

Solar photocatalytic degradation of amoxicillin using Ni:TiO₂ nanocatalyst stabilized on ceramic plates

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ABSTRACT

The main aim of this study was to investigate the photocatalytic degradation of amoxicillin in an aqueous medium using Ni:TiO₂ nanoparticles stabilized on ceramic surfaces under natural sunlight irradiation. Ni:TiO₂ nanoparticles were synthesized using a hydrothermal method and characterized using X-ray diffraction, scanning electron microscope, and Fourier-transform infrared spectroscopy techniques. The nanoparticles were then stabilized on the ceramic surface in a furnace. The effects of operational parameters such as the doping percentage (doping ratio), initial pH, contact time, and initial amoxicillin concentration on the photocatalytic degradation efficiency (PDE) of amoxicillin were examined in the presence of natural sunlight irradiation. The reusability of the stabilized nanoparticles was also studied. Based on these results, the amoxicillin PDE under natural sunlight irradiation was enhanced by increasing the doping percentage of synthesized nanoparticles and the contact time, while increasing the initial pH and the initial concentration of amoxicillin led to a reduction in the amoxicillin PDE. The results revealed that 78.4% PDE was obtained for amoxicillin using Ni:TiO₂ nanoparticles under optimal conditions for the photocatalytic process. This efficiency rate was higher than the PDE of TiO₂ nanoparticles and the degradation efficiency of solar irradiation by 22.97% and 66.1%, respectively. Moreover, the amoxicillin PDE was reduced after each reuse of the Ni:TiO₂ nanoparticles stabilized on the ceramic.

Keywords: Antibiotic; Stabilization; Photocatalyst; Ni:TiO₂; Hydrothermal; Sunlight

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1. Introduction

Pharmaceutical compounds constitute an important group of environmental pollutants found in surface and groundwater [1,2]. These compounds usually originate and find their way to aquatic environments from various sources, including the pharmaceutical industry, effluents from hospitals and medical centers, as well as wastes from humans and livestock [1,3]. Due to their extensive and often unnecessary use in veterinary and human medicine, antibiotics are one of the leading causes of contaminating aquatic environments [4]. Many antibiotics (even minor quantities) have noxious effects on large groups of living organisms, including bacteria and algae [5,6]. In this regard, the development of antibiotic-resistant bacteria appears to be a major concern from an environmental point of view, and the one which might bring on acute and chronic diseases as well as costly treatment procedures and hospital care [7,8]. One of the major classifications of antibiotics relies on the presence of the beta-lactam ring in its structure. Antibiotics are accordingly divided into two beta-lactam and non-beta-lactam categories [9]. Beta-lactams (such as amoxicillin, penicillin, and ampicillin) constitute more than 65% of the antibiotics used in the world, among which, amoxicillin has the highest consumption rate [10]. Amoxicillin is a semi-synthetic antibiotic used in medicine to treat various human infections and in veterinary medicine as a growth promoter [11]. It is poorly metabolized in the body; thus, about 80%–90% of this enters the environment unchanged and in its original form [7,11]. It is also hardly degraded by common biological processes of wastewater treatment (conventional plug flow activated sludge) and cannot be optimally removed from the sewage [6,12]. Therefore, applying effective technologies is necessary to purify and remove these compounds from water and wastewater. Various methods such as adsorption [13], membrane processes [14], electrochemical methods [15], and advanced oxidation processes (AOPs) [16,17] have already been used to eliminate amoxicillin and various other pharmaceutical compounds from aquatic environments. Among these methods, advanced oxidation processes such as Fenton, photo-Fenton as well as ultrasonic processes, and photocatalytic and nano-photocatalytic methods have been reported as appropriate and effective approaches to decompose amoxicillin in aqueous media [7,8,11,16,18]. The main mechanism involved in these processes acts based on the production of active and oxidizing hydroxyl radicals (OH^{\bullet}). Such radicals can then react unselectively with resistant organic pollutants and oxidize them [7,19].

The nano-photocatalytic method using titanium dioxide (TiO_2) nanocatalyst has been recognized as an appropriate high-efficient technology for the degradation of amoxicillin in aqueous media [3,11]. TiO_2 nanocatalyst incorporates features and properties such as low cost, significant sustainability, and higher activity [20–22]. This nanocatalyst has a broad bandgap (3.2 eV) and is further excited at ultraviolet wavelengths while its activity reduces within the visible wavelengths [20,23], which limits the use of this catalyst in the presence of sunlight as a sustainable and available source of energy. Thus, the nanocatalyst should undergo further modifications to enhance

the absorption of visible light and improve photocatalytic activity. This would then result in the effective use of the sunlight's natural energy for TiO_2 nano-photocatalytic processes. As previously stated by researchers, doping these nanoparticles with metal ions to reduce their bandwidth, is one of the most effective strategies to modify their structures [20]. Due to the possible health and environmental related hazards of applying such nanoparticles and to make them easily recovered and separated after utilization, the catalytic nanoparticles should be first stabilized on neutral surfaces [23,24]. Moreover, the photocatalytic activity of stabilized nanoparticles has been demonstrated to be superior to the nanoparticles used as suspension [25,26]. In that regard, previous studies have shown that different materials such as bentonite [27], silica gel [23], glass [25], zeolite [24], and cement [28] are capable of being employed as substrates for stabilizing the catalysts.

The application of the photocatalytic oxidation process along with using different catalysts for the degradation of antibiotics in aqueous media has been evaluated in various previously published studies. However, according to the available literature and reports, so far, the use of a photocatalytic process in which the $\text{Ni}:\text{TiO}_2$ nanoparticles catalyst are stabilized on the surface of ceramic and under sunlight irradiation has not been investigated to decompose amoxicillin in an aqueous medium. Therefore, in this study, we aimed to analyze the photocatalytic degradation of amoxicillin in an aqueous medium using $\text{Ni}:\text{TiO}_2$ nanoparticles in the presence of sunlight irradiation.

2. Materials and methods

2.1. Chemicals

In this study, the amoxicillin standard was purchased from Sigma-Aldrich Company. Titanium dioxide, nickel(II) oxide, *n*-butylamine, and other laboratory materials were purchased from Merck Co., Germany. All chemicals used had a laboratory-grade and were in their pure form.

2.2. Nanocatalyst synthesis

$\text{Ni}:\text{TiO}_2$ nanocatalyst was synthesized through the mild hydrothermal method. We first prepared a solution of compounds of TiO_2 (2 moles), nickel oxide (0.01 moles), *n*-butylamine (0.5 mL), and 1 normal hydrochloric acid (10 mL), which were thoroughly mixed (doping percentage = 1%). To prepare different percentages of nanoparticles, two moles of TiO_2 nanoparticles (1.62 g) were doped with values of 0.005, 0.01, 0.015, and 0.02 moles of nickel oxide; as a result, 0.5%, 1.0%, 1.5%, and 2.0% of TiO_2 nanoparticles doped with nickel were obtained, respectively. The prepared acidic solution was added to the Teflon liner under mixing conditions and each liner was placed in a general-purpose autoclave. The autoclave was then put inside an oven for 12 h at a temperature of about 120°C. The resulting solution was rinsed several times with double-distilled water after quenching and dried at room temperature [29].

2.3. Stabilization of nanocatalyst on the ceramic plates

We used circular ceramic plates with a diameter of 8.5 cm and a thickness of 8 mm as the stabilization substrate.

The surface of the ceramics was first sandblasted to create a rough and appropriate surface for better adhesion of nanoparticles. The plates were then rinsed several times with ion-free water and dried at room temperature. Subsequently, we prepared a suspension of Ni:TiO₂ nanocatalysts with a concentration of 3% in distilled water. The suspension was shaken for 45 min and then underwent ultra-sonication for 10 min to be homogenized. After homogenization, the prepared homogenous suspension was coated evenly on the ceramic surfaces using a 10 mL pipette while stirring (a volume of 10 mm of homogenous suspension of Ni:TiO₂ nanocatalysts were poured on each piece of ceramic). The coated ceramic plates were dried at room temperature for 24 h. Finally, each plate was placed inside a furnace at 450°C for 3 h for calcination and stabilization of nanoparticles on the ceramic surface [25].

2.4. Reactor used

This was a batch scale study in which six one-liter glass beakers (a photocatalytic reactor) were used. The working volume of each reactor was considered to be 200 mL. The ceramic substrate and the light source were located at the bottom and top of the reactor, respectively. Direct sunlight was the main light source used. Accordingly, the study was conducted during the days of July from 12:00 to 14:00. A plate mixer was also used for the mixing the process in the reactors.

2.5. Photodegradation experiments

We first prepared a stock solution with a concentration of 1,000 mg/L of amoxicillin. Then, each reactor was filled with an amoxicillin aqueous solution of a certain concentration.

Necessary modifications were made in them according to the predetermined variables. The reactors were placed on a shaker and the rotation speed and mixing time were set. Several samples were taken from each reactor and analyzed after the specified duration. The variables considered in this study included initial concentrations of amoxicillin (10, 20, 40, and 80 mg/L), contact time (30, 60, 90, 120, 150, and 180 min), the doping percentage of nanoparticles (0.5%, 1%, 1.5%, and 2%) and the initial pH (3, 5, 7, 9, and 11). The samples containing amoxicillin were measured using an HPLC instrument (KZUER Co., Model: AZURA, Germany), equipped with a C18 column and a PDA detector, at a wavelength of 190 nm [9].

2.6. Characterization techniques

A scanning electron microscope (SEM) (TESCAN, Model: Mira3, Czech Republic) was employed to determine the morphology of the catalyst surface. X-ray diffraction device (XRD) (PANalytical, Model: X'Pert Pro MPD, the Netherlands) was also used to examine the crystallographic characteristics as well as the size of nanoparticles. The XRD pattern of the nanoparticles synthesized was prepared at a 2θ angle of 10° to 80° and then analyzed. The Fourier-transform infrared spectroscopy (FT-IR) (Model: AVATAR, Thermo, USA) was applied to examine the chemical bonds as well as to determine the type of functional groups.

3. Results and discussion

3.1. Characteristics of Ni:TiO₂ nanocatalysts

SEM images of un-doped TiO₂ and Ni:TiO₂ nanocatalysts are shown in Fig. 1a and b respectively. The morphological

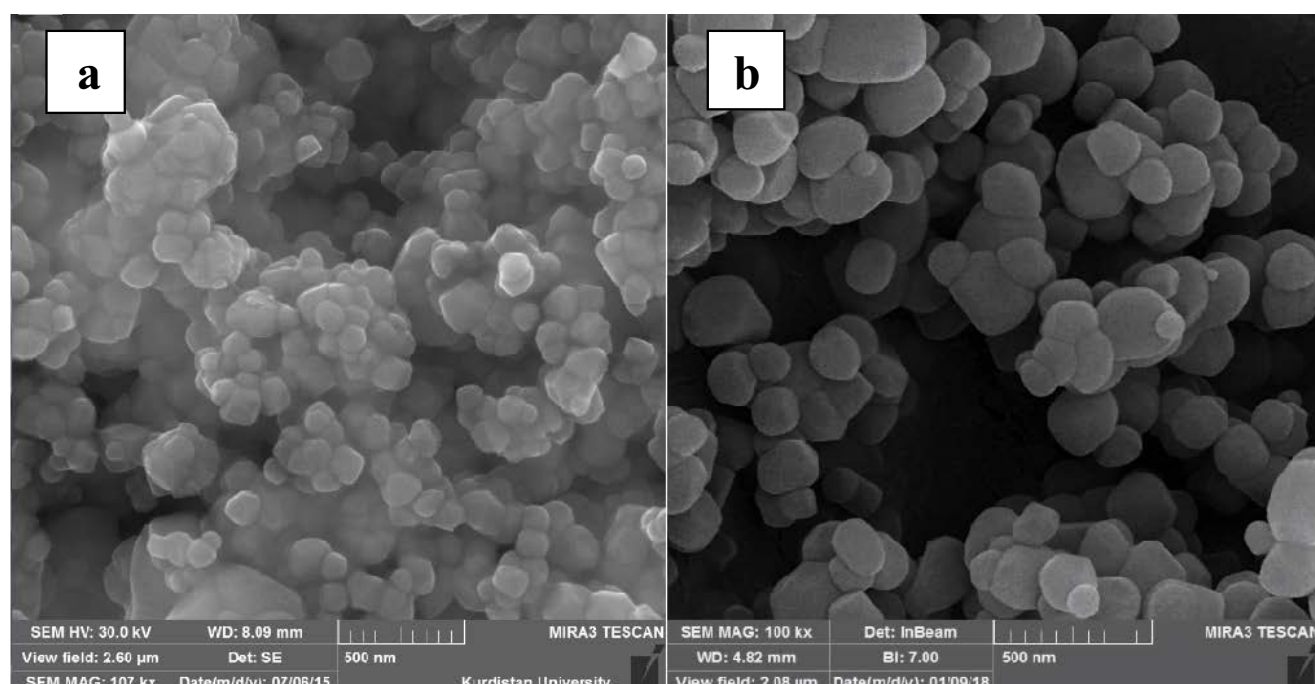


Fig. 1. Characteristic SEM images of synthesized nanoparticles: (a) bare TiO₂ and (b) Ni:TiO₂.

analysis of these nanocatalysts demonstrates their spherical distribution at the nanoscale. Based on SEM images, the mean diameter of TiO₂ and Ni:TiO₂ nanoparticles are about 98.88 and 85.45 nm, respectively. Compared with the average size of TiO₂ nanoparticles, the average size of the Ni:TiO₂ nanoparticles has been reduced due to the presence of nickel in its composition. To explain such behavior of nanoparticles, one can say that the amount of bandgap has reduced due to the presence of nickel in the composition of TiO₂ nanoparticles, which at the same time, has reduced the size of their crystals [30]. Moreover, the agglomeration rate among the doped nanoparticles has not declined compared with the non-doped nanoparticles [31]. The tetragonal morphology of the particles has altered to spherical, which could be attributed to the effect of the surfactant used.

The XRD pattern for TiO₂ and Ni:TiO₂ nanoparticles is shown in Fig. 2. The size of bare TiO₂ nanoparticles and Ni:TiO₂ nanoparticles was calculated using the Scherrer formula according to Eq. (1) [32].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D : size of crystals' nanoparticles in nanometers; λ : powder X-ray wavelength in nanometers; β : width of the highest peak at the half-height in radians; and θ : diffraction angle of the highest peak in degrees

The large peaks identified for bare TiO₂ and Ni:TiO₂ nanoparticles are almost identical; however, the peak intensity of Ni:TiO₂ nanoparticles shows a significant decrease. Besides, as can be seen in this figure, the widening of the Ni:TiO₂ peak is related to the dopant used and the structure created after the doping process. It is assumed that some portion of the nickel has infiltrated into the TiO₂ lattice and nickel ions are uniformly distributed in the structure of semiconductor crystals [33].

The peaks formed in the XRD patterns and the Miller index corresponding to the 2θ of bare TiO₂ and Ni:TiO₂ nanoparticles indicate the formation of the anatase phase (JCPDS, Card No. 21-1272). Revealed by the results, the crystalline structure of TiO₂ was not affected by nickel doping and no specific diffraction peak related to nickel oxide was observed. This phenomenon may have occurred due to the very small volume of nickel or the dispersion of nickel particles in the TiO₂ lattice. It was found that adding nickel dopant to TiO₂ reduces the intensity of the peaks, indicating a decrease in the size of crystals. This confirms that nickel ions have been successfully incorporated into the TiO₂ crystal lattice [30]. In addition, doping TiO₂ with dopant materials generally reduces the lattice parameters of this catalyst [34]. The decreased size of the crystals as a result of adding nickel reflects that the presence of this element prevents the growth of crystals as well as the phase transition. As a result, reducing the particles' size will lead to an increase in the specific surface area of the catalyst, which affects the photocatalytic process efficiency [35].

The FT-IR spectroscopy of TiO₂ and Ni:TiO₂ nanoparticles is shown in Fig. 3. As seen in Fig. 3, the strong peaks that appeared in the 400–800 cm⁻¹ range in both TiO₂ and Ni:TiO₂ graphs are related to the bonds of anti-symmetric and symmetric stretching vibrations of Ti–O and Ti–O–Ti.

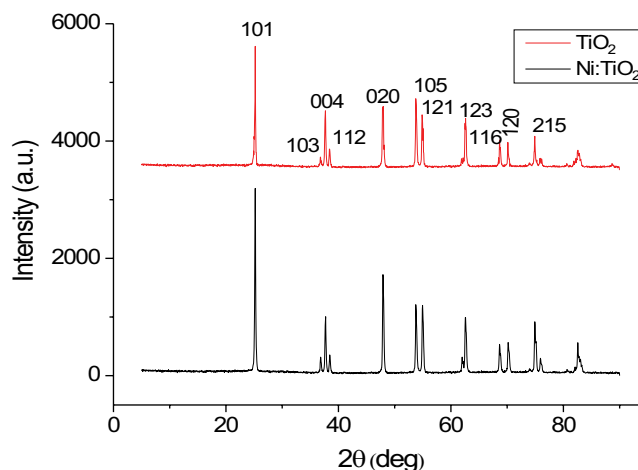


Fig. 2. XRD pattern of TiO₂ and Ni:TiO₂ nanoparticles.

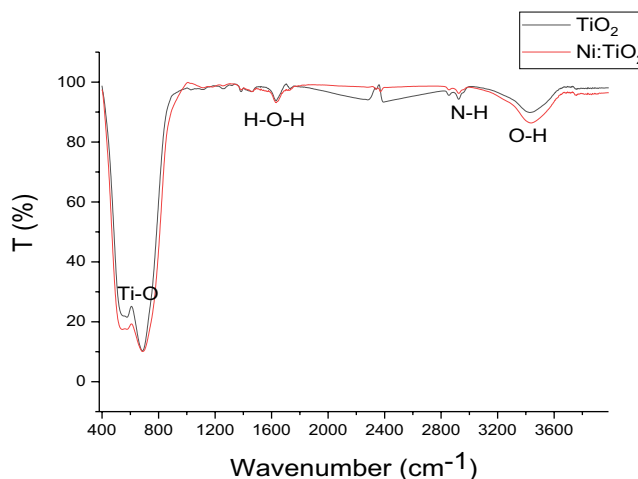


Fig. 3. FT-IR spectroscopy of pure TiO₂ and Ni:TiO₂ nanoparticles.

The band observed in the 500 cm⁻¹ range in the present study is related to Ti–O–Ti and Ti–O vibrations. In the modified Ni:TiO₂ samples, the shape of the band observed in the 500 cm⁻¹ range is different compared with the pure TiO₂ samples due to the modifications made as well as the presence of symmetric Ti–O–Ti and anti-symmetric Ti–O groups. In addition, the intensity of the band is lower in the modified samples, indicating that the bands are weakened. The number of bands in the doped samples is higher than in the non-doped samples due to the presence of more molecules. In addition, the peaks seen in the area of 1,620–1,635 and 3,300–3,450 cm⁻¹ ranges are attributed to the bending vibration of water molecules absorbed on the TiO₂ surface and the stretching vibration of O–H groups, respectively. These groups seem to be highly effective in improving photocatalytic activity. Moreover, the presence of a band between 2,800–3,000 cm⁻¹ reflects the presence of a small amount of organic matter in the sample, which could be due to the applying the surfactant, *n*-butylamine [36].

In their study, Ganesh et al. [31] observed some weak transition bands between 3,400–3,600 and 1,625 cm⁻¹ in

ranges in the FT-IR spectrum of TiO_2 and Ni:TiO_2 nanoparticles at concentrations of 0.1%, 0.5%, 1%, and 5%, which gradually decrease with increasing nickel percentage in the TiO_2 lattice. These bands are related to vibrations of the O–H bending groups of water molecules adsorbed on the titanium surface. A peak seen in the $650\text{--}830\text{ cm}^{-1}$ range is attributed to different vibrational modes of TiO_2 . A wide peak is seen below the $1,200\text{ cm}^{-1}$ range due to Ti–O–Ti vibrations. The downward movement and sharpening of the Ti–O–Ti peak with increasing nickel can lead to a reduction in the particles' size [31].

3.2. Effective operational parameters in amoxicillin photocatalytic degradation

3.2.1. Effect of dopant percentage

The effect of the doping percentage (0.5%, 1%, 1.5%, and 2%) of Ni:TiO_2 nanoparticles on the efficiency of photocatalytic degradation of amoxicillin under sunlight is shown in Fig. 4. Based on the results given in this figure, the photocatalytic degradation efficiency (PDE) of amoxicillin has increased with the increased percentage of nanoparticles' doping percentage. As the doping percentage of Ni:TiO_2 nanoparticles increases, the number of active sites at the catalyst surface increases, resulting in an increase in the production of OH and O_2 radicals in the environment. Moreover, the presence of nickel in the composition of Ni:TiO_2 nanoparticles reduces the bandgap and the size of the crystals. This phenomenon prevents the electron/hole pair recombination [30]. Since nickel doping in the TiO_2 structure acts as a crystal size inhibitor, increasing the dopant percentage reduces the size of the crystals, which thereby enhances the surface area of nanoparticles. This phenomenon will increase the PDE of pollutants [34]. It has been reported that the photocatalytic removal efficiency of "Bisphenol A" under visible light radiation increased as the percentage of nickel increased in the composition of Ni:TiO_2 nanoparticles [30]. In another study, it was found that increasing the nickel percentage in the structure of TiO_2 increased the photocatalytic removal efficiency of the acidic dye in the photoelectrocatalytic process using Ni:TiO_2 [33].

3.3. Effect of pH

Considering the surface charge of the catalyst and the nature of organic compounds, pH is seen as one of the effective parameters in photocatalytic processes. pH changes affect adsorption capacity, target compound separation, electric charge distribution on the catalyst surface, and the capacity bond oxidation potential [37]. The effects of pH at values 3, 5, 7, 9, and 11 in the photocatalytic degradation of amoxicillin in a solution under the following conditions are shown in Fig. 5: Initial amoxicillin concentration (20 mg/L), the doping percentage of nanoparticles (1.5%), and the reaction time (120 min).

According to Fig. 5, the photocatalytic degradation efficiency of amoxicillin has reduced with increasing the pH value. The highest and lowest PDE rates of amoxicillin was obtained at $\text{pH} = 3$ (84.9%) and $\text{pH} = 11$ (36.75%),

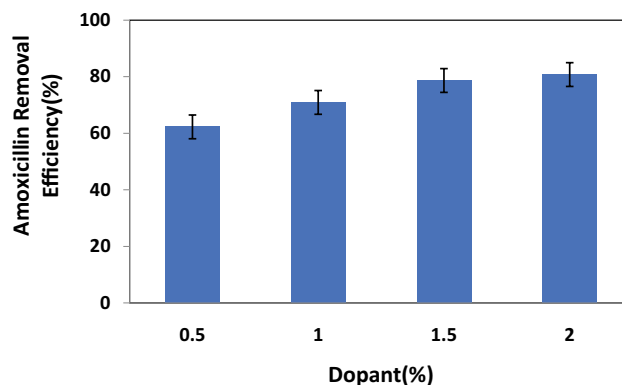


Fig. 4. Effect of doping percentage of Ni:TiO_2 nanoparticles on the amoxicillin PDE under sunlight radiation ($\text{pH} = 7$; contact time = 120 min; initial concentration of amoxicillin = 20 mg/L).

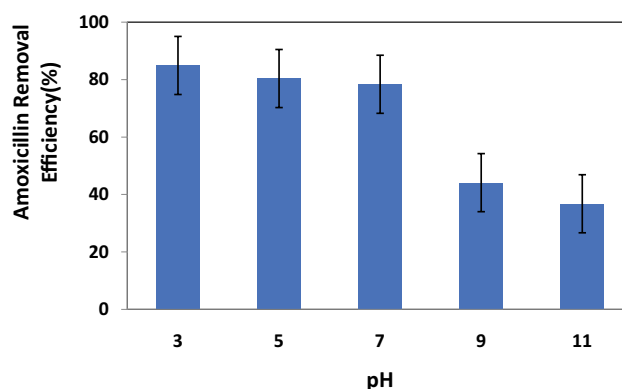


Fig. 5. Effect of pH on the PDE of amoxicillin under sunlight (doping percentage of nanoparticles = 1.5%; contact time = 120 min; initial concentration of amoxicillin = 20 mg/L).

respectively. The contaminants' removal efficiency increases in photocatalytic processes at low pHs due to the increased hydroxyl radicals in the medium [38].

In acidic pHs, the pores produced by light radiation on the catalyst surface act as an oxidizing agent. These cavities are transferred to the catalyst surface in the capacity band and react with water molecules and OH ions adsorbed on the catalyst surface, producing OH and H radicals. These radicals degrade the pollutants adsorbed on the catalyst surface [39]. Amoxicillin molecules have three degradation constants belonging to the functional groups of carboxyl ($\text{pK}_a = 4.2$), amine ($\text{pK}_a = 7.4$), and phenol ($\text{pK}_a = 9.6$). Thus, they can be found at various pHs in cationic, neutral (anionic), and anionic forms. The amoxicillin pK_a falling in the acidic pH range can be known as one of the reasons for its greater elimination rate in acidic pHs [40].

It was reported that the highest photocatalytic removal efficiency of amoxicillin occurred at $\text{pH} = 4$ and the degradation rate of amoxicillin decreased by increasing the medium pH [8]. Nevertheless, by examining the photocatalytic degradation of tetracycline in the pH range of 5–11, the highest tetracycline PDE obtained at $\text{pH} = 5$ [37]. Examining the efficacy of the CuFe_2O_4 catalyst in removing

amoxicillin from aqueous media, the highest amoxicillin PDE was obtained at a pH of 4 and the degradation efficiency decreased with increasing pH [40].

3.4. Effect of time

The effects of reaction time on the photocatalytic degradation of amoxicillin by Ni:TiO₂ nanoparticles in the presence of sunlight are given in Fig. 6 at different times of 30, 60, 90, 150, 120, and 180 min at pH 7, the doping percentage of 1.5, and amoxicillin concentration of 20 mg/L. According to this figure, one can see that the rate of amoxicillin photocatalytic degradation has increased by increasing the reaction time. The lowest amoxicillin degradation rate obtained in 30 min was equal to 28.15%, while the highest rate in 180 min was 84.56%.

As the reaction time increases, the amount of energy received at the nanocatalyst surface rises, enhancing the number of active sites at the catalyst surface. As a result, more active electrons/holes and radicals are produced in the medium, resulting in the increased photocatalytic degradation of amoxicillin. In addition, over longer times, amoxicillin molecules find the opportunity to come into contact with active radicals in the medium [4,33]. Similar results have been obtained regarding the effect of time on the PDE in previous studies [31,33,41].

3.5. Effect of initial amoxicillin concentration

Fig. 7 shows the effect of initial amoxicillin concentration on its PDE rate by Ni:TiO₂ nanoparticles in the presence of sunlight at different concentrations of 10, 20, 40, and 80 mg/L at pH 7, the nanoparticles' doping percentage of 1.5, and the reaction time of 120 min. As demonstrated in Fig. 7, increasing the initial concentration of amoxicillin has reduced its PDE rate. The highest percentage of amoxicillin degradation at a concentration of 10 mg/L was obtained as 96%, while the lowest degradation percentage at a concentration of 80 mg/L was equal to 30.5%.

The variables of doping percentage, contact time, and pH were kept constant at all concentrations. As a result, the amounts of radicals produced for different concentrations of pollutants are almost identical. Therefore, the rate of pollutant degradation is higher at lower concentrations and the efficiency rate increases. Moreover, as the initial concentration of amoxicillin increases, the density of its molecules in the medium increases. Thus, the percentage of radiation rays reaching the catalyst surface reduces, thereby, decreasing the production of active hydroxyl radicals. On the other hand, the production of the active radicals decreases at higher concentrations due to the occupation of active sites of the catalyst surface by amoxicillin molecules. In addition, the reaction of OH⁻ and O₂ molecules is inhibited due to the lack of direct contact with the electron/hole produced at the catalyst surface by increasing the number of amoxicillin molecules on the catalyst surface. As a result, the oxidizing species of OH[•] and O₂ are inhibited. Hence, the removal efficiency of amoxicillin will be lower in samples with higher concentrations [8,42]. It was observed that the removal efficiency of amoxicillin using Fe:Ni nanoparticles reduced from 94%

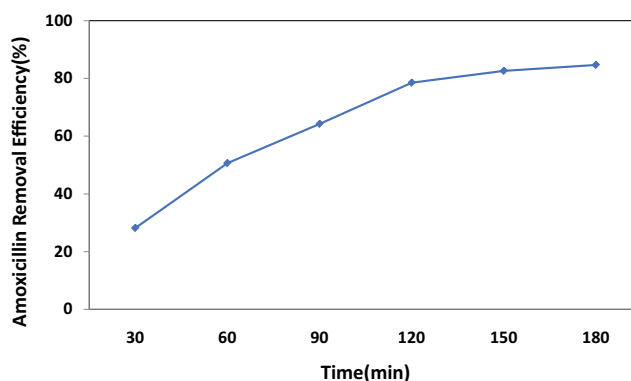


Fig. 6. Effect of reaction time on the PDE rate of amoxicillin under sunlight illumination (dopant percentage = 1.5%; pH = 7; initial amoxicillin concentration = 20 mg/L).

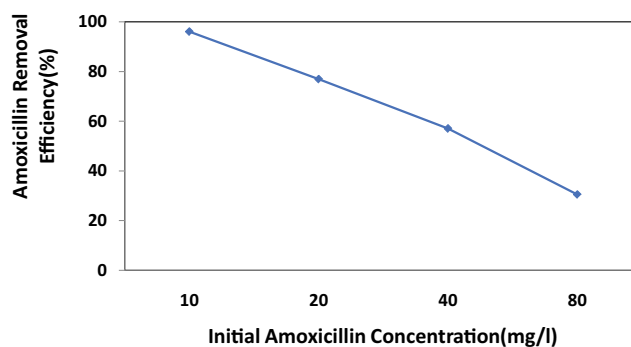


Fig. 7. Effect of the initial concentration of amoxicillin on its photocatalytic degradation efficiency under sunlight (dopant percentage = 1.5%; pH = 7; initial amoxicillin concentration 20 mg/L).

to 72% by increasing the initial concentration of amoxicillin from 40 to 100 mg/L in 20 min [8]. In another study, it was indicated that increasing the initial concentration of ampicillin will reduce its PDE rate using ZnO/polyaniline nanocomposite in an aqueous solution in the presence of sunlight [42]. It was also found that increasing the initial concentration of tetracycline from 27 to 103 mg/L in the photocatalytic degradation process of this antibiotic has reduced its removal efficiency from 91.4% to about 69.3% in a 90-min timeframe [37]. In a study, the highest amoxicillin photocatalytic removal efficiency was obtained using the CuFe₂O₄ catalyst at low concentrations. According to it, the removal efficiency decreased by increasing the initial concentration of amoxicillin. It was suggested that in conditions, where all parameters such as the catalyst concentration, H₂O₂ concentration, reaction time, and pH are the same, the production rates of oxidizing agents are the same as well. Thus, the complete elimination of the pollutant does not occur at higher concentrations, which, in turn, reduces the process efficiency [40].

3.6. Comparison of amoxicillin removal efficiency

Fig. 8 shows the removal efficiency of amoxicillin using sunlight without nanoparticles, with bare TiO₂ nanoparticles,

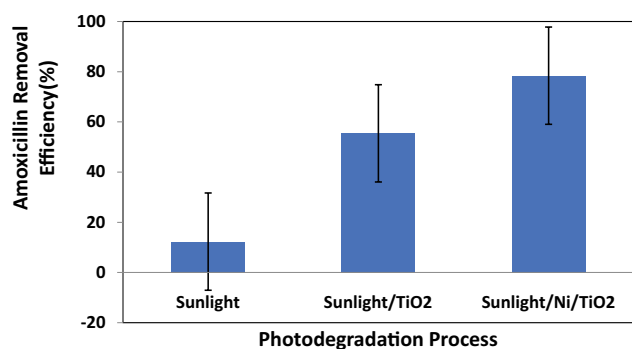


Fig. 8. Comparison of amoxicillin removal efficiency using sunlight alone, TiO₂ nanoparticles under sunlight, and Ni:TiO₂ nanoparticles under sunlight (dopant percentage = 1.5%; pH = 7; initial amoxicillin concentration 20 mg/L).

and Ni:TiO₂ nanoparticles with the initial concentration of amoxicillin of 20 mg/L, the time of 120 min, and the pH of 7. According to this figure, the PDE of amoxicillin using sunlight without nanoparticles, with bare TiO₂ nanoparticles, and Ni:TiO₂ nanoparticles are 12.3%, 55.43%, and 78.4%, respectively.

As seen in Fig. 8, the PDE of amoxicillin using Ni:TiO₂ nanoparticles under sunlight is higher than its PDE rates using bare TiO₂ nanoparticles, and the sunlight without nanoparticles. Adding nickel as a dopant to TiO₂ reduces the bandgap energy of the nanocatalyst. Nickel metal also prevents the electron/hole recombination in the nanocatalyst, expands the effective absorption of light in the visible area, and improves the efficiency of TiO₂ photocatalytic activity. Therefore, the efficiency of pollutant removal in the doped nanoparticles will be much higher than that of the pure nanoparticles [31,43,44].

3.7. Reusability of Ni:TiO₂ nanoparticles

The stability of catalysts especially immobilized catalysts is of great consideration during photocatalysis. The stability of the as-prepared catalyst can be performed as a valuable strategy to show the suitability of the catalyst. The reusability test may show the stability of the catalyst on the surface of the support. In this study, the reusability of Ni:TiO₂ nanoparticles is demonstrated four times in Fig. 9. As can be seen in the figure, the PDE rate of amoxicillin at each re-use of the nanocatalyst has slightly decreased compared with the previous time so that the PDE rate of amoxicillin has reduced by about 14% during the four stages of re-use of the stabilized nanocatalyst. The results of previous studies [41,45,46] regarding the reuse of catalysts suggest that the PDE rate is reduced by only about 10% in four to five re-uses of these catalysts. One reason for the decrease in the PDE rate after reuse is the removal of some nanoparticles from the ceramic surface during the preparation process of the catalyst for reuse. In a study, Sun et al. [45] investigated the reusability of TiO₂ nanocatalyst in Cr(VI) removal four consecutive times. According to their results, the chromium removal efficiency was reduced by about 11% after four re-uses. They stated that the reason for

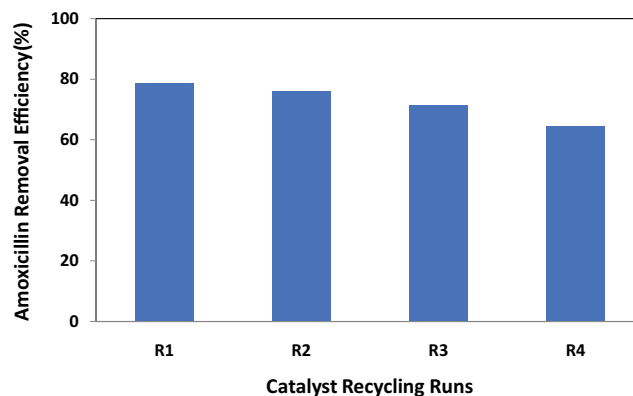


Fig. 9. Effect of the number of reuses of Ni:TiO₂ nanoparticles stabilized on the ceramic surface in the photocatalytic degradation of amoxicillin under sunlight (dopant percentage = 1.5%; pH = 7; initial amoxicillin concentration 20 mg/L).

the reduction in the removal efficiency during re-use of the catalyst may be due to the producing by-products such as Cr(III) and the absorption of these products on the active sites of the catalyst. The results of the study by Topkaya et al. [46] also indicated the reusability of pure ZnO and ZnO:TiO₂ composite catalysts in the photocatalytic degradation process composition during two times of re-use. The researchers suggested that during photocatalytic reactions, the degraded products may remain on the catalyst surfaces, and thus, reduce their photocatalytic activity. Our observations confirmed that the release of catalysts into the solution after the reaction is not considerable. However, the photocorrosivity of Ni:TiO₂ nanostructures should be evaluated via a separate study in the future. In this manner, if we monitor the drop in the photocatalytic activity concerning the removal of the target pollutant, it may be due to both the detachment of nanocatalyst into the solution and/or the photocorrosivity of the catalyst. Therefore, we should design a study to show the role of each occurrence separately.

4. Conclusion

We analyzed the photocatalytic degradation of amoxicillin in an aqueous medium using Ni:TiO₂ nanoparticles under sunlight irradiation in this study. Ni:TiO₂ nanoparticles were first synthesized by a mild hydrothermal technique and stabilized on the ceramic surface. The properties of these nanoparticles were studied using FT-IR, XRD, and SEM techniques. The photocatalytic degradation of amoxicillin was then carried out in batch reactors under sunlight irradiation. The effects of parameters such as the doping percentage of nanoparticles, initial pH, initial concentration of amoxicillin, and contact time on the photocatalytic degradation of amoxicillin were subsequently examined. The amoxicillin concentrations were measured using HPLC. As revealed by the results, increasing the doping percentage of nanoparticles synthesized and the reaction time within the specified range in the presence of sunlight increased the PDE rate of amoxicillin by about 18% and 56%, respectively. However, increasing the initial pH and initial concentration of amoxicillin in the prescribed

range reduced the PDE rate of amoxicillin by about 48% and 65%, respectively. Based on the results, among the parameters studied, changes in the initial concentration of amoxicillin and changes in the doping percentage of synthesized nanoparticles respectively showed the highest and lowest effect on the PDE of amoxicillin using Ni:TiO₂ nanoparticles stabilized on the ceramic in the presence of sunlight irradiation. Meanwhile, evaluating the reusability of ceramic-stabilized nanoparticles demonstrated that the PDE of amoxicillin at each time of reuse of the nanocatalyst decreases slightly compared with the previous time; hence, the PDE of amoxicillin is reduced by about 14% after four times of reuse of the stabilized nanocatalyst.

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Data availability statement

All data that support the findings of this study are included in the article.

Conflict of interest

The authors declare that they have no conflict of interest.

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