Photocatalytic Degradation of Ceftriaxone in Aqueous Solutions by Immobilized TiO_2 and ZnO Nanoparticles: Investigating Operational Parameters

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Abstract

The main objective of this study was to investigate the degradation of Ceftriaxone with immobilized TiO_2 and ZnO as heterogeneous catalysts. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) was used to characterize the surface of both catalysts. Photodegradation was compared using direct photolysis (UV alone), TiO_2/UV, and ZnO/UV processes in a photoreactor with high-pressure mercury lamp irradiation. Special attention was given to the influence of the initial concentration of Ceftriaxone, initial pH and light intensity (LI), on photodegradation processes. The results showed that photodegradation involving UV/TiO_2 process was more effective than that involving UV/ZnO process. Either of the experiments was performed in the same operational conditions of C_0, light intensity, desired value of pH for both catalysts, and the apparent rate constant (k_{app}) appears to be about 0.022 min^{-1} for UV/TiO_2 process (pH = 5) and about 0.0081 min^{-1} for UV/ZnO process (pH = 8). For both systems, the photodegradation of Ceftriaxone followed the pseudo-first-order kinetics.

Keywords: Photocatalysis, UV/TiO_2, UV/ZnO, Immobilization, Ceftriaxone

1. Introduction

Over the past two decades, heterogeneous photocatalysis for degradation of organic contaaminants such as pharmaceuticals has been an effective technique for water treatment [1]. Among all the pharmaceuticals that cause pollution, antibiotics play an important role because of their high utilization in human and veterinary medicine and the difficulty of their reduction in the future [2]. Ceftriaxone is an antibiotic that is useful for the treatment of a number of bacterial infections. It is a third-generation cephalosporin and has a broad-spectrum activity against Gram-positive bacteria and expanded Gram-negative ones. Heterogeneous photocatalysis is a procedure dealing with environmental pollution because of its capability in oxidizing organic contaminants. Among photocatalysts, TiO_2 and ZnO have attracted considerable attention due to their photoactivity under UV irradiation, availability, low toxicity and cost [3]. Despite the extensive use of titanium dioxide, zinc oxide can be a good alternative to TiO_2 due to some advantages. ZnO is a mineral and anti-inflammable material and could provide the broad-spectrum of UV absorbance. In addition, ZnO yields rational and favorable results due to its higher quantum efficiency and photocatalytic activity like as TiO_2 [4, 5]. Very few researches have directly studied on the photocatalytic degradation efficiency of ZnO and TiO_2 under UV light irradiation and in immobilized system. The immobilization of catalysts on the glass plate eliminates the problem of the separation of nanopowders from the solution in suspension systems during photocatalysis.

A number of research studies have addressed on the use of immobilized photocatalysts mostly for the removal of azo dyes. For instance, Behnajady et al. evaluated the removal of dye by the use of immobilized ZnO photocatalyst which attached on support with a simple method [6]. In addition, Khataee et al. investigated the photodegradation of three commercial textile dyes (C.I. Acid Orange 10, C.I. Acid Orange 12 and C.I. Acid Orange) from aqueous solution in the presence of immobilized TiO_2 catalyst under UV light illumination [7]. Han et al. were applied tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater [8]. Furthermore, heterogeneous photocatalytic treatment of organic dyes was examined by Rajeshwar et al. in air and aqueous media [9]. Over the past years, the use of immobilized photocatalysts was developed in degrading other organic pollutants such as pharmaceuticals. Alatrache et al. examined the photocatalytic efficiency of immobilized TiO_2 (Degussa P25 and Millennium PC500) for degrading sulfamethoxazole. Both catalysts indicated very similar activities in the photocatalytic degradation of pollutant [10]. In another study, Darvishi et al. investigated the photocatalytic activity of immobilized ZnO nanoparticles on glass plates for removing formaldehyde in an aqueous phase. The results indicated that at pH = 7, the immobilized ZnO nanoparticles could be an efficient photocatalyst for treating wastewaters containing formaldehyde [11]. Despite the widespread use of Ceftriaxone and the probability of its presence in wastewaters, the study of the degradation of this antibiotic has not been reported mostly in the literature.

Junejo et al. investigated the degradation of antibiotics such as cefdinir, cefditoren, cefixime, ceftriaxone sodium and doxycycline applying synthesized novel amoxicillin derived silver nanoparticles (Amp-Ag (0) NPs) in aqueous solution. Based upon the results it has been revealed that Amp-Ag (0) NPs had an excellent catalytic activity as catalyst for the 100% reduction of these antibiotics [12]. In another study, Guo et al. evaluated the electro-catalytic performance of titanium dioxide/Nano-graphite (TiO_2/Nano-G) composite synthesized by a sol-gel method, by the yield of $^{\bullet}OH$ radicals, degradation of methyl orange and ceftriaxone sodium. The results demonstrated that degradation rate of ceftriaxone sodium within 120 min by TiO_2 (40)/Nano-G electrode was 97.7% [13].

This paper represents the photodegradation of Ceftriaxone in the presence of immobilized TiO_2 and ZnO nanocatalysts. The influence of various parameters such as the initial concentration of Ceftriaxone, initial pH and light intensity (LI) was evaluated and the photocatalytic efficiency was examined. Chemical oxygen demand (COD) was applied to examine the mineralization of Ceftriaxone, and the kinetic study was also carried out.

2. Materials and methods

2.1. Reagents

Ceftriaxone was obtained from Exir Daroo Co. (Tehran, Iran) and used in the photocatalytic experiments. TiO_2-P25 (80% anatase and 20% rutile, surface area 50 ± 10 m^2 g^{-1}, average size = 21 nm) was purchased from Degussa Company, and ZnO nanoparticles (particle size < 100 nm) was provided from Aldrich. All of the other chemicals used in the study were of analytical grade and were provided from Merck.

2.2. Preparation of catalysts

Heat attachment method was applied for immobilizing TiO_2 and ZnO nanoparticles on the sand-blast glass plate. Initially,the glass plate was placed in a solution of HF (5%) for 12 h and then was covered with NaOH (0.1 N) solution for 24 h. Secondly, the prepared suspension (4 g L^{-1} TiO_2 or ZnO) was sonicated (Elma T/460H, 35 kHz and 170 W) for 15 min to enhance the dispersion of the nanoparticles in the solution. After that, the suspension was poured on the glass plate, placed in an oven at 90 °C for 12 h, and then put in the furnace at 475 °C for 4 h.

2.3. Analysis

The morphology of TiO_2 and ZnO samples was investigated by means of Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). A Hitachi S–4160 and DME–Danish Micro Engineering A/S were applied for the SEM and AFM analysis, respectively. UV–Vis absorption spectra were recorded on a double beam Shimadzu (1700-Japan) spectrophotometer, and a Shimadzu UVmini–1240 spectrophotometer was applied for recording the spectrum of antibiotic in its λ_{max}. The chemical oxygen demand (COD) was performed (standard potassium dichromate titration method) to indicate the mineralization of Ceftriaxone [14].

2.4. Procedure

The photocatalytic efficiencies of the immobilized TiO_2 and ZnO were evaluated by analyzing the change in concentrations of antibiotic solutions by measuring absorbance values using a spectrophotometer at a wavelength of 276 nm. A borosilicate glass photoreactor (dimensions of 14 × 14 × 5 cm^3, and a support for holding glass plate) was used for carrying out all the experiments. In separate experiments using TiO_2 and ZnO, the specified concentration of Ceftriaxone solution was poured into the photoreactor containing photocatalyst and stirred magnetically for 30 min in the dark to reach complete equilibration of adsorption of Ceftriaxone onto the catalyst surface. Following that, the UV lamp (15 W, λ_{max} = 254 nm, Philips) was switched on and the reaction mixture was irradiated by UV–Vis light. For all solutions, 120 min photocatalytic runs were performed to obtain and examine the true degradation proficiency of immobilized TiO_2 and ZnO [15].

3. Results and discussions

3.1. Catalyst Characterization

Figure 1 (a and b) shows the surface images of immobilized TiO_2 and ZnO nanoparticles analyzed by SEM. A well-defined morphology clearly demonstrates the formation of a uniform distribution of TiO_2 and ZnO nanoparticles. The results indicated a significant density of nanoparticles over the surface of the substrate with no agglomeration of nanoparticles. In order to explore the surface of both catalysts, the plates were also observed by AFM images represented for the three–dimensional (Figure 2a and 2b) AFM micrographs. The three–dimensional images provide additional information on the morphology of the substrates compared to the two–dimensional ones. The high degree of uniformity in the distribution of heights and suitable roughness can also be seen in the AFM images of both catalysts (with the average roughness of about 29.4 and 50.85 nm for TiO_2 and ZnO nanoparticles, respectively).

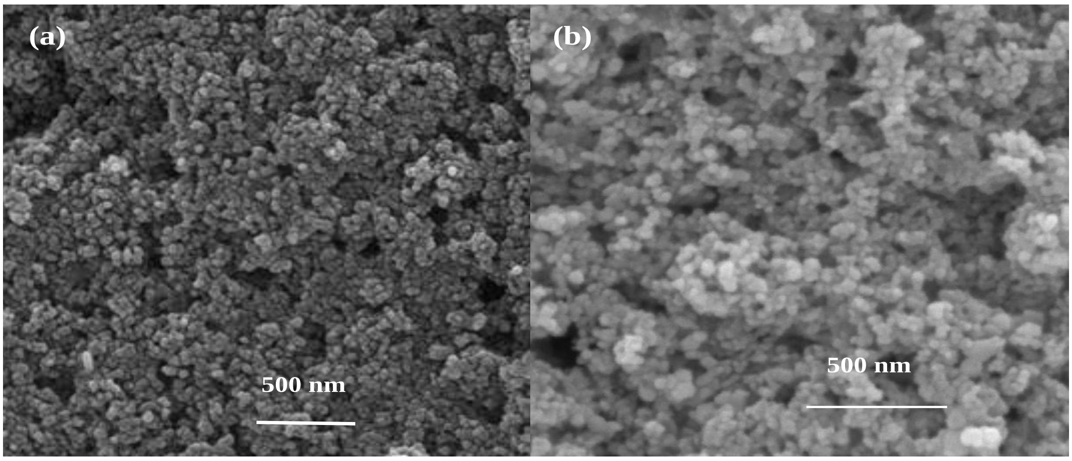

Figure 1: SEM patterns of (a) TiO_2 and (b) ZnO nanocatalysts immobilized on glass plate

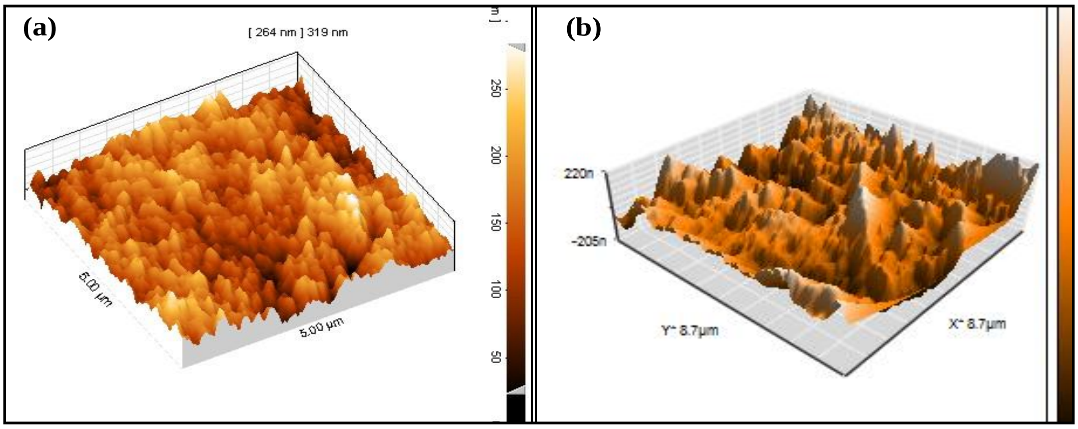

Figure 2: AFM images of immobilized (a) TiO_2–3D (b) ZnO–3D

3.2. UV-Vis spectra changes

Figure 3 (a and b) shows the variations of the absorption spectra of Ceftriaxone and UV measurements during the photocatalytic degradation using TiO_2 and ZnO nanoparticles. The decrease of absorption spectra, corresponding to Ceftriaxone, at its λ_{max} is postulated by degradation of antibiotic at $C_0 = 10$ mg L^{-1}, pH = 6.5 and LI = 17 W m^{-2}. The results in Figure 3, show that the TiO_2 was more active than ZnO nanocatalyst for the degradation of Ceftriaxone.

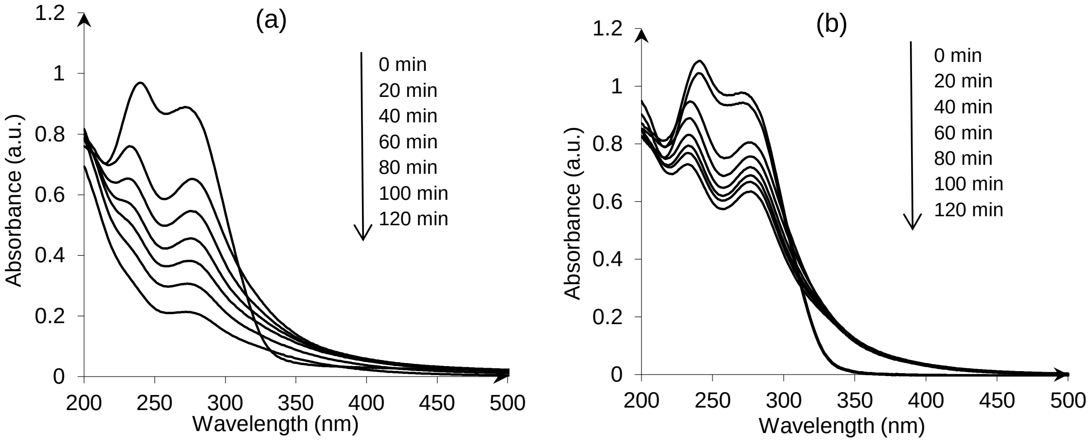

Figure 3: UV-Vis spectra changes for degrading Ceftriaxone in the presence of immobilized (a) TiO_2 and (b) ZnO nanocatalysts

Furthermore, the photolysis of Ceftriaxone was compared with the degradation of Ceftriaxone in the presence of TiO_2 and ZnO photocatalysts (Figure 4). The photolysis efficiency was about 28.8% during 120 min for removal of Ceftriaxone in the same operational conditions.

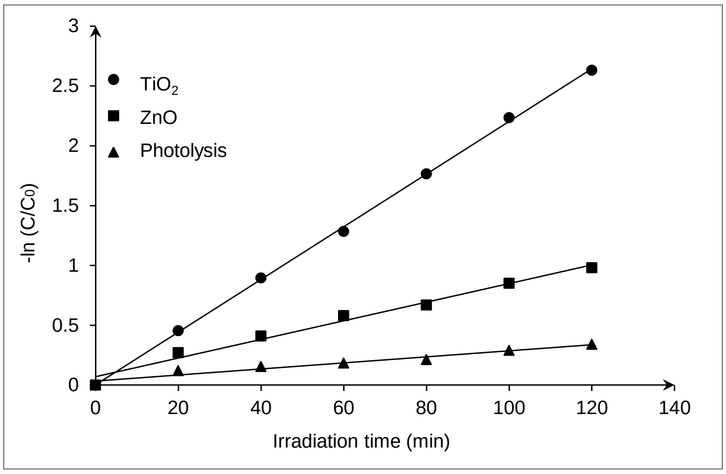

Figure 4: Degradation efficiency of Ceftriaxone for photolysis state and in the presence of immobilized TiO_2 and ZnO nanocatalysts (Light Intensity (LI) = 17 W m^{-2}, pH = 6.5, $C_0 = 20$ mg L^{-1})

3.3. The Effect of Operational Parameters on Photocatalytic Efficiency

3.3.1. The effect of initial concentration of Ceftriaxone

The effect of the initial concentration of Ceftriaxone on the degradation efficiency of TiO_2 and ZnO is shown in Figure 5a and b, respectively. By varying the initial concentration of Ceftriaxone from 10 to 40 mg L^{-1} (pH = 6.5, LI = 17 W m^{-2}), the photodegradation efficiency decreased from 93 to 48.6% at 120 min irradiation time in the presence of TiO_2. Additionally, at the same operational conditions, for ZnO nanocatalyst, the photodegradation efficiency varied from 86.7 to 38.7%. The results represent that the photocatalytic activity of

TiO_2 is better than ZnO in degrading of Ceftriaxone. Besides, the photocatalytic degradation is relatively promising at low concentrations of organic pollutants. This result is in accordance with the Achilleos et al.'s study in degrading Diclofenac in the presence of TiO_2-P25 [16]. In addition, Chong et al. demonstrated that the transformation of contaminant decreases with increasing initial concentration of it [17].

It is assumed that for a solution with high concentration of a pollutant, a fraction of light might be absorbed by the contaminant molecules instead of catalysts [18, 19]. Moreover, the obtainability of the generated active species on the surface of catalysts is inadequate for increased contaminant concentrations. The formation of organic intermediates during photocatalytic process may occupy the active sites on the surface of catalyst and results in a reduction in the photocatalytic degradation of the pollutant [20].

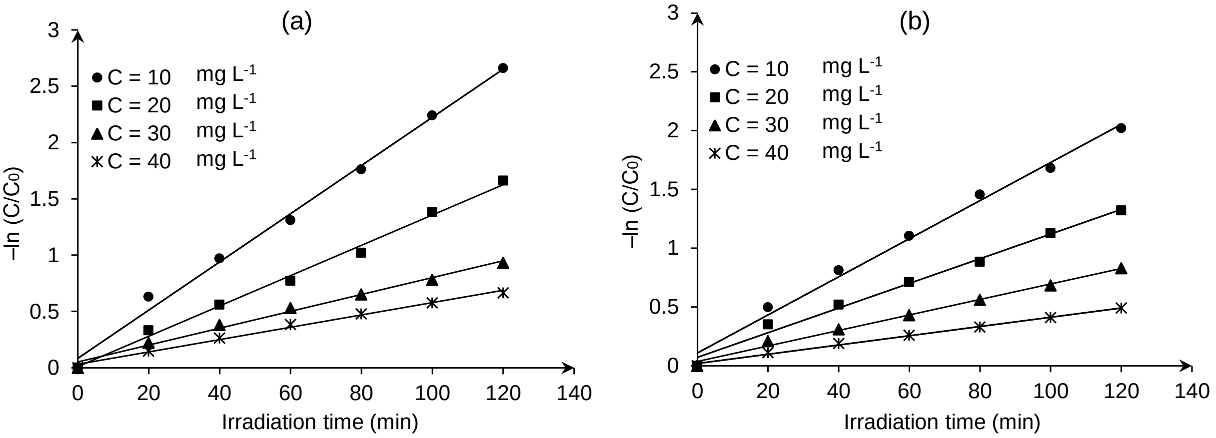

Figure 5: Effect of initial concentration of Ceftriaxone on photodegradation efficiency in the presence of immobilized (a) TiO_2 and (b) ZnO nanocatalysts (LI = 17 W m^{-2}, pH = 6.5)

3.3.2. Effect of pH

Research shows that pH has a promising effect on the photodegradation of many organic contaminants and can influence the surface charge of the catalyst and other physical or chemical properties [19, 21]. A series of experiments were conducted to examine the influence of pH on the photodegradation efficiency of Ceftriaxone by changing the initial pH from 5 to 8 in the presence of TiO_2. Figure 6a shows the relationship between pH and the degradation efficiency of Ceftriaxone in the presence of TiO_2 (C_0 = 20 mg L^{-1}, LI = 17 W m^{-2}) after irradiating under UV light for 120 min. The degradation efficiency of Ceftriaxone increased from 63.1 to 92.8% by decreasing pH from 8 to 5, implying that the photodegradation of Ceftriaxone in the presence of TiO_2 was desirable in acidic solutions than in alkaline ones.The role of pH in photocatalytic removal of Ceftriaxone can be explained by considering the properties of both the catalyst and Ceftriaxone at different pH values. The point of zero charge (pzc) for TiO_2 is 6.25; thus, the surface of TiO_2 will be positively charged at pH < 6.25, and negatively charged at pH > 6.25, and neutral for pH = 6.25 [22]. Also, Ceftriaxone has electron rich aromatic rings tending to be adsorbed on the positively charged surface of catalyst. Considering the pK_a values of Ceftriaxone (pK_{a1} = 1.72, pK_{a2} = 3.15 and pK_{a3} = 4.34), it is presumed that ionic species of Ceftriaxone varies from neutral charge at acidic pH values to negative charge at neutral and alkaline pH, which confirms the acceleration in the catalytic degradation of Ceftriaxone.

The same procedure was carried out to examine the effect of the initial pH value on the photodegradation efficiency of Ceftriaxone solution in the presence of ZnO. From Figure 6b, it can be inferred that the degradation of Ceftriaxone has better efficiency at pH = 8 than acidic media. The degradation percentage varies from 62.8 to 85.98% by changing the pH form 5 to 8. Due to the pzc of ZnO (pzc = 9), the surface of ZnO will be positively and negatively charged for pH < 9 and pH > 9, respectively. As mentioned, due to the structure of Ceftriaxone, the adsorption on the positively charged surface is more favorable. When pH is greater than 9 (pH > 9), both ZnO and Ceftriaxone are negatively charged and hence, the adsorptionon the surface of ZnO is restricted due to the repulsive forces, resulting in a reduction in the photodegradation efficiency [23]. Furthermore, High degradation proficiency of Ceftriaxone in alkaline condition can be influenced by two factors. One is the tendency of large quantities of OH^- ions on ZnO surface to form $^{\bullet}OH$ radicals [18]; the other is the hydrolysis of the Ceftriaxone due to instability of the β-lactam ring at high pH as reported by Houand Pool [24]. These factors cause a better degradation of Ceftriaxone at pH = 8 than other pH values. On the other hand, ZnO dissolves under lower pH values (pH < 4.5) and does not have any activity.

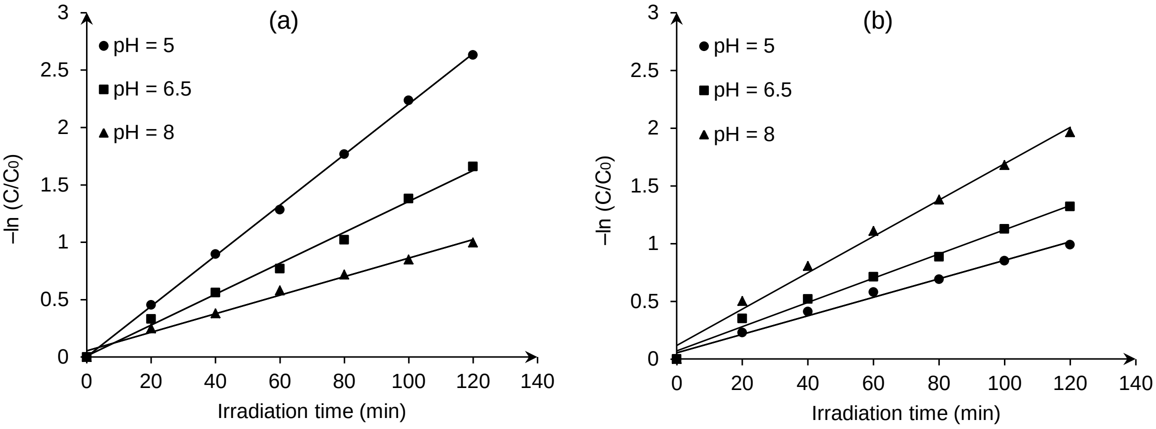

Figure 6: Effect of the initial pH of solution on photodegradation efficiency of Ceftriaxone in the presence of immobilized (a) TiO_2 and (b) ZnO nanocatalysts (LI = 17 W m^{-2}, C_0 = 20 mg L^{-1})

3.3.3. Effect of Light Intensity

A set of experiments were carried out in order to investigate the effect of the irradiation intensity on the photocatalytic degradation of Ceftriaxone. The light intensity varied in the range of 5.9 to 17 W m^{-2}. As represented in Figure 7, the photodegradation efficiency raises as the intensity of the UV lamp is increased. Light intensity specifies the proportion of the photons which are absorbed by the photocatalysts at a certain wavelength. As a consequence, the photons are efficiently transformed into active species that participate in the degradation process [25, 26]. According to Cassano and Alfano [27], the rate of photocatalysis and electrone-hole generation in the photodegradation process are profoundly related to the light intensity. Thus, higher light intensity will produce higher photons and electron-hole pairs, resulting in high degradation rates.

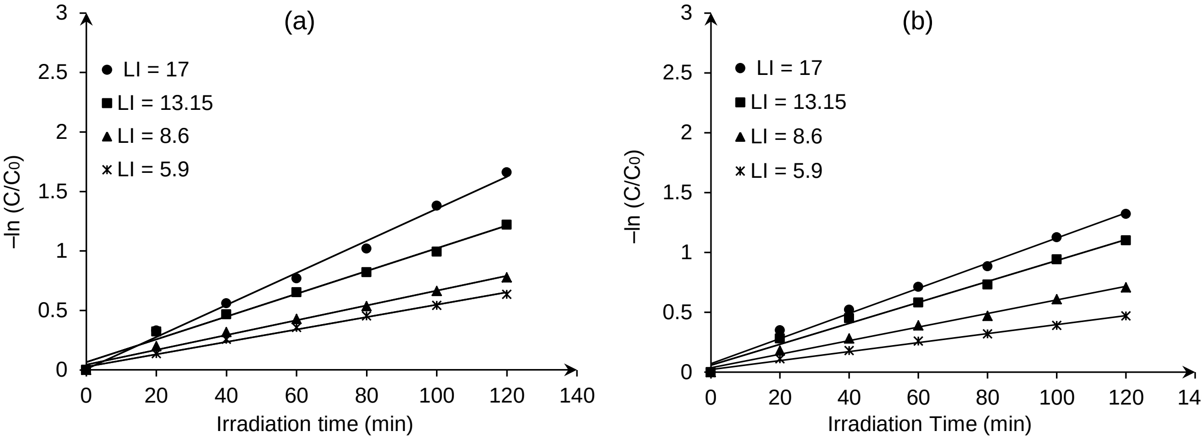

Figure 7: Effect of light intensity on photodegradation efficiency of Ceftriaxone in the presence of immobilized (a) TiO_2 and (b) ZnO nanocatalyst (C_0 = 20 mg L^{-1}, pH = 6.5)

3.4. Reusability of the catalyst

In order to estimate the reusability efficiencies of immobilized TiO_2 and ZnO, ten runs were tested sequentially for the Ceftriaxone antibiotic under UV irradiation. For this purpose, the used catalysts were regenerated by washing them with distilled water and then by drying at 100 °C. The results indicate that in both systems the reused catalysts could degrade Ceftriaxone in aqueous solution and maintain their photocatalytic efficiencies even after ten cycles. Figure 8 shows a slight decrease (about 4%) in the activity of the catalysts. Through the photocatalytic removal of Ceftriaxone, degradation products may remain on the catalyst surfaces and block their active sites, consequently causing a decrease in their activities [5].

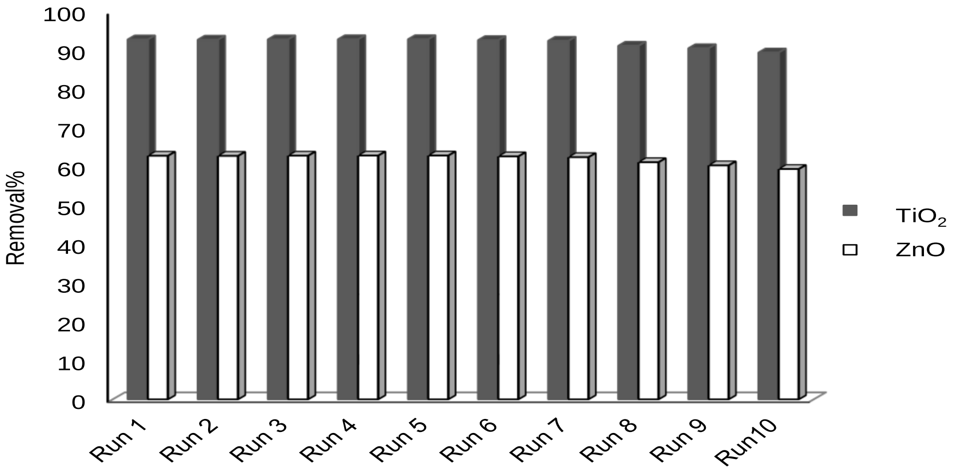

Figure 8: Efficiency of the reused catalysts over the ten degradation experiments (■ Immobilized TiO_2, ☐ Immobilized ZnO)

3.5. Kinetic Studies

To identify the apparent reaction rate constant (k_{app}) values for the degradation of Ceftriaxone, a pseudo-first order kinetics model was applied. Generally, most photocatalytic degradation reactions of organic contaminants are explained in terms of the Langmuir–Hinshelwood (L–H) model for low concentrations. The following equation shows the calculation of the rate:

$$\text{Ln}\left[\frac{C_0}{C}\right] = k_{app}\, t$$

Where k is the apparent rate constant, C and C_0 are the concentration at time t and initial concentration [28].
The calculated k_{app} values and correlation coefficients (R^2) for the photocatalytic degradation reactions during 120 min for both catalysts are given in Table 1. In all cases, the R^2 values are greater than 0.99, indicating that it was appropriate to assume a pseudo-first order kinetics model for the present degradation reactions.

Table 1: The apparent first–order rate constants and correlation coefficients for Ceftriaxone degradation at different operational conditions at 25 °C

Run	**Operational conditions**			**Kinetic values & removal% (TiO_2)**			**Kinetic values & removal% (ZnO)**		
	[Ceftriaxone]$_0$ (mg L^{-1})	**pH**	**LI (W m^{-2})**	**k_{app} (min^{-1})**	**R^2**	**R%**	**k_{app} (min^{-1})**	**R^2**	**R%**
1	10	6.5	17	0.0214	0.9948	93.%	0.0162	0.9914	86.7%
2	20	6.5	17	0.0135	0.9945	80.9%	0.0105	0.9907	73.3%
3	30	6.5	17	0.0075	0.9914	60.7%	0.0066	0.9932	56.4%
4	40	6.5	17	0.0055	0.9927	48.6%	0.0039	0.9956	38.7%
5	20	5	17	0.022	0.9994	92.8%	0.008	0.9901	62.8%
7	20	8	17	0.0081	0.9907	63.1%	0.0158	0.9906	85.9%
9	20	6.5	13.5	0.0096	0.9902	70.5%	0.0088	0.9905	66.7%
10	20	6.5	8.6	0.0062	0.9911	54.1%	0.0057	0.9912	50.7%
11	20	6.5	5.9	0.0052	0.9935	47%	0.0038	0.9939	37.5%

3.6. Mineralization efficiency

In order to investigate the mineralization of Ceftriaxone, a series of designation (COD) was carried out within 8 h of irradiation time in the presence of immobilized TiO_2 and ZnO catalysts. A solution of Ceftriaxone (20 mg L^{-1}) was degraded and monitored at different irradiation times to follow COD removal. The COD measurements are shown in Table 2. A decrease in COD indicates the gradual degradation of Ceftriaxone through the photocatalysis process.

Table 2: COD removal percent for Ceftriaxone degradation in the presence of immobilized TiO_2 and ZnO nanocatalysts during 480 min

Irradiation time (min)	**COD removal%**		
	TiO_2	**ZnO**	**Photolysis**
0	0	0	0
120	38.3%	12.5%	1.7%
280	70%	37.5%	3.4%
420	81.7%	56.3%	5.2%
480	96.7%	75%	6.9%

Conclusion

To evaluate the photocatalytic activity of TiO_2 and ZnO nanoparticles in degrading Ceftriaxone in aqueous solutions at different operational conditions (Initial concentration of Ceftriaxone, LI and pH), a set of experiments was done and the results were compared. The results indicated that in examining the pH of the solution, the degradation efficiency depended on the structure of the compound and pH_{pzc} of the photocatalysts. Besides, the low initial concentration of the antibiotic in the presence of high light intensity showed higher degradation proficiency. Also, the results of both Ceftriaxone degradation in favorable conditions and the UV-Vis spectra changes indicated better degradation efficiency of TiO_2 than ZnO. The comparison of k_{app} and R^2 values of both systems confirmed the accuracy of the obtained results.

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