RESEARCH ARTICLE
• Arch Hyg Sci 2018;7(4): 288-294
• Journal Homepage: http://jhygiene.muq.ac.ir

# Photocatalytic Degradation of Ciprofloxacin Pharmacy Pollutant in Batch Photoreactor

**Reza Moradi[a*], Amin Ganjali[b], Ahmad Reza Yari[c], Mohamad Hassan Mahmoudian[c]**

[a]Young Researchers and Elite Club, Arak Branch, Islamic Azad University, Arak, Iran.
[b]Department of Experimental Science, Kahnooj Branch, Islamic Azad University, Kahnooj, Iran.
[c]Research Center for Environmental Pollutants, Qom University of Medical Sciences, Qom, Iran.

***Correspondence** should be addressed to Dr Reza Moradi, **Email:** reza.moradi_bi@yahoo.com

**A-R-T-I-C-L-EI-N-F-O**

**Article Notes:**
Received: June 5, 2018
Received in revised form: Dec 22, 2018
Accepted: Dec 27, 2018
Available Online: Dec 29, 2018

**Keywords:**
Photo-Fenton process,
Ciprofloxacin,
Pollutant,
Photocatalytic,
Batch reactor,
Iran.

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

**Background & Aims of the Study:** Pharmaceutical compounds have a variety of forms and applications. Specific amounts of toxic organic compounds in the process of their manufacturing and utilization cause environmental pollution problems. So, degradation and removal these compounds are necessary. The aim of this paper is the study photocatalytic degradation of ciprofloxacin drug in aqueous solution using photo-Fenton process in a batch photoreactor.

**Materials and methods:** This is an experimental study on a laboratory scale. $Fe^{2+}$ ions as a homogeneous catalyst applied for the degradation of ciprofloxacin in aqueous solution. The study was performed on synthetic wastewaters that contain ciprofloxacin as a pollutant. The effect of operational parameters such as pH, $Fe^{2+}$ concentration and $H_2O_2$ concentration on reaction kinetics were studied and the optimum conditions were determined for the photocatalytic degradation of ciprofloxacin using one factor at the time (OFAT) experimental design method.

**Results:** The optimal conditions were obtained at pH =3, $Fe^{2+}$ concentration at 35 ppm and $H_2O_2$ concentration at 25 ppm. A first order reaction with rate constant (k=0.0291 $min^{-1}$) was observed for the photocatalytic degradation reaction. The chemical oxygen demand (COD) analysis of the ciprofloxacin under optimum conditions showed 92% reduction COD in a 49 min period.

**Conclusions:** The results showed that the photo-Fenton process can be a suitable alternative method to degradation of pharmaceutical compounds from synthesis wastewaters.

**Please cite this article as**: Moradi R, Ganjali A, Yari AR, Mahmoudian MH. Photocatalytic Degradation of Ciprofloxacin Pharmacy Pollutant in Batch Photoreactor. Arch Hyg Sci 2018;7(4):288-294

## Background

The medicinal chemistry is rooted of all branches of chemistry and biology sciences. Ciprofloxacin is an antibiotic used to treat a number of bacterial infections such as bone and joint infections, intra-abdominal infections, certain type of infectious diarrhea, respiratory tract infections, skin infections, typhoid fever and urinary tract infections.

Environmental pollution is one of the important problems in human health. In recent years, due to the excessive use of drugs, it can be concluded that pharmaceutical substances are present in aquatic environments (1). These compounds are often excreted via urine or feces since they are not metabolized, entering the wastewaters and eventually reaching groundwaters, if they are not degraded or removed during the wastewater treatment process (2, 3). Pharmaceuticals and personal care products (PPCPs) have gained increasing environmental attention due to their incomplete removal by conventional wastewater treatment plants (WWTPs) (4-7). The presence of fluorine atom in the antibiotic composition of ciprofloxacin has been stabilized and therefore is considered as a pollutant in the environment.

In among water pollutants, pharmacy wastewater pollutants such as ciprofloxacin (8, 9) under the photocatalytic degradation process to produce less harmful products indicates some potential for photocatalytic treatments of wastewater using catalyst and UV light. Among different techniques for the removal or degradation of medicines in water, the traditional processes, such as adsorption (10, 11) electrocoagulation–electrooxidation (12) ozonation (13, 14) $H_2O_2$ oxidation, photo-oxidation (15) and combination of several techniques have been applied (16). Advanced oxidation processes (AOPs) offer a highly reactive, nonspecific oxidant namely hydroxyl radical ($OH^•$), that oxidize a broad range of pollutants quickly and non-selective in water and wastewater. In the oxidation process, a wide range of organic compounds will be converted into harmless compounds such as $CO_2$, $H_2O$, and inorganic acids. The Fenton's reagent is one of the most popular AOPs and it is an economic, simple and effective treatment process to oxidize recalcitrant organic compounds. The photo-Fenton process consists of a combination of the Fenton reagent ($Fe^{2+}/H_2O_2$) and UV light. The mechanism of the photo-Fenton reaction is usually described by the following (Eqs.1-5) (17-19):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^• \quad (1)$$

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

$$Fe^{3+} + H_2O + h\upsilon \rightarrow Fe^{2+} + OH^• + H^+ \quad (3)$$

$$H_2O_2 + h\upsilon \rightarrow 2OH^• \quad (4)$$

$$OH^• + pharmaceutical\ compounds \rightarrow Oxidized\ products \quad (5)$$

In the presence of UV light, the degradation rate of the photo-Fenton reaction was increased by the $Fe^{3+}$ photo-reduction (Eq. (3)) that generates new hydroxyl radical and regenerates $Fe^{2+}$ ions, and $Fe^{2+}$ ions can further react with $H_2O_2$ (20). As can be seen in Eq. (4), photolysis of $H_2O_2$ can produce hydroxyl radical directly. So the catalytic activity of photo-Fenton process can be enhanced by the synergistic effects.

**Aims of the study:**

In this study, photocatalytic degradation of ciprofloxacin in aqueous solution using photo-Fenton process was employed to enhance the degradation rate of ciprofloxacin. The reaction kinetics of ciprofloxacin was studied. The effects of an operational parameter such as pH, $Fe^{2+}$ concentration and $H_2O_2$ concentration on the process were studied and optimized by one factor at the time the experiment design.

## Materials & Methods

### Materials

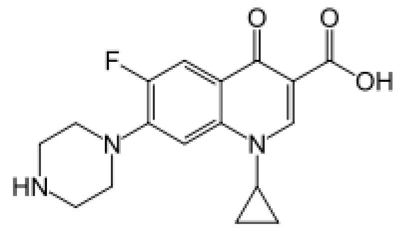
Ciprofloxacin was obtained from Farabi Pharmaceutical Company (Iran). The structure and characteristics of ciprofloxacin are shown in Table 1.

The pH values were adjusted at the desired level using dilute NaOH and $H_2SO_4$. Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) as the source of $Fe^{2+}$, $H_2O_2$ (30% w/w) were all Merck products (Germany). Double distilled water was used for the preparation of solutions.

### Apparatus

Fig. 1 shows the schematic diagram of Batch photoreactor which was used for photocatalytic decomposition of ciprofloxacin. In this equipment, a basin with 1 L capacity with a mercury lamp Philips 15W (UV-C) was used in photoreactor. The residual ciprofloxacin was measured using UV/Vis Spectrophotometer, Jenway (6505). For the COD measurement, COD meter analyzer model AL250 AQUALYTIC was used. pH values were measured with Horiba M12 pH meter.

**Table 1) The structure and characteristics of ciprofloxacin.**

| Name | Formula | Structure | $\lambda_{max}$ (nm) | MW (g/mol) |
|---|---|---|---|---|
| Ciprofloxacin | $C_{17}H_{18}FN_3O_3$ |  | 275 | 331.346 |

## Procedures

For the photodegradation, 35 ppm ciprofloxacin solutions were prepared as initial concentration. The suspension pH values were adjusted at the desired level using dilute NaOH 0.1N and $H_2SO_4$ 0.1N. Then, hydrogen peroxide and iron ion were added to the solution. The prepared suspension was transferred to reaction flask (Pyrex). The degradation reaction took place under the radiation of a mercury lamp at the top of reaction flask. The concentration of the samples was determined (at 7 min intervals) using a Spectrophotometer (UV-Vis Spectrophotometer, Jenway (6505)) at $\lambda_{max}$=275 nm. The degree of photodegradation (X) as a function of time is given by (Eq.6):

$$X = \frac{C_{\circ} - C}{C_{\circ}} \quad , \qquad (6)$$

where $C_0$ and C are the concentration of ciprofloxacin at t=0 and t, respectively.

# Results

## The effects of pH

pH is one of the main factors that can affect the degradation of organic compounds in the photocatalytic process. The effect of pH in degradation rate was studied from pH 3 to 11. The results of pH using photo-Fenton process are shown in Fig. 2. The degradation of ciprofloxacin decreases with increasing pH. It can be seen that the best results obtained in acidic solution, (pH=3).

## The effect of $Fe^{2+}$ concentration

The concentration of $Fe^{2+}$ is one of the main parameters that influence the photo-Fenton process. At this stage, the effect of different concentration of $Fe^{2+}$ between 20 to 40 ppm to obtaining optimum concentration was tested. The results are shown in Fig. 3. So, maximum $Fe^{2+}$ concentration=35 ppm was obtained.

## The effect of $H_2O_2$ concentration

Fig. 4 shows the relationship between the degradation rate of ciprofloxacin and $H_2O_2$ concentration for the photo-Fenton process. The effect of $H_2O_2$ concentration on the degradation of ciprofloxacin was performed at a range of 5-25 ppm. The degradation rate increases with an increase of $H_2O_2$ concentration.

## Reaction kinetics study

Photocatalytic degradation reaction kinetics of ciprofloxacin completely correspond the kinetic of pseudo-first-order reaction model reaction (9,21). In the kinetic equation of first order relationship between [*ciprofloxacin*] and time (t) is in (Eq.7):

$$ciprofloxacin \xrightarrow{k} product$$

$$[ciprofloxacin] = [A]$$

$$\frac{-d[A]}{dt} = k[A], \qquad (7)$$

The integral Eq.7 is in Eq.8:

$$\frac{-d[A]}{dt}=k[A]\rightarrow\frac{d[A]}{[A]}=-kdt\rightarrow\int_{[A]_0}^{[A]}\frac{d[A]}{[A]}=$$

$$K\int_0^t dt\Rightarrow\ln[A]-\ln[A]_0=-kt\Rightarrow\ln\frac{[A]_0}{[A]}=kt. \qquad (8)$$

In which that k is the apparent first order rate constant (that is affected by [*A*]) and t the reaction time.

A plot of $\ln\left(\frac{[A]_0}{[A]}\right)$ versus *t* for optimum condition of photocatalytic degradation of ciprofloxacin is shown in Fig. 5. The linear plot suggests that the photodegradation reaction approximately follows the pseudo first order kinetics with a rate constant k=0.0291 $min^{-1}$.

**Photocatalytic mineralization of ciprofloxacin**

The COD test is commonly used to indirectly measure the amount of ciprofloxacin in synthesized solution as organic matter. In this paper, the COD test was used to confirm that the organic pollutants are decomposed and are converted into the minerals matter. The results of these experiments are shown in Fig. 6. The degradation of ciprofloxacin under optimal operational conditions and the removal 92% from organic pollutant have been performed in 49 min period. These results can be confirmed by the decomposition of organic matter that was present in the drug sewage sample. The COD removal efficiency (%) has been calculated by (Eq.9):

$$COD \text{ removal efficiency (\%)} = \frac{COD_0 - COD}{COD_0}\times 100, \qquad (9)$$

where $COD_0$ and COD are COD values at *t*=0 and t, respectively.

In Table 2, the amount of COD removal efficiency (%) obtained from the ciprofloxacin solution is shown in various times.

**Table 2) The COD removal efficiency (%) of ciprofloxacin**

| time (min) | 0 | 7 | 14 | 21 | 28 | 35 | 42 | 49 |
|---|---|---|---|---|---|---|---|---|
| COD removal efficiency (%) | 0 | 20 | 39 | 57 | 68 | 76 | 89 | 92 |

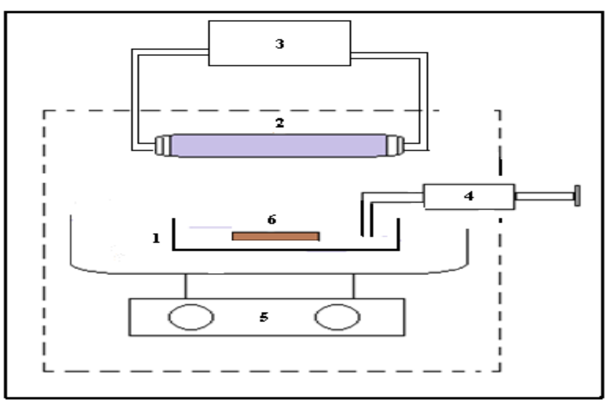



**Figure 1) Schematic diagram of Batch photoreactor 1) reaction flask (Pyrex), 2) UV lamp, 3) power supply, 4) sampling , 5) heater stirrer, 6) magnet.**

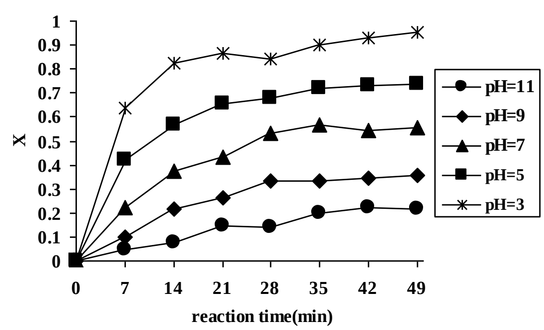



**Figure 2) Effect of pH in degradation of ciprofloxacin ($Fe^{2+}$ concentration=35 ppm, $H_2O_2$ concentration=25 ppm, drug concentration= 35 ppm, irradiation time=49 min).**

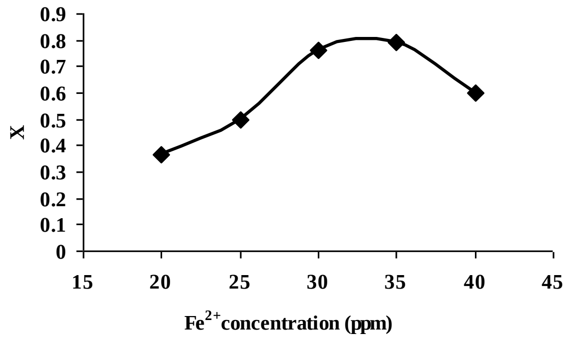



**Figure 3) Effect of $Fe^{2+}$ concentration in degradation of ciprofloxacin (pH=3, $H_2O_2$ concentration=25 ppm, drug concentration= 35 ppm, irradiation time=49 min).**

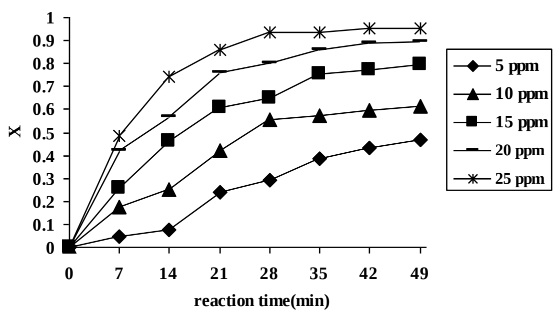



**Figure 4) Effect of $H_2O_2$ concentration in degradation of ciprofloxacin (pH=3, $Fe^{2+}$ concentration=35 ppm, drug concentration= 35 ppm, irradiation time=49 min).**

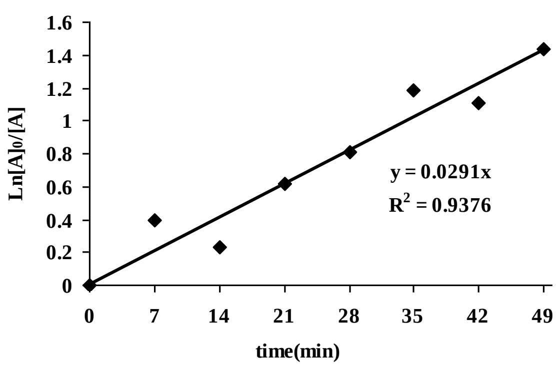



**Figure 5) Kinetic for degradation of ciprofloxacin in photo-Fenton process (pH=3, $Fe^{2+}$ concentration=35 ppm, $H_2O_2$ concentration=25 ppm, drug concentration=35 ppm, irradiation time=49 min).**

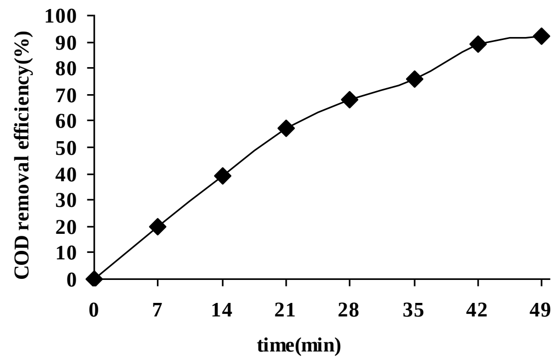



**Figure 6) COD removal efficiency of ciprofloxacin (pH=3, $Fe^{2+}$ concentration=35 ppm, $H_2O_2$ concentration=25 ppm, drug concentration= 35 ppm, irradiation time=49 min).**

## Discussion

In this paper, degradation of ciprofloxacin as drug sewage is used in the batch photoreactor. In this process, the effect of operational parameters such as $Fe^{2+}$ and $H_2O_2$ concentration and pH, was studied. pH is the most effective factor in this process. The photo-Fenton reactions are strongly pH dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency. pH changes on photo-Fenton process performance are shown in Fig. 2. The degradation rate in acidic condition is higher than that in alkaline condition. There is also the photocatalytic degradation of ciprofloxacin in acidic solutions, which is due to the formation of hydroxyl radical as it can be inferred from $H_2O_2$ oxidation. In higher pH iron ions the sludge is exited from the reaction. At pH above 3, the degradation rate of ciprofloxacin decreased because the $Fe^{3+}$ starts to precipitate as Fe $(OH)_3$ and cause the decomposition of $H_2O_2$ into $O_2$ and $H_2O$. Also complexes formation $Fe^{2+}$ in higher pH reduced its concentration in the reaction and thus of reproduction $Fe^{2+}$ is prevented according to the Eq. 2 (22-24).

The results of $Fe^{2+}$ ion concentration is shown in Fig. 3. From results, it can be seen that the degradation rate of ciprofloxacin increased with increasing the $Fe^{2+}$ concentration to 35 ppm according to the Eq.1. Addition concentration of $Fe^{2+}$ above 35 ppm in the process decreases the degradation rate. Because hydroxyl radical was consumed by the side reaction according to the Eq.10, the degradation rate is decreased (25).

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \qquad (10)$$

Fig. 4 showed the effect of $H_2O_2$ concentration from 5 to 25 ppm. The degradation rate will increase with increasing $H_2O_2$ concentration. Because hydroxyl radical will be produced by some reactions as shown in Eqs.1,3,4 (26).

The mineralization of ciprofloxacin was monitored by the COD during the process. The COD analysis is showing that the organic pollutant was decomposed and converted into minerals such as intermediates, $CO_2$, $H_2O$, and inorganic compounds.

## Conclusion

In this study, photocatalytic degradation of ciprofloxacin was investigated by the photo-Fenton process ($UV/Fe^{2+}/H_2O_2$). The results demonstrated that the photo-Fenton process was a powerful method for degradation of ciprofloxacin. Various factors are affecting the degradation process such as pH, initial concentration $Fe^{2+}$ and $H_2O_2$ concentration were analyzed and optimized. The results show that pH, $Fe^{2+}$ and $H_2O_2$ concentration at 3, 35 ppm and 25 ppm was optimum conditions for this reaction recpectively. Kinetics of photocatalytic decomposition reaction was determined. Pseudo-first-order model reaction with a rate constant ($k=0.0291\ min^{-1}$, $R^2=0.9376$) has corresponded to the experimental data of photocatalytic degradation of ciprofloxacin. The COD analysis of the ciprofloxacin under optimum conditions showed 92% reduction COD in a 49 min period. The results of COD experiments indicated that ciprofloxacin was mineralised completely after 49 min of the process.

## Footnotes

**Conflict of Interest:**

The authors declared no conflict of interest.

## References

1. Elmolla ES, Chaudhuri M. Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process. Journal of hazardous materials. 2010;173(1-3):445-9. Link

2. Ikehata K, Jodeiri Naghashkar N, Gamal El-Din M. Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: a review. Ozone: Science and Engineering. 2006;28(6):353-414. Link

3. Hojat Ansari S, Giahi M. Photochemical Degradation of Fluocinolone Acetonidin Drug in Aqueous Solutions Using Nanophotocatalyst ZnO Doped by C, N, and S. Iranian Journal of Chemistry and Chemical Engineering (IJCCE). 2017;36(3):183-9. Link

4. Carballa M, Omil F, Lema JM. Comparison of predicted and measured concentrations of selected pharmaceuticals, fragrances and hormones in Spanish sewage. Chemosphere. 2008;72(8):1118-23. Link

5. Halling-Sørensen B, Nielsen SN, Lanzky P, Ingerslev F, Lützhøft HH, Jørgensen S. Occurrence, fate and effects of pharmaceutical substances in the environment-A review. Chemosphere. 1998;36(2):357-93. Link

6. Joss A, Andersen H, Ternes T, Richle PR, Siegrist H. Removal of estrogens in municipal wastewater treatment under aerobic and anaerobic conditions: consequences for plant optimization. Environmental science & technology. 2004;38(11):3047-55. Link

7. Lai WW-P, Lin HH-H, Lin AY-C. $TiO_2$ photocatalytic degradation and transformation of oxazaphosphorine drugs in an aqueous environment. Journal of hazardous materials. 2015;287:133-41. Link

8. Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999− 2000: A national reconnaissance. Environmental science & technology. 2002;36(6):1202-11. Link

9. El-Kemary M, El-Shamy H, El-Mehasseb I. Photocatalytic degradation of ciprofloxacin drug in water using ZnO nanoparticles. Journal of Luminescence. 2010;130(12):2327-31. Link

10. Peng H, Pan B, Wu M, Liu Y, Zhang D, Xing B. Adsorption of ofloxacin and norfloxacin on carbon nanotubes: hydrophobicity-and structure-controlled

process. Journal of hazardous materials. 2012;233:89-96. Link
11. El-Shafey E-SI, Al-Lawati H, Al-Sumri AS. Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date palm leaflets. J Environ Sci. 2012;24(9):1579-86. Link
12. Linares-Hernández I, Barrera-Díaz C, Bilyeu B, Juárez-GarcíaRojas P, Campos-Medina E. A combined electrocoagulation–electrooxidation treatment for industrial wastewater. Journal of hazardous materials. 2010;175(1-3):688-94. Link
13. Garoma T, Umamaheshwar SK, Mumper A. Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation. Chemosphere. 2010;79(8):814-20.
14. Nawrocki J, Kasprzyk-Hordern B. The efficiency and mechanisms of catalytic ozonation. Applied Catalysis B: Environmental. 2010;99(1-2):27-42. Link
15. Chatzitakis A, Berberidou C, Paspaltsis I, Kyriakou G, Sklaviadis T, Poulios I. Photocatalytic degradation and drug activity reduction of chloramphenicol. Water Research. 2008;42(1-2):386-94. Link
16. Lin AY-C, Lin C-F, Chiou J-M, Hong PA. $O_3$ and $O_3/H_2O_2$ treatment of sulfonamide and macrolide antibiotics in wastewater. Journal of hazardous materials. 2009;171(1-3):452-8. Link
17. Nazari S, Yari AR, Mahmodian MH, Tanhaye Reshvanloo M, Alizadeh Matboo S, Majidi G, et al. Application of $H_2O_2$ and $H_2O_2$/Fe0 in removal of Acid Red 18 dye from aqueous solutions. Archives of Hygiene Sciences. 2013;2(3):104-10. Link
18. Gonzalez-Olmos R, Martin MJ, Georgi A, Kopinke F-D, Oller I, Malato S. Fe-zeolites as heterogeneous catalysts in solar Fenton-like reactions at neutral pH. Applied Catalysis B: Environmental. 2012;125:51-8. Link
19. Yu L, Chen J, Liang Z, Xu W, Chen L, Ye D. Degradation of phenol using $Fe_3O_4$-GO nanocomposite as a heterogeneous photo-Fenton catalyst. Separation and Purification Technology. 2016;171:80-7. Link
20. Pérez-Moya M, Graells M, Castells G, Amigó J, Ortega E, Buhigas G, et al. Characterization of the degradation performance of the sulfamethazine antibiotic by photo-Fenton process. Water Research. 2010;44(8):2533-40. Link
21. Babić S, Zrnčić M, Ljubas D, Ćurković L, Škorić I. Photolytic and thin $TiO_2$ film assisted photocatalytic degradation of sulfamethazine in aqueous solution. Environmental science and pollution research. 2015;22(15):11372-86. Link
22. Kang S-F, Liao C-H, Po S-T. Decolorization of textile wastewater by photo-Fenton oxidation technology. Chemosphere. 2000;41(8):1287-94. Link
23. Safarzadeh-Amiri A, Bolton JR, Cater SR. The use of iron in advanced oxidation processes. Journal of Advanced Oxidation Technologies. 1996;1(1):18-26. Link
24. Gogate PR, Pandit AB. A review of imperative technologies for wastewater treatment II: hybrid methods. Advances in Environmental Research. 2004;8(3-4):553-97. Link
25. Lima MJ, Silva CG, Silva AM, Lopes JC, Dias MM, Faria JL. Homogeneous and heterogeneous photo-Fenton degradation of antibiotics using an innovative static mixer photoreactor. Chemical Engineering Journal. 2017;310:342-51. Link
26. Bobu M, Yediler A, Siminiceanu I, Schulte-Hostede S. Degradation studies of ciprofloxacin on a pillared iron catalyst. Applied Catalysis B: Environmental. 2008;83(1-2):15-23. Link