

Original Research

Gentamicin Removal by Photocatalytic Process from Aqueous Solution

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Abstract

The entry of gentamicin antibiotics into the aquatic environment has raised many concerns. Today, modern nanotechnology-based approaches have been employed to overcome such problems. The present study was conducted to investigate the efficiency of the UV/ZnO photocatalytic process in removing antibiotic gentamicin from aqueous solution. So we investigated the effects of parameters, including initial gentamicin concentrations (20, 60, and 100 mg/L), zinc oxide concentrations (0, 200, 350, and 500 mg/L), contact times (10, 30, 60, and 120 min), pH (5, 6, and 7), and type of radiation (sun and UV-C). The sample size and the number of test procedures were determined to be 576, taking into account the levels of effective variables and through the full factorial. All experiments were carried out in a double-compartment reactor at laboratory temperature using a magnetic stirrer at 150 rpm. The change of gentamicin concentrations were measured using a DR5000 spectrophotometer. Data analysis and charting were done through Design Expert 8 and Excel 2010 software. Results showed that the maximum removal efficiency of gentamicin of about 93% was obtained under UV-C irradiation at pH of 5, contact time of 30 min, ZnO concentration of 200 mg/L, and initial gentamicin concentration of 20 mg/L. In addition, the maximum removal efficiency of gentamicin (84.32%) under sunlight occurred at pH 6, contact time of 60 min, ZnO concentration of 200 mg/L, and initial gentamicin concentration of 20 mg/L. The results demonstrated that the photocatalytic UV/ZnO process exposed to UV-C or natural sunlight could be an effective process for removing antibiotic gentamicin from the aqueous solution.

Keywords: gentamicin, antibiotic removal, zinc oxide, photocatalysis, photocatalytic

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Introduction

In recent years, the production of sewage and effluent containing pharmaceutical compounds and the entry of these compounds into the environment have been regarded as major environmental threats [1-2]. The pharmaceutical materials can be found in aquatic environments (underground and surface) through the discharge of sewage and waste water from treatment plants, agricultural runoff, direct emissions from manufacturing plants, improper disposal of drug waste from houses, veterinary clinics, and medical centers [3-4]. The amounts of these compounds may be low in aquatic environments, but their continuous entry due to cumulative effects can be considered a potential risk for aquatic ecosystems and existing microorganisms [5-6]. The presence of antibiotics in the environment can lead to the development of antibiotic-resistant pathogens that potentially threaten ecosystem performance and human health [7-8]. The annual consumption of antibiotics in the world is estimated to be between 100,000 and 300,000 tons [9]. About 30% to 90% of them remain active after excretion due to lack of complete metabolism in the body so that active antibiotics are 3,000 tons per year in the best conditions and 180,000 tons per year in the worst conditions being introduced into the environment [10]. This is while the U.S. Environmental Protection Agency has set a standard of 1 mg/L for the presence of antibiotics in wastewater [11]. Aminoglycosides are antibiotics that are largely excreted without absorption from the body. These antibiotics belong to the family of aminated carbohydrates, whose major effect is to inhibit protein synthesis in bacteria [12]. Aminoglycosides are the most commonly used antibiotics for the treatment of life-threatening infections, such as drug-resistant *Mycobacterium tuberculosis* and aerobic gram-negative bacteria like *Pseudomonas aeruginosa*. These compounds are also applied as synergistic agents along with other drug combinations in the treatment of diseases such as endocarditis [13-14].

Gentamicin is one of the most important aminoglycosides with the scientific name of gentamicin sulfate, the brands of Garamycin and Gemycin, molecular formula $C_{21}H_{43}N_5O_7$, and molecular weight of 477.596 [15]. This antibiotic is a water-soluble combination used to treat chronic infections caused by gram-negative bacteria such as *Pseudomonas* due to inhibiting protein synthesis in bacteria by binding to the 30S subunit of ribosomes [12]. Various methods have been used to eliminate drug compounds from aqueous solutions, including membrane processes (reverse osmosis [16], adsorption on activated carbon [17], and advanced oxidation processes or AOPs), ozonation [18-19], electrocoagulation [20], Fenton and photo-Fenton [21], ultrasonic [22], peroxidation with UV [23-24], adsorption [25-26], solar degradation [27], and photocatalytic processes [28-29]. In general, a number of disadvantages have been mentioned in the field of membrane processes, such as high equipment costs, maintenance costs, high

energy consumption for start-ups, and the efficiency of these processes, the limitation of mass transfer, limitation of removal of organic compounds, membrane vulnerability due to attack of oxidizing materials, blockage of membrane pores by large molecules, prolonged time [30-31], the need for reverse washing, and resin regeneration [32].

Photocatalytic decomposition is a modern treatment process as well as being clean and environmentally friendly, which is of particular importance in solving environmental and global issues with light radiation and semiconductors, such as TiO₂, ZnO, NiO, and WO₂ [33-34]. In this process, the electrons of catalytic band capacity are excited by UV irradiation and are transmitted to the conduction band; during this transfer, holes are formed in the surface of the catalyst. These excited electrons are transmitted to the conduction band together with the holes in the capacity band, which lead to intensifying the production of hydroxyl radicals, which play an essential role in the photocatalytic process [35]. Among the semiconductor metal oxides, the use of zinc oxide (ZnO) nanoparticles has been considered for having high effective surface, high catalytic activity, low toxicity, low cost and, and in some cases, more efficacy than some metal oxides [36-37].

Zinc oxide (ZnO), a unique and widely used mineral, is one of the zinc compounds recognized as safe by the U.S. Food and Drug Administration [38-39]. This nanoparticle is a wide band gap semiconductor of ev3.2 with energy gap of ev3.37 [40]. Moreover, this nanoparticle is excitable under ultraviolet radiation at a visible wavelength range of 200 to 400 nm, and shows maximum absorption in the wavelength range 385-360 nm. The zinc oxide nanoparticles have been widely used in industrial applications such as dye-sensitized solar cells (DSCs), pigments, photocatalysts, sensors, catalysts, gaseous sensors, semiconductors, piezoelectric devices, and UV-absorbent materials [41]. According to the materials mentioned, the present study was carried out to investigate the photocatalytic removal of antibiotic gentamicin from aqueous solution using zinc oxide nanoparticles.

Materials and Methods

This experimental study was conducted on various concentrations of synthetic solution containing antibiotic gentamicin. Antibiotic gentamicin with a purity of 99% was purchased from Iran Daru Pharmaceutical Co. in Tehran. ZnO nanoparticles with a purity of +99%, a size of 10-30 nm, milky white dye, and a density of 5.66 g/m³ were prepared from Nano Sani Co. in Mashhad, Iran. Sulfuric acid and sodium hydroxide used in experiments with a purity of +99% were obtained from Merck Co. (Germany).

A reactor was recruited to perform the photocatalytic process with the simultaneous effect of ultraviolet/zinc oxide nanoparticles. The reactor consisted of two main

parts: the main chamber (reaction chamber), with a useful volume of 3 l, a wall thickness of 1 cm, and a height of 25 cm to fulfill all stages of the test, and the secondary chamber with a volume of 10 l, a wall thickness of one cm and a height of 40 cm involving the main chamber, in which the continuous flow of water was maintained by a pump to reduce the temperature resulting from UV radiation. The radiation source, UV-C (125 watt), with a length of 12 cm and a diameter of one cm, as well as quartz coating with an outer diameter of 2.5 cm, an inner diameter of 2 cm, and a length of 20 cm were mounted in the middle of the reactor lid. All components of the reactor were wrapped in two layers of aluminum foil to prevent ultraviolet reflection. Gentamicin salt and deionized distilled water were used to make a synthetic solution. The stock solution of gentamicin at 1,000 mg/L was prepared weekly and stored in dark conditions at 4°C. Other concentrations of antibiotic gentamicin were prepared from the stock solution with appropriate dilution ratios; sulfuric acid and sodium hydroxide were utilized to adjust solution pH. Then the concentrations of 1 to 100 mg/L of antibiotic were prepared to plot the calibration curve by spectrophotometer at pH values of 5, 6, and 7. The read data were inserted into Excel and the curves were plotted.

The experiments were done in combination form (radiation-ZnO) to determine the effects of parameters affecting gentamicin removal efficiency, including the duration of radiation (10, 30, 60, and 120 min), pH (5, 6, and 7), concentrations of ZnO nanoparticles (0, 200, 350, and 500 mg/L), initial gentamicin concentrations (20, 60, and 100 mg/L) and type of radiation (UV-C and sunlight). The sample size of the test procedures was determined

to be 576 through the full factor. The samples extracted from the reactor were centrifuged at 4,000 rpm for 30 min to settle ZnO nanoparticles. After centrifuging, the samples were introduced into a spectrophotometer to read out absorption rate. The point with the highest peak was selected as the maximum absorption. Finally, the removal percentage was obtained using the calibration curve. At the end, the analysis of the data resulting from the experiments was carried out through Design Expert 8 and Excel 2010 software.

Results and Discussion

Effect of Initial Gentamicin Concentration on Process Efficiency

Comparing the mean removal efficiencies at different gentamicin concentrations in the presence of both types of radiation (UV-C and sunlight) showed that maximum efficiency occurred at a concentration of 20 mg/L and at about 92.69 and 84.32 percentages, respectively. In addition, according to Fig. 1a), the decrease in efficacy was observed by increasing the antibiotic concentrations from 20 to 60 mg/L and then increasing to 100 mg/L.

Effect of Zinc Oxide Concentration on Process Efficiency

The highest mean removal efficiency in the presence of both types of radiation (UV-C and sunlight) occurred at a concentration of 200 mg/L ZnO and about 92.69 and 84.32 percentages, respectively. It can

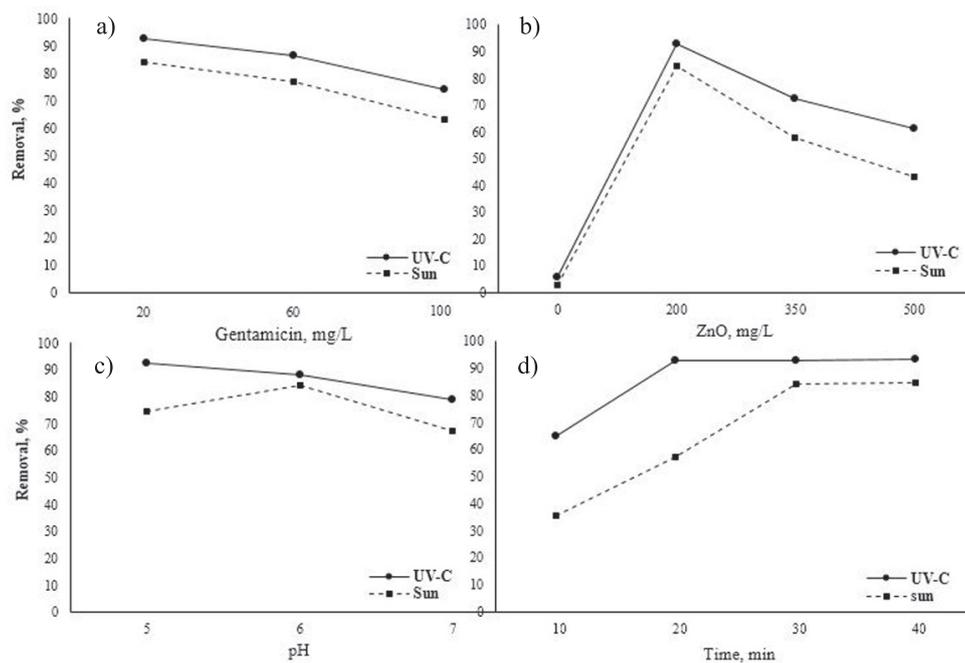


Fig. 1. Effects of: a) initial gentamicin concentrations, b) zinc oxide concentrations, c) pH changes, and d) contact time changes on process efficiency.

also be deduced from Fig. 1b) that gentamicin removal efficiency was elevated by increasing the concentration from 0 to 200 mg/L, and the reduction in removal efficiency was seen by increasing the concentration from 200 to 350 – and sometimes 500 mg/L.

Effect of pH Changes on Process Efficiency

According to Fig. 1c), the maximum mean removal efficiency with UV-C radiation exposure occurred at pH of 5 and about 92.69%. Efficiency was decreased by increasing pH from 5 to 6 and then 7. Maximum removal efficiency in the presence of sunlight was at pH of 6 and about 84.32%. Efficiency was improved by increasing pH from 5 to 6, and decreased with rising from 6 to 7.

Effect of Contact Time Changes on Process Efficiency

In exposure to UV-C radiation, maximum mean efficiency occurring at 30 min was about 93%. As shown in Fig. 1d), the increase in removal was observed by increasing the time from 10 min to 30 min. This efficiency did not change significantly with an increase in time from 30 min to 60 and 120 min. In exposure to sunlight, the increase in removal was seen with increasing radiation time from 10 min to 30 min and sometimes 60 min; however, no significant changes were observed in efficiency with an increase in time from 60 to 120 min., and maximum efficiency was about 84.32% at 60 min.

Optimal Conditions in the Process

According to Fig. 2, the efficiency of removing antibiotics exposed to UV-C radiation reached 92.69% at the ZnO concentration of 200 mg/L and the gentamicin concentration of 20 mg/L, irradiation time of 30 min, and pH of 5.

The best antibiotic removal efficiency at exposure to sunlight was observed at 84.32% at a ZnO concentration of 200 mg/L, a gentamicin concentration of 20 mg/L, irradiation time of 60 min, and pH 6. Solution pH is one of the factors affecting the advanced oxidation process (AOP). In these processes, pH changes influence the oxidation rate through the production of hydroxyl radicals [42]. In the present study, maximum removal efficiency when using UV-C was obtained about 93% in acidic pH 5 and the lowest efficiency in neutral pH 7, because acidic pH has a greater potential than neutral pH in producing hydroxyl radicals. In this regard, Emad S. Elmolla and Malay Chaudhuri analyzed amoxicillin, ampicillin, and coloxacillin antibiotics using the Fenton process and reported that hydrogen peroxide is more stable at low pH due to the formation of oxonium ions, and oxonium ions improve H₂O₂ stability [43]. Naddeo et al. reported an increase in the decomposition of diclofenac, amoxicillin, and carbamazepine after exposure to UV irradiation

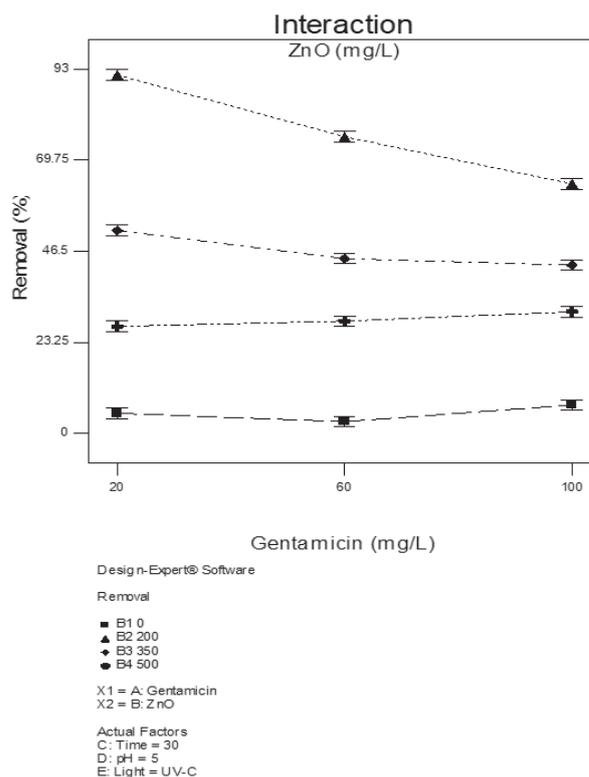


Fig. 2. Optimal conditions in the photocatalytic process under UV-C radiation

following a decline in solution pH [44]. Emad S. Elmolla and Malay Chaudhuri stated that pH 5 was optimized for complete decomposition of amoxicillin, ampicillin, and coloxicillin antibiotics using UV/TiO₂ [45]. The highest removal efficiency occurred at ZnO 200 mg/L. The decrease in removal efficiency was observed by increasing the catalyst concentration from 200 to 350 and 500 mg/L.

Reducing the efficiency due to this increase in concentration can be due to the adhesion of catalyst particles, increased light diffusion in high concentrations of catalyst, and an increase in the amount of catalyst, which in turn leads to the prevention of hydroxyl radical production and even consumption of produced hydroxyl radicals [46]. In line with this study, Rodrigo A. Palominos et al. suggested values over 1.5 g/L for TiO₂ and 1 g/L for ZnO for tetracycline decomposition [29]. Giusy Lofrano et al. stated that the optimal amount of TiO₂ was 1.6 g/L for the photocatalytic decomposition of antibiotic chloramphenicol within 120 min [47]. The short contact time is a factor that has a significant impact on process performance in terms of cost and energy. The optimal contact time provides sufficient opportunity to generate active hydroxyl radicals and their attack into antibiotic molecules.

In exposure to UV-C irradiation, maximum mean efficiency occurred at the contact time of 30 min. The efficiency had no significant elevation with increasing the contact time from 30 to 60 and 120 min. The reason for

the increase in removal efficiency at the initial reaction times can be the creation of more holes and corrosion at the nanoparticle surface, thereby increasing removal efficiency [48-49]. Prados-Joya et al. observed that increasing the elimination of antibiotic nitroimidazole depends on prolonged exposure to UV and high-intensity radiation [50]. Jung YJ et al. stated that 20 min contact time decomposes over 99% of the primary amoxicillin compound with the UV/H₂O₂ advanced oxidation process [51]. Shaojun et al. concluded that UV eliminated 73% of tetracycline in the contact time over 300 min [52]. Maximum removal efficiency was at a concentration of 20 mg/L. The reduction in efficacy was almost significant because of increasing antibiotic concentrations from 20 to 60 and then 100 mg/L. This phenomenon maybe attributed to the ability to occupy an active site of the catalyst with high antibiotic values. EL Sayed et al. by studying the photocatalytic decomposition of antibiotic metronidazole using copper oxide nanoparticles, found that removal efficiency was reduced by increasing the initial pollutant concentration [53]. In a similar study, Shaojun et al. observed that the rate of tetracycline photolysis under UV was decreased dramatically by increasing the initial tetracycline concentration from 10 to 40 mg/L [40]. Perhaps the difference in the results of the above studies can be attributed to laboratory conditions, different materials, and equipment.

Conclusions

The results obtained from the present study demonstrated that the UV/ZnO photocatalytic process could remove gentamicin in short contact times. So that the removal efficiency of gentamicin antibiotic in the optimal conditions of pH 5 and 7, contact time 30 and 60 min, ZnO 200 mg/L and initial gentamicin 20 mg/L was 92.69% and 84.32% at the presence of UV-C and sunlight irradiation, respectively. Reductions in removal were observed occasionally with an increase in irradiation time, catalyst concentrations, and antibiotic levels. So, zinc oxide has good efficiency as a photocatalyst in removing gentamicin from aqueous solutions along with UV-C and sometimes the sun.

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Ethical Clearance

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