

Determination of Effective Parameters on Removal of Organic Materials from Pharmaceutical Industry Wastewater by Advanced Oxidation Process (H₂O₂/UV)

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A-R-T-I-C-L-E-I-N-F-O

Article Notes:

Received: Dec 5, 2015

Received in revised form:
Jun 15, 2016

Accepted: Feb 26, 2016

Available Online: Mar 29,
2016

Keywords:

Advanced oxidation process, COD removal, pharmaceutical industry effluent, Iran.

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

Background & Aims of the Study: Pharmaceutical wastewater is one of the major complex and toxic industrial effluents that contain little or no biodegradable organic matters.

Materials & Methods: In this study, H₂O₂/UV base advance oxidation process (AOP) was used to remove organic materials from pharmaceutical industry effluent. Experiments were conducted for the chemical oxygen demand (COD) removal using medium pressure mercury vapor UV lamp coupled with hydrogen peroxide (H₂O₂/UV).

Results: Results indicated that the efficiency of COD removal depends on the concentration of initial H₂O₂, oxidation time and pH as well. The efficiency of COD removal in low H₂O₂ concentration was very low even in coupled with UV light, which can be attributed to the low hydroxyl radicals ([•]OH) generation. In high concentration of H₂O₂ (500 mg/L) and optimum pH (pH=4), 87.496% of removal efficiency could be achieved during 70 minutes of oxidation time.

Conclusions: For high concentration of H₂O₂ (500 mg/l) in pH 3 and 7, the maximum COD removal efficiency was 28.5% and 15.2% respectively, indicating significant roles of pH and H₂O₂ concentration in oxidation efficiency of H₂O₂/UV process in removing the COD.

Please cite this article as: Azizi E, Ghayebzadeh M, Dargahi A, Hemati L, Beikmohammadi M, Sharafi K. Determination of Effective Parameters on Removal of Organic Materials from Pharmaceutical Industry Wastewater by Advanced Oxidation Process (H₂O₂/UV). Arch Hyg Sci 2016;5(2):69-74.

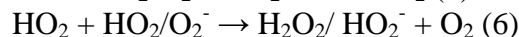
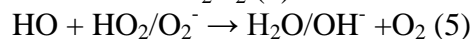
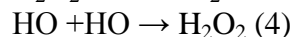
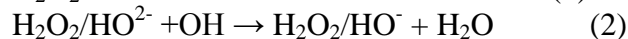
Background

Pharmaceutical wastewater is characterized by high concentrations of organic matter and toxic pollutants (1). This wastewater contains the main agents and solvents which were used in washing and cleaning processes; also reactants and catalysts used in manufacturing processes (2). In many cases, effluents of these industries contain little or no biodegradable organic matters. Therefore, the pollutant loads in terms of biological oxygen demand (BOD)

may be negligible and chemical oxygen demand (COD) would be higher than the BOD (3). In fact, many pharmaceutical compounds are only partially removed during biological treatment processes in sewage treatment plants and consequently released into surface waters (4,5). For pharmaceutical wastewater treatment several different alternatives were suggested include anaerobic-aerobic (6) or membrane (7,8) bioreactors, electrochemical oxidation (9), biochemical combined method (10) and advanced oxidation processes (AOPs) (11-13). The application of UV process is uncommon

for pharmaceutical compounds removal from wastewater. However, many studies have been conducted about the organic pollutant removal from industrial effluents such as pharmaceutical industries, focused on UV treatment process in combination with O₃ or H₂O₂, because of no byproducts formation and being effective process for degrading organic matters in aqueous systems (5,14).

Hydrogen peroxide in combination with ultraviolet photolysis (H₂O₂/UV) is one of the most effective methods in AOPs for treatment of wastewaters which are contain the toxic organic pollutants (15). The main reactions of •OH generation in H₂O₂/UV process is shown as follows (16,17):



H₂O₂/UV advanced oxidation method appears to be the most promising method, in terms of cost-effectiveness and ease of operation (18). As compared to other AOPS such as chemical oxidation by ozone and ozone/hydrogen peroxide with off-gas and VOCs problems; they have not been observed in the UV-based AOP (19).

Aims of the study:

In this study, the applicability of H₂O₂/UV oxidation for treating pharmaceutical effluents from a drug manufacturing plant that produce various antiseptics and disinfectant solutions was tested under laboratory conditions.

Materials & Methods

Characteristics of raw wastewater and Sampling

The pharmaceutical wastewater was a real sample from a pharmaceutical mill situated in Kermanshah industrial town, Iran. Samples were collected from the entrance of treatment plant, prior to any treatment processes. Samples were shipped into 10 L drums and stored in a

refrigerator at 4°C before the experiments. Some characteristics of the samples are tabulated in Table 1.

Table1) Characteristics of studied wastewater

Parameter	Value
BOD ₅ (mg/L)	240
COD (mg/L)	1580
BOD ₅ /COD	0.16
TDS(mg/L)	757
TSS (mg/L)	103
pH	7.8
EC (µmoh/cm ²)	297

Oxidation reactor

Figure 1 shows a schematic of UV/H₂O₂ reactor. A custom-made reactor of Plexiglas with 2 liter capacity, included a medium pressure (MP) UV lamp with a 254 nm maximum wavelength and intensity of 50-W (0.315 W/cm²) housed inside a quartz box with 6 cm in diameter used for all irradiations. To avoid energy wasting, the reactor was covered with aluminum foil sheet. In order to establish equalized conditions throughout the reactor, a circulating pump was used inside the reactor with Q_{max} 300 lit/h and, H_{max} 0.6 m. A cooling water flow was used to surround the reactor in order to control the inside temperature of the reactor.

Chemicals and reactions

All the experimental analysis was made according to standard methods (20). COD tests were performed as recommended in the closed reflux method 5220-C. Merck analytical quality chemicals such as hydrogen peroxide %35 (H₂O₂), sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄), were used for preparation of reagents. The pH was measured by a Jenway 3040 brand pH-meter.

Experimental procedure

The main objective of this study was to evaluate the performance of advanced oxidation process in oxidizing of refractory organic matter in pharmaceutical industry sewage. Complex organic compounds can be broke down into simpler one by the oxidation process

using adsorption techniques to remove. Laboratory scale experiments involved treating the pharmaceutical wastewater by H_2O_2/UV process and consequently filtration the oxidized wastewater by granular activated carbon as adsorbent material to remove the COD in a batch system. After turning on the UV lamp, required amount of H_2O_2 injected into the reactor and at intervals of 10 minutes, the sampling was done.

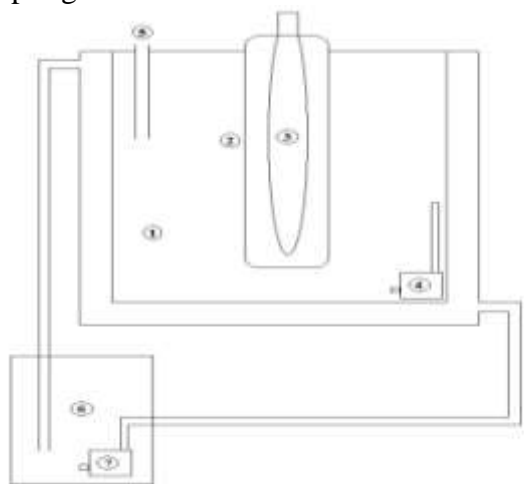


Figure 1) 1- Reactor, 2- Quartz cover, 3- UV lamp, 4- circulator pump, 5- chemicals injection vessel, 6- cooling water, 7- cooling water circulator

Results

The use of H_2O_2 in conjunction with UV, enhances the degradation of organic compounds due to the contribution of $OH\cdot$ radicals generated from the direct photolysis of H_2O_2 , i.e. with a quantum yield of two $OH\cdot$ radicals formed per quantum of radiation which are absorbed so as to oxidize pharmaceutical compounds. The study of the effect of oxidation conditions such as pH, initial H_2O_2 concentration and oxidation time on oxidation performance in COD removal revealed the following results:

pH

pH is a very effective factor in advanced oxidation processes (21). Alkaline conditions have been reported as an unsuitable things for advanced oxidation processes (22,23). In order to study the effect of pH on the process, pH

range (3,4,7) was considered as variable and other parameters as constant. Figure 2 shows the effect of pH variations on COD removal. In general, the COD removal increased in acidic condition (low pH values). However, in $pH < 4$, the efficiency reduced sharply. pH 4 was found the optimum pH for H_2O_2/UV process with 87.6% COD removal.

COD removal by H_2O_2 concentration with time

With UV/H_2O_2 advanced oxidation, organic matters will be degraded by UV direct photolysis and the OH radical oxidation pathway (24). To determine the effect of H_2O_2 concentration, its range (50, 200 and 500 mg/L) was considered as variable and other parameters as constant. Some experiments were performed at different contact times (10, 20, 30, 40, 50, 60 and 70 minutes). Figure 3 presents the effect of H_2O_2 concentration on the COD removal. In general the COD removal increased with time. It was also observed that through increasing H_2O_2 concentration from 50 to 500 ml/L, COD removal increased.

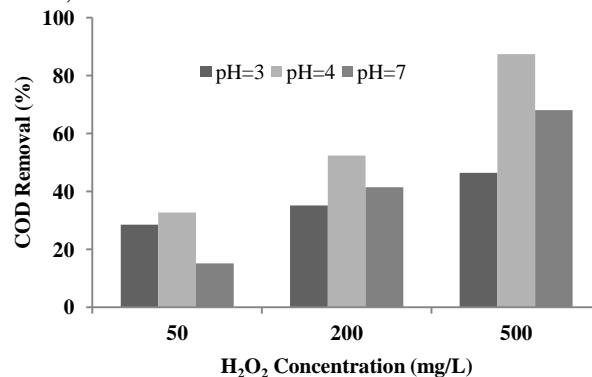


Figure.2) Effect of pH on H_2O_2/UV Oxidation performance

Kinetic study

To determine the effect of hydrogen peroxide concentration on the kinetic constants (k_{ap}) of COD removal, some experiments were designed at different H_2O_2 concentration (50, 200 and 500 mg/L) and condition of $COD_0 = 1580$ mg/L and $pH=4.0$ and $T=25\pm 1$ °C. The results are shown in Figure 5. The value of the

parameter k (min^{-1}) was determined by fitting the experimental data to Eq. 1 and 2 (25):

$$\ln \frac{C_t}{C_0} = -kt \quad (1)$$

$$k = \frac{1}{t} \ln \frac{C_0}{C_t} \quad (2)$$

Where:

C_0 = Initial COD concentration at instant $t=0$ (mg/L)

C_t = COD concentration at instant t (mg/L)

k = First order rate constant (min^{-1})

t = Time of reaction (min)

This is known as a kinetic equation for a first-order reaction. The pseudo-first-order kinetic model seems to be well applicable to the COD removal under the given test conditions (Figure 4). The estimated values of k are given in Figure 5.

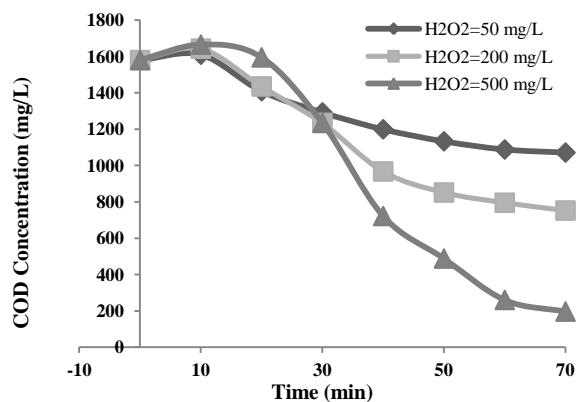


Figure 3) Effect of H_2O_2 concentration and contact time on the COD removal efficiency in pH 4

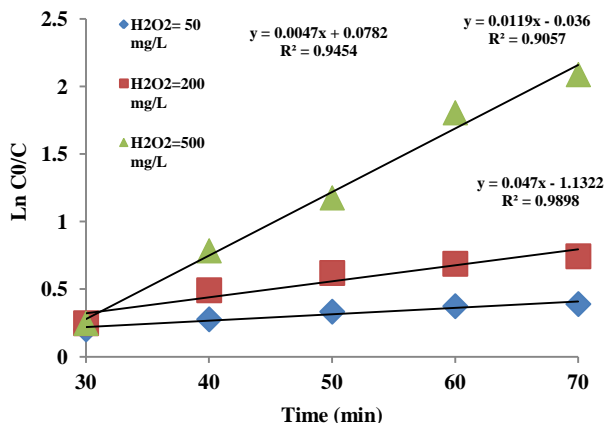


Figure 4) First-order kinetics of various H_2O_2 concentrations (pH=4)

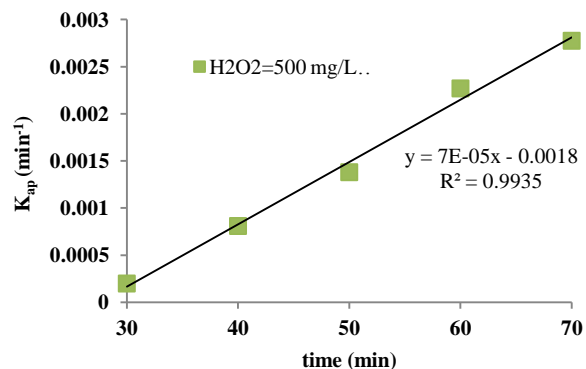


Figure 5) Plot of K for COD removal in initial $\text{H}_2\text{O}_2 = 500$ mg/L and pH=4

Discussion

Applicability of $\text{H}_2\text{O}_2/\text{UV}$ advanced oxidation process for COD removal from a pharmaceutical industry effluent was investigated, suitable pH and H_2O_2 concentration for operation were determined. pH 4 and 500 mg/L H_2O_2 concentration was found an optimum 87.6% COD removal result. A relative increase in the COD up to 20 minutes of onset of oxidation in all trials was recorded. This may be due to the residual concentration of H_2O_2 that has oxidized dichromate result in the increase of COD value. Increasing the amount of H_2O_2 resulted in the COD removal increase. Maximum removal of COD was achieved in 500 mg/L of H_2O_2 . According to Jung et al. study on amoxicillin removal by UV and UV/ H_2O_2 processes only 10% removal was achieved after 80min of UV irradiation with the addition of 0.5 mM H_2O_2 . But when H_2O_2 concentration increased to 10 mM, TOC removal increased to higher than 50% after 80 min irradiation time (18). A detail kinetic modeling was developed to understand the mechanisms and kinetics of the COD removal by the technique used. The results showed that the initial H_2O_2 concentration was the main factor that affect the kinetic constant K . It can be observed that the value of k increases linearly with oxidation time (figure 5). The k of COD removal increased with the increase of H_2O_2 concentration similar to the

results obtained by Cristtenden et al. (17). Also according to Jung et al. (18) study on removal of amoxicillin by UV and UV/H₂O₂ processes, the degradation rate of amoxicillin fitted pseudo first-order kinetics, and the rates increased up to six fold with increasing H₂O₂ addition at 10 mM H₂O₂ compared to direct photolysis (UV only). A plot of K as a function of UV intensity I₀ for (H₂O₂)=500 mg/L (Figure 5) gives a straight line, which shows that when OH radicals efficiently are available, a maximum rate can be observed and K value increases with time. Similar results was showed in Mohey El-Dein et al. study for kinetic model of the azodye Reactive Black 5 by UV/H₂O₂ process (26). The success key of the study was high efficiently removal of the COD. So H₂O₂/UV advanced oxidation process operated in suitable condition mentioned is suggested as an effective method for the treatment of pharmaceutical effluent of Bakhtarbioshimi industry in Kermanshah, Iran.

Conclusion

Briefly, we conclude that advanced Oxidation Process (H₂O₂/UV) has high efficiency in the removal of organic matter from organic Materials from Pharmaceutical Industry Wastewater. For high concentration of H₂O₂ (500 mg/L) in pH 3 and 7, the maximum COD removal efficiency was 28.5% and 15.2% respectively, indicating significant roles of pH and H₂O₂ concentration in oxidation efficiency of H₂O₂/UV process in removing COD.

Footnotes

Acknowledgments:

The authors wish to gratefully acknowledge the Deputy and Research Center staff of Kermanshah University of medical sciences for financial assistance and the Environmental chemistry laboratory staff of the Public Health School, Kermanshah University

of medical sciences for providing necessary laboratory facilities.

Conflict of Interest:

The authors declared no conflict of interest.

References

1. Wei X, Wang Z, Fan F, Wang J, Wang S. Advanced treatment of a complex pharmaceutical wastewater by nanofiltration: Membrane foulant identification and cleaning. *Desalination* 2010;251(1-3):167-75.
2. Oktem YA, Ince O, Sallis P, Donnelly T, Ince BK. Anaerobic treatment of a chemical synthesis-based pharmaceutical wastewater in a hybrid up flow anaerobic sludge blanket reactor. *Bioresour Technol* 2008;99(5):1089-96.
3. Madukasi EI, Dai X, He C, Zhou J. Potentials of phototrophic bacteria in treating pharmaceutical wastewater. *Int J Environ Sci Technol* 2010;7(1):165-74.
4. Andreozzi R, Canterino M, Marotta R, Paxeus N. Antibiotic removal from wastewaters: The ozonation of amoxicillin. *J Hazard Mater* 2005;122(3):243-50.
5. Rosario-Ortiz FL, Wert EC, Snyder SA. Evaluation of UV/H₂O₂ treatment for the oxidation of pharmaceuticals in wastewater. *Water Res* 2010;44(5):1440-8.
6. Shreeshivadasan C, Thomas W, Paul S. Treatment of pharmaceutical wastewater containing tyrosine in an anaerobic-aerobic reactor system. *Water Practice Technol* 2010;5(1).
7. Clara M, Strenn B, Gans O, Martinez E, Kreuzinger N, Kroiss H. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Res* 2005;39(19):4797-807.
8. Chang CY, Chang JS, Vigneswaran S, Kandasamy J. Pharmaceutical wastewater treatment by membrane bioreactor process – a case study in southern Taiwan. *Desalination* 2008;234(1-3):393-401.
9. Babu BR, Venkatesan P, Kanimozhi R, Basha CA. Removal of pharmaceuticals from wastewater by electrochemical oxidation using cylindrical flow reactor and optimization of treatment conditions. *J Environ Sci Health A Tox Hazard Subst Environ Eng* 2009;44(10):985-94.
10. Serrano D, Suárez S, Lema J, Omil F. Removal of persistent pharmaceutical micro pollutants from sewage by addition of PAC in a sequential membrane bioreactor. *Water Res* 2011;45(16):5323-33.
11. Rosal R, Rodríguez A, Perdígón-Melón J, Mezcuca M, Hernando M, Letón P, et al. Removal of pharmaceuticals and kinetics of mineralization by O₃/

H₂O₂ in a bio treated municipal wastewater. *Water Res* 2008;42(14):3719-28.

12. Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ Int* 2009;35(2):402-17.

13. Melero JA, Martínez F, Botas JA, Molina R, Pariente MI. Heterogeneous catalytic wet peroxide oxidation systems for the treatment of an industrial pharmaceutical wastewater. *Water Res* 2009;43(16):4010-8.

14. Huber MM, Canonica S, Park GY, von Gunten U. Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. *Environ Sci Technol* 2003;37(5):1016-24.

15. Sun JH, Sun SP, Fan MH, Guo HQ, Qiao LP, Sun RX. A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process. *J Hazard Mater* 2007;148(1-2):172-7.

16. Kim I, Yamashita N, Tanaka H. Performance of UV and UV/H₂O₂ processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. *J Hazard Mater* 2009;166(2-3):1134-40.

17. Crittenden JC, Hu S, Hand DW, Green SA. A kinetic model for H₂O₂/UV process in a completely mixed batch reactor. *Water Res* 1999;33(10):2315-28.

18. Jung YJ, Kim WG, Yoon Y, Kang JW, Hong YM, Kim HW. Removal of amoxicillin by UV and UV/H₂O₂ processes. *Sci Total Environ* 2012;420(0):160-7.

19. Yuan F, Hu C, Hu X, Qu J, Yang M. Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H₂O₂. *Water Res* 2009;43(6):1766-74.

20. Glesteria LA GE, Eaton AD. Standard methods for the examination of water and wastewater. Washington DC: APHA; 2005.

21. Catalkaya EC, Kargi F. Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: A comparative study. *J Hazard Mater* 2007;139(2):244-53.

22. Pera-Titus M, García-Molina V, Baños MA, Giménez J, Esplugas S. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Appl Catal B: Environ* 2004;47(4):219-56.

23. Azbar N, Yonar T, Kestioglu K. Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere* 2004;55(1):35-43.

24. Pereira VJ, Linden KG, Weinberg HS. Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Res* 2007;41(19):4413-23.

25. Khan H, Ahmad N, Yasar A, Shahid R. Advanced oxidative decolonization of Red CI-5B: effects of dye concentration, process optimization and reaction kinetics. *Polish J Environ Stud* 2010;19(1):83-92.

26. El-DeinAM, Libra JA, Wiesmann U. Kinetics of decolonization and mineralization of the azo dye reactive black 5 by hydrogen peroxide and UV light. *Water Sie Technol* 2001;44(5):295-301.