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Photocatalytic degradation of ciprofloxacin in the presence of synthesized ZnO nanocatalyst: The effect of operational parameters

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ABSTRACT

This study was aimed at investigating the photocatalytic degradation of ciprofloxacin (CIP) antibiotic in aqueous solution using immobilized ZnO nanoparticles on glass plate. X-ray diffraction, atomic force microscopy, and scanning electron microscopy were applied to characterize the nanoparticles. To do so, the ZnO nanoparticles were synthesized through the chemical precipitation method and were immobilized on a glass plate. The degradation of CIP was under UV-C light irradiation. The effects of operational parameters (initial concentration of CIP**,** pH, and light intensity) on the activity of synthesized ZnO photocatalyst and the kinetics of reaction were investigated. With the initial concentration of 10 mg L^{-1} of CIP, pH = 6.8 and light intensity = 42 W m^{-2}, the photodegradation efficiency was found to be 69.5%. The results showed that the reaction followed a pseudo-first-order kinetic. The results of the mineralization studies also represented a decreasing trend of total organic carbon over time.

Keywords*: ZnO nanoparticles, Advanced oxidation processes (AOPs), Photocatalytic degradation, Immobilization, Ciprofloxacin.*

1. Introduction

Water pollution through such contaminants as heavy metals and organic compounds has become a global problem and has caused growing concerns [1]. During the last decades, the use of pharmaceuticals, an important group of organic compounds, especially antibiotics has extremely grown. These compounds are non-biodegradable and can enter the aquatic environment by human and veterinary sources. Among antibiotics, Ciprofloxacin (CIP) [1- cyclopropyl- 6- fuoro- 1,4- dihydro- 4- oxo- 7- (1- piperazinyl)- 3- quinolone carboxylic acid], is a fluoroquinolone broad-spectrum antibiotic, which is an active antibiotic against gram-positive and gram-negative bacteria and has been widely used over the past years [2,3].

The presence of antibiotics in the environment has resulted in the generation of more harmful bacteria which are resistant to antibiotics. Therefore, it is necessary to develop a beneficial method to remove these compounds from water sources like wastewater [4].

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Advanced oxidation processes (AOPs) such as UV/H_2O_2 process, electrochemical method, electro-Fenton process, photo-Fenton, and photocatalysis have been applied for the removal and degradation of antibiotics from groundwater, surface water, and wastewater [5,6]. Of these processes, heterogeneous photocatalysis has been used for the degradation and mineralization of a large range of organic pollutants. For this purpose, different catalysts such as TiO_2, ZnO, ZnS, Al_2O_3, Fe_2O_3, and CdS have been used. Faghihian *et al*. investigated the photodegradation of some organic pollutants, using immobilized TiO_2–zeolite as photocatalyst and higher activity obtained for TiO_2 supported on zeolite X compared to pure TiO_2 [7]. In another study, the photocatalytic activity of MCM-41/ZnO and MCM-48/ZnO nano-composites was examined for the photodegradation of Congo Red as a dye pollutant [8]. In addition, the coating of Mn doped ZnO nanocomposite thin film on glass was studied by Habibi *et al*., and was used to degrade an azo dye from the aqueous solution [9]. Also, the photocatalytic degradation of dimethyldisulfide was studied by zeolite A containing nano CdS, and this catalyst was found to be highly efficient under UV irradiation [10].

Furthermore, the photocatalytic degradation of the acid Red 206 in water was evaluated applying $CuFe_2O_4$ supported on Clinoptilolite by solid-state dispersion (SSD) method [11]. Another study investigated the comparison of the photoefficiency of Ni (II) and NiS incorporated into zeolite P for photodecolorization of Eriochrome Black T dye solution under UV light irradiation [12]. Besides, Mesoporous photocatalyst of CeO_2/SBA-15 was synthesized by Pouretedal *et al*., and the results represented that the dispersed CeO_2 in SBA-15 illustrates a photodegradation of Congo Red (CR) in the aqueous solution [13].

Of these catalysts, TiO_2 and ZnO semiconductors are the most effective. ZnO has a wide band gap with an energy gap (EG) of about 3.3 eV, and because of band to band transition, it absorbs UV irradiation. ZnO is applied in many areas, including solar cells, sensors, and photoluminescence materials. As a photocatalyst, ZnO has some important advantages such as low price and high photocatalytic activity (sometimes, activity bigger than TiO_2). The biggest advantage of ZnO is that it absorbs a larger fraction of the UV spectrum, compared with TiO_2 [14]. Photocatalysis processes have been applied in slurry and immobilized systems. The efficiency of photocatalysis is high when being slurry, but separating the catalyst from the suspension is difficult. To solve this problem, photocatalytic degradation in the immobilized form has been applied. In this technique, the photocatalyst is immobilized into an inert surface such as glass, stainless steel, or ceramic [15].

Some studies have investigated the photocatalytic degradation of CIP in various conditions. Babic´ *et al*., investigated the photolytic degradation of enrofloxacin, CIP, and norfloxacin in rivers and synthetic wastewater. The results showed that the antibiotics were degraded very quickly, and photodegradation followed pseudo-first-order kinetics [16]. Batchu *et al*. examined the removal of Roxithromycin, erythromycin, CIP, and sulfamethoxazole under direct and indirect irradiation of various light sources. The results provided a faster degradation of antibiotics under ultraviolet and simulated solar illumination, representing a better photochemical conversion of antibiotics in aqueous solutions [17]. Furthermore, Liu *et al*. synthesized NaCl/TiO_2 catalyst by surface molecular imprinted technology using the photocatalyst for photocatalytic degradation of CIP. In this study, chlorine was used to dope TiO_2 by the solid state method. The obtained results indicated that the molecular imprinted photocatalyst demonstrated higher selectivity and photodegradation efficiency for CIP degradation than the non-imprinted photocatalyst [18]. Also, the CIP and ibuprofen (IBU) degradation were estimated by Xiao *et al*. by means of ultrasound radiation in aqueous solutions in the presence of matrix organic compounds. The higher degradation rates of antibiotics by ultrasound indicated potential benefits of sonolysis in comparison with the other AOP processes [19]. Besides, the photooxidation of CIP was evaluated by Vasconcelos *et al*. at the pH of 9, confirming that the photoelimination of CIP is very fast, and the kinetics depend on pH value [20].

In this study, the photocatalytic degradation of CIP antibiotic under UV-C light was investigated using synthesized ZnO nanoparticles in immobilized system, and the effect of operational parameters on the degradation efficiency was evaluated. The kinetic of the reaction was examined, and the progress of mineralization was assessed by the total organic carbon (TOC) measurements.

2. Experimental

2.1. Materials

Pure ciprofloxacin (CIP) (Fig. 1) was purchased from Sina Daru pharmaceutical Co., Tehran, Iran. Zinc acetate (Zn $(OAc)_2$), NaOH (0.1 M), HCl (0.1 M) and HF (5%) were obtained from the Merck. The solutions were prepared by dissolving the required amount of CIP antibiotic in distilled water before each experiment.

2.2. Synthesis of ZnO nanoparticles and immobilizing on glass plate

Zn $(OAc)_2$ (2 g) was dissolved in 50 ml of distilled water and stirred by a magnetic stirrer at room temperature. Then, NaOH or HCl was added to the obtained solution dropwise in order to adjust the value of pH at 8. The obtained white precipitate was filtered and washed several times with double distilled water until the pH reached the neutral pH level. Then, the precipitate was dried at 90 °C for 12 h. Finally, the prepared white powder was calcined at 500 °C for 2 h [21,22].

For the immobilization of ZnO nanoparticles on a glass plate (a sand blast glass with the dimensions of 5 × 5 × 0.5 cm^3), the heat attachment method was used. First, the glass plate was placed in HF (5%) solution for about 12 h and then washed with distilled water.

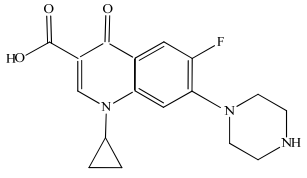

Fig. 1. Chemical structure of ciprofloxacin.

After that, the plate was covered with NaOH (0.1 N) solution for 24 h, then the suspension of ZnO nanoparticles (4 g L^{-1}) that had already been sonicated in ultrasonic bath (T/460 H, Windaus) under the frequency of 35 kHz for 90 min was slowly poured into the cleaned glass plate. Finally, the solution was dried in an oven at 90 ºC for 12 h and calcinated at 400 ºC for 3 h in a furnace and was washed with distilled water in order to remove the weakly attached ZnO nanoparticles [23].

2.3. Photocatalytic study

The Photocatalytic reaction was carried out in a batch photoreactor. The photoreactor was a borosilicate glass dish with the dimensions of 14 × 14 × 5 cm^3 containing a support for holding glass plate (Fig. 2). To start the experiment, the immobilized ZnO on the glass plate was placed into the reactor, and 500 mg L^{-1} of CIP solution with desired concentration was prepared and poured into the reactor. The solution was agitated for 30 min in the dark to reach the adsorption equilibrium. Afterwards, while the solution was being stirred by the magnetic stirrer, the UV lamp (15 W, UV-C, λ_{max} = 254 nm, manufactured by Philips, Holland) was switched on and the solution was illuminated with a desired light intensity from the top to start the reaction. The light intensity was calculated by measuring the electricity current using a Lux–UV–IR meter (Leybold Co.). Then, at certain reaction intervals, 5 ml of the sample was withdrawn, and the concentration of the CIP was determined by means of an UV–Vis spectrophotometer (Shimadzu, 1700, Japan) at λ_{max} = 271.4 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 CIP through the adsorption on ZnO was not very significant and could be neglected.

2.4. Method of analysis

The absorbance of the solution during the degradation process was measured by UV–Visible Spectrophotometer (Shimadzu 1700, Japan). For the characterization of immobilized ZnO nanoparticles, X-ray diffraction (XRD), (Siemens D500, Germany), Atomic Force Microscopy (AFM) (Nanosurf Mobile S, Nanosurf Company, Switzerland) and Scanning Electron Microscopy (SEM) (MIRA3 FEG-SEM, Tescan Company, Czech) techniques were applied. The mineralization content of CIP was determined on the basis of the TOC measurements. TOC measurements were performed by total organic carbon analyzer (Shimadzu TOC–V_{CSH}). Ultraviolet spectrophotometric screening method (Shimadzu 1700, Japan) was used to measure nitrate and ammonium ions during the photodegradation of CIP. To detect the trace of Zn (leaching from the surface of the substrate) in the solution, the Atomic Absorption Spectroscopy (AAS) (VARIAN, model AA240) was employed.

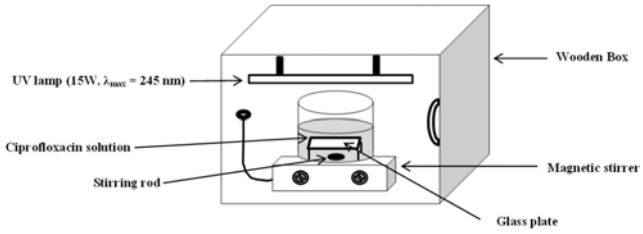

Fig. 2. Experimental set up for photocatalytic degradation of ciprofloxacin using ZnO immobilized nanoparticles.

3. Results and Discussion

3.1. Characterization of ZnO nanoparticles

The crystal structure of the synthesized ZnO nanoparticles was analyzed via X-ray powder diffraction. The XRD pattern (Fig. 3) shows seven different peaks at 2θ = 31, 34, 36, 48, 57, 63, 67, which depicts the hexagonal phase of ZnO [24]. The peaks in ZnO XRD pattern indicate the narrow size distribution of nanoparticles in the samples, implying that the diffraction peaks are almost strong. These results confirmed that the peak positions matched well with the standard data for bulk ZnO [9].

The average diagonal size of immobilized ZnO nanoparticles in photochemical reaction was calculated using the Debye–Sherrer equation [9,25]:

$$D = \frac{0.89\lambda}{\beta cos\theta}$$

where β is the width of the peak at half maximum, λ is the radiation wavelength, and θ the Bragg angle [9]. The crystallite size for ZnO nanoparticles was about 11.5 nm.

Fig. 4 shows the SEM images of the synthesized immobilized ZnO nanoparticles.

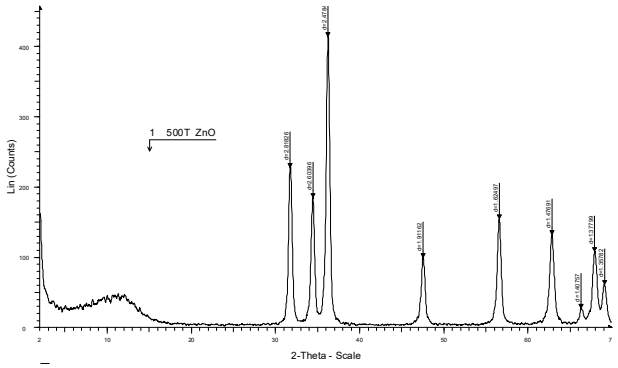

Fig. 3. XRD pattern of synthesized ZnO nanoparticles immobilized on glass plate.

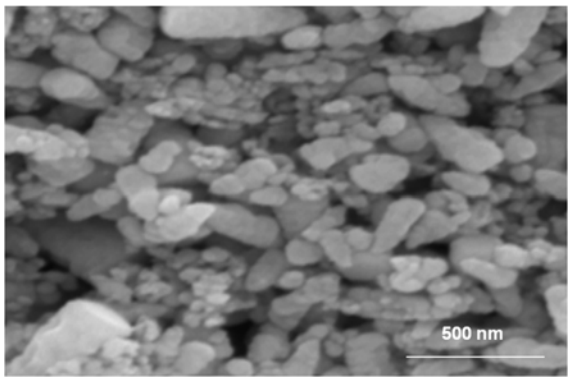

Fig. 4. SEM images of synthesized ZnO nanoparticles immobilized on glass plate

It can be observed that the surface of coated glass has a suitable roughness, and as a result, ZnO immobilization on glass plate is satisfactory.

The information related to the surface roughness of immobilized ZnO nanoparticles using AFM technique is shown in Table 1 and Fig. 5, respectively. Also, the remaining negligible amount of Zn in the solution (by Atomic Absorption Spectrometry–AAS) indicates a suitable immobilizing of nanoparticles on the glass plate through heat attachment technique [26].

3.2. Influence of operational parameters

3.2.1. Effect of initial concentration of ciprofloxacin

To investigate the effect of initial concentration of CIP on photocatalytic efficiency, a set of experiments were done at light intensity = 42 W m^{-2} and pH = 6.8 with different initial concentration of antibiotic (C_0 = 5, 10, 15, and 20 mg L^{-1}). The results (Fig. 6) show a clear reduction of degradation efficiency with an increase in the initial concentration of CIP. The data suggest that the CIP degradation at higher initial concentrations may be limited by the saturation of ZnO surface, which, at higher concentrations, there would be a competition for engaging the active sites and fewer photons will reach the catalyst surface [7]. This leads to a decrease in the generation of electron–hole pairs and hydroxyl radicals (•OH). These results are in agreement with Najjar *et al.*'s (2015) research in degrading an azo dye, indicating that the availability of enough surface adsorption sites at the lower concentration of contaminant results in faster degradation [27].

3.2.2. Effect of initial pH of the solution

To investigate the effect of initial pH of the solution on the photocatalytic degradation of CIP, the pH of the solution was adjusted to 5.3, 6.8 and 8.3 ($[CIP]_0$ = 10 mg L^{-1}, light intensity = 42 W m^{-2}). The results in Fig. 7 indicate that the best pH for the degradation of CIP is the natural pH value (pH = 6.8). The effect of initial pH on the photocatalytic degradation of pollutants is complex, with the results generally depending on the type of pollutant and the zero point charge (zpc) of the photocatalyst. The surface charge properties of the photocatalyst vary by changing the pH of the solution, thus it has a considerable effect on the electrostatic interaction between the catalyst surface and the pollutant molecules. The effect of pH on CIP antibiotic degradation can be examined by considering the properties of both the catalyst and antibiotic in different pH values. For ZnO, the zero point charge is 9.0 ± 0.3 [28] and, consequently, the ZnO surface is positively charged at pH < 9 and negatively charged at pH > 9 [9]. On the other hand, CIP has pk_a at 6.09 and 8.2. At acidic pH, both ZnO and CIP are positively charged; therefore, the adsorption on the surface of ZnO is restricted. With pH of more than 6.09, the surface of CIP is negative, but ZnO has a positive surface, causing the adsorption of antibiotic on ZnO surface and an increase in the rate of degradation. When the pH of solution is > 8, the CIP will appear in an anionic form (CIP-O^-), which hinders the oxidization of species and finally decreases the efficiency of CIP removal [29-31].

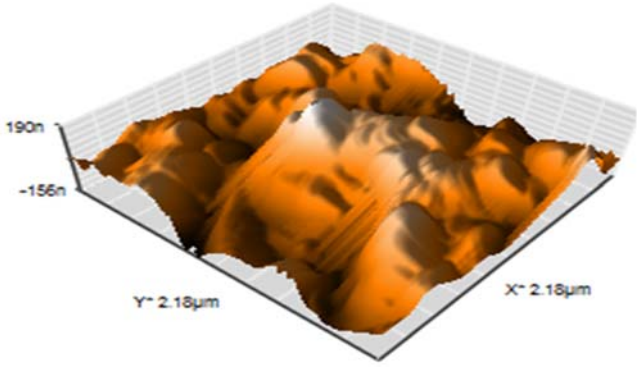

Fig. 5. AFM images of immobilized ZnO nanoparticles on glass plate.

Table 1. Morphologic and surface roughness information of immobilized ZnO nanoparticles.

Key attributes	Area (µm²)	$S_{m\ (nm)}$	$S_{v\ (nm)}$	$S_{p\ (nm)}$	$S_{y\ (nm)}$	$S_{q\ (nm)}$	$S_{a\ (nm)}$
Values	4.77	39.318	49.437	367.3	163.58	-203.72	4.955

S_a: The Roughness Average, S_m: The Mean Value, S_q: The Root Mean Square, S_v: The Valley Depth, S_p: The Peak Height and S_y: The Peak-Valley Height.

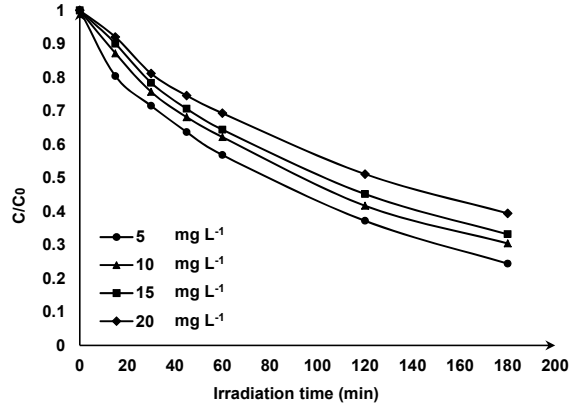

Fig. 6. Effect of ciprofloxacin initial concentration on photocatalytic degradation of ciprofloxacin using immobilized ZnO nanoparticles on glass plate (pH = 6.8, Light intensity = 42 W m^{-2}).

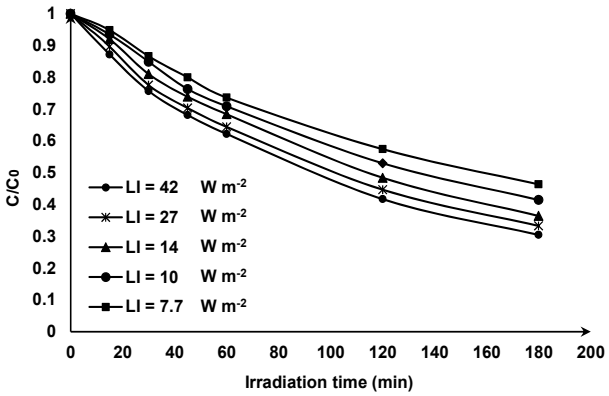

Fig. 8. Effect of light intensity on photocatalytic degradation of ciprofloxacin using immobilized ZnO nanoparticles on glass plate (C_0 = 10 mg L^{-1}, pH = 6.8).

3.2.3. The Effect of Light Intensity

As for the effect of light intensity on photocatalytic degradation of CIP (C_0 = 10 mg L^{-1}, pH = 6.8), a light intensity in the range of 7.7 to 42 W m^{-2} was investigated. Fig. 8 reveals that higher light intensity increased the rate of photocatalytic degradation. When the light intensity increases, the rate of the generation of photoactive species (electron-hole pairs) enhances on the semiconductor surface, raising the rate of CIP photocatalytic degradation [32,12].

3.3. Kinetics Studies

To study the kinetics of photodegradation process, the semi-logarithmic plot (Fig. 9) of CIP concentration versus irradiation time in the presence of immobilized ZnO was evaluated. With different CIP concentrations (pH = 6.8, LI = 42 W m^{-2}), the correlation coefficients (R^2) were estimated, the results of which are shown in Fig. 10. The results indicate the conformation of pseudo-first-order kinetics for the reaction.

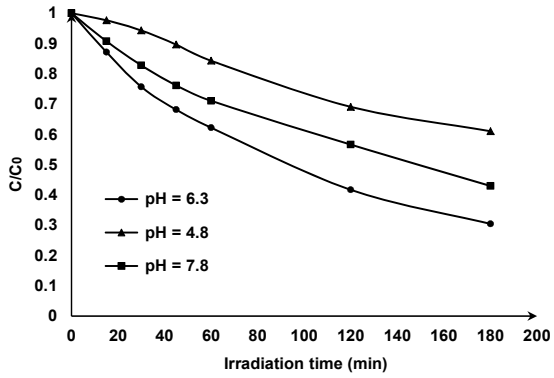

Fig. 7. Effect of initial solution pH on photocatalytic degradation of ciprofloxacin using immobilized ZnO nanoparticles on glass plate (C_0 = 10 mg L^{-1}, Light intensity = 42 W m^{-2}).

3.4. Mineralization Studies

In order to study the mineralization of CIP antibiotic, the concentrations of TOC, and NO_3^-, NH_4^+ ions were measured. Table 2 shows that the TOC of the solution (C_0 = 10 mg L^{-1}, light intensity = 42 W m^{-2} and pH = 6.8) has decreased about 69% after 180 min. The reduction of TOC and the increase of ions concentrations in the solution represent the mineralization of CIP solution. The measurement of UV absorption of CIP solution at 220 and 275 nm in the presence of HCl as a reagent enables rapid determination of nitrate. For determination of ammonium ions a solution of CIP was prepared using different reagents such as $ZnSO_4$, NaOH, Rochelle ($KNaC_4H_4O_6.4H_2O$) and after 10 min the intensity of absorbance peak was measured by a spectrophotometric method [33]. The results are shown in Table 2.

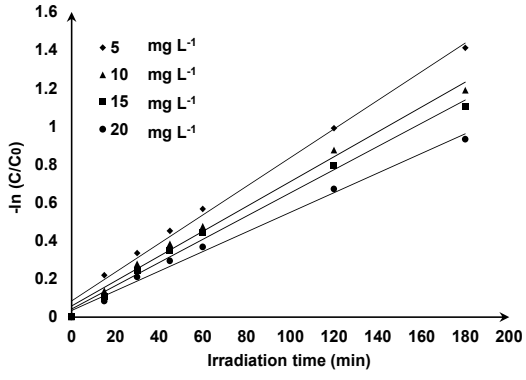

Fig. 9 The semi-logarithmic plot of ciprofloxacin concentration versus irradiation time in the presence of immobilized ZnO nanoparticles on glass plate (pH = 6.8, Light intensity = 42 W m^{-2}).

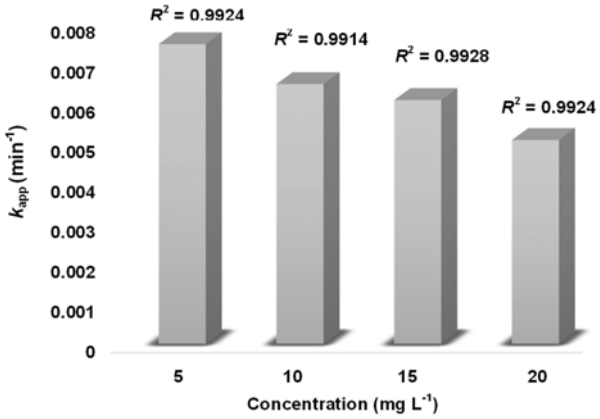

Fig. 10. Variation of k_{app} versus irradiation time for ciprofloxacin degradation in the presence of immobilized ZnO nanoparticles on glass plate (pH = 6.8, Light intensity = 42 W m^{-2}).

Table 2. TOC and ions measurements for photocatalytic degradation of ciprofloxacin antibiotic using immobilized ZnO nanoparticles.

Time (min)	0	60	180
TOC	3.766	2.937	1.174
NO_3^- concentration (mg L^{-1})	0.89	8.8	15.5
NH_4^+ concentration (mg L^{-1})	0.02	1.71	2.67

4. Conclusions

The results of the study showed that the immobilization of ZnO nanoparticles on the glass plate was significantly efficient in the photocatalytic degradation of ciprofloxacin antibiotic. The examination of the degradation efficiency of the catalyst by evaluating the operational parameters indicated that the low initial concentration of the contaminant and high light intensity are more favorable in the progress of degradation process. Besides, the results revealed that the surface charge of both the catalyst and the antibiotic are as crucial factors in determining the optimal pH for degradation experiments. The correlation coefficients and semi-logarithmic plot of CIP represented that the photodegradation of CIP follows pseudo-first-order kinetics. Moreover, the mineralization studies were carried out by measuring the decreasing trend of TOC as well as and the ions conversion to obtain the desirable photodegradation process.

Acknowledgements

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