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Removal of pharmaceutical pollutants from aquatic environments using heterogeneous photocatalysis

Mahmood Hajiani*, Azam Gholami, and Mohammad Hossein Sayadi

[1]*Department of Environmental Engineering, Faculty of Natural Resources and Environment, University of Birjand, Birjand, Iran*

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ABSTRACT

Penicillin is one of the emerging pollutants that has toxic effects on food chains and aquatic environments. It creates many problems for human health and other living organisms. Conventional wastewater treatment methods cannot remove penicillin; therefore, modern approaches are necessary to remove it from sewage. In this study, we examined the ability of TiO_2 photocatalysis in the degradation of penicillin in aqueous solutions. The effects of different factors such as adsorption, pH, catalyst dosage, the initial concentration of penicillin, and time were examined. The results showed that photolysis and adsorption had negligible effects on penicillin degradation. The maximum degradation (94.5%) was observed at an ambient pH of 5, 0.1 g/l of TiO_2, and 20 mg/l of penicillin for 90 min. The photodegradation of penicillin followed a first-order kinetic reaction, and the rate constant (k) was 0.0213 min^{-1}. A TOC analysis was conducted to determine the fate of the pollutant. The results showed that 41% of the organic carbon was removed in 120 min. Based on the results, TiO_2 photocatalysis is an economically feasible procedure with good efficiency in removing penicillin from the aquatic environment.

1. Introduction

Rapid population growth, urbanization, and industrialization have increased the amount of organic and inorganic pollutants in the environment and caused environmental pollution. Among different types of pollutants, pharmaceutical compounds such as antibiotics are considered one of the significant environmental issues due to their high consumption rate [1,2]. These emerging pollutants are discharged from hospitals, health centers, and pharmaceutical industries into the waters. Although the concentrations of antibiotics are low (µg/l or ng/l) [3], their accumulation in the environment in the long term can threaten the health of food chains and living organisms. Most of the consumed antibiotics are excreted from humans and livestock and discharged to aquatic environments [4]. The residuals of antibiotics in the environment increase the threat of antibiotic-resistant bacteria [4]. Penicillin is one of the popular antibiotics with a high consumption rate to prevent and treat bacterial infections in humans and animals [5]. This antibiotic prohibits the production of peptidoglycan and eventually leads to bacterial cell

*Corresponding author: Tel.: +985631026516
E-mail: hajiani@birjand.ac.ir
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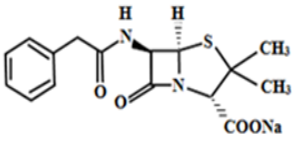
death [6]. More than 20,000 tons of penicillin are produced annually to treat different bacterial diseases [7]. The popularity of penicillin in treatment and its low absorption in the body has increased its amount in wastewater. Penicillin cannot be efficiently removed from wastewater by conventional methods such as biological processes [8], reverse osmosis [9], and adsorption by activated carbon [10]. In other words, the mentioned approaches move the contaminants from one place to another. Therefore, an effective method is necessary to achieve the total elimination of antibodies from environments [1]. Advanced oxidation processes (AOPs) such as ozonation [11], Fenton, and photo-Fenton [12], UV [13], sonolysis [4], electrochemical oxidation [14], and photocatalysis [15,16] are promising approaches for the removal of pharmaceutical compounds from wastewater. In these methods, the free hydroxyl ($OH^{\cdot}$) radical is a powerful oxidant that can decompose organic matter to H_2O and CO_2 [1, 17]. Naddeo et al. studied the efficiency of ozonation and enhanced ozonation by sonolysis in the degradation of some antibiotics. Their results revealed that the combination of ozonation and sonolysis considerably increased the efficiency of the removal rate of the pharmaceutical compounds [18]. Salehnia et al. applied the Electro-Fenton process to remove penicillin G from an aqueous solution at a laboratory scale with variable flow, voltage, and penicillin concentrations. At optimum conditions (pH=3, 50 mg/L of antibiotic, and reaction time 20 min), 100% of the penicillin was removed [19]. Sheikh Mohammadi and Sardar used chestnut shells as an inexpensive adsorbent to remove penicillin G from the aquatic environment. The results showed at a pH of 3 and an adsorbent dose of 0.1 g/L, 92% of the pollutant was removed in 120 min [20]. Among the different alternatives of AOPs, photocatalysis has proven to have a high potential to remove antibiotics from aquatic environments. In this method, semiconductors utilize light energy to degrade organic pollutants. When a semiconductor such as TiO_2 absorbs photon energy more than its bandgap, an excited electron (e^-) is transferred from the valance band to the conduction band, and a hole (h^+) is built. The electron-hole pair with a high activity state acts as a reductant and oxidant. Studies have proven the ability of TiO_2 in the photodegradation of different antibiotics [21,22]. TiO_2 as a semiconductor is an inexpensive, safe, strong oxidant, and highly chemical stable catalyst frequently used in the photocatalytic degradation of organic pollutants [23]. The present study was carried out to examine the ability of the TiO_2 photocatalysis in the degradation of penicillin G. The effects of different parameters such as pH, TiO_2 dosage, initial penicillin concentrations, and time of radiation were studied to manipulate the process to find the optimum conditions.

2. Materials and methods

2.1. Materials

Penicillin G ($C_6H_{17}N_2NaO_4S$) was purchased from Sigma-Aldrich. Some of its properties are given in Table 1. The TiO_2 with 99.5% purity was supplied from Degussa (P-25 ca. 80% anatase and 20% rutile). The NaOH and HCl were bought from Merck.

Table 1. The properties of penicillin G.

Penicillin G sodium salt	
Antibiotic class	β-lactam
Structural formula	
Molecular formula	$C_{16}H_{17}N_2NaO_4S$
Molecular weight	356.37 g/mol
Solubility in water	100 mg/ml

2.2. Photoreactor

A 200ml Pyrex glass cylinder was used as a photoreactor (Figure 1). A UV lamp (6w) was placed in the middle of the reactor. The light source was kept in a quartz tube to prevent contact between the water and the lamp. Aluminum foil covered the outer walls of the reactor to prevent light transmission. An air pump was used for aeration and having a homogenous solution. The sampling was conducted from an outlet at the top of the reactor.

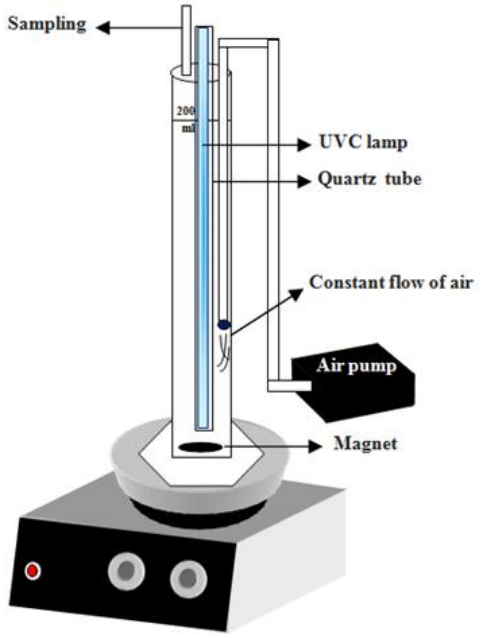


Fig. 1. A schematic picture of the photoreactor.

2.3. Photocatalytic experiments

A series of experiments were conducted to find the optimum values of pH, amount of catalyst, initial concentration of antibiotic, and radiation time. Different values of pH (5, 7, 9, and 11), TiO_2 (0.1, 0.5, and 1 g/l), concentrations of penicillin (10, 20, 30 mg/l), and contact time (5, 15, 30, 60, 90, 120 minutes) were studied. A magnetic stirrer (70 rpm) and an aeration pump (1.5 l/min) were used to mix the samples. NaOH and HCl were used to adjust the pH. Photocatalytic experiments were conducted in a reactor with 100 cc samples of the antibiotic aqueous solution containing TiO_2. The solution was stirred in the dark reactor for 30 minutes at room temperature to find the adsorption of penicillin on the surface of TiO_2. Then, the UV lamp was turned on, and samples were taken at selected time intervals via a syringe. All the samples were then centrifuged, and the concentration of penicillin in the samples was measured by a spectrophotometer (Shimadzu, Bio spec-1601). The maximum absorbance wavelength was found at 290 nm by depicting absorbance wavelength in the range of 200 to 400 nm (Figure 2). The removal (R) of penicillin was calculated as follows:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial antibiotic concentration and C_t is the penicillin concentration at time t.

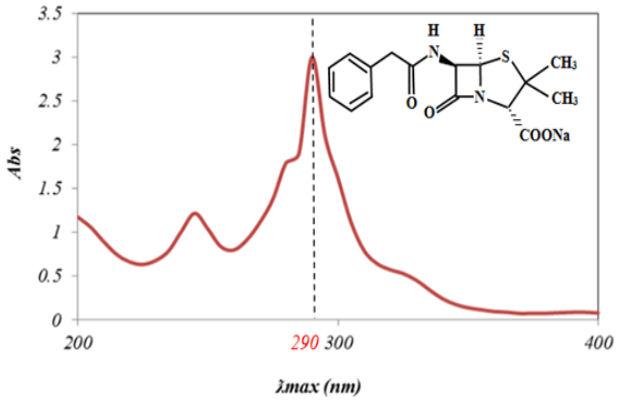


Fig. 2. Absorbance wavelength in the range of 200 to 400 nm.

3. Results and discussion

3.1. pH effect on the photodegradation of penicillin

The pH plays a significant role in photocatalysis, affecting both catalysts and pollutants. It directly affects the catalysts' properties, surface charges, interactions between solvent and catalyst, and intermediate products [24]. These factors are essential in the photocatalysis process. The effects of different pH (3, 5, 7, 9, and 11) in the photodegradation of penicillin are shown in Figure 3. The initial concentration of penicillin and TiO_2 were 20 mg/l and 0.1 g/l, respectively. By increasing the pH from 7 to 11, the degradation of antibiotics decreased from 70% to 47% in 120 minutes. In acidic conditions, the efficiency of the process at pH 3 is lower than at pH 5. The maximum degradation of penicillin was observed at pH 5 (95%) after two hours. TiO_2 has an amphoteric property, and its surface charge is directly dependent on its pH. Its point of zero charge is about pH 6.7. Therefore, its surface charge in alkaline conditions (pH >6.7) is negative and has a positive charge for acidic situations (pH < 6.7). Moreover, the efficiency of the process is directly related to the surface charges of the catalyst and the pollutant's distribution. Therefore, the ionic nature of the antibiotic causes an electrostatic interaction between the catalyst and pollutant [13,17,24]. At pH 5, the positive surface charges of TiO_2 and negative charges of penicillin increase the electrostatic interaction between the catalyst and pollutant, causing a rise in the photo degradation of the antibiotic. Furthermore, in acidic conditions, more hydroxyl radicals are produced due to the high availability of H, and the dissolved oxygen

produces superoxide radicals; finally, these radicals destroy the penicillin according to the following reactions:

$$2HO_2 \rightarrow O_2^{\circ} \quad (2)$$

$$H_2O_2 + O_2^{\circ} \rightarrow OH^{\circ} + OH^{-} + O_2 \quad (3)$$

$$e^{-} + O_2 \rightarrow O_2^{\circ -} \quad (4)$$

$$O_2^{\circ -} + 2H^{+} \rightarrow 2HO^{\circ} \quad (5)$$

Jallouli et al. found the same results for pH in the photodegradation of ibuprofen by UV-LED/ TiO_2 in water and wastewater [25].

3.2. TiO_2 concentration effect on the photodegradation of penicillin

Catalyst dosage is one of the parameters directly affecting photocatalysis. Different concentrations of TiO_2 (0.1, 0.5, and 1 g/l) were used to study the effect of TiO_2 dosage on the photodegradation of penicillin. Experimental conditions were a pH of 5 and a penicillin concentration of 20 mg/l; the samples were kept in the dark for 30 minutes. The maximum degradation of antibiotics happened at 0.1 g/l TiO_2 (Figure 4). It was observed that the degradation of the pollutants decreased by increasing the TiO_2 concentration. The efficiency of the process for 0.1, 0.5, and g/l of TiO_2 was 95, 80, and 68 %, respectively. With the increase in the catalyst amount, the rate of photocatalytic reactions increased. This trend continued and caused more production of hydroxyl radicals and light absorbance. However, the increase of catalyst dosages beyond the optimum point led to a decrease in the efficiency of the process [17,26,27]. Studies have shown that the accumulation of catalysts in the solutions and prevention of light penetration leads to a decrease in the degradation of pollutants [24,28]. In this study, it was observed that an increase in TiO_2 had an adverse effect on the efficiency of the process because the turbidity created in the solution due to the increase of photocatalyst limited the hitting light on the catalyst surface and caused a decline in the production of reactive radicals [29,30].

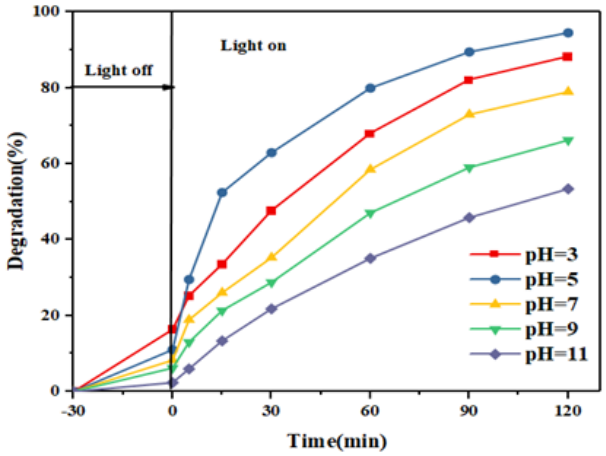


Fig. 3. Penicillin degradation in different pHs (initial concenter penicillin 2 mg/l, TiO_2 0.1 g/l).

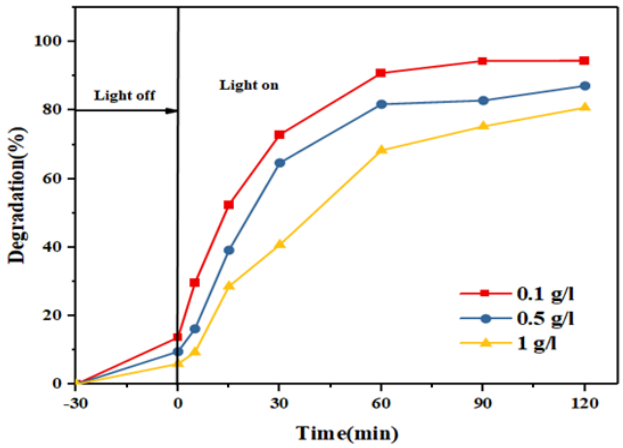


Fig. 4. Effect of TiO_2 concentration (pH 5, penicillin concentration 20 mg/l).

3.3. Initial concentration of penicillin effect on the photodegradation of penicillin

Figure 5 shows the effect of different penicillin concentrations (10, 20, and 30 mg/l) on the degradation of the antibiotic. Based on the optimum conditions in the previous steps, the experimental conditions were a pH of 5 and a catalyst dosage of 0.1 g/l. An increase in the initial concentration of antibiotics from 10 to 20 mg/l caused a rise in the process efficiency; however, further increases in the penicillin concentration from 20 to 30 mg/l led to a decrease in the degradation. The maximum photodegradation was 95%, with an initial penicillin concentration of 20 mg/l. The interaction between oxidizing agents and pollutants increased with an increase in the antibiotic concentration. Besides, the natural oxidation processes between the electron-hole

pairs and penicillin improved with the high availability of the antibiotic on the catalyst surface. However, further increases in penicillin, while the intensity of irradiation, catalyst dosage, and time of irradiation were constant, caused a reduction in the efficiency of the processes. Because adsorbed intermediate products on the catalyst's surface eventually decreased free sites and the rate of reactions [31,32]. Initially, access to active sites on the surface of TiO_2 was more readily available; however, after a while, the free sites were filled, and the rate of the reactions and the production of hydroxyl radicals were reduced [15,24]. Therefore, less production of hydroxyl radicals had adverse effects on the photocatalytic activity of TiO_2 [33].

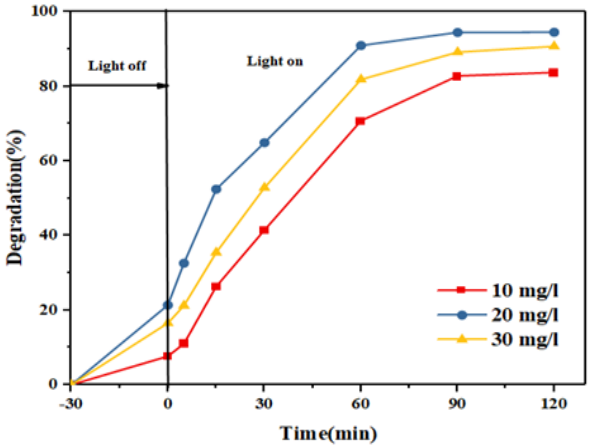


Fig. 5. Effect of penicillin concentration (pH 5, dosage of TiO_2 0.1 mg/l).

3.4. The time effect on the photodegradation of penicillin

The photocatalytic degradation of penicillin was studied at different time intervals (5, 15, 30, 60, 90, and 120 min). The results showed that the concentration of antibiotics decreased in the photoreactor as time passed. However, the rate of antibiotic degradation was much higher in the first 60 min (Figure 6) because the overall conditions of the process were desirable for antibiotic degradation. After 90 min, the rate of removal was in equilibrium. The removal of the pollutants was proportional to the irradiation time; however, the degradation efficiency after a particular time was low because the active sites on the catalyst's surface and the production of hydroxyl radicals were reduced [6,34].

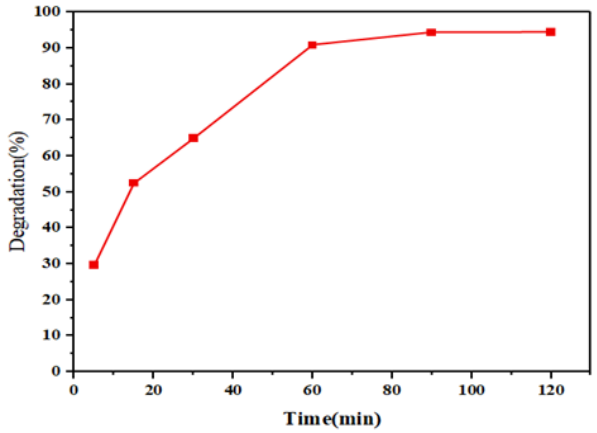


Fig. 6. Effect of time on the photocatalysis.

3.5. Kinetic photodegradation of penicillin

A series of experiments with different concentrations of penicillin were conducted at pH 5 and TiO_2 0.1 g/l in 120 min to study the kinetics of photocatalysis. Figure 7 shows –ln (C/C_0) as a function of irradiation time. The kinetic was studied based on the Langmuir-Hinshelwood mechanism [1,17,28]:

$$\ln\left(\frac{C_t}{C_0}\right) = -Kt \qquad (6)$$

As shown in Figure 7, the obtained line suggests that the process follows the pseudo-first-order kinetic. The best R^2 (96%) was observed at an initial penicillin concentration of 20 mg/l with a constant (k) of 0.0213 min^{-1}.

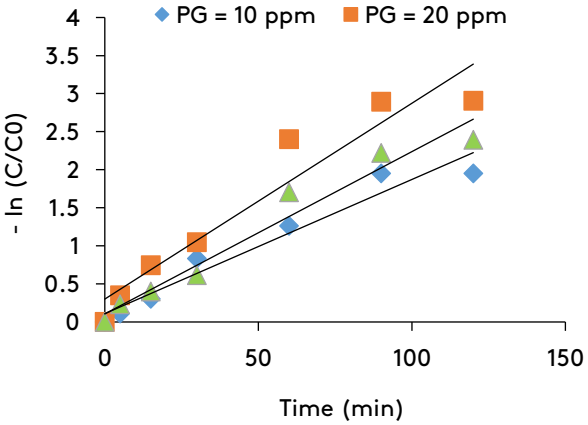


Fig.7. Kinetic photodegradation of penicillin.Elmolla

Elmolla and Chaudhuri's study showed that the photocatalytic degradation of amoxicillin, ampicillin, and cloxacillin followed a first-order kinetic reaction [35]. Moreover, with an increase in the initial concentration of the antibiotic, the k value decreased. In a study by Zhang et al., the

degradation of chloramphenicol also followed a first-order kinetic reaction [36]. The values of k for different values of penicillin concentration are presented in Table 2.

Table 2. k values for different penicillin concentrations of kinetic analysis.

Concentration (mg/l)	Equation	R^2	K
10	Y=0.0257x+0.301	0.9205	0.02371
20	Y=0.0213x+0.1058	0.9592	0.0213
30	Y=0.0176x+0.1098	0.9492	0.0176

3.6. Mineralization of antibiotic

Total Organic Carbon (TOC) analysis was conducted to study the variation of organic carbon during the photocatalytic degradation of penicillin. The experimental condition included a pH of 5, TiO_2 of 0.1 g/l, and a penicillin concentration of 20 mg/l. It is proposed that the photocatalysis process can mineralize organic pollutants. TOC analysis was conducted three times to investigate this hypothesis, and the mineralization was calculated using the following equations [15,24,28]:

$$-\frac{d\,[TOC]}{dt} = KC^n \quad (7)$$

$$-\frac{d\,[C]}{dt} = KC^n \quad (8)$$

where C, k, and n are antibiotic concentration, the reaction rate constant, and reaction order, respectively. Figure 8 shows that most TOC removals happened in the first 20 min of 120 min. The maximum degradation of TOC was 41% in 120 min. Yi et al. showed that after 60 minutes of irradiation, tetracycline TOC was 40% [37].

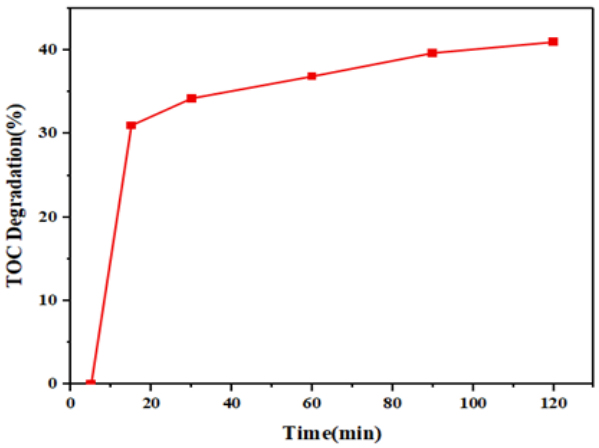


Fig. 8. Mineralization of the antibiotic.

4. Conclusion

In this study, the efficiency of the TiO_2 photocatalysis in the degradation of penicillin was examined in laboratory conditions. While adsorption and photolysis had negligible effects on the removal of the antibiotic, heterogeneous photocatalysis was the dominant process. At optimum conditions (pH of 5, TiO_2 of 0.1 g/l, and an initial penicillin concentration of 20 mg/l), the maximum removal (95%) occurred during 90 min. A first-order kinetic reaction was observed at different antibiotic concentrations in 2 hr; 41% of TOC was removed after 120 min. While complex nanocomposites with very complex synthesis procedures have been used in some studies to degrade pharmaceutical compounds, the results of this study revealed the sole use of TiO_2 nanoparticles as an environmentally friendly photocatalyst could effectively remove penicillin from aqueous solutions in heterogeneous photocatalysis.

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