RESEARCH ARTICLE

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Chemical Oxygen Demand Removal from Synthetic Wastewater Containing Non-beta Lactam Antibiotics Using Advanced Oxidation Processes: A Comparative Study

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A-B-S-T-R-A-C-T

Background & Aims of the Study: Pharmaceuticals are considered as an emerging environmental problem due to their continuous discharge and persistence to the aquatic ecosystem even at low concentrations. The purpose of this research was the investigation of advanced oxidation processes (Fenton and Fenton-like) efficiency for the removal of non-beta lactam Antibiotics of azithromycin and clarithromycin from synthetic wastewater.

Materials & Methods: In this laboratory scale study, samples of synthetic wastewater were prepared from azithromycin and clarithromycin antibiotics. Concentration of samples was 200 mg/L. Chemical oxygen demand (COD) index was selected as the parameter for evaluation in this study. Fenton and Fenton-like oxidation processes were done on synthetic wastewater of azithromycin and clarithromycin. In Fenton (Fe^{2+}/H_2O_2) and Fenton-like (Fe^{0}/H_2O_2) processes the influence of pH, iron and hydrogen peroxide on the removal efficiency of the antibiotics were studied and the optimum values for each parameter were determined.

Results: The optimum condition for Fenton in removal of azithromycin and clarithromycin were pH= 7 and 7, Fe^{2+} 0.45 mmol/L and 0.45 mmol/L, hydrogen peroxide 0.16 mmol/L and 0.2 mmol/L, and contact time of 1 h and 1 h, respectively. The optimum condition for Fenton-like in removal of clarithromycin and azithromycin were pH= 7 and 7, Fe^{0} 0.3 mmol/L and 0.36 mmol/L, hydrogen peroxide 0.3 mmol/L and 0.38 mmol/L, contact time of 30 min and 30 min.

Conclusions: The findings of this study demonstrate that the Fenton and Fenton-like processes under optimum conditions can play an important role in the removal of azithromycin and clarithromycin antibiotics from industrial wastewater.

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Background

Pharmaceuticals continuously discharge to the aquatic ecosystem. Their persistence in the environment emerges environmental issues and impact the human and veterinary health (1).

Studies have shown after passing through wastewater treatment, pharmaceuticals are released directly into the environment. Microbial resistant is one of the greatest concerns related to antibiotics use and their disposal in environment.

Antibiotics have been widely used in human and veterinary medicine to prevent or treat microbial infections. Thus, large quantities of these pharmaceutical agents are metabolized in the body and the rest are excreted in their native form or as metabolites. These pharmaceuticals may accumulate in soil and may be mobile in soil and can contaminate ground water (2-4). They are present in the effluent of sewage treatment plants, indicating their poor biodegradability in municipal sewage and sewage treatment plants that can be emitted into the receiving water systems. Hence, biological treatment process of wastewater for removal antibiotic is insufficient and a pretreatment process is often required.

One of the new technologies used in the pretreatment of water supplies and industrial sewage containing toxic material is "advanced oxidation processes (AOPs)". The reason for the use of AOPs is due to production of hydroxyl radicals (•OH) which have high efficacy in breaking down organic material because •OH is capable of mineralizing them ultimately to CO_2 and H_2O (5-7).

Fenton-like and Fenton are advanced oxidation processes that use Fe° and Fe2+ in reaction with H2O2, respectively, to produce •OH as follows:

(1) $Fe^{\circ} \rightarrow Fe^{2+} + 2e^{-}$

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

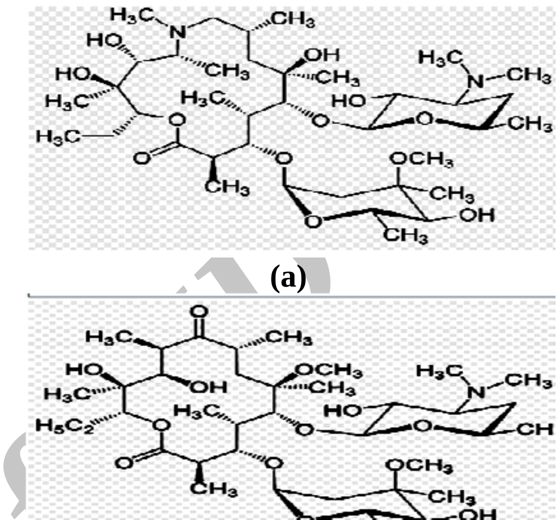
Aims of the study: In this study Fenton and Fenton- like oxidation processes were done on synthetic wastewater of azithromycin and clarithromycin and the effects of important variables such as H_2O_2 and Fe° dosage, pH and reaction time in these processes on antibiotics removal were examined.

Materials & Methods

This study was performed to determine the optimum conditions, including Fe^{2+} and H_2O_2 dosages, and pH for the Fenton process; and Fe° and H_2O_2 dosages and pH for Fenton-like process, for obtaining maximum "chemical oxygen demand (COD)" removal.

For all experiments, the synthetic wastewater was produced by dissolving 0.2 g antibiotic in 1000 mL distilled water.

Based on our analysis 1 mg/L of azithromycin is equivalent to 1.95 mg/L COD and 1 mg/L of clarithromycin is equivalent to 1.75 mg/L COD. Figure 1 shows molecular structure of azithromycin and claritromycin.



(a)

(b)

Figure 1) Molecular structure of azithromycin (a) and claritromycin (b)

The iron powder (95%) with particle size of 70-100 µm, $FeSO_4$. $7H_2O$ (98%), Sulfuric acid (96%) and NaOH (98%) (in order to pH adjustment), and hydrogen peroxide with the technical grade (30% w/w and density of 1.13 kg/L) were purchased from the Merck Company. COD measurements were performed by the closed reflux titrimetric method (8). The COD samples were measured after filtration through a Millipore membrane filter with a pore size of 0.45 µm. Initial and residual H_2O_2 amounts were determined by the spectrophotometry method (presence of H_2O_2 leads to overestimating COD) (9).

Each experiment was conducted three times. The Fenton and Fenton-like oxidation experiments were performed in a cylindrical glass reactor with a magnetic stirrer using a constant speed of 200 rpm. The stages of experiments for Fenton-like process were similar to Fenton process. The only difference between these processes was use of Fe° for Fenton-like and Fe^{2+} for Fenton.

The experiments were performed in three stages. In the first stage, the initial concentrations of (Fe° or Fe^{2+} and H_2O_2) were kept the same from run to determine the optimum pH for the solution. While maintaining the optimum pH determined during the first stage and the same Fe° or Fe^{2+}concentration, the optimum level for H_2O_2 was measured and determined during the second stage. Finally, while maintaining the optimum pH from the first stage and the H_2O_2 optimum concentration from the second stage, the optimum concentration for the Fe° or Fe^{2+} was measured and determined in the third stage. All experiments were performed at 20°C.

Data analysis: The data were analyzed using one-way analysis of variance (ANOVA). P-values less than 0.5 were considered as statistically significant.

Results

Fenton and Fenton- like oxidation processes were done on synthetic wastewater of azithromycin and clarithromycin.

In Fenton (Fe^{2+}/H_2O_2) and Fenton-like (Fe°/H_2O_2) processes, the influence of pH, iron and hydrogen peroxide on the removal efficiency of antibiotics were studied and the optimum values for each parameter were determined.

Figure 2 compares the effects of the pH value on the Fenton and Fenton-like processes in removal of azithromycin COD (2-a) and clarithromycin COD (2-b). To elucidate the role of pH on final COD, pH was altered within a range of 3 to 11 for each process, and H_2O_2 and Fe (Fe° or Fe^{2+}) concentrations for each process were fixed at 0.1 mM/L and 0.1 mM/L, respectively.

The minimum final COD (each tow antibiotics) for each tow processes of Fenton and Fenton-like was obtained at pH=7.0, while at pH <7.0 and pH>7.0, higher values of final COD was observed. Considering the above indicated results, optimum pH for each process was selected as 7.0.

Figure 3 shows the effect of the initial H_2O_2 on the decreasing of final COD. As presented in Figure 3a, azithromycin COD removal efficiency was increased (the final COD was decreased) by increasing the H_2O_2 concentration from 0.1 to 0.38 mM/L and 0.05 to 0.2 mM/L for Fenton-like and Fenton, respectively, and increase in the concentration of H_2O_2 up to 0.38 mM/L for Fenton-like and 0.2 for Fenton did not significantly affect the removal of COD.

Also according to figure 3b, the clarithromycin final COD was decreased by increasing of H_2O_2 added (increasing the H_2O_2 concentration from 0.1 to 0.3 mM/L and 0.04 to 0.16 mM/L), while clarithromycin final COD remained constant with increasing H_2O_2 up to 0.3 mM/L and 0.16 for Fenton-like and Fenton processes, respectively (in each process for removal of antibiotics, pH controlled at 7.0 and the Fe° or Fe^{2+} dosage was Fixed at 0.1 mM/L).

Conclusively, the optimal doses for removal azithromycin and clarithromycin COD by the Fenton were 0.2 and 0.16, and by the Fenton-like process were 0.38 and 0.3, respectively.

To obtain the optimum concentration of Fe^{0} or Fe^{2+} for COD removal from solution, the investigation was carried out with various amounts of the Fe^{0} or Fe^{2+}.

Figure 4 shows that the increase of either Fe^{0} or Fe^{2+} enhanced the efficiency of Fenton-like and Fenton processes for COD removal of azithromycin and clarithromycin. Experiments show that COD removal efficiency significantly increases (final COD decreased) in dosages of 0.36 mM/L and 0.42 mM/L (Fe^{0} and Fe^{2+}, respectively) for azithromycin and 0.3 mM/L and 0.45 mM /l (Fe^{0} and Fe^{2+}, respectively) for clarithromycin.

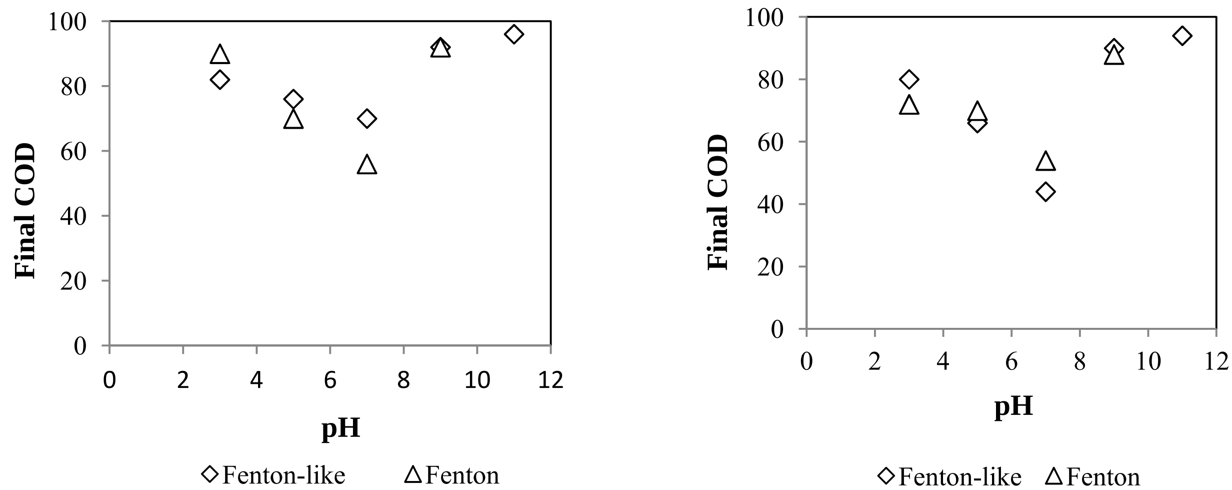
Figure 5 presents changes in COD values of azithromycin and clarithromycin during Fenton-like and Fenton oxidation as a function of treatment time. Degradation of azithromycin and clarithromycin by Fenton-like and Fenton oxidation could be expressed as first order reaction according to the following equation:

$dCOD/dt = -k_{COD} \times COD$

Where k_{COD} (min^{-1}) is the first-order COD abatement rate constant for azithromycin or clarithromycin by Fenton-like and Fenton.

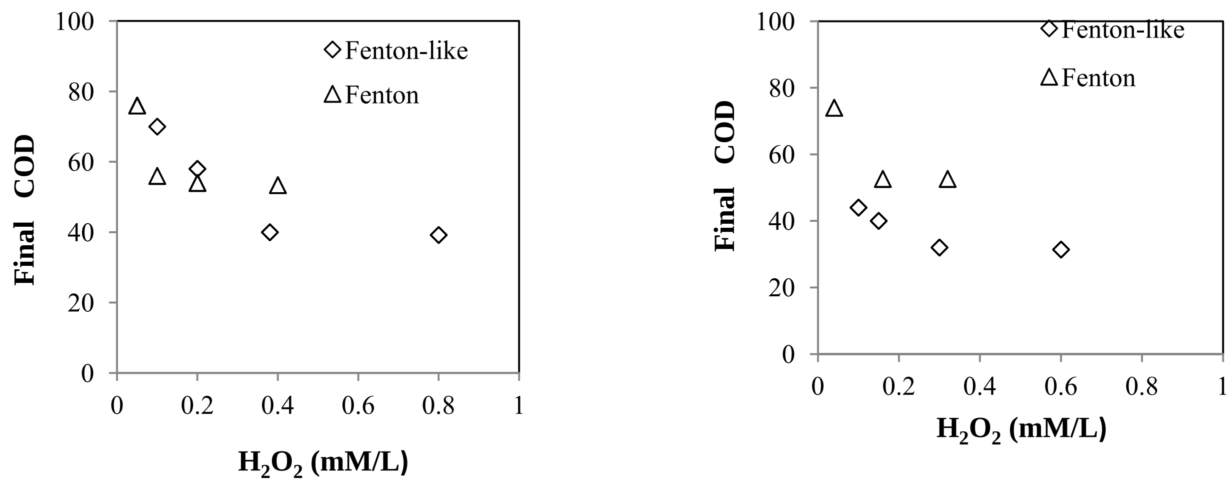
Table 1) Rate constants of mineralization in antibiotics by Fenton and Fenton-like

Process	Azithromycin		Clarithromycin	
	$K(s^{-1})$	$t_{1/2}(min)$	$k(s^{-1})$	$t_{1/2}(min)$
Fenton-like	0.074	9.3	0.079	8.7
Fenton	0.028	24.7	0.027	25.6



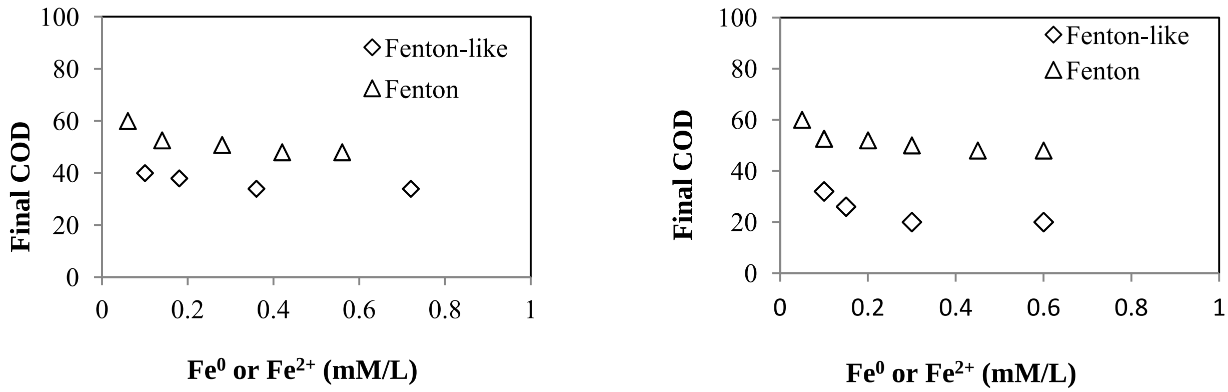
(a) **(b)**

Figure 2) Effects of pH on chemical oxygen demand (COD) removal rates obtained for azithromycin (a) and clarithromycin (b) antibiotics by "Fenton" and "Fenton-like" processes



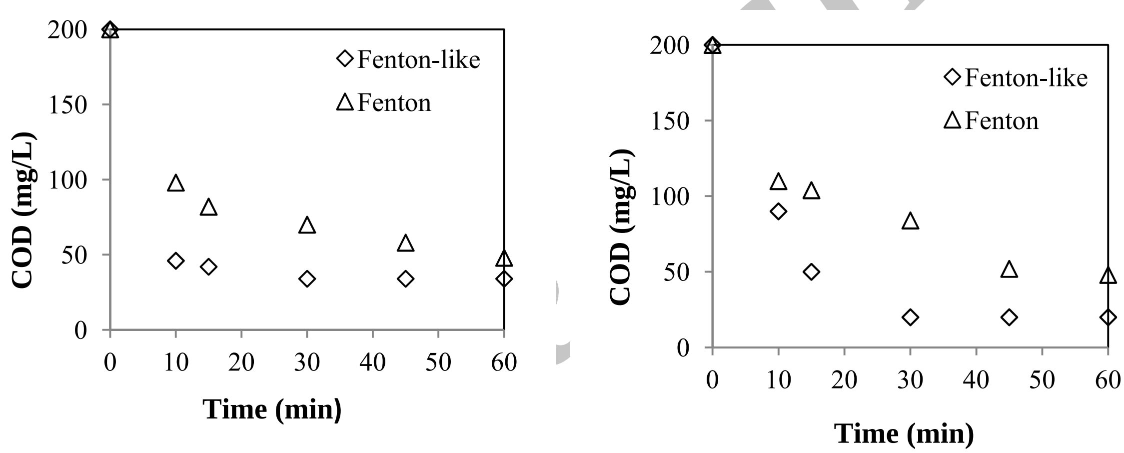
(a) **(b)**

Figure 3) Effects of H_2O_2 on chemical oxygen demand (COD) rates obtained for azithromycin (a) and clarithromycin (b) antibiotics by "Fenton" and "Fenton-like" processes



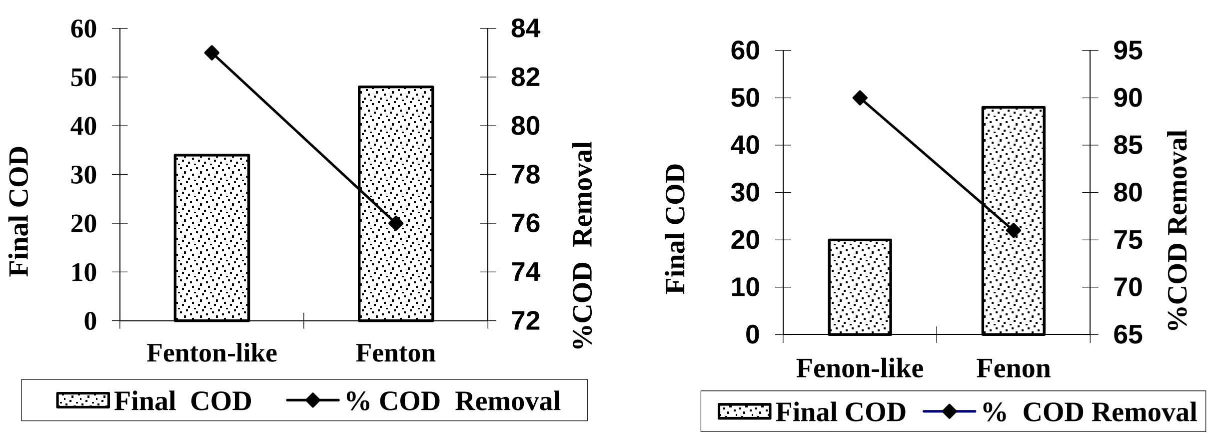
(a) (b)

Figure 4) Effects of Fe^0 or Fe^{2+} on chemical oxygen demand (COD) removal rates obtained for azithromycin (a) and clarithromycin (b) antibiotics by "Fenton" and "Fenton-like processes"



(a) (b)

Figure 5) Chemical oxygen demand (COD) abatement rates for "Fenton" and "Fenton-like" experiments



(a) (b)

Figure 6) Comparison of "Fenton" and "Fenton-like" processes for chemical oxygen demand (COD) removal: azithromycin (a) and clarithromycin (b)

Discussion

The pH value affects the final COD and AOPS processes are strongly affected by pH. It was observed that the minimum final COD for each antibiotic at pH 7.0 that can be compared to pH >7.0 and pH <7.0. The high removal efficiency of COD was achieved at pH 7.0 which might be due to:

a) The generation of OH radicals according to Equations 1 and 2; b) at this pH, the amount of the dissolved Fe^{2+} increases. At pH values higher than 7.0, the degradation strongly decreases because of: 1- iron precipitates as hydrous oxyhydroxide ($Fe_2O_3 \cdot nH_2O$) 2- at alkaline solutions H_2O_2 is unstable and decomposes to give O_2 and H_2O. The decrease in the COD removal efficiency at pH <7 could be because of the scavenging effect of $^{\bullet}OH$ by H^+ as shown in Equation 12 (10, 11).

(3) $^{\bullet}OH + H^+ + e^- \rightarrow H_2O$

Xing *et al.* for removal of the antibiotic fermentation wastewater COD used a combination of coagulation and Fenton-like processes. The pH of the wastewater entering the Fenton-like process was set to 4 and the COD removal efficiency after combined process was measured as %93.5 (12).

The degradation of antibiotics was increased by augmenting the concentration of H_2O_2 added to optimum dosage that, and this can be due to produced $^{\bullet}OH$ radicals (ferrous ions completely oxidized; consequently, the generation of hydroxyl radicals increased).

Addition of H_2O_2 exceeding optimum dosage for Fenton and Fenton-like processes did not improve removal of COD, because H_2O_2 acts as a scavenger of the $^{\bullet}OH$ to produce the perhydroxyl radical ($HO_2^{\bullet}$) according to reaction 4 (H_2O_2 itself contributes to the OH scavenging capacity).

(4) $H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet}$

The decrease in COD removal efficiency with reduction of H_2O_2 concentration can be explained by partial oxidation of Fe^{2+} in H_2O_2 concentrations lower than optimum values (13,14). Arslan-Alaton *et al.* used Fenton-like process for removal of penicillin COD from the wastewater. The optimum H_2O_2 amount for the COD removal was achieved at 1.5 mM (15).

As presented in figure 4, increasing the iron in its Fe^{2+} or Fe° form has a significant effect on the removal efficiency of azithromycin or clarithromycin COD. Experiments show that in the optimum dosage of Fe^{2+} or Fe°, final COD significantly decreases (in the other hand the removal efficiency of COD distinctly increased with higher amounts of Fe^{2+} or Fe°).

The best result of antibiotics removal were achieved at optimum dosages of Fe° (0.36 mM/L) or Fe^{2+} (0.42 mM/L) for azithromycin, and at optimum dosages of Fe° (0.3 mM/L) or Fe^{2+} (0.45 mM/L). Addition of Fe° or Fe^{2+} above mentioned optimum dosage did not affect the removal efficiency (a slight increase in removal efficiency was observed). Because in overdoses of Fe^{2+} ions or Fe°, ferrous ions reacted with OH radicals as a scavenger as observed in reaction 5 (the formation of orange-brown iron precipitate ($Fe(OH)_3$ flocculates), consequently, the COD removal could decrease.

(5) $Fe^{2+} + {}^{\bullet}OH \rightarrow OH^- + Fe^{3+}$

According to equations 6 and 7, it must be noted that the formed Fe^{3+} again enters a reaction with hydrogen peroxide that leads to an increase in the removal efficiency (16, 17).

(6) $Fe^{3+} + H_2O_2 \rightarrow H^+ + FeOOH^{2+}$

(7) $FeOOH^{2+} \leftrightarrow OH_2^{\bullet} + Fe^{2+}$

Fana *et al.* study used a Fenton-like process in the removal of sulfasalazine from wastewater. The amount of the iron used was 0.35 mM and a COD removal efficiency of 84.2% was achieved (18).

The experimental data were fitted by first order kinetics. Table 1 presents the Pseudo-first-order kinetic constants for the Fenton-like and Fenton processes studied and the experimental half-life time.

Major COD mineralization occurred for the Fenton-like process (each tow antibiotics) in 30 min and Fenton process (each tow antibiotics) in 60 min and Fenton-like process showed more COD mineralization rate than the Fenton process. According to table 1 Fenton-like process has significant role on mineralization of azithromycin an clarithromycin in comparison with the Fenton process (15).

Figure 6 shows comparison of Fenton-like and Fenton oxidation efficiency for removal of azithromycin or clarithromycin antibiotics from synthetic wastewater. According to Figure 6 (a) and 6 (b), Fenton-like oxidation shows the best efficiency for removal of azithromycin or clarithromycin, whereas Fenton oxidation shows a slow degradation.

At optimum reaction conditions for azithromycin or clarithromycin COD_0 adjusted to 200 mg/L, 83 and 76% azithromycin COD removals were achieved by Fenton-like (after 30 min) and Fenton (after 60 min), respectively, also 90 and 76% clarithromycin COD removals were achieved by Fenton-like (after 30 min) and Fenton (after 60 min), respectively.

Conclusions: In conclusion, COD removal rates obtained for Fenton-like process were higher than Fenton process.

Footnotes

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None declared.

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Conflict of Interest:

The authors declare no conflict of interest.

References

1. Elmolla ES, Chaudhuri M. The feasibility of using combined Fenton-SBR for antibiotic wastewater treatment. Desalination 2012;285:14-21.
2. Kulik N, Trapido M, Goi A, Veressinita Y, Munter R. Combined chemical treatment of pharmaceutical effluents from medical ointment production. Chemosphere 2008;70(8):1525-31.
3. Elmolla ES, Chaudhuri M. Combined photo-Fenton–SBR process for antibiotic wastewater treatment. J Hazard Mater 2011;192(3):1418–26.
4. Farabi Pharmaceutical Co. Properties of Azithromycin. Available from: http:// www.Farabipharma.ir. Accessed 6 May, 2012. (Full Text in Persian)
5. Arsene D, Musteret CP, Catrinescu C, Apopei P, Barjoveanu G, Teodosiu C. Combined oxidation and ultrafiltration processes for the removal of priority organic pollutants from wastewaters. Environ Eng Manag J 2011;10(12):1967-76.
6. Zaharia C, Suteu D, Muresan A, Muresan R, Popescu A. Textile wastewater treatment by homogeneous oxidation with hydrogen peroxide. Environl Eng Manage J 2009;8(6):1359-69.
7. Ayyasamy PM, Shunthi K, et al. Two-stage removal of nitrate from grand water using biological and chemical treatments. J Biosci Bioeng 2007;104(2):129-134.
8. APHA, AWWA, WPCF. Standard Methods for the Examination of Water and Wastewater. 21st ed. Washington DC: American Public Health Association; 2005.
9. Lee E, Lee H, Kim YK, Sohn K, Lee K. Hydrogen peroxide interference in chemical oxygen demand during ozone-based advanced oxidation of anaerobically digested livestock wastewater. Int J Environ Sci Technol 2011;8(2):381-8.
10. Hang S, Kwon B, Lee J, Kim I. Degradation of 2-chlorophenol by Fenton & Photo Fenton Processes. Korean J Chem Eng 2008;25(1):46-52.
11. Wang S. A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater. Dyes Pigm 2008;76(3):714-20.
12. Xing Z, Sun D, Yu X. Treatment of antibiotic Fermentation wastewater using the combined Polyferric Sulfate coagulation with Fenton-like oxidation. J Environ Prog Sustain Energy 2010;29(1):42-51.

13. Ai Z, Yang P, Lu X. Degradation of 4-chlorophenol by a microwave assisted photocatalysis method. J Hazard Mater 2005;124(1-3):147-52.

14. Ciner F, Akal Solmaz SK. Decolorization of reactive dye containing wastewater using fenton, fenton-like and chemical coagulation. Proceedings of the 10th International Conference of Environmental Science and Technology 5-7 September 2007, Kos Island, Greece. Greece; 2007.

15. Arslan-Alaton I, Gurses F. Photo-Fenton-like and photo-Fenton-like oxidation of Procaine Penicillin formulation effluent. J Photochem Photobiol A Chem 2004;165(1-3):165-75.

16. Elmolla ES, Chaudhuri M. Photo-Fenton treatment of antibiotic wastewater. Nature Environ Pollut Technol 2010;9(2):365-70.

17. Barbusinski K, Majewaski J. Discoloration of azo dye Acid Red 18 by Fenton reagent in the presence of iron powder. Polish J Environ Stud 2003;12(2):151-55.

18. Fan X, Hao H, Shen X, Chen F, Zhang J. Removal and degradation pathway study of sulfasalazine with Fenton-like reaction. J Hazard Mater 2011;190(1-3):493-500.