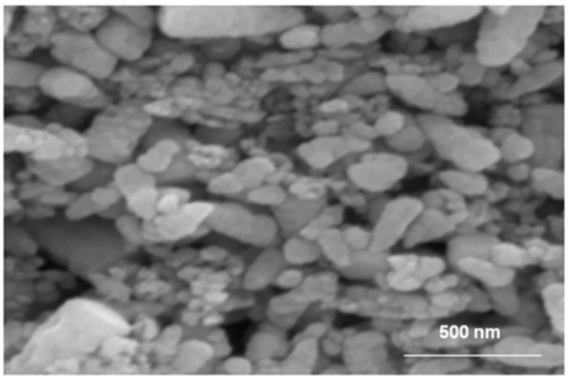

Fig. 4. SEM images of synthesized ZnO nanoparticles immobilized on glass plate

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 ($CIP\text{-}O^-$), which hinders the oxidization of species and finally decreases the efficiency of CIP removal [29-31].

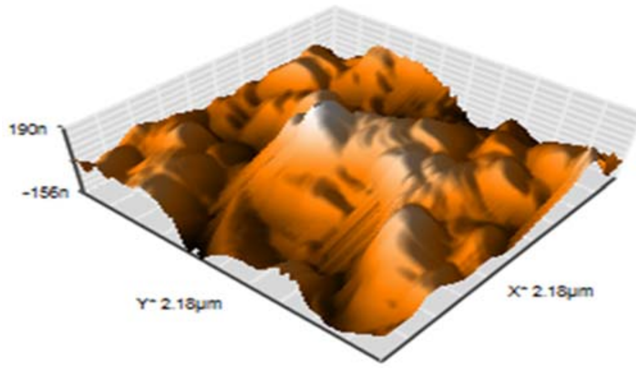

Fig. 5. AFM images of immobilized ZnO nanoparticles on glass plate.

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

Key attributes	Area (µm^2)	$S_{m\ (nm)}$	$S_{v\ (nm)}$	$S_{p\ (nm)}$	$S_{y\ (nm)}$	$S_{q\ (nm)}$	$S_{a\ (nm)}$
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.

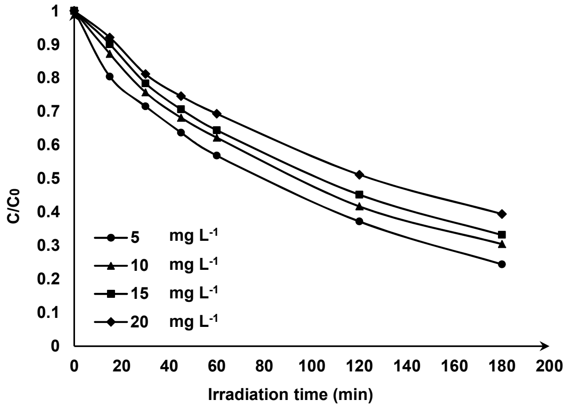

Fig. 6. Effect of ciprofloxacin initial concentration on photocatalytic degradation of ciprofloxacin using immobilized ZnO nanoparticles on glass plate (pH = 6.8, Light intensity = 42 W m^{-2}).

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.

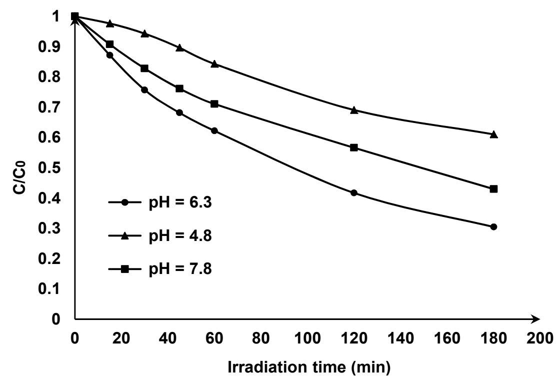

Fig. 7. Effect of initial solution pH on photocatalytic degradation of ciprofloxacin using immobilized ZnO nanoparticles on glass plate (C_0 = 10 mg L^{-1}, Light intensity = 42 W m^{-2}).

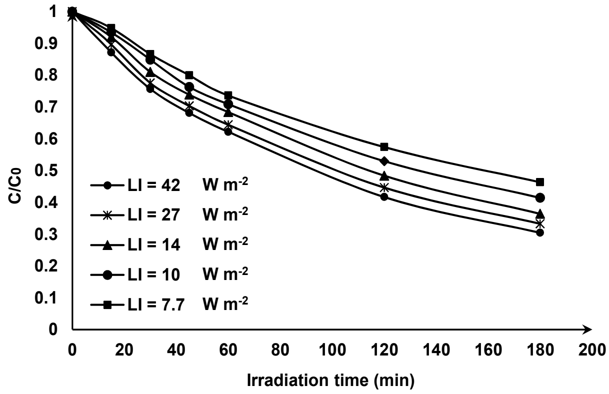

Fig. 8. Effect of light intensity on photocatalytic degradation of ciprofloxacin using immobilized ZnO nanoparticles on glass plate (C_0 = 10 mg L^{-1}, pH = 6.8).

3.4. 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.

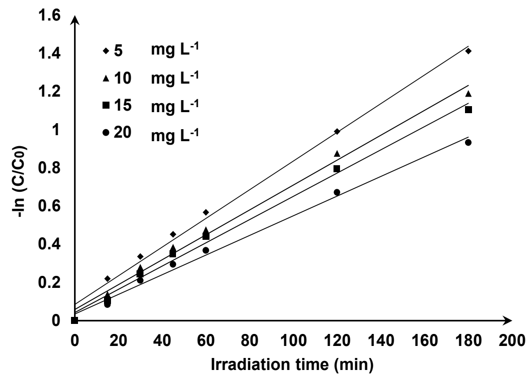

Fig. 9 The semi-logarithmic plot of ciprofloxacin concentration versus irradiation time in the presence of immobilized ZnO nanoparticles on glass plate (pH = 6.8, Light intensity = 42 W m^{-2}).

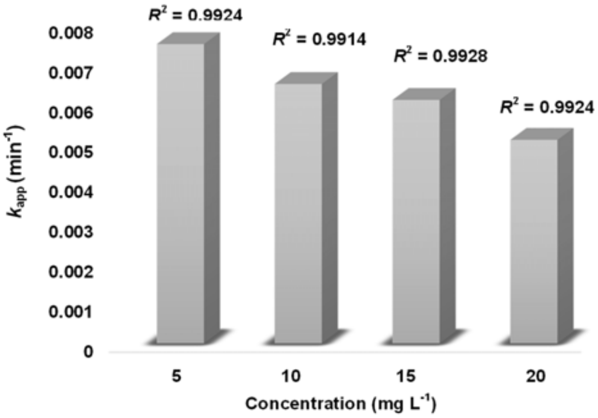

Fig. 10. Variation of k_{app} versus irradiation time for ciprofloxacin degradation in the presence of immobilized ZnO nanoparticles on glass plate (pH = 6.8, Light intensity = 42 W m^{-2}).

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.

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