Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

Vol. 9	No. 2	pp. 365-370	2010

Original Research Paper

Photo-Fenton Treatment of Antibiotic Wastewater

Emad S. Elmolla and Malay Chaudhuri
Department of Civil Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskander, 31750 Tronoh, Perak, Malaysia

Nat. Env. Poll. Tech.
ISSN: 0972-6268
www.neptjournal.com

Key Words:
Antibiotic wastewater
Amoxicillin
Biodegradability
Cloxacillin
Photo-Fenton treatment

ABSTRACT

The study examined photo-Fenton treatment of an antibiotic wastewater containing amoxicillin and cloxacillin, and evaluated the effect of operating conditions (H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio) on biodegradability (BOD_5/COD ratio) improvement and mineralization. The optimum operating conditions for treatment of the antibiotic wastewater was observed to be H_2O_2/COD molar ratio 2.5 and H_2O_2/Fe^{2+} molar ratio 20 (COD/H_2O_2/Fe^{2+} molar ratio 1/2.5/0.125) at pH 3 and reaction time 30 min. Under optimum operating conditions, complete degradation of amoxicillin and cloxacillin occurred in one minute, biodegradability improved from 0.09 to 0.50 ± 0.01 in 30 min, and COD and DOC removal were 67 ± 1% and 51 ± 2%, respectively in 30 min. The study indicated that the photo-Fenton process can be used as pretreatment for antibiotic degradation and biodegradability improvement of antibiotic wastewater containing amoxicillin and cloxacillin.

INTRODUCTION

Pharmaceuticals can reach the aquatic environment though various sources, such as pharmaceutical wastewater, hospital effluent and excretion from humans and livestock (Ikehata et al. 2006, Nikolaou et al. 2007, Yang et al. 2008). Pharmaceuticals including antibiotics and other drugs have been observed in surface water (Kolpin et al. 2002, Anderson et al. 2004, Rabiet et al. 2006), groundwater (Rabiet et al. 2006), sewage effluents (Carballa et al. 2004, Nikolaou et al. 2007) and even in drinking water (Stackelberg et al. 2004).

Among all the pharmaceuticals that cause contamination of the environment, antibiotics occupy an important place due to their high consumption rates in both veterinary and human medicine. Problem that may be created by the presence of antibiotics at low concentration in the environment is the development of antibiotic resistant bacteria (Walter & Vennes 1985). In recent years, the incidence of antibiotic resistant bacteria has increased and many people believe the increase is due to the use of antibiotics (Alexy et al. 2004). Furthermore, the presence of antibiotics in wastewaters has increased in recent years and their abatement will be a challenge in the near future.

Biological treatment is limited to wastewaters which contain biodegradable substances and which are not toxic to the biological culture. Antibiotic wastewater has high chemical oxygen demand (COD) and low biochemical oxygen demand (BOD), and hence biological treatment is unsuitable for the wastewater. Advanced oxidation processes (AOPs) such as Fenton, photo-Fenton and Fenton-like processes constitute a promising technology for the treatment of wastewaters containing non-easily removable (non-biodegradable) organic compounds (Pera-Titus et al. 2004).

Oxidation with Fenton's reagent is based on hydroxyl radicals ($OH^{\bullet}$) produced by catalytic decomposition of hydrogen peroxide in reaction with ferrous ion. In the photo-Fenton process,

additional reactions occur in the presence of light that produce hydroxyl radicals or increase the production rate of hydroxyl radicals (Pignatello et al. 1999), thus increasing the efficiency of the process. There have been studies on treatment of amoxicillin wastewater and penicillin formulation effluent by AOPs (Arslan-Alaton & Dogruel 2004, Arslan-Alaton et al. 2004, Zhang et al. 2006). However, no study on treatment of antibiotic wastewater containing amoxicillin and cloxacillin by the photo-Fenton process has been reported.

The present study examined photo-Fenton treatment of an antibiotic wastewater containing amoxicillin and cloxacillin, and evaluated the effect of operating conditions (H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio) on biodegradability (BOD_5/COD ratio) improvement and mineralization. In addition, degradation of antibiotics under optimum operating conditions was also evaluated.

MATERIALS AND METHODS

Antibiotic wastewater: Antibiotic wastewater was obtained from a local pharmaceutical industry. The antibiotic wastewater characteristics are summarized in Table 1.

Chemicals and antibiotics: Hydrogen peroxide (30%, w/w) and ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) were obtained from R & M Marketing, Essex, U.K. Analytical grade of amoxicillin (AMX) was obtained from Sigma and cloxacillin (CLX) from Fluka to construct HPLC analytical curves for the determination and quantification of the antibiotics. Sodium hydroxide and sulphuric acid were obtained from HACH Company, USA. Potassium dihydrogen phosphate (KH_2PO_4) was procured from Fluka, and acentonitrile (HPLC grade) from Sigma.

Analytical methods: Antibiotic concentration was determined by HPLC (Agilent 1100 Series) equipped with micro-vacuum degasser (Agilent 1100 Series), quaternary pumps, diode array and multiple wavelength detector (DAD) (Agilent 1100 Series) at wavelength 204 nm. The data were recorded by a chemistation software. The detection column was ZORBAX SB-C18 (4.6 mm × 150 mm, 5 μm) and the column temperature was set at 60°C. Mobile phase was made up of 55% buffer solution (0.025 M KH_2PO_4 in ultra purified water) and 45% acentonitrile, and flow rate 0.5 mL/min. Chemical oxygen demand (COD) was determined according to the Standard Methods (APHA 2005). If the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 to decompose hydrogen peroxide to oxygen and water (Talinli & Anderson 1992). pH was measured using a pH meter (HACH Sension 4) and a pH probe (HACH platinum series pH electrode model 51910, HACH Company, USA). Biodegradability was measured by 5-day biochemical oxygen demand (BOD_5) test according to the standard methods (APHA 2005). Dissolved oxygen was measured using an YSI 5000 dissolved oxygen meter. The seed for BOD_5 test was obtained from a municipal wastewater treatment plant. TOC analyser (Model 1010, O & I Analytical) was used for determining dissolved organic carbon (DOC).

Experimental procedure: Batch experiments were preformed in a 1200 mL Pyrex reactor with 1000 mL of the antibiotic wastewater. The required amount of iron ($FeSO_4 \cdot 7H_2O$) was added to the wastewater and mixed by a magnetic stirrer to ensure complete homogeneity during reaction. Thereafter, necessary amount of hydrogen peroxide (H_2O_2) was added simultaneously with pH adjustment to the required value using H_2SO_4 or NaOH and the mixture was subjected to UV irradiation at room temperature (22 ± 2°C). The source of UV light was a UV lamp (Spectroline model EA-160/FE 230 volts 0.17 amps, Spectronics Corporation, New York USA) with nominal power of 6 W emitting radiations at wave length 365 nm. Samples were taken at pre-selected time intervals using a syringe. The samples were filtered through a 0.45 μm membrane syringe filter for COD, BOD_5 and DOC

measurement and filtered through a 0.20 μm membrane syringe filter for measurement of antibiotic concentration by HPLC.

RESULTS AND DISCUSSION

Effect of H_2O_2/COD molar ratio: The effect of H_2O_2/COD molar ratio on COD removal and biodegradability (BOD_5/COD ratio) improvement are shown in Fig. 1. The operating conditions were pH 3, initial COD 670 mg/L and sCOD 575 mg/L (17.97 mM), DOC 165 mg/L, reaction time 30 min and H_2O_2/Fe^{2+} molar ratio 50. To study the effect of H_2O_2/COD molar ratio on biodegradability improvement and mineralization of the antibiotic wastewater, initial H_2O_2 concentration was varied in the range 17.97-53.9 mM. The corresponding H_2O_2/COD and COD/H_2O_2/Fe^{2+} molar ratio were 1, 1.5, 2, 2.5 and 3, and 1.0/1.0/0.02, 1.0/1.5/0.03, 1.0/2.0/0.04, 1.0/2.5/0.05 and 1.0/3.0/0.06, respectively. It was expected that as the H_2O_2/COD molar ratio increased, more hydroxyl radicals would be available to attack the substrate and, therefore, degradation would increase. The COD concentration deceased from 300 mg/L at H_2O_2/COD molar ratio 1 to 222 mg/L at H_2O_2/COD molar ratio 2.5, and then increased slightly at H_2O_2/COD molar ratio 3. The BOD_5 varied from 97 to103 mg/L at H_2O_2/COD molar ratio 1 to 3. The COD removal percent was 45 ± 1, 51 ± 1, 57 ± 1, 59 ± 1 and 58 ± 1 at H_2O_2/COD molar ratio 1, 1.5, 2.0, 2.5 and 3.0, respectively. The BOD_5/COD ratio was 0.34 ± 0.01, 0.41 ± 0.02, and 0.43 ± 0.01, 0.44 ± 0.01 and 0.42 ± 0.01 at H_2O_2/COD molar ratios 1, 1.5, 2.0, 2.5 and 3.0, respectively.

The effect of H_2O_2/COD molar ratio on mineralization of organic carbon in terms of DOC removal is shown in Fig. 2. The results show that DOC concentration deceased from 105 ± 1 mg/L at H_2O_2/COD molar ratio 1 to 83 ± 2 mg/L at H_2O_2/COD molar ratio 2.5, and then increased slightly at H_2O_2/COD molar ratio 3. The DOC removal percent was 32 ± 3, 34 ± 1, 36 ± 1, 49 ± 1 and 48 ± 1 at H_2O_2/COD molar ratio 1, 1.5, 2.0, 2.5 and 3.0, respectively.

The results show that COD and DOC removal and biodegradability (BOD_5/COD ratio) improved with increasing H_2O_2/COD molar ratio. Addition of H_2O_2 in excess of H_2O_2/COD molar ratio 2-2.5 did not improve removal. This is presumably due to auto-decomposition of H_2O_2 to oxygen and water and scavenging of $OH^{\cdot}$ by H_2O_2 as in reactions (1) and (2) (Buxton et al. 1988). Moreover, the excess H_2O_2 reacts with ferric ions to form hydroperoxyl radical as in reaction (3) (Kavitha & Palanivelu 2005).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad ...(1)$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \quad ...(2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad ...(3)$$

Based on these results, it may be considered that optimal H_2O_2/COD molar ratio is 2-2.5 for biodegradability improvement, COD and BOD removal and mineralization of the antibiotic wastewater. A H_2O_2/COD molar ratio 2.5 was used in all subsequent experiments.

Effect of H_2O_2/Fe^{2+} molar ratio: In photo-Fenton process, iron and hydrogen peroxide are two major chemicals determining the operation cost as well as efficiency. The effect of H_2O_2/Fe^{2+} molar ratio on COD removal and biodegradability (BOD_5/COD ratio)) are shown in Fig. 3. The operating conditions were pH 3, initial COD 670 mg/L and sCOD 575 mg/L (17.97 mM), DOC 165 mg/L, reaction time 30 min and H_2O_2/COD molar ratio 2.5. To study the effect of H_2O_2/Fe^{2+} molar ratio on biodegradability improvement and mineralization of the antibiotic wastewater, experiments were conducted at constant H_2O_2 concentration (44.9 mM) and varying Fe^{2+} concentration in the range

0.3-4.5 mM. The corresponding H_2O_2/Fe^{2+} and $COD/H_2O_2/Fe^{2+}$ molar ratio were 10, 20, 50, 100 and 150, and 1.0/2.5/0.25, 1.0/2.5/0.125, 1.0/2.5/0.05, 1.0/2.5/0.025 and 1.0/2.5/0.017, respectively. The COD removal percent was 67 ± 1, 67 ± 1, 59 ± 1, 46 ± 1 and 30 ± 1 at H_2O_2/Fe^{2+} molar ratio 10, 20, 50, 100 and 150, respectively. The BOD_5/COD ratio was 0.48 ± 0.04, 0.50 ± 0.01, 0.44 ± 0.01, 0.32 ± 0.02 and 0.19 ± 0.02 at H_2O_2/Fe^{2+} molar ratio 10, 20, 50, 100 and 150, respectively. It may be noted that a wastewater is considered biodegradable if the BOD_5/COD ratio is 0.40 (Al-Momani et al. 2002).

The effect of H_2O_2/Fe^{2+} molar ratio on mineralization of organic carbon in terms of DOC removal is shown in Fig. 4. The DOC concentration deceased from 126 ± 3mg/L at H_2O_2/Fe^{2+} molar ratio 150 to 83 ± 3 mg/L at H_2O_2/Fe^{2+} molar ratio 20, and then increased slightly at H_2O_2/Fe^{2+} molar ratio 10. The DOC removal percent was 48 ± 1, 51 ± 2, 45 ± 1, 36 ± 1 and 24 ± 2 at H_2O_2/Fe^{2+} molar ratio 10, 20, 50, 100 and 150, respectively.

The results show that COD and DOC removal and BOD_5/COD ratio increased with decrease of H_2O_2/Fe^{2+} molar ratio up to 20. Further decrease of H_2O_2/Fe^{2+} molar ratio below 20 did not improve COD and DOC removal. This may be due to direct reaction of $OH^{\cdot}$ radical with metal ions at high concentration of Fe^{2+} as in reaction (4) (Joseph et al. 2000).

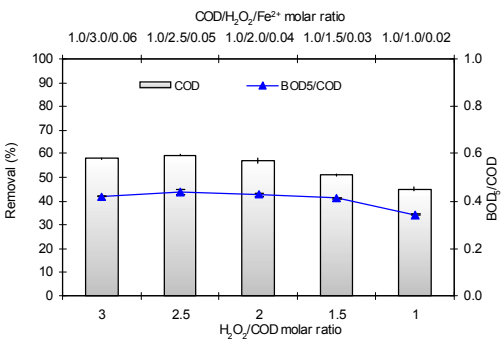

Fig. 1: Effect of H_2O_2/COD molar ratio on COD removal and BOD_5/COD ratio.

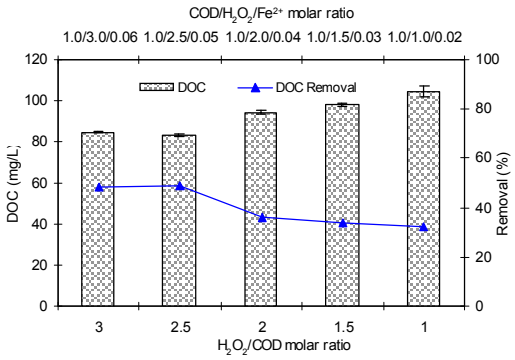

Fig. 2: Effect of H_2O_2/COD molar ratio on mineralization in terms of DOC removal.

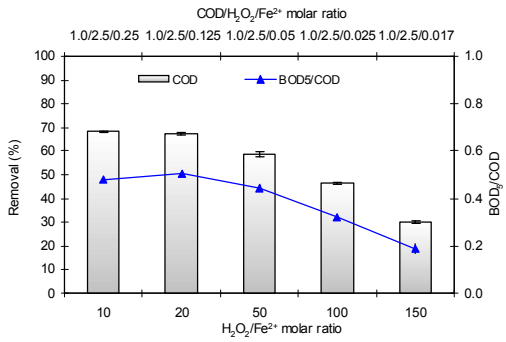

Fig. 3: Effect of H_2O_2/ Fe^{2+} molar ratio on COD removal and BOD_5/COD ratio.

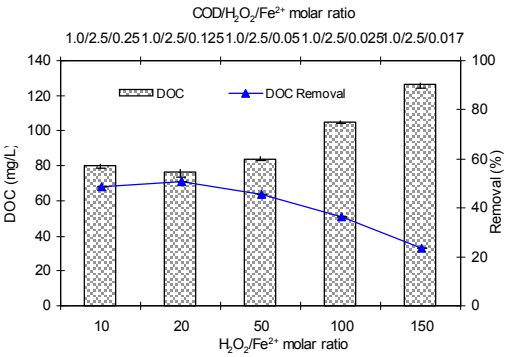

Fig. 4: Effect of H_2O_2/ Fe^{2+} molar ratio on mineralization in terms of DOC removal.

Table 1: Antibiotic wastewater characteristics.

Parameter	Value	Parameter	Value
Amoxicillin (mg/L)	138 ± 5	Total Suspended Solids (mg/L)	70 ± 5
Cloxacillin (mg/L)	84 ± 4	Phosphate (mg P/L)	7.5
COD (mg/L)	670 ± 20	Nitrate (mg NO_3-N/L)	5.1
Soluble COD (sCOD) (mg/L)	560 ± 20	Ammonia (mg NH_3-N/L)	11.1
DOC (mg/L)	160 ± 5	Sulphate (mg SO_4^{2-}/L)	0.7
BOD_5 (mg/L)	65 ± 10	Chloride (mg Cl^-/L)	5.92
Biodegradability (BOD_5/COD)	0.09	Turbidity (NTU)	45
pH	6.8	Conductivity (μS/cm)	125

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \quad ...(4)$$

The optimum H_2O_2/Fe^{+2} molar ratio for treatment of the antibiotic wastewater is 20.

Degradation of antibiotics under optimum operating conditions: To study the degradation of amoxicillin and cloxacillin in the antibiotic wastewater, an experiment was conducted under optimum operating conditions (H_2O_2/COD molar ratio 2.5, H_2O_2/Fe^{+2} molar ratio 20) at pH 3. Complete degradation of amoxicillin and cloxacillin occurred in one min reaction. This agrees well with the results reported by Trovó et al. (2008) on degradation of amoxicillin, bezafibrate and paracetamol by the photo-Fenton process. They observed 90 and 89% amoxicillin degradation in one minute reaction in distilled water and in sewage treatment plant effluent, respectively.

CONCLUSIONS

- Photo-Fenton process is effective in the treatment of antibiotic wastewater containing amoxicillin and cloxacillin.
- Under optimum operating conditions (COD/H_2O_2/Fe^{2+} molar ratio 1/2.5/0.125) at pH 3, complete degradation of the antibiotics occurred in one min, biodegradability improved from 0.09 to 0.50 ± 0.01 in 30 min, and COD and DOC removal were 67 ± 1% and 51 ± 2%, respectively in 30 min.
- Photo-Fenton process can be used as pretreatment for antibiotic degradation and biodegradability improvement of antibiotic wastewater containing amoxicillin and cloxacillin.

ACKNOWLEDGEMENT

The authors are thankful to the management and authorities of Universiti Teknologi PETRONAS for providing facilities for this research.

REFERENCES

Alexy, R., Kümpel, T. and Kümmerer, K. 2004. Assessment of degradation of 18 antibiotics in the closed bottle test. Chemosphere, 57(6): 505-512.

Al-Momani, F., Touraud, E., Degorce-Dumas, J.R., Roussy, J. and Thomas, O. 2002. Biodegradability enhancement of textile dyes and textile wastewater by VUV photolysis. Journal of Photochemistry and Photobiology, 153(1-3): 191-197.

Anderson, P.D., D'Aco, V.J., Shanahan, P., Chapra, S.C., Buzby, M.E., Cunningham, V.L., Duplessie, B.M., Hayes, E.P., Mastrocco, F.J., Parke, N.J., Rader, J.C., Samuelian, J.H. and Schwab, B.W. 2004. Screening analysis of human pharmaceutical compounds in US surface waters. Environmental Science and Technology, 38(1): 838-849.

APHA 2005. Standard Methods for the Examination of Water and Wastewater. 18th ed., American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC., USA.

Arslan-Alaton, I. and Dogruel, S. 2004. Pre-treatment of penicillin formulation effluent by advanced oxidation processes. Journal of Hazardous Materials, B112(1-2): 105-113.

Arslan-Alaton, I., Dogruel, S., Baykal, E. and Gerone, G. 2004. Combined chemical and biological oxidation of penicillin formulation effluent. Journal of Environmental Management, 73(2): 155-163.

Buxton, G.V., Greenstock, C.L., Helman, W.P. and Ross, A.B. 1988. Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}OH/^{\bullet}O^{-}$) in aqueous solution. Journal of Physical and Chemical Reference Data, 17(2): 513-886.

Carballa, M., Omil, F., Lema, J.M., Llompart, M., Garcia-Jares, C., Rodriguez, I., Gomez, M. and Ternes, T. 2004. Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water Research, 38(12): 2918-2926.

Joseph, J.M., Destaillats, H., Hung, H-M. and Hoffmann, M.R. 2000. The sonochemical degradation of azobenzene and related azo dyes: Rate enhancements via Fenton's reactions. Journal of Physical Chemistry A, 104(2): 301-307.

Kavitha, V. and Palanivelu, K. 2005. Destruction of cresols by Fenton oxidation process. Water Research, 39(13): 3062-3072.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. and Buxton, H.T. 2002. Pharmaceuticals, hormones and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environmental Science and Technology, 36(6): 1202-1211.

Ikehata, K., Naghashkar, N.J. and El-Din, M.G. 2006. Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review. Ozone Science and Engineering, 28(6): 353-414.

Nikolaou, A., Meric, S. and Fatta, D. 2007. Occurrence patterns of pharmaceuticals in water and wastewater environments. Analytical and Bioanalytical Chemistry, 387(4): 1225-1234.

Pera-Titus, M., Garc1a-Molina, V., Baños, M.A., Giménez, J. and Esplugas, S. 2004. Degradation of chlorophenols by means of advanced oxidation processes: A general review. Applied Catalysis B: Environmental, 47(4): 219-256.

Pignatello, J.J., Liu, D. and Huston, P. 1999. Evidence for an additional oxidant in the photo assisted Fenton reaction. Environmental Science and Technology, 33(11): 1832-1839.

Rabiet, M., Togola, A., Brissaud, F., Seidel, J.L., Budzinski, H. and Elbaz-Poulichet, F. 2006. Consequences of treated water recycling as regards pharmaceuticals and drugs in surface and ground waters of a medium-sized Mediterranean catchment. Environmental Science and Technology, 40(17): 5282-5288.

Stackelberg, P.E., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Henderson, A.K. and Reissman, D.B. 2004. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Science of the Total Environment, 329(1-3): 99-113.

Talinli, I. and Anderson, G.K. 1992. Interference of hydrogen peroxide on the standard COD test. Water Research, 26(1): 107-110.

Trovó, A.G., Melo, S.A.S. and Nogueira, R.F.P. 2008. Photodegradation of the pharmaceuticals amoxicillin, benzafibrate and paracetamol by the photo-Fenton process-Application to sewage treatment plant effluent. Journal of Photochemistry and Photobiology A: Chemistry, 198(2-3): 215-220.

Yang, L., Yu, L.E. and Ray, M.B. 2008. Degradation of paracetamol in aqueous solutions by TiO_2 photocatalysis. Water Research, 42(3): 3480-3488.

Walter, M.V. and Vennes, J.W. 1985. Occurrence of multiple-antibiotic resistant enteric bacteria in domestic sewage and oxidative lagoons. Applied and Environmental Microbiology, 50(4): 930-933.

Zhang, G., Shulan, J. and Beidou, X. 2006. Feasibility study of treatment of amoxillin wastewater with a combination of extraction, Fenton oxidation and reverse osmosis. Desalination, 196(1-3): 32-42.