Korean J. Chem. Eng., **31**(11), 2014-2019 (2014)
DOI: 10.1007/s11814-014-0119-y

pISSN: 0256-1115
eISSN: 1975-7220

Investigation of photocatalytic degradation of clindamycin antibiotic by using nano-ZnO catalysts

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(*Received 1 February 2014 • accepted 20 April 2014*)

Abstract−The photocatalytic degradation of clindamycin (CLM) was studied by a batch reactor using UV irradiation and ZnO catalyst. The effects of several parameters such as pH, catalyst loading, light intensity and irradiation time were evaluated in the removal process. The results showed that the degradation of CLM was effective in alkaline conditions. The optimum catalyst loading in an aqueous solution containing 25 mM of CLM and UV lamp of 50 W was observed at 3.0 g/L of catalyst loading. The process followed pseudo-first order kinetics, and the apparent rate constant (k) decreased with increasing the initial concentration of CLM. The photocatalytic process had higher removal efficiency in synthetic than actual wastewater in optimum conditions.

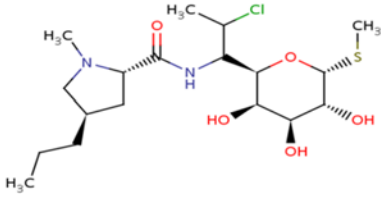
Keywords: Clindamycin, Degradation, Photocatalytic, ZnO Nanoparticles

INTRODUCTION

Antibiotics are widely used to control bacteria in humans and other animals. Due to their therapeutic properties they have become commonplace. Antibiotics were consumed about at a rate of 100,000 to 200,000 tons in 2003 [1]. Lincosamides are one of the most common antibacterial agents that have a wide clinical application against a broad spectrum of pathogenic microorganisms, particularly, gram-positive aerobic and gram-positive and negative anaerobic bacteria. This class of antibiotics was first identified in 1960, and its mechanism of action is via inhabitation of protein synthesis [2]. Clindamycin (CLM) is a Lincosamide antibiotic; its structure and properties are shown in Table 1. From the special features of wastewater industry manufacturer of CLM, high content of chemical oxygen demand (COD), color, salts and antibiotics have been considered [3].

There are several physical, chemical and biological methods for removal of antibiotics according to the chemical and physical properties of the material [4]. Recently, the use of advanced oxidation processes (AOPs) for complete destruction of contaminants has been popular. AOPs are based on the production of reactive species such as hydroxyl radicals that oxidized a wide range of organic pollutants quickly and non-selectively [5,6]. AOPs include photocatalytic systems like the combination of semiconductor and lighting, and oxidants. The heterogeneous photocatalysts are an important destructive technology that leads to higher mineralization of organic pollutants [7,8]. ZnO has a direct wide band gap of 3.5 eV at room temperature (this property is the same of TiO_2) [9], but produces more OH radicals than TiO_2 [10], and has high reaction and mineralization rates (Rashed and El-Amin, 2007). ZnO also has greater numbers of active size with high surface activity [11]. Nano-ZnO, which has high surface to volume ratio, high absorption of UV radiation and long life [12] has been widely applied as catalyst [13,14]. ZnO is also a suitable material owing to high optical activity, chemical stability, availability and low cost [15,16]. The relevant reactions at the semiconductor surface causing the degradation of organic pollutants can be expressed as follows [10]:

Table 1. Properties and chemical structure of the CLM antibiotic

Chemical structure	
Chemical formula	$C_{18}H_{33}ClN_2O_5S$
Molar weight	424.983
Boiling point	255 °C
Solubility in water	30.6 g/L

$$ZnO+hv\ (UV) \rightarrow ZnO\ (e^- CB+h^+ VB) \quad (1)$$

$$ZnO\ (h^+ VB)+H_2O \rightarrow ZnO+H^++OH^{\cdot} \quad (2)$$

$$ZnO\ (h^+ VB)+OH^- \rightarrow ZnO+OH^{\cdot} \quad (3)$$

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$$ZnO\ (e^{-}\ CB)+O_2 \rightarrow ZnO+O_2^{-\bullet} \quad (4)$$

$$O_2^{-\bullet}+H^{+} \rightarrow HO_2^{\bullet} \quad (5)$$

$$Organic+OH^{\bullet} \rightarrow Degradation\ products \quad (6)$$

Moreover, ZnO is used widely for degradation of organic compounds such as C.I. Acid Red 249, rhodamine B, methylene blue, acid red 14, metronidazole, amoxicillin, ampicillin and cloxacillin antibiotics [17-20].

Since studies on CLM antibiotic removal are rare in aqueous environments, this study investigated the photocatalytic degradation of CLM under UV radiation using ZnO catalyst in several condition such as light intensity, pH, catalyst loading and irradiation time.

MATERIALS AND METHODS

1. Chemicals

CLM (99%, Chemical Reagent Co.) was prepared from commercial sources. Nano-ZnO, with an average diameter of 12-6 nm and surface area of 40-150 g/m^2, was purchased from Nano Pars Spadana (Isfahan, Iran). Methanol (HPLC grade) and hexanesulfonic acid and citric acid were obtained from Merck Company, Germany. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were purchased from HACH Company, USA.

2. Photocatalytic Reactor

The photodegradation studies were performed in a batch reactor system (Fig. 1). The reactor consisted of a cylinder of 5 cm diameter and height (500 cm) made of stainless steel, with a magnetic stirrer. In the center of the reactor we put a quartz sheath in which a radiation source by using UV lamps (Philips TL-50 W/05 at λ_{max} 366 nm) was placed and the samples were passed around the quartz sheath in rotational mode. Intensity of the light source used in this study was about 2.87×1019 quanta per second that was standardized via ferrioxalate actinometry [21].

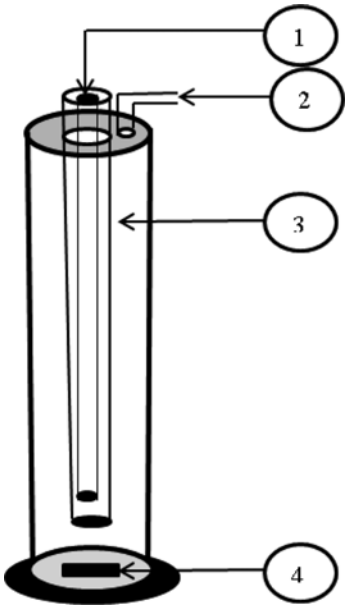

Fig. 1. Photocatalytic reaction device diagram.
1. UV lamp
2. Sample input
3. Quartz cell
4. Magnetic stirrer

3. Experimental Procedure

The used concentration of CLM in this study was 25 mM. The studied variables influencing the process were as follows: pH (5, 7, 9, 10 and 11), nano-ZnO (0.5, 1.5, 3, 4 and 5 g/L) and contact time (15, 30, 60, 75, and 90 min). To optimize the variables, the analytical method of one factor at a time was used; each experimental factor was optimized separately and independently of other factors. The UV lamps used were with a power of 50 W and the output intensity light of 12 W/cm^2 that was at the center of the reactor and with distance of 5 cm from the wall. Nano-ZnO used in this study was suspension; for creating these conditions, the nanoparticles were poured into a flask, and it was placed in an ultrasonic bath (model Elmai S-89) for 20 min at 60 °C. The required concentration of the nanoparticles was lifted from suspension and added to the synthetic wastewater containing CLM. It was done both for oxygen supply and mixing with aeration by an aerator pump. Aeration kept the nanoparticles in suspended state and prevented from settling in the bottom of the reactor. During aeration and suspension of nanoparticles, UV irradiation was performed on the samples. After contact with nano-ZnO and ultraviolet irradiation, the samples were collected and for separation and settling the particles were centrifuged with 8,000 rpm for 15 min by a centrifuge (model Hettich). Then, supernatants were filtered through filters 0.2 μm, PTFE (poly tetra fluoro ethylene) Mann Company Germany.

The stability of ZnO nanoparticles based on the amount dissolved in the solution was performed by atomic absorption spectroscopy (SHIMADSO AA680) [22]. To compare the efficiency of CLM removal in actual and synthetic wastewaters, the actual wastewater was prepared from a pharmaceutical factory in Tehran, Iran. All of conditions for actual wastewater were the same for the synthetic samples. The characteristics of actual wastewater are listed in Table 2. Chemical oxygen demand (COD) test was done for investigation of the mineralization efficiency during photodegradation of CLM. The closed reflux method by using of standard $K_2Cr_2O_7$ and Mohr salt was applied for this test. Experiments conducted in this study were taken from the book of standard methods for the analysis of water and wastewater [23]. For analysis of the data from the experiments, Sigma plot and SPSS software were used.

4. Analytical Method

CLM concentration was determined by high performance liquid chromatography (HPLC, Shimadzu, LC10A HPLC) equipped with a UV detector (SPD-10AV) at 274 nm. Separations were performed on an Agilent C-18 column (250 mm×4.6 mm, with 20 μm particle size). The flow rate was fixed at 1 mL/min and with mobile phase of 80 : 20 (v/v) methanol/buffer. The buffer solution consisted of 10 mM hexanesulfonic acid and 20 mM citric acid, adjusted at pH

Table 2. The characteristic of selected pharmaceutical industry's effluent

Parameter	Value
Total COD (mg/L)	1380
Soluble COD (mg/L)	1184
pH	6.8
TSS (mg/L)	136
VSS (mg/L)	94

4 with NaOH and sulfuric acid. The observed retention time for this antibiotic was 4 min. Measurement of pH was by a pH meter (Metrohm 827, Swiss) with glass electrode. All chemicals used for HPLC analysis were HPLC reagent grade.

RESULTS AND DISCUSSION

1. Photodegradability of CLM

Effect of nano-ZnO and UV irradiation was investigated separately for CLM concentration of 25 mM in conditions as follows: nano-ZnO 3 g/L, irradiation intensity 50 W and pH 10. The findings are given in Fig. 2. About 20% removal of CLM was observed after 90 min of magnetic stirring without UV irradiation, which is attributed to the adsorption of CLM molecules on the ZnO surface. According to this result, it can be said that nano-ZnO has a low efficiency in removal of CLM and alone irradiation needs more time for better efficiency. This test showed that a hybrid of both methods is more effective than each one alone. Then, we can conclude that a great part of degradation by photocatalytic reaction occurred by the UV/ZnO process.

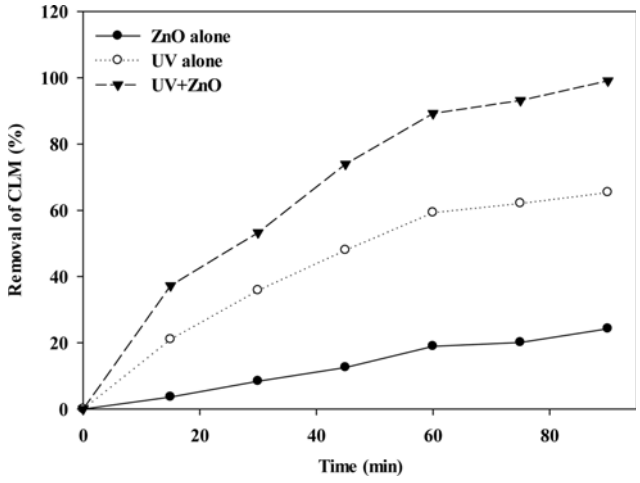

Fig. 2. Photodegrability of CLM in condition of: CLM 25 mM, ZnO loading, 3 g/L, pH 10 and UV irradiation 50 W.

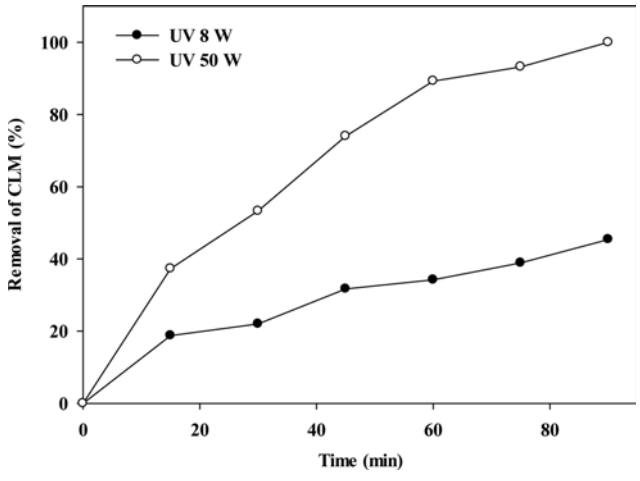

Fig. 3. Effect of light intensity on the photocatalytic degradation of CLM.

2. Effect of Light Intensity

The effect of light intensity on the performance of nanophotocatalytic process was done at fixed concentration of CLM (25 mM, pH 10) and catalyst loading (3 g/L). The light intensity was varied with two UV lamps between 8 and 50 W. As shown in Fig. 3, with increasing the UV light intensity, the removal efficiency increased. Thus, at light intensity 8 W, removal efficiency was 45% and in intensity of 50 W, CLM was completely removed. It can be deduced that with increasing of light power, the production of hydroxyl radicals through photo dissociation of water is more. Also, with production of photons by UV lamp, electrons transferred from the valence band to the conduction band of ZnO catalyst; this process is a function of wavelength and power of the light [24]. These results accord well with previous studies on removal of metronidazole antibiotic [20], degradation amoxicillin, and cloxacilinantibiotics [17].

3. Effect of pH

pH is one of the most affecting parameters on the photocatalytic processes. In this study the effect of pH in the range of 5-11 on the photocatalytic process was examined at a fixed concentration of CLM (25 mM) and nano-ZnO (3 g/L). Fig. 4 shows the removal rate of CLM is a function of pH. It was observed that the removal of CLM increased by increasing pH. The maximum removal efficiency was obtained at pH 10 (complete removal), and at pH 11 the efficiency was not significant in comparison with pH 10, and, therefore, pH 10 was selected as the optimum figure. Nano-ZnO creates electron pairs when exposed to photons with energy equal to or greater than the energy hole empty. In neutral and alkaline pH, the released electrons have the ability to react with oxygen as an electron receptor, which causes this oxygen atom to convert to radical. The created electron holes are separated electrons from the molecules of organic materials, and convert them to the form of R+ and or react with water molecules or hydroxyl ions, and produce hydroxyl free radicals, which may eventually lead to the decomposition of organic matters.

At acidic pH values, nano-ZnO, because it loses its oxygen (in reaction with H^+ ions), tends to be in ionic form of Zn^{2+}, soluble in water and eventually loses its photocatalytic properties [25].

$$ZnO+2H^+ \rightarrow Zn^{2+}+H_2O$$

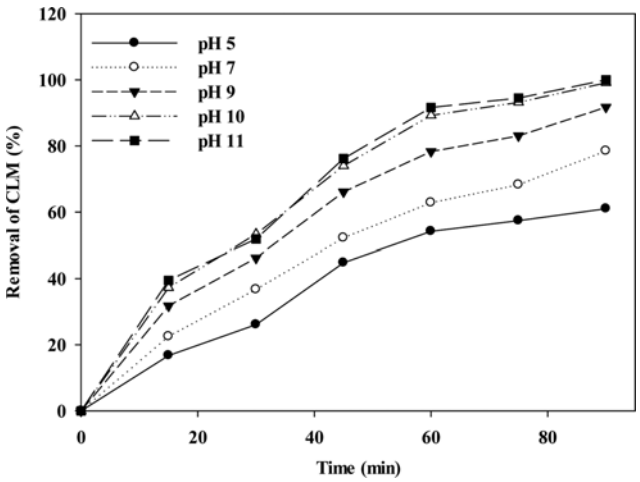

Fig. 4. Effect of pH on the photocatalytic degradation of CLM.

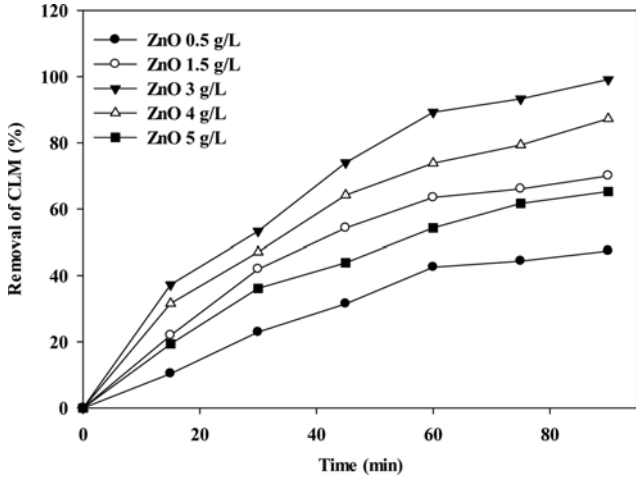

Fig. 5. Effect of catalyst loading on the photocatalytic degradation of CLM.

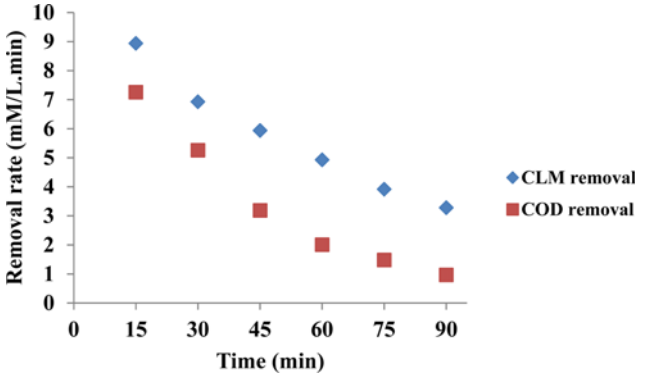

Fig. 6. Plots of CLM and COD removal vs. irradiation time (CLM 25 mM, ZnO loading, 3 g/L, pH 10 and UV irradiation 50 W).

pH_{PZC} for ZnO nanoparticles is ca. 10.9 and when the pH of solution is lower than pH_{pzc} the surface of ZnO tends to be more positive charge [26-28]. Thus, considering that absorption on the surface of nanoparticles depends on pK_b (9.42) and pH_{pzc}, it can be seen that removal efficiency for CLM in photocatalytic process is more in alkaline pH. This is well seen in the results of the study by Lizama et al. [11]. Therefore, in removal of RB-19 dye, the optimum efficiency was observed at pH 11. This is due to faster and more formation of hydroxyl radicals [11]. In another study, Kansal et al. [29] found the same result and the maximum removal efficiency was observed at pH 10 [29].

4. Effect of Catalyst Loading

Impact of different concentrations of nano-ZnO (0.5-5 g/L) was investigated in the degradation of CLM (Fig. 5). Overall, because of increase in the number of available adsorption and catalytic sites causing an increase in the number of active sites on the surface of nano-ZnO catalyst, by increasing concentration of nano-ZnO the removal efficiency increases [30,31]. The results also showed that with increasing the concentration of nano-ZnO, CLM removal efficiency increased up to a certain amount, and then there was a decrease in the rate of removal. Thus, at concentration of 0.5 to 3 g/L, removal efficiency increased and maximum removal was observed at a concentration of 3 g/L (completely removal). However, with increasing concentrations to higher than 3 g/L, there was a downward trend, and at the concentration of 5 g/L, removal efficiency decreased to 65%.The cause of this decrease can be attributed to increased turbidity caused by the increasing of nano-ZnO. Higher turbidity decreased the penetration of UV light into the solution and thus this contact with contaminant becomes less [32]. Chen et al. [33] found similar results in a study of the decomposition of methyl orange by the nanophotocatalytic process by nano-ZnO; they observed that in the range of concentrations 0.4-5 g/L, maximum removal efficiency was at concentration of 2.5 g/L [33]. In another study, in photocatalytic process by using different nanoparticles of TiO_2, ZnO, CdS and ZnS in the removal of dyes, the results accorded with the findings obtained in this research [29].

5. Effect of Irradiation Time

Contact time is an important factor in improving the performance of photocatalytic processes. In this study, times of 0-90 min (15 min intervals) were investigated. The results showed that by increasing the contact time there was an increase in the efficiency of clindamycin. But, as can be seen in Fig. 6, the trend of increasing at early 60 minutes is faster. After this time, removal efficiency was lower. At 15 min the rate of removal was 8.94 mM/min and this reached to 3.28 mM/min in 90 min. In the first times, CLM is oxidized quickly by the produced free radicals. After this time, with production of intermediates, free radicals are consumed.

Moreover, the same results were observed for mineralization of CLM; in order to determine the mineralization, the chemical oxygen demand (COD) test was applied. This was done in 25 mM concentration of CLM at optimum condition (catalyst dose 3 g/*l*, pH 10 and UV irradiation 50 W) with contact times of 15-90 min (15 min intervals). The findings showed that the photocatalyst process had lower rate in reduction of COD than CLM (Fig. 6). Less reduction of COD than CLM happened at the same contact times, and for complete mineralization longer time is required. Liu et al. [34] achieved approximately 97.7% color removal with significant reduction of TOC (57.6%) and COD (72.2%) within 3 h [34]. This can be confirmed by other studies [4,10].

6. Kinetics of Photocatalytic Degradation

Photocatalytic degradation rate was calculated as the rate of destruction of clindamycin under optimum operating conditions (ZnO concentration 3 g/L, irradiation time 90 min, pH 10). CLM concentrations used were as follows: 25, 50, 100 and 150 mM. The linearity of the plots suggests that the photocatalytic reaction approximately followed the pseudo-first order kinetics by use of the following equation:

$$-dC/dt=kC$$

Integration from above equation leads to the following relation:

$$\ln(C/C_0)=-kt$$

where k and t are the apparent reaction rate constant and time, respectively. C and C_0 are the reactant concentration at time t=t and t=0. Linear plot of $-\log(C/C_0)$ versus of time (t) is shown in Fig. 7. Degradation of CLM at different concentration showed that with increasing of concentration the rate constant decreased; thus, its value is from about 0.04 1/min in 25 mM reached to 0.01 1/min at 150 mM (Table 3). Elmolla and Chaudhuri [17] in study of degradation

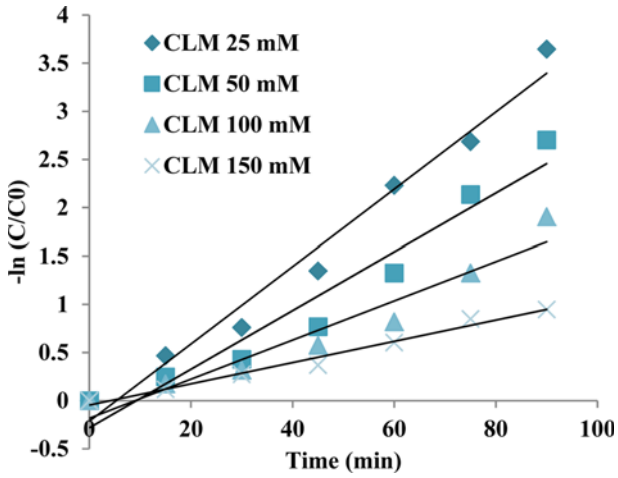

Fig. 7. Plot of ln C/C_0 versus time for photodegradation of CLM (ZnO loading 3 g/L, pH 10 and UV irradiation 50 W).

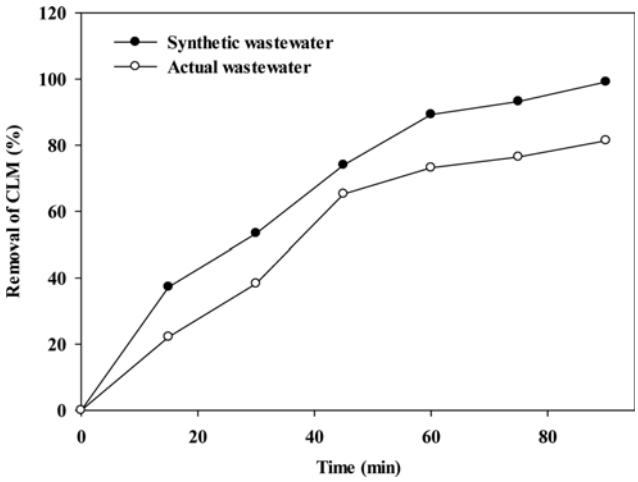

Fig. 8. Photocatalytic degradation of CLM in synthetic and actual wastewater.

Table 3. Reaction rate constant of CLM photocatalytic decomposition with different concentrations

Experiments	ZnO concentration (g/L)	Concentration of CLM (mM)	k (Constant)	R^2
1	3	25	0.042	0.9999
2	3	50	0.035	0.9949
3	3	100	0.023	0.9986
4	3	150	0.011	0.9867

amoxicillin, ampicillin and cloxacillin antibiotics found that cloxacillin exhibited the highest rate constant (0.029 min^{-1}) followed by amoxicillin (0.018 min^{-1}) and ampicillin (0.015 min^{-1}) [17].

7. Performance in Actual Wastewater

Condition of synthetic samples with actual is not identical. There are no intervening elements in synthetic samples. While in actual samples, there are several ingredients including different organic and inorganic compounds. As a result, it is possible that these compounds are affected in the photocatalytic process and to make changes in the efficiency of it. Therefore, in this study, the performance of the nanophotocatalytic process in the synthetic and actual wastewater containing CLM was compared. For this, the synthetic and actual wastewater containing 25 mM of CLM was contacted with 50 W of UV light and 3 g/L nano-ZnO at pH 10. As can be seen from Fig. 8, the removal of CLM in actual wastewater compared to synthetic had lower efficiency (about 10%). Probably there are two reasons for this decline: 1) consumption of produced hydroxyl radicals in process for damaging of compounds other than antibiotics used in the study, and 2) reducing of penetration UV light due to increasing in turbidity of actual wastewater.

8. Reusability of Photocatalyst

In this study the reusability of ZnO photocatalyst of CLM was also investigated. After first contact of ZnO with CLM, the solution containing ZnO was filtered; ZnO residue was washed several times with double distilled water in ultrasonic bath and followed by filtration and drying at 110 °C in an electric oven. In the same terms, the dried nano-ZnO was applied for the removal of CLM. To obtain the dissolution rate of Zn^{2+} ions, atomic absorption spectrophotometry (AAS) was used for analyzing the filtrate [35]. The results showed there was negligible amount of zinc oxide nanoparticles loss in this study (0.09% in 3 h of contact time). Observations showed that ZnO nanoparticles had high reusability, so that in this study, after 10 times of applications in optimal conditions, the removal efficiency decreased by only 11%. The reusability of ZnO is due to its stability in neutral solution and negligible [12].

Same study by Nageswara Rao et al. [35] showed that after five reuses during 2 h of reaction time, amount of ZnO losses was negligible (0.04%) [35]. Pardeshiand and Patil [36] in photocatalytic degradation of resorcinol found that for reusability of ZnO after four reuses, removal efficiency was reduced only 8% [36].

CONCLUSION

Complete degradation of CLM (25 mM) occurred by nanophotocatalytic process at the time of 90 minutes, with 3 g/L of ZnO nanocatalyst in the presence of UV lamps of 50 watts at pH 10. With increasing concentration of CLM, the reaction rate decreased and followed pseudo-first order kinetics. The results indicated that ZnO nanoparticles have great stability and loss amount was negligible. Furthermore, nanoparticles are reusable. This process had a lower performance for the actual wastewater than for the synthetic samples. UV/ZnO photocatalys has a good performance for CLM degradation in aqueous solution.

ACKNOWLEDGEMENT

The authors highly appreciate Tehran University of Medical Sciences for financial support of the study (No. 13452).

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