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A comparative study of photocatalytic degradation of the antibiotic cefazolin by suspended and immobilized TiO_2 nanoparticles

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ABSTRACT

In this study, the photodegradation of cefazolin was investigated in the presence of suspended and immobilized TiO_2 on a glass plate. The effects of the operational parameters such as the catalyst dosage for the suspended system, the initial pH of the solution, the initial concentration of the cefazolin, and light intensity were examined and compared in both systems. Scanning electron microscopy and atomic force microscopy were used to determine the surface properties of the immobilized catalyst on glass. The favorable conditions obtained for the photodegradation of cefazolin were pH 5, light intensity = 17 W m^{-2}, and $[\text{cefazolin}]_0 = 20$ mg L^{-1} in both the systems. Also, in the slurry system, the most suitable catalyst dosage was 400 mg L^{-1}. The kinetic examination, following the pseudo-first-order reaction kinetics, was made based on the Langmuir–Hinshelwood model.

Keywords: Antibiotic; Cefazolin; Photodegradation; Immobilization

1. Introduction

Among all the pharmaceuticals containing water and wastewater contaminants, antibiotics play an important role due to their high consumption in human medicine and veterinary. This has aroused a concern about environmental pollution [1]. At present, wastewater treatment plants are not capable of entirely detoxifying these kinds of pollutants, and there is often a high probability of observing them in the drinking water [2].

Of various treatment techniques to purify the wastewater containing pharmaceutical compounds, the advanced oxidation processes (AOPs) have been proved more feasible in comparison with other techniques such as activated carbon adsorption, air stripping, and reverse osmosis because these techniques only transfer the contaminants from one phase to another without destroying them [3]. Among the different AOPs, heterogeneous photocatalysis has been shown to be an effective way for wastewater treatment because it is an adaptable and inexpensive technique for the degradation of various organic pollutants [4]. Semiconductor photocatalysis based on titania, which

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is induced by UV–Vis illumination, is an economical and harmless technology for wastewater treatment. It has many applications over the past several years due to high production of hydroxyl radicals and eco-friendly process [5–7]. Among the research studies on the photocatalytic degradation of pharmaceutical contaminants, Dimitrakopoulou et al. investigated the UV-TiO_2 photocatalytic degradation of amoxicillin (AMX) in aqueous suspensions. The results showed that semiconductor photocatalysis based on TiO_2-P25 under UV-A irradiation is an efficient method for the degradation of AMX in water [8]. Also, the photochemical conversion of oxytetracycline (OTC) was investigated by Zhao et al. through the photocatalysis process using NF-TiO_2 film and photolysis under visible and solar light illumination. The effect of solution pH on the photolytic and photocatalytic degradation of the antibiotic OTC was estimated to clarify the different mechanisms at various pH values and light wavelengths. This comparative study of the photolysis of OTC with different initial concentrations of OTC under solar light irradiation, and in the presence of scavengers of reactive oxygen species, displayed a self-photosensitization pathway [9]. Furthermore, in another study by Zhao et al. the comparison of the adsorption, desorption, and photodegradation of OTC using nano-TiO_2 particles and TiO_2/5A zeolite composite system under different operational conditions were evaluated. The adsorption results demonstrated that 5A had much more ability in adsorption of OTC compared to TiO_2 except at high pH values (pH 11). In addition, under the optimal conditions the 15% T5A composite photocatalysis represents a better OTC removal than unsupported TiO_2 [10].

In another study, Elmolla and Chaudhuri investigated the treatment of an antibiotic wastewater including AMX, cloxacillin, and ampicillin in the presence of UV-A/ZnO photocatalysis. The results showed that UV/ZnO photocatalysis can be a useful process in degrading AMX, ampicillin, and cloxacillin in aqueous solution [11]. Gurkan et al. also examined the photocatalytic degradation of cefazolin over N-doped TiO_2 under UV light and solar light irradiation, showing higher photocatalytic efficiency in the removal of cefazolin for the N-doped TiO_2 compared to TiO_2-P25. The N-doped TiO_2 also represented better photocatalytic activity under sunlight irradiation [12].

The present study was mainly aimed at investigating the photocatalytic degradation of cefazolin (a first-generation cephalosporin antibiotic) as a model antibiotic pollutant in aqueous solutions under UV light illumination and in the presence of TiO_2 suspension and immobilized TiO_2 on a glass plate. Another objective was to examine the effects of catalyst concentration, cefazolin's initial concentration, pH, and light intensity on the photocatalytic degradation of cefazolin. The third objective was to evaluate and compare the efficiency and kinetics of photocatalytic reactions.

2. Materials and methods

2.1. Materials

TiO_2-P25 (80% anatase and 20% rutile, surface area $50 \pm 10\ m^2\ g^{-1}$) and cefazolin were purchased from Degussa and Dana Pharmaceutical Company (Iran), respectively. NaOH and HNO_3 (Merck) were used to adjust the initial pH of the solution.

2.2. Preparation of the catalyst

For the preparation of TiO_2 immobilized on glass plates, heat attachment method was used. In this method, the suspension containing $10\ g\ L^{-1}$ TiO_2-P25 was prepared in distilled water and, pH was adjusted with diluted HNO_3 to around three. At first, the glass plate was placed in a solution of HF (5%) for 12 h and then washed with distilled water. After that, the plate was covered with NaOH (0.1 N) solution for 24 h. The prepared suspension, after sonication (Elma T/460H, 35 kHz and 170 W) for 30 min, was poured on the glass plate and placed in an oven at 100°C for 12 h. Then, the glass plate was placed in the furnace at 475°C for 4 h.

2.3. Characterization techniques

Immobilized TiO_2 nanoparticles were characterized by Scanning Electron Microscopy (SEM) (Tescan-Wega II) and Atomic Force Microscopy (AFM) (DME—Danish Micro Engineering A/S). The Chemical Oxygen Demand (COD) was directly measured (standard potassium dichromate titration method) to indicate the mineralization of cefazolin. To detect the trace of Ti in the solution, Atomic Absorption Spectrometry (AAS) (VARIAN, model AA240) was employed.

2.4. Photocatalytic study

For the investigation of the photocatalytic activity of TiO_2 nanoparticles toward degradation of cefazolin, the100 mL solution containing desired amounts of cefazolin and photocatalyst was prepared and agitated for 30 min in the dark to reach the adsorption equilibrium. Then, the suspension was transferred into a photoreactor. The photoreactor was a borosilicate petri dish (diameter = 12 cm, height = 2.5 cm), which contained the solution and catalyst. Afterward, while the solution was being stirred by the magnetic stirrer, the

UV lamp (15 W, $\lambda_{\max} = 254$ nm, Philips) was switched on and irradiated with a desired light intensity from the top of the solution to start the reaction. The measurement of light intensity was conducted by a Lux–UV–IR meter (Leybold Co.) (Fig. 1 shows the distribution of light intensity versus light wavelength). Then, at certain reaction intervals, 5 mL of sample was withdrawn, and the catalyst was removed by centrifuging (5,000 rpm). The concentration of the remaining cefazolin was determined by means of an UV–Vis spectrophotometer (Shimadzu, UVmini-1240) at $\lambda_{\max} = 271$ nm. Since in all the experiments the absorbance changes in the samples before and after 30 min of adsorption equilibrium were very low, the removal of cefazolin through the adsorption of TiO_2 was very insignificant and could be neglected.

The investigation of the degradation process with immobilized TiO_2 was similar to the suspension method except that the photoreactor was a borosilicate glass dish with the dimensions of 14 × 14 × 5 cm and contains a support for holding glass plate.

3. Results and discussion

3.1. Catalyst characterization

Fig. 2(a) shows SEM image of a cross-section taken from the immobilized TiO_2 nanoparticles on the glass plate. In the picture, the thickness of the prepared plate is about 17 μm. Fig. 2(b)–(d), depicts SEM image of the prepared surface in three magnifications and shows that the particles are almost uniformly distributed over the surface of the glass plate.

The two-dimensional (Fig. 3(a)) and three-dimensional (Fig. 3(b)) images of immobilized TiO_2 nanoparticles on the glass plate were prepared by AFM (Table 1 shows the roughness characteristics). The results show the formation of the substrate with a suitable surface roughness of 34.1 nm. Surface skewness (*Ssk*) amount indicate the asymmetry of the height distribution histogram. The surface Kurtosis (*Sku*) is another parameter to infer the distribution of heights. The *Sku* is three for Gaussian distribution and less than three for broader distribution of heights. The *Sp* is the maximum height of peaks and the value of *S10z* represents the average height of the five highest peaks and five shortest peaks.

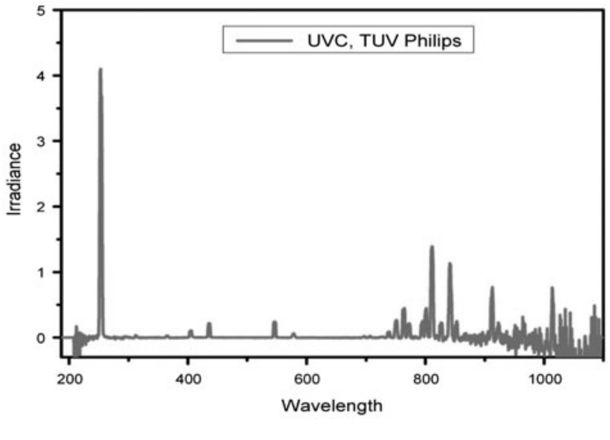

Fig. 1. The distribution of light intensity versus light wavelength.

3.2. Effects of operational parameters under UV–Vis

3.2.1. Effect of catalyst dosage on photodegradation of cefazolin

To investigate the effect of the catalyst dosage on the photodegradation of the cefazolin, the degradation experiments were carried out by varying the TiO_2 concentration within the range of 200–600 mg L^{-1}, whereas the other operational parameters remained constant ($[\text{cefazolin}]_0 = 20$ mg L^{-1}, pH 5 and light intensity = 17 W m^{-2}). As the results show (Fig. 4), the degradation of the antibiotic improved significantly by increasing the amount of the catalyst up to 500 mg L^{-1}, which is due to an increase in the number of the reaction sites. However, further increase in TiO_2 concentration (higher than 500 mg L^{-1}) caused a decrease in the antibiotic degradation. This may be due to the decreasing light penetration, increasing light scattering [13,14], agglomeration, and sedimentation of TiO_2 under high catalyst concentration [15], which inversely affect the photocatalytic reaction. Zhao et al. [10], verified the above results and represented that, in degrading OTC in the presence of TiO_2 and TiO_2/5A, the higher load of the catalyst can inhibit the light penetrating into the solution. Besides, Chong et al. [16], reported similar results in their study, demonstrating that the excess dosage of TiO_2 could cause a light-screening effect that decreases the surface area of TiO_2 catalyst being exposed to light irradiation and eventually decreases the photocatalytic efficiency. Therefore, to avoid excess catalyst dosage and to have efficient absorption of photons, experiments should be carried out below the saturation level of TiO_2 particles.

3.2.2. Effect of cefazolin initial concentration on the photocatalytic degradation

To determine the effect of the antibiotic concentration on the photocatalytic degradation, different concentrations of the antibiotic (within the range of 20–80 mg L^{-1}) were examined with the other operational parameters (e.g. light intensity (17 W m^{-2}) and pH 5) remaining constant (Fig. 5).

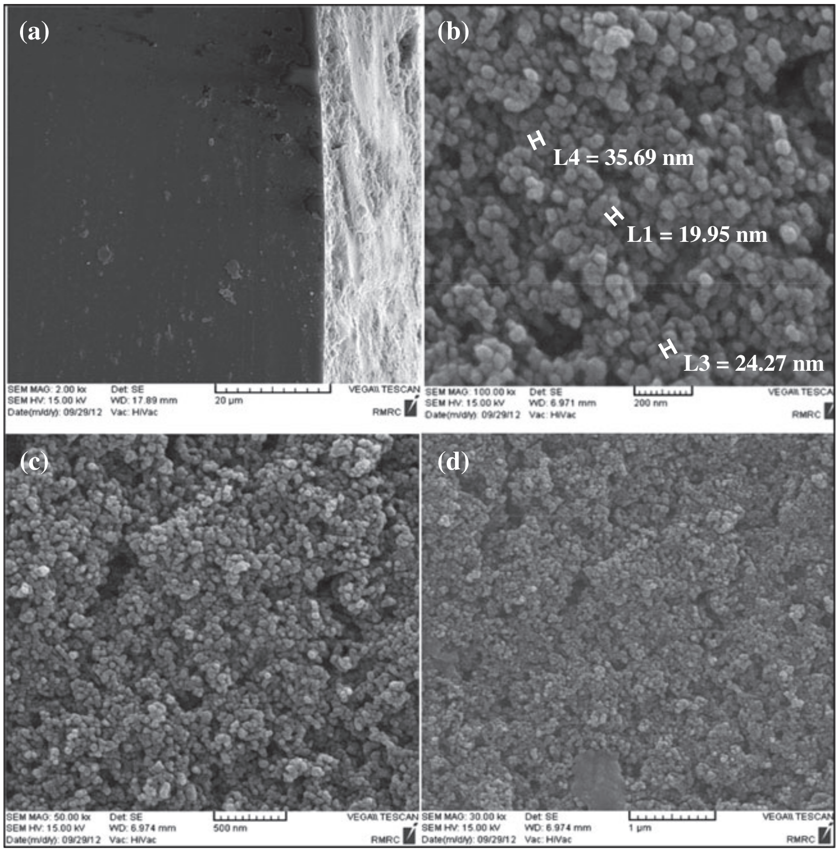

Fig. 2. SEM images of immobilized TiO_2 nanocatalyst: (a) cross-section, and magnifications of, (b) 100 kx, (c) 50 kx, and (d) 30 kx.

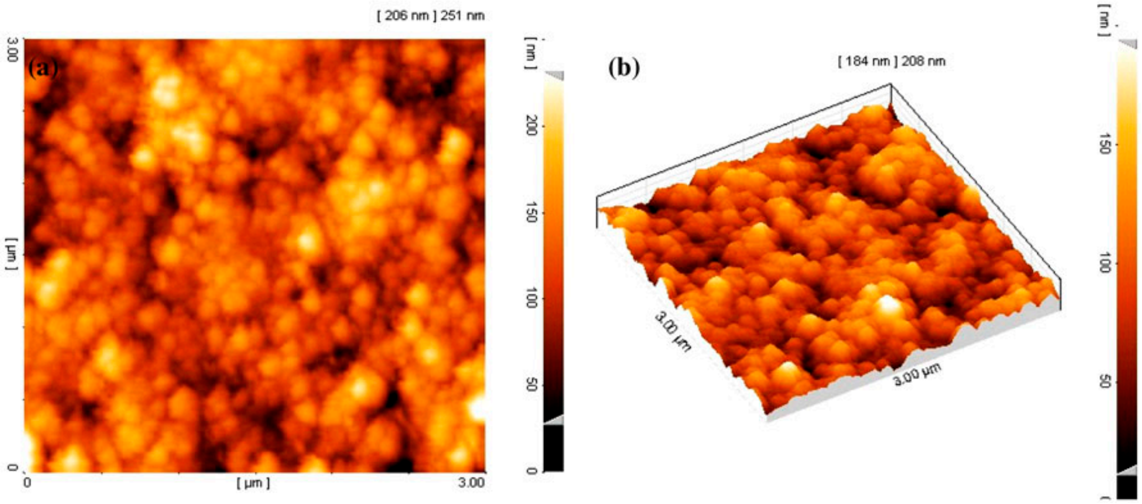

Fig. 3. AFM images of immobilized TiO_2 nanocatalyst: (a) two-dimensional and (b) three-dimensional.

In both cases (TiO_2 suspension and immobilized TiO_2 on the glass plates), by increasing the initial concentration of the cefazolin, the elimination process decreased. During the photocatalytic oxidation, the concentration of organic compound depends on the efficiency of the photon over the time. According to

Table 1
Morphological data and surface roughness for immobilized TiO_2 obtained from AFM image

Projected area (μm^2)	RMS roughness (nm)	Average roughness (nm)	Surface skewness *Ssk*	Surface Kurtosis *Sku*	Ten point height *S10z* (nm)	Maximum peak height *Sp* (nm)
9	42.4	34.1	0.05	2.94	281	319

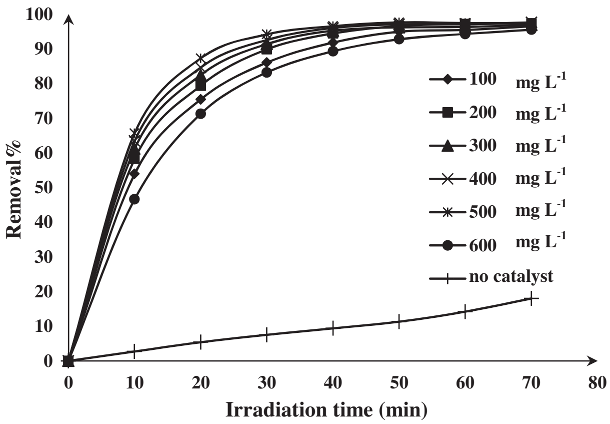

Fig. 4. Effect of TiO_2 amount on photodegradation of cefazolin in suspension ($[\text{cefazolin}]_0 = 20$ mg L^{-1}, light intensity (LI) = 17 W m^{-2}, pH 5).

Gaya and Abdullah's study [17], at higher contaminant concentrations, the photon efficiency decreases, as the catalyst surface may be saturated, leading to the deactivation of the catalyst by preventing the production of electron–hole pairs and thus causing hydroxyl radicals and ultimately the photocatalytic degradation process to lessen [18].

3.2.3. Effect of pH on photodegradation of cefazolin

Since the pH of the solution determines the surface charge properties of the photocatalyst and consequently the adsorption behavior of the contaminant, the influence of the initial pH on degradation process of cefazolin was investigated by carrying out a series of experiments with different values of pH (pH 5, 7, and 9) and constant amounts of other parameters ($[\text{cefazolin}]_0 = 20$ mg L^{-1}, light intensity = 17 W m^{-2}). Fig. 6 shows the degradation rate for the decomposition of cefazolin as a function of pH operating in two different states of TiO_2, that is, suspension (Fig. 6(a)) and immobilization on the glass plate (Fig. 6(b)). According to the results, pH had a great effect on the antibiotic degradation, and the highest photodegradation was achieved at pH 5.

The results show that the degradation percentage in the favorable pH (pH 5) is 96.47% for TiO_2 suspension and 46.17% for the immobilized TiO_2 during 60 min irradiation time. The surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively. Ahmed et al. [19] showed that the pH of a solution determines the surface charge of photocatalyst and ionization of an organic pollutant. They also reported that the electrostatic interaction between semiconductor surface, solvent molecules, substrate, and generated radicals

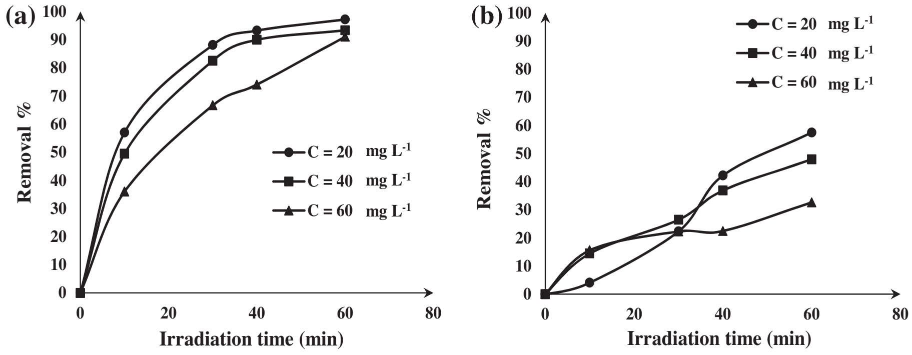

Fig. 5. Effect of cefazolin initial concentration on photocatalytic activity: (a) TiO_2 suspension and (b) immobilized TiO_2 (light intensity = 17 W m^{-2}, pH 5).

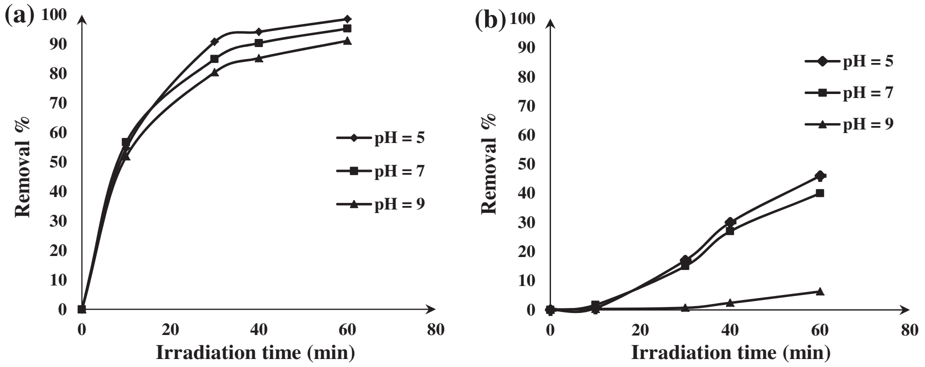

Fig. 6. Effect of pH on photodegradation of cefazolin: (a) TiO_2 suspension and (b) immobilized TiO_2 ($[\text{cefazolin}]_0$ = 20 mg L^{-1}, light intensity = 17 W m^{-2}).

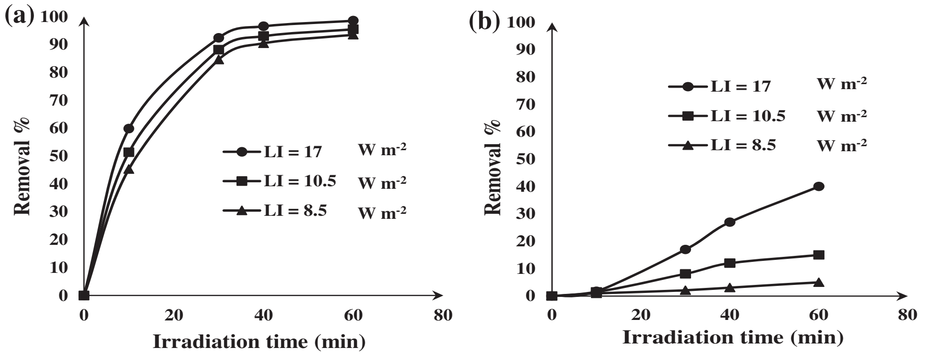

Fig. 7. Effect of light intensity on photodegradation of cefazolin in the presence of: (a) TiO_2 suspension and (b) immobilized TiO_2 ($[\text{cefazolin}]_0$ = 20 mg L^{-1}, pH 5).

during photocatalytic process was heavily reliant on the pH of the solution. According to the cefazolin structure with electron rich aromatic rings, its adsorption on the surface of TiO_2 nanoparticles with positive charge is desirable and this is the reason of an increase in the reaction rate and photocatalytic activity. Furthermore, at the end of the experiments, the pH of the solution was measured for initial pH 7 revealing a reduction in the pH to 6.1 and 6.5 in the suspension and immobilized system, respectively. This decrease can be attributed to the generation of organic acids during the degradation process [20].

3.2.4. Effect of light intensity on cefazolin photodegradation

The effect of light intensity on the degradation of cefazolin (20 mg L^{-1}) was examined by varying the power of light from 8.5 to 17 W m^{-2}. Fig. 7 shows the degradation rate of the cefazolin in the presence of both states of the catalysts in different light intensities. As seen, the rate rises by increasing the UV light intensity due to decreasing the distance of light source from the solution surface. The results are in accordance

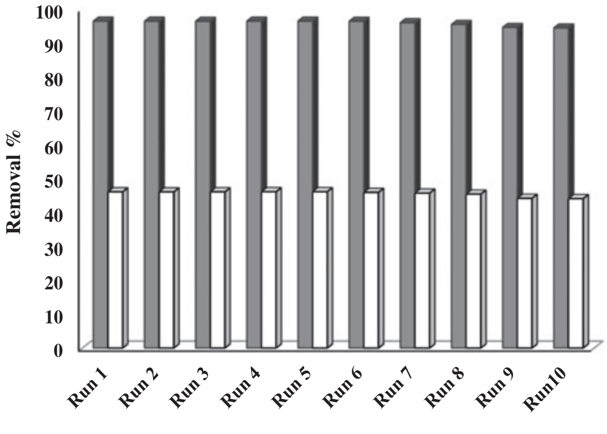

Fig. 8. Efficiency of the reused catalysts over the 10 degradation experiments (▇ suspended TiO_2☐ immobilized TiO_2).

Table 2
Effect of TiO_2 on cefazolin degradation in terms of COD removal

Irradiation time (min)	COD (mg L^{-1}) (TiO_2 suspension)	COD (mg L^{-1}) (immobilized TiO_2)	COD (mg L^{-1}) (no catalyst)
0	58	58	58
60	35	42	–
120	13	32	–
180	2	27	56

with Ahmed et al. [21], who reported that the electron–hole formation in the photodegradation process was strongly dependent on the light intensity. Increasing in the light intensity causes an increase in the amount of produced hydroxyl radicals and eventually in the acceleration of photocatalytic degradation of pollutant.

3.3. *Efficiency of the recycled catalyst*

The used catalysts were regenerated by washing with distilled water and then by drying it at a temperature of 100°C. The photodegradation efficiency of the suspended and immobilized regenerated catalysts was evaluated in the photodegradation of the cefazolin. It was observed that in both systems the reused TiO_2 samples could degrade cefazolin in aqueous solution and preserve their photocatalytic efficiencies (with a little decrease (about 2%)) even after ten cycles (Fig. 8). Insignificant decrease in the immobilized catalyst efficiency can be the advantage of the photocatalytic process. A minor decrease in the efficiency of the reused catalysts can be due to the deposition of hydroxides on the photocatalyst surface which can block its active sites [22].

3.4. *Degradation of antibiotic and mineralization*

To evaluate the COD and mineralization of the cefazolin through degradation process, the aqueous solution of cefazolin with the initial concentration of 20 mg L^{-1} and pH 5 was exposed to UV irradiation with the light intensity of 17 W m^{-2} in the absence and presence of both catalysts (catalyst amount in the case of suspended TiO_2 was 400 mg L^{-1}). COD measurement results are shown in Table 2. As it can be seen, the percentages of decrease in COD value are 78% for TiO_2 suspension, 45% for the immobilized TiO_2, and 3.5% in the absence of the catalyst at the time of 120 min. This represents a high efficiency of TiO_2 suspension in the removal of pollutants.

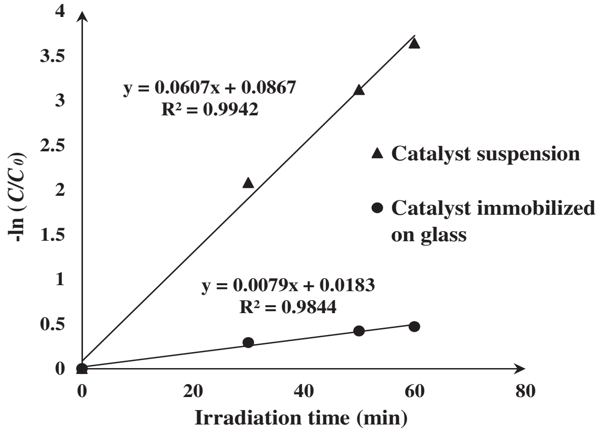

Fig. 9. Plot of $-\ln(C/C_0)$ versus time for the degradation of cefazolin in the presence of TiO_2 suspension and immobilized TiO_2 ($[\text{cefazolin}]_0 = 20$ mg L^{-1}, pH 5, light intensity = 17 W m^{-2}).

4. Kinetic study

To study the kinetics of photocatalytic degradation of cefazolin, a number of experiments were conducted under desired operating conditions ($[TiO_2]_{\text{suspension}} = 400$ mg L^{-1}, initial cefazolin concentration = 20 mg L^{-1} and solution pH 5). Fig. 9 shows the plots of $-\ln([\text{antibiotic}]/[\text{antibiotic}]_0)$ versus irradiation time for the photodegradation of cefazolin and shows the apparent rate constant (k_{app}) in the presence of TiO_2 suspension (0.0607 min^{-1}) and immobilized TiO_2 (0.0079 min^{-1}). The good linearity of the $-\ln(C/C_0)$ versus irradiation time plot, with R^2 values of >0.98 in both cases, suggests that the photocatalytic reaction approximately followed the pseudo-first-order kinetic.

5. Conclusions

The degradation of cefazolin antibiotic in the presence of TiO_2 photocatalyst in two states (suspension and immobilized TiO_2 on the glass plate) was investigated under UV irradiation. The desired conditions for the photocatalytic degradation of cefazolin were found to be: pH 5, light intensity = 17 W m^{-2}, initial concentration of 20 mg L^{-1} of cefazolin in both states, and the catalyst dosage of 400 mg L^{-1} in TiO_2 suspension. The semi-logarithmic graphs of the concentration of the cefazolin versus irradiation time yield straight lines indicated a pseudo-first-order reaction kinetic. The efficiency of the TiO_2 catalyst which was reused 10 times declined by about 2% compared to the fresh catalyst. Eventually, according to the results, the rate of the photodegradation of the cefazolin in the presence of TiO_2 suspension was higher than that in the immobilized TiO_2. However, using immobilization method did not cause separation problems of dissolved catalyst during the experiments.

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