ISSN: 0975-766X
CODEN: IJPTFI
Research Article

Available Online through
www.ijptonline.com

APPLICATION OF RESPONSE SURFACE METHODOLOGY ON CEFIXIME REMOVAL FROM AQUEOUS SOLUTION BY ULTRASONIC/ PHOTOOXIDATION

Ali Almasi[1], Abdollah Dargahi[2], Mitra Mohammadi[1*], Ali Azizi[3], Amir Karami[2], Fateme Baniamerian[4], Zahra saeidimoghadam[4]

[1]Department of Environmental Health Engineering, School of Health, Social Development and Health Promotion Research Center, Kermanshah University of Medical science, Kermanshah, Iran.

[2]PhD Student in Environmental Health Engineering, School of Health, Hamadan University of Medical Sciences, Hamadan, Iran.

[3]Social Medicine Specialist, Assistant Professor of Social Medicine, Faculty of Medicine, Kermanshah University of Medical Sciences, Kermanshah, Iran

[4]Department of environmental health engineering, public health school, Kermanshah university of Medical Sciences, Kermanshah, Iran.

Email: m.mohamadi725@gmail.com

Received on 02-08-2016 *Accepted on 28-08-2016*

Abstract

This study investigated the ultra-photooxidation of cefixime in aqueous solution using a WO_3/UV photocatalyst. Effect of contact time (50-100 min), cefixime initial concentration (40-80 mg/L) and WO_3 dose (100-200 mg/l) on antibiotic removal was surveyed. A pilot scale of Pyrex reactor with volume of 1 L was applied. Interactive effect of independent variable on cefixime removal was studied by response surface methodology. Based on obtained result, cefixime concentration in ultra - UV/WO_3 was the most effective in removal efficiency. In the sonolysis process the maximum and minimum COD removal rate reach to 21.2% and 10.15% respectively. The maximum removal in UV/WO_3 process reach to 83.3% by catalyst dose of 200 mg/L, contact time of 100 min and cefixime concentration of 40 mg/L. Photocatalytic process was as applicable technology which can be applied extensively and preferably for cefixime removal.

Key words: Photocatalistic, Cefixime, Sonication, Response Surface Methodology.

Introduction

Recently, Pharmaceutics drug presence in the environment considered as noticeably problem in the world. The harmful effects of antibiotic in the environment which release into soil, surface water, and biological resistance microorganism is undeniable issue (1-4). The annual antibiotic consumption in the world has been valued around between 100000-200000 tons. it can be deducted that in optimistic condition almost 30000 tons and in the worst condition, approximately 180000 tons of antibiotic entrance in the environment (5,6). Presence of antibiotic has been detected in surface water, groundwater, effluent and even in drinking water in value of nanogram/L to µg/L (7, 8). Chemical formula Cefexime is $C_{16}H_{15}N_5O_7S_2$.

Up to now, various physical, chemical and biological methods have been carried out for remediation antibiotics in aqueous solution (9, 10). In recent decades, advanced oxidation processes have been studied in order to reducing of antibiotic residue from aqueous solution (11-13). Generally, AOPs related to methods in which active hydroxyl radicals ($OH^{\bullet}$) generation, with a high oxidative potential that reacts and destruct organic pollutant. AOP_s processes are applicable and functional methods for removal of pharmaceutics drug wastewater (14).

The sonolytic system along catalyst usage, being able to oxidize the antibiotic and converted (15). Sonochemical processes caused by acoustic radiation with high intensity from liquids in frequencies that generated cavitation. Ultrasound radiation increases the chemical and physical change in the liquid environment through generation and consequently, the destruction in bubble cavitation (16). Up to now applying the integrated of sonolysis and Photocatalytic processes from aqueous solution for cifiximie was not studied. The general objective of this research was to determination the removal of cifiximie by combination of sonolysis and Photocatalytic processes from aqueous solution. The present study modeled and analyzed removal of cefixime from aqueous solution, in Photocatalytic aprocesses using RSM. The specific objectives were 1) to assess the effect of catalyst dose, contact time and cefixime concentration on photocatalytic degradation efficiency, 2) to identify COD, and 3) to assess the effect of ultrasonic radiation on photocatalytic efficiency.

Material and Method

- **Chemical**

The chemical and cifixime with 99% purity was purchased from Merc co, Germany. Synthetic solution were prepared with distilled deionizes water.

- **Collection of samples and Operation of Ultrasound and Photo catalytic processes**

All the experiment was carried out in batch flow. A pilot scale of Pyrex reactor with volume of 1 L was applied. The ultrasonic bath equipped by adjustable temperature and time was used. Different cifixime concentration was arranged which started to reactor of ultrasonic equipment (DSA 100-SK 2-4, 0) within temperature of 22˚C. Fixed frequency of 40 Hz and power of 100 watt was performed. In order to assess the system analysis, chemical oxygen demand (COD) sampling was collected from influent and effluent of ultrasound system. To the effluent of ultrasound reactor were added the different dose of WO_3 and placed in magnetic stirred with velocity of 350 rpm. Radiation source was a low pressure of mercury lamp with wave length of 254 nm (Philips, Germany Co) that had been adjusted in 5 cm of Pyrex reactor. All the experimental of catalytic photooxidation processes was carried out in environment temperature and according to standard method for water and wastewater examination (17).

- **Statistical analyses**

Central composite design (CCD) was used to study the three different factors: A: cefixime concentration (40-80 mg/l), B: dose of WO_3 (100-200 mg/l) and C: contact time (50-100 min). The variables were considered at three levels, 1 (minimum), 0 (central) and 1 (maximum) which assessed based on the full face-centered CCD experimental plan. Totally 20 runs were performed and 5 runs repeated was conducted due to prove the accuracy of experimental runs that in table.1 were neglected. Fitting the quadratic polynomial regression model has been derived based on resulted data of RSM method. The obtained results through CCD were surveyed by the analysis of variance (ANOVA).

Table-1: Experimental range and levels of the independent variables.

Run	Antibiotic concentration (mg/L)	time (min)	WO_3 (mg/L)	COD removal (%)
1	60	50	150	62.4
2	40	100	200	83.3
3	60	75	150	67.2
4	60	75	100	55.4
5	80	100	200	61.8
6	80	100	100	45.3
7	40	50	100	61.3
8	40	100	100	63.5
9	80	50	100	43.5
10	60	100	150	68.4
11	60	75	200	73.2
12	40	75	150	71.6
13	40	50	200	78.1
14	80	50	200	62.2
15	80	75	150	51.8

Result

- **Statically analysis**

Based on obtained result, antibiotic concentration in UV/WO_3 was the most operative factors. Contact time was the less effective in photooxidation process. By increasing cefixime concentration, the removal efficiency decreased and increment of contact time and dose of catalyst led to increasing of COD removal. Fitting model has been verified according to predicted model via correlation coefficient, R^2, Adjusted R^2 and Pred R^2 between the experimental and model predicted values (Table 2). The great amount of R^2 and Adjusted R^2 exhibition statiscally significant of model. In UV/WO_3 process, the Pred R^2 and adjusted R^2 are nearby to 1 and exactly are, 0.91 and 0.89, respectively. The validity and reliability of analysis has represented by adequate precious and it should be 4 value or more (18). Adequate precious of this result are 25.89 that it is remarkably over than 4 values.

Table-2.The ANOVA result for the equation of the design expert software.

Processes	Modified equation with significant	Type of Model	Adeq. precision	R^2	Adjusted R^2	Predicted R^2	SD	CV	P-value
UV/WO_3	Y= +63.87 – 9.5A+9.14B +1.3C	linear	25.89	0.902	0.91	0.89	3.44	4.39	0.000

- **Ultrasonic process (sonolysis)**

The maximum COD removal was achieved in 40 mg/L of cefixime concentration, and the removal reduced by increasing the antibiotic concentration with regard to statically significant difference ($p<0.05$). In overall the removal in sonolysis process was not effective considerably, and the maximum and minimum COD removal rate reaches to to 21.2% and 10.15%, respectively. Base on obtained result the maximum and minimum COD removal rate were in 40 mg/L and 80 mg/L on cifixime concentration, respectively.

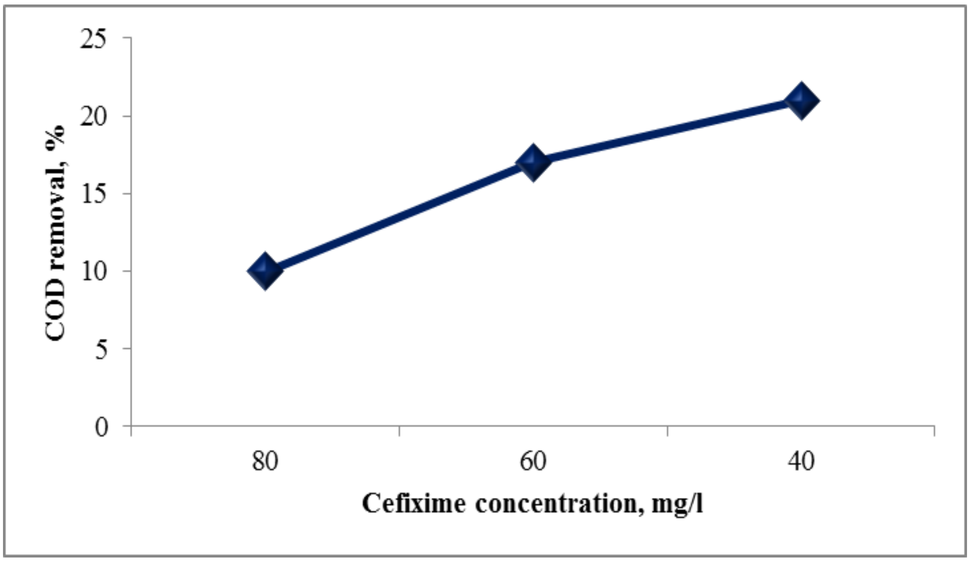

Figure-1.The influent and effluent COD Concentration in Ultrasound process.

Photocatalytic process

- **Effect of contact time on the cifixime Removal**

After being passed the ultrasonic process then its effluent COD was used as influent COD for this unit, the removal of cefixime has been analyzed in all stages of experiment. By increasing contact time from 50 to 100 min, increment of COD removal was revealed. It was apparent the optimal COD removal was at the first 50 min and subsequently the slight increment of removal rate was taken place.

- **Effect of initial cefixime concentration and of WO3 dose on the removal efficiency**

Through considering the effect of cefixime concentration on the process performance, the highest removal was accomplished in 40 mg/L of antibiotics concentration. For instance in the initial concentration of cefixime of 40 mg/L and contact time of 100 min, the removal reach to 83.3%. By explore the catalyst dose on COD removal, it was also observed by increasing catalyst concentration, the system performance increased.

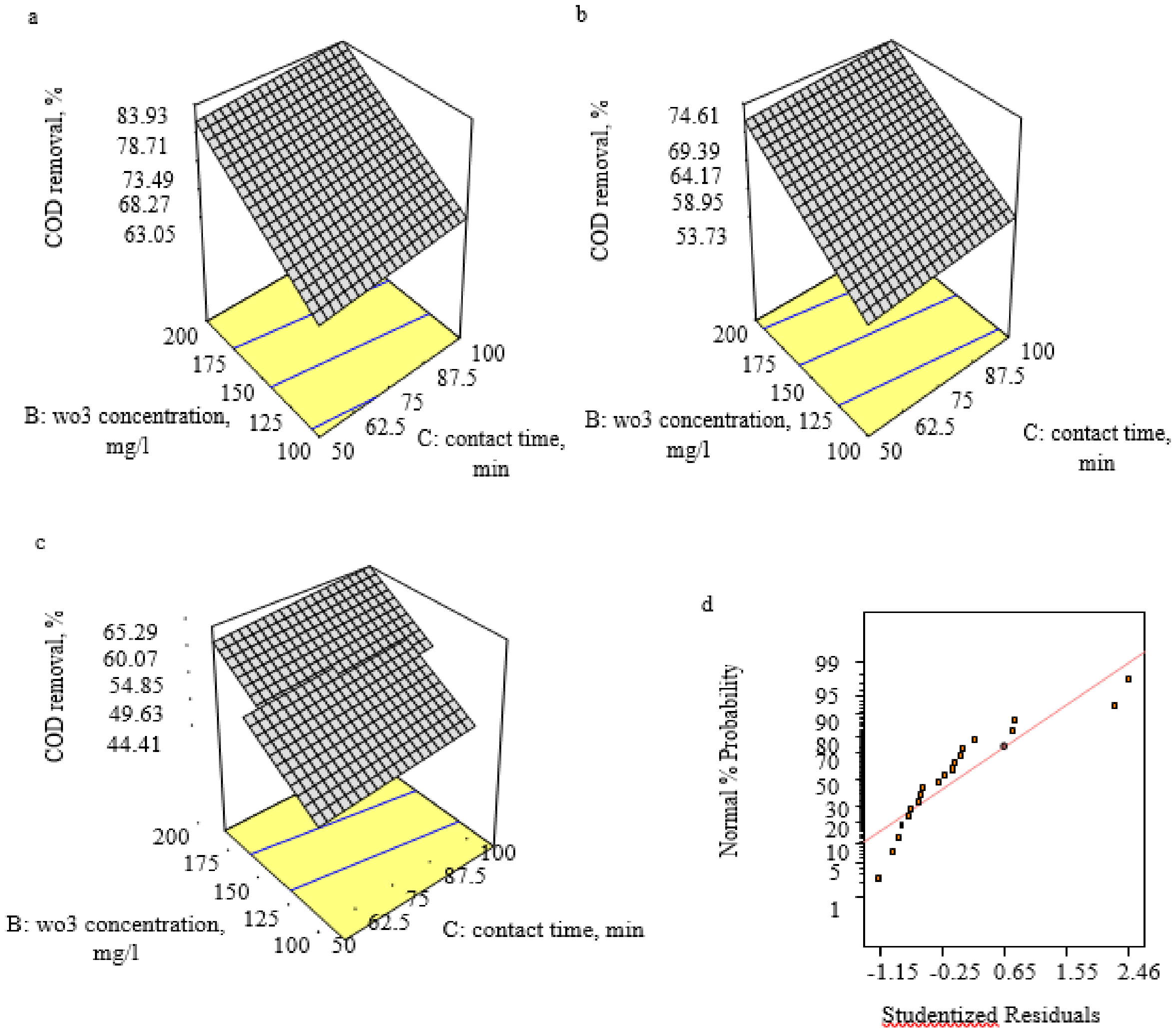

Figure-2: Response surface plot for COD Removal of cefixime with UV/WO_3 in cefixime concentration of (a) 40 mg/l (b) 60 mg/l (c) 80 mg/l (d) Normal Plot of Residuals for COD removal.

Discussion

It was revealed that by increasing dose of catalyst, the removal efficiency increased. There was a significant difference of catalyst dose on the process performance ($p < 0.05$). It was found that COD analysis within 40 mg/L of cefixime concentration, catalyst dose of 200 mg/l and contact time of 100 min, the prosperous mineralization has been occurred. Generally it can be concluded, Photocatalytic degradation was appropriate for antibiotic removal in low concentration, nevertheless in high concentration due to high level of catalyst which pose to increasing economical point of view. Generally by employing individual sonolysis is the drastic removal were not reflected, that it may be assigned to low amount of hydroxyl radical ($OH^{\bullet}$) generation in the presence of ultrasonic processes (19, 20).

- **Effect of initial cefixime concentration**

Base on result, by reducing initial concentration of cefixime the of degradation rate increased. This reason can be explained in same condition the catalyst dose and contact time in aqueous solution were equal, therefore antibiotic reaction with $OH^{\bullet}$ in low concentration was more, and that has led to increasing the degradation through free radical (21). Due to the equal concentration of hydroxyl radical that generated in entirely aqueous solution, so low antibiotic concentration solution with the same hydroxyl radical, increased conversion in comparison to high antibiotic concentration. In high concentration of cefixime, the great number of photons absorbed, and in conclusion , the available photon for catalyst activation reduced, thus in low concentration the excess of converted were be higher at a time (22).

- **Effect of contact time**

By increasing contact time, COD removal rate increased, this high performance by increasing contact time which due to the exited WO_3 particles increasing, thus by hole creation in catalyst surface and as a result, the absorption surface area and also removal rate increased as well (23). Nonetheless in the first 50 min of reaction, the optimum removal was observed, and by further increment of contact time, the increasing trend of COD removal reduced. It can be reasoned to fast degradation in the first 50 min of reaction through free radical due to electron excitation of catalyst particles.

- **Effect of catalyst dose**

By increasing the WO_3 particles, the COD removal was higher, that is due to increment the number of absorbed photon, and so in conclusion the available active site increased and also increasing of antibiotic molecules absorption as well (24-26). In high catalyst dose, most of initial active site may be inactive through collision on the surface of catalyst particles. Generally the slight increase of catalyst dose caused the reduced reaction time of Photo catalytic processes, thus the catalyst dose should be equilibrated because of two opposite impact of removal rate increment, owing to increment of available site and the removal rate reducing due to turbidity increment of catalyst dose and thus as a result the decreasing of UV light.

Conclusion

UV/WO_3 process was confirmed as an appropriate and satisfactory technology with regard to considerably reduce of cefixime from aqueous solution. The advantages of process are high efficiency, lack of sludge generation and simple operation. The maximum COD removal in UV/WO_3 process reach to 83.3% by under condition, WO3 dose of 200 mg/L, contact time of 100 min and cefixime concentration of 40 mg/L. Finally, it can be deducted, sono-photochemical processes effect, direct photolysis by UV radiation, acoustic cavitation and hydroxyl radicals for antibiotic destruction accompanied processes and pretreatment were identified for high COD removal. The result of this work has been revealed, sonolysis and Photocatalytic processes has led to proper removal of cefixime.

Authors' contributions

All authors contributed to this project and article equally. All authors read and approved the final manuscript.

References:

1. Martinez JL. Environmental pollution by antibiotics and by antibiotic resistance determinants. Environmental Pollution. 2009; 157(11): 2893–902.
2. Pirsaheb M, Mohamadi M, Mansouri AM, Zinatizadeh AA, Sumathi S, Sharafi K. Process modeling and optimization of biological removal of carbon, nitrogen and phosphorus from hospital wastewater in a continuous feeding &intermittent discharge (CFID) bioreactor. Korean Journal of Chemical Engineering. 2015;32(7):1340-53..
3. Arfaeinia1H, Sharafi K, Banafshehafshan S, Hashemi S E. Degradation and biodegradability enhancement of chloramphenicol and azithromycin in aqueous solution using heterogeneous catalytic ozonation in the presence of MGO nanocrystalin comparison with single ozonation. International Journal Of Pharmacy & Technology. 2016; 8(1): 10931-10948.
4. Arfaeinia H, Ramavandi B, Sharafi K, Hashemi S E. Reductive Degradation Of Ciprofloxacin In Aqueous Using Nanoscale Zero Valent Iron Modificated By Mg-Aminoclay. International Journal Of Pharmacy & Technology. 2016; 8(2): 13125-13136.

5. Elmolla S, Chadhuri M. Comparison of different advanced oxidation processes for treatment antibiotic aqueous solution. Desalination. 2010; 256: 43-7.
6. Seungmin, Sanghyun C, Seban L, Seungkwan H, Jeehyeong .Addition of sonochemical reactor to the solar photocatalytic compound parabolic concentrators system. Japanese Journal of Applied physics. 2011; 50: 7-14.
7. Peerayeh SN, Karmostaji A, Sarasiabi SS, Javadpour S, Davoodian P, Moradi N. In Vitro Activity of Tigecycline and Colistin against clinical isolates of Acinetobacter baumannii in Hospitals in Tehran and Bandar-Abbas, Iran. Electronic Physician. 2014; 6(3): 919-24.
8. 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). Archive Hygiene Sciences 2016;5(2): 69-74.
9. Sharif MR, Soltani B, Moravveji A, Erami M, Soltani N. Prevalence and Risk Factors associated with Extended Spectrum Beta Lactamase Producing Escherichia coli and Klebsiella pneumoniae Isolates in Hospitalized Patients in Kashan (Iran). Electronic Physician. 2016; 8(3): 2081-7.
10. Saghafinia MS, Emadian SM, Vossoughi M. Performances Evaluation of Photo-Fenton Process and Sonolysis for the Treatment of Penicillin G FormulationEffluent. Procedia Environmental Sciences. 2011; 8: 202 –8.
11. Puckowski A, Mioduszewska K, Łukaszewicz P, Borecka M, Caban M, Maszkowska J, Stepnowski P. Bioaccumulation and analytics of pharmaceutical residues in the environment: A review. Pharmaceutical and Biomedical Analysis. 2016; 16 (3): In Press, Corrected Proof.
12. Taghavi SM, Momenpour M, Azarian M, Ahmadian M, Souri F, Taghavi SA, et al. Effects of Nanoparticles on the Environment and Outdoor Workplaces. Electronic Physician, 2013; 5(4): 706-12,
13. Dobaradaran S, Nabizadeh R, Mahvi AH, Mesdaghinia AR, Naddafi K, Yunesian, et al. Survey on degradation rates of trichloroethylene in aqueous solutions by ultrasound. Iranian Journal of Environmental Health Science & Engineering. 2010; 4: 307-12.
14. Yuan F, Hu C, Hu X, Qu J, Yang M. Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H2O2. Water Research. 2009; 43: 1766-74.
15. Michael I, Rizzo L, McArdell CS, Manaia CM, Merlin C, Schwartz T, et al. Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review. Water Research. 2013; 47: 957-95.

16. MullaiP, Vishali S. Biodegradation of penicillin-G wastewater using Phanerochate chrysosporium – An equilibrium andkinetic modeling. African Journal of Biotechnology. 2007; 6 (12): 1450- 4.
17. Sioi M, Bolosis A, Kostopoulou E, Poulios I. Photocatalytic treatment of colored wastewater from medical laboratories: photocatalytic oxidation of hematoxylin. Photochemistry and Photobiology A: Chemistry. 2006; 184(1): 18-25.
18. APHA (2008), Standard method for the examination of water and wastewater, 19th ed. American Public Health Association, Washington, D.C.
19. M. Pirsaheb, M. Mohamadi, Amir Mohammad Mansouri, A. A. L. Zinatizadeh, S. Sumathi, K. Sharafi. Process modeling and optimization of biological removal of carbon, nitrogen and phosphorus from hospital wastewater in a continuous feeding & intermittent discharge (CFID) bioreactor. Korean Journal of Chemical Engineering. 2015, 32(7): 1340-1353.
20. Homem V, Santos L. Degradation and removal methods of antibiotics from aqueous matrices–A review. Journal of environmental management. 2011; 10: 2304- 47.
21. Verma A, Kaur H, Dixit D. Photocatalytic, Sonolytic and sonophotocatalytic degradation of 4-Chloro-2-nitro phenol. Archive of environmental protection. 2013; 39 (2): 17-28.
22. Dargahi A, Pirsaheb M , Hazrati S, Fazlzadehdavil M, Khamutian R, Amirian T. Evaluating efficiency of H2O2 on removal of organic matter from drinking water, Desalination and Water Treatment, 2015, 54 (6): 1589-1593
23. Konstantina T, Elpida, P. Modeling of arsenic immobilization by zero valent iron. Soil Biology. 2007; 43: 356-67.
24. Kashif N, Ouyang F. Parameters effect on heterogeneous photocatalysed degradation of phenol inaqueous dispersion of TiO2. Environmental Sciences. 2009; 21(4): 527-533.
25. Kümmerer K. Antibiotics in the aquatic environment – A review – Part I. Chemosphere. 2009; 75(4):417- 34.
26. Daneshvar N, Rasoulifard M H, Khataee A R, Hosseinzadeh F. Removal of C.I. Acid Orange 7 from aqueous solution by UV irradiation in the presence of ZnO Nano powder. Water and Wastewater Treatment. 2006; 95-101.

Corresponding Author:
Mitra Mohammadi*,
Email: *m.mohamadi725@gmail.com*