Fenton (F) methods (Conditions: DCP=200 mg/L and pH=2.5)

	Initial hydrogen peroxide concentration (mg/L)							
	580		500		400		300	
	S.F	F	S.F	F	S.F	F	S.F	F
Degradation efficiency (%)	88.7	70.0	86.2	69.0	83.3	53.3	82.8	48.3
Mineralization efficiency (%)	85.6	39.1	83.2	36.1	79.6	27.4	75.2	25.6

Table 2. Effect of hydrogen peroxide concentration on the degradation and mineralization efficiency of DCP at 15 mg/L of Fe^{2+} by Sono-Fenton (S.F) and Fenton (F) methods (Conditions: DCP=200 mg/L and pH=2.5)

	Initial Hydrogen peroxide concentration (mg/L)							
	580		500		400		300	
	S.F	F	S.F	F	S.F	F	S.F	F
Degradation efficiency (%)	86.7	68.5	82.7	65.5	81.0	53.3	80.0	45.7
Mineralization efficiency (%)	84.6	35.4	80.2	31.5	73.5	24.8	68.7	19.3

Table 3. Effect of hydrogen peroxide concentration on the degradation and mineralization efficiency of DCP at 10 mg/L of Fe^{2+} by Sono-Fenton (S.F) and Fenton (F) methods (Conditions: DCP=200 mg/L and pH=2.5)

	Initial Hydrogen peroxide concentration (mg/L)							
	580		500		400		300	
	S.F	F	S.F	F	S.F	F	S.F	F
Degradation efficiency (%)	83.1	64.3	81.7	61.5	79.7	50.3	74.1	35.9
Mineralization efficiency (%)	77.5	30.9	74.3	29.1	68.7	22.5	54.5	15.3

efficiencies for 580 mg/L and 300 mg/L of H_2O_2 were found to be 83.1 and 74.1% where the difference in the efficiency was 9.0%. The decrease in efficiency within each set can be attributed to the decrease in the H_2O_2 concentration, but the difference between the initial and final degradation efficiencies is due to the reduction in Fe^{2+} concentration.

The difference between the degradation efficiencies of Sono-Fenton and Fenton increased within each set as the concentration of H_2O_2 decreased from 580 to 300 mg/L. In the first set, the difference between Sono-Fenton and Fenton was 18.7% at 580 mg/L of H_2O_2 and was 34.5% at 300 mg/L of H_2O_2. Similarly, in the second set the difference between Sono-Fenton and Fenton was found to be 18.2 and 35.3%. In the last set, the difference was 18.8 and 38.2%, respectively. The decrease of efficiency in Sono-Fenton was negligible when compared with Fenton. It should be noted that the reduction of H_2O_2 concentration is given more importance than that of Fe^{2+}. In general, degradation of H_2O_2 produces harmless products (H_2O and O_2). Thus, although a higher concentration of H_2O_2 is used, it cannot cause serious problem in the effluent, which will be discharged after treatment. However, the concentration of Fe^{2+} is critically important in the treated effluent. It is necessary to reduce the required concentration of Fe^{2+} while maintaining the degradation efficiency as 80%.

High degradation efficiency of Sono-Fenton when compared with Fenton may result from the continuous generation of H_2O_2 within the system apart from the H_2O_2 amount added from outside after the reduction of hydrogen peroxide concentration up to 31%. In the case of Fenton, the only source of hydrogen peroxide was added externally. Hence, the degradation is dependent on the concentration of H_2O_2. The mineralization efficiency was almost the same as that of degradation efficiency for DCP in the case of Sono-Fenton, where there was large difference between the degradation and mineralization efficiency in the Fenton method because the mineralization of the intermediate products formed immediately after the degradation of DCP.

2-2. Effect of Ferrous Ion Concentration

Next, we carried out investigations to find the effect of ferrous ion at lower concentration. The catalytic role of iron as well as the sonolytic generation of ferrous ion suggests the feasibility of Sono-Fenton at reduced ferrous concentration. As mentioned in the previous section, the experiments were conducted in three sets while the Fe^{2+} concentration was also reduced from 20 mg/L to 10 mg/L. The degradation efficiency of DCP (200 mg/L and pH 2.5) was calculated. Tables 1, 2 and 3 show the degradation efficiencies of DCP for various concentrations of hydrogen peroxide and ferrous ion.

As indicated before, an increase in the difference between initial and final degradation efficiencies (5.9 to 9%) at various H_2O_2 concentrations was observed in Sono-Fenton. This due to the decrease in the ferrous ion concentration from first set to third set. As expected, the Sono-Fenton showed a promising result with effective degradation of DCP even at lower concentration of hydrogen peroxide and ferrous ion. The optimal concentration of Fenton's reagent for the degradation of DCP by Sono-Fenton was found to be 10 mg/L of Fe^{2+} and 400 mg/L of H_2O_2.

2-3. Effect of pH

Based on the previously examined results (H_2O_2=400 mg/L, Fe^{2+}= 10 mg/L), investigation of the efficiency of Sono-Fenton at neutral pH was conducted. It is well known that Fenton's processes are efficient in the acidic range from pH 2 to 4 [20]. Since the degradation efficiency of Sono-Fenton is different from the Fenton process, we investigated the possibility of DCP degradation at various ranges of pH using the Sono-Fenton method.

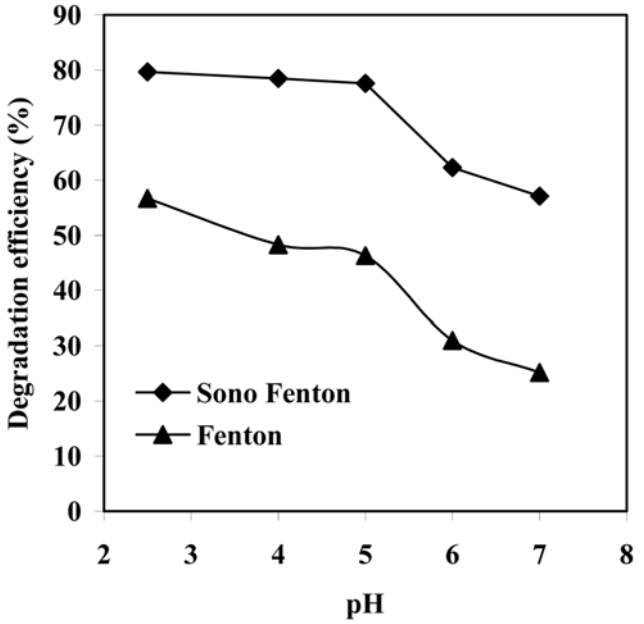

Fig. 2. Effect of pH on the degradation efficiency with respect to decrease in COD concentration by Sono-Fenton (S.F) and Fenton (F) methods (Conditions: DCP=200 mg/L, Fe^{2+}=10 mg/L and H_2O_2=400 mg/L).

Fig. 2 shows that Sono-Fenton was efficient from pH 2.5 to pH 5.0 while degradation efficiency was maintained at 77.6%. The larger difference in the degradation efficiency between pH 2.5 and 7 was found to be 22.6% in Sono-Fenton, whereas it was 31.5% in the Fenton method. As the pH was increased, Sono-Fenton was more efficient than the Fenton. The high efficiency resulted from the continuous production of hydroxyl radical with respect to the change of pH, which effectively degrades DCP in system. Therefore, Sono-Fenton could be applicable even at slightly acidic pH 5, which might alleviate the problem caused by the acidic effluent from the treatment plants during Fenton's method.

3. Kinetics of DCP Degradation by Sono-Fenton Method

In the Sono-Fenton method, the generated hydroxyl radicals play a predominant role in the degradation of DCP. The hydroxyl radical could attack DCP and degrade it as shown below:

$$C_6H_4OHCl_2(DCP) + {}^{\bullet}OH \longrightarrow 2Cl^- + \text{Oxidized product} \quad (10)$$

Thus, the rate of degradation of DCP can be expressed as follows:

$$\frac{d[DCP]}{dt} = -k[DCP]_0[\bullet OH] \quad (11)$$

The concentrations of Fe^{2+}, H_2O_2 and pH were maintained at 10 mg/L, 400 mg/L and 5.0, respectively. The hydroxyl radical specified in Eqs. (10) and (11) is the total concentration of the hydroxyl radicals formed from the the Sono-Fenton process. This hydroxyl radical is assumed to be present in excess for the reaction. Hence,

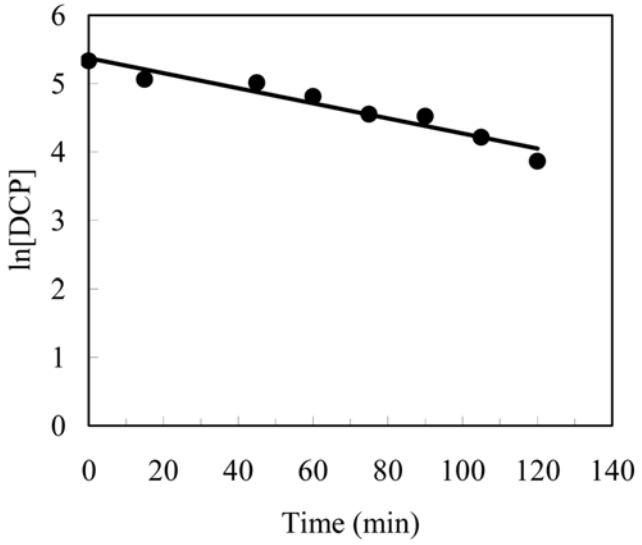

Fig. 3. Logarithmic relationship between concentration of DCP and reaction time (Conditions: DCP=200 mg/L, H_2O_2=400 mg/L, Fe^{2+}=10 mg/L, pH=5).

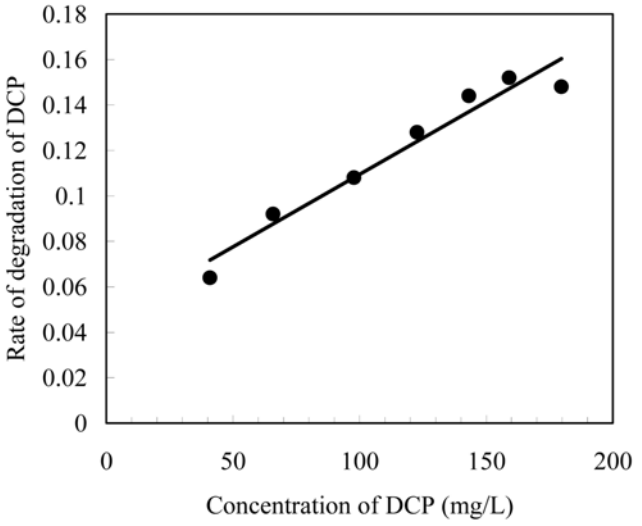

Fig. 4. Rate of degradation of DCP as a function of concentration of DCP (Conditions: DCP=200 mg/L, H_2O_2=400 mg/L, Fe^{2+} =10 mg/L, pH=5).

the kinetics can be assumed to follow pseudo-first order.

The obtained data was plotted in Fig. 3. The rate constant of the reaction could be determined by the slope of the plotted graph [28]. The reaction rate constant was calculated to be 7×10^{-4} min^{-1}. This result is similar to previous work on the degradation of p-CP using the Fenton method by Kwon et al. [20] and confirms that the degradation of DCP follows a pseudo-first order reaction.

CONCLUSIONS

The Sono-Fenton method showed promising results for the degradation of DCP when compared with Fenton. There was around 50% reduction in the Fe^{2+} concentration and 31% reduction in the H_2O_2 concentration. The Sono-Fenton process proved a broad range of working pH. The degradation kinetics of DCP follows pseudo first order reaction and the reaction rate constant was 7×10^{-4} min^{-1}. Based on the present investigations, Sono-Fenton can be applied to degrade DCP from wastewater and can reduce the amount of required hydrogen peroxide and ferrous ion. In addition, Sono-Fenton is a green process because it is well adopted at near neutral pH. Therefore, Sono-Fenton will be a viable alternative technology to the existing methods for treating DCP in wastewater. Scale-up studies with higher frequency of sonication may bring down the cost of this process for industrial applications. Further studies are required in these aspects.

ACKNOWLEDGMENT

This research was supported by the Program for the Training of Graduate Students in Regional Innovation (CN-06-1-016) which was conducted by the Ministry of Commerce Industry and Energy of the Korean Government.

REFERENCES

1. U. G. Ahlborg and J. M. Thunberg, *C R C Critical Reviews in Toxicology*, **7**, 1 (1980).
2. H. C. Lee, J. H. In, J. H. Kim, K. Y. Hwang and C. H. Lee, *Korean J. Chem. Eng.*, **22**, 882 (2005).
3. J. Balfanz and H. J. Rehm, *Appl. Microbio. Biotech.*, **35**, 662 (1991).
4. A. Farrell and B. Quilty, *Wat. Res.*, **36**, 2443 (2000).
5. E. Munaf, R. Zein, R. Kurniadi and I. Kuriadi, *Envi. Tech.*, **18**, 355 (1997).
6. S. H. Lin, C. L. Pan and H. G. Lee, *J. Haz. Mat.*, **65**, 289 (1990).
7. Metcalf and Eddy, *Wastewater engineering: Treatment disposal and reuse*, Mc Graw-hill, New York, USA (1995).
8. Y. O. Kim, H. U. Nam, Y. R. Park, J. H. Lee, T. J. Park and T. H. Lee, *Korean J. Chem. Eng.*, **21**, 801 (2004).
9. M. A. Boncz, H. Bruning and W. H. Rulkens, *Wat. Sci. and Tech.*, **47**, 17 (2003).
10. S. Contreras, M. Rodriguez, A. F. Momani, C. Sans and S. Esplugas, *Wat. Res.*, **37**, 3164 (2003).
11. V. Kavitha and K. Palanivelu., *J. Envi. Sci. and Health*, **A38**, 1215 (2003).
12. J. G. Lin, C. Chang and J. Wu, *Wat. Sci. and Tech.*, **33**, 75 (1996).
13. N. H. Ince, G. Tezcanti and R. K. Belen, *Appl. Catal.*, **29**, 167 (2001).
14. J. P. Lorimer, T. J. Manson and K. Fiddy, *Ultrasonics*, **29**, 338 (1991).
15. C. Petrier, A. Jeunet, J. L. Luche and G. Reveredy, *J. Am. Chem. Soc.*, **114**, 3148 (1992).
16. L. K. Weavers, F. H. Ling and M. R. Hoffmann, *Environ. Sci. Technol.*, **32**, 2727 (1998).
17. D. L. Sedalk and A. W. Anders, *Environ. Sci. Technol.*, **25**, 777 (1991).
18. H. R. Eisenhauer, *J. WPCF*, **36**, 1116 (1964).
19. I. Casero, S. Dolores, R. Soledad and P. B. Dolores, *Wat. Res.*, **31**, 1985 (1997).
20. B. G. Kwon, D. S. Lee, N. Kang and J. Yoon, *Wat. Res.*, **33**, 2110 (1999).
21. Standard methods for examination of water and wastewater, APHA-

AWWA-WEF, American Public Health Association, Washington, D.C. (1995).
22. G. H. Jeffery, J. Bassett, J. Mendham and R. C. Denny, Volgel's textbook of quantitative chemical analysis (1998).
23. V. Kavitha, *Degradation of phenolic compounds in wastewater by Fenton processes*, PhD. Thesis, Centre for Environmental Science, Anna University, Chennai (2003).
24. K. Makino, M. Magdl and P. Reise, *J. Phy. Chem*., **87**, 1369 (1983).
25. C. Minero, M. Lucchiari, D. Vione and V. Maurino, *Envi. Sci. Tech.*, **39**, 8936 (2005).
26. M. R. Hoffmann, I. Hua and R. Hochemer, *Ultrasonics Sonochemistry*, **2**, 163 (1996).
27. Y. Yasman, V. Bultov, V. V. Gridin, S. Agur, N. Galil, R. Armon and I. Schechter, *Ultrasonics Sonochemistry*, **11**, 365 (2004).
28. B. R. Puri, L. R. Sharma and S. M. Pathania, *Principles of physical chemistry*, Vishal publishing and co., Jalandhar (2002).