Environment and Water Engineering

Homepage: www.jewe.ir

Investigating photocatalytic removal of Doxycycline antibiotic using ZnO@g C₃N₄ nanocomposite in aqueous environments

Shahrzad Forghani Darmiyan[1], Mohammad Reza Rezaei[1✉], and Mohammad Hossein Sayadi Anari[2]

[1]Department of Environment, Faculty of Natural Resources and Environment, University of Birjand, Birjand, Iran
[2]Department of Environment, Faculty of Natural Resources and Environment, Shahid Bahonar University of Kerman, Kerman, Iran

ARTICLE INFO	ABSTRACT
  *Corresponding author: M. R. Rezaei ✉ mrrezaei@birjand.ac.ir	Antibiotics are stable compounds with low biological degradation that are generally not removable by conventional wastewater treatment processes. This study aimed to investigate the photocatalytic removal of the antibiotic Doxycycline using the ZnO@g-C₃N₄nanocomposite in aqueous environments. The ZnO@g-C₃N₄ nanocomposite was synthesized for the first time and evaluated for the photocatalytic degradation of the antibiotic Doxycycline in aqueous environments under UV-C light. After that, the nanocomposite was analyzed and evaluated using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), photoluminescence spectroscopy (PL), thermogravimetric analysis (TGA), and energy-dispersive X-ray spectroscopy (EDAX). Effective parameters such as pH, pollutant dose, catalyst dose, and time were assessed in the photocatalytic section. The results of this experiment showed that the best degradation and removal efficiency of Doxycycline as a pollutant in aqueous environments under optimal conditions (pH=5, pollutant concentration: 50 *mg/l*, catalyst dose: 0.5 *g/l*, and time: 90 *min*) was 84.14%. The degradation kinetics tests indicated that it follows a second-order kinetic model. According to the obtained results, the ZnO@g-C₃N₄ nanocomposite can be introduced as an environmentally friendly and suitable catalyst for the degradation of pollutants of pharmaceutical origin.

1. Introduction

Water is always regarded as an essential material for life on Earth and human health. Over recent years, the interference of factors such as industrial activities, domestic wastewater, and agriculture has put this valuable resource undergo changes. Water is the primary necessity for human survival. Irreversible damages to the environment, including pharmaceutical, hormonal, pesticide, and insecticide pollutants, have been caused by excessive use. Various sources such as pharmaceutical industries, hospital wastewater, human and animal excretion, and municipal wastewater treatment plant discharges may cause pharmaceuticals to penetrate water and soil (Moosavi et al., 2019). Iran is categorized as one of the countries with the highest consumption of pharmaceuticals in general and antibiotics in particular, which account for a significant portion of this consumption (Jafari et al., 2020).

Recently, the COVID-19 pandemic has significantly increased the use of antibiotics. After being consumed, Antibiotics enter urban sewage and aquatic environments through various ways, including blood, secretions, and excretion, which leads to water pollution and disruptions in purification processes (Kümmerer et al., 2000).

Doxycycline is a tetracycline-class antibiotic with a molecular formula of <C₂₂H₂₄N₂O₈, HCl,½>C₂H₆O,½H₂O. It shows lipid solubility and a low affinity for binding to serum calcium. Notably, this medicine is used to treat various bacterial infections such as acne, intestinal and urinary tract infections, eye infections, gonorrhea, and chlamydia (Bajpai et al., 2012; Ghazi Tabatabai et al., 2018). During the outbreak of COVID-19, Doxycycline was widely prescribed alongside other medications. It was especially recommended for lung inflammations. Studies have claimed that antibiotic

concentrations in surface and groundwater environments range between 1–100 µg/l, while in pharmaceutical manufacturing wastewater, concentrations can be higher than 100 µg/l (Moosavi et al., 2019). Photocatalytic degradation is one of the most innovative methods praised by researchers.

Photocatalysts are catalysts that are activated by light. These catalysts mostly consist of semiconductor metal oxides, generating electron-hole pairs upon absorbing photons. It should be mentioned that photocatalytic degradation is an effective and energy-efficient technology. This technology produces CO_2 and H_2O after the complete degradation of pollutants (Ahmadpour et al., 2020). Additionally, zinc oxide (ZnO) is a valuable material that is observable as a white powder in its pure form, and it is naturally occurring as the mineral zincite. Regarding the features, it has high transparency, a wide energy band gap, and high electron mobility. Additionally, it is widely used in photocatalytic processes since it has high conductivity and strong oxidative power, which makes it an important and active material for photocatalytic applications (Shokri et al., 2020). Graphitic carbon nitride (g-C₃N₄) has been reported as a polymeric semiconductor. It has also been regarded as a new-generation photocatalyst carrying simple synthesis, suitable electronic band structure, and high physicochemical stability (Esrafili et al., 2018). Its noticeable stability in acidic and basic environments, together with the appropriate band gap, has led to investigations into its photocatalytic properties for water splitting and pollutant degradation (Shan et al., 2016). In this material, nitrogen atoms replace carbon atoms within a graphite framework which can form a layered, two-dimensional structure. Additionally, by interacting with UV light, in this process, Zinc oxide acts as a photocatalyst. This causes electrons to rise to the conduction band. In a study, Shokri et al. (2020) investigated the photocatalytic removal of Doxycycline antibiotics from aqueous solutions via Zinc oxide particles immobilized on glass. They investigated how operational and kinetic parameters affect the way ZnO shows effective photocatalytic performance under UV light for removing Doxycycline from aqueous solutions. The antibiotic removal efficiency for an initial concentration of 75 mg/l, pH 6.5, light intensity of 40 W/m², and 4 hr of reaction time was 45.2, 48.8, and 52.7 % for Aldrich ZnO nanoparticles, Merck ZnO microparticles, and synthesized ZnO nanoparticles, respectively. Mineralization tests also showed a reduction in COD over time (Shokri et al., 2020).

The main purpose of this research was to analyze the photocatalytic removal of Doxycycline antibiotics using ZnO-GCN nanocomposite. The effects of catalyst dosage, initial pollutant concentration, temperature, pH, and reaction time on Doxycycline removal were also studied.

2. Materials and Methods

In order to study the photocatalytic removal of the antibiotic Doxycycline using ZnO-GCN nanocomposite in aqueous environments, the desired nanocomposite was synthesized as described in detail below. Then, its photocatalytic activity for the removal of Doxycycline under specified parameters was evaluated.

2.1 Synthesis of GCN

In the present study, g-C₃N₄ (GCN) was synthesized through thermal condensation of melamine powder. Initially, 12 g of melamine powder was placed in a porcelain crucible, and then it was heated in a furnace at 550 °C for 240 min. After cooling for 24 hr, the resulting material was collected and weighed. Next, 0.5 g of the obtained substance was added to a 50 ml volumetric flask, which contained 20 ml of deionized water. After that, it was subjected to sonication for 60 min to ensure uniform dispersion.

2.2 Synthesis of ZnO@g-C₃N₄ nanocomposite

Preparing the nanocomposite requires 0.406 g of ZnO nanoparticles to be weighed and dissolved in 100 ml of deionized water. The sonicated GCN solution was transferred to a beaker with a magnetic stirrer, and then it was stirred at 90 °C for 120 min. Once the solution temperature reached 65 °C and was measured by a thermometer, the ZnO solution was added dropwise while stirring continued. Then, the mixture was heated to 90 °C. It was removed from the stirrer, cooled, and centrifuged at 5500 rpm for 10 min. This process was repeated three times. Each time, rinsing the sample with deionized water was practiced. The final residue was dried at 70 °C in an oven for 15 hr. Then the desired sample was collected and again ground in a mortar until a smooth and smooth powder can then be obtained.

2.3 Preparation of Doxycycline Stock Solution

Pharmaceutical-grade Doxycycline has been used to prepare the Doxycycline stock solution (Razak Pharmaceutical Company). First, 1 *g* of Doxycycline was accurately weighed and dissolved in a 1000 *ml* volumetric flask with deionized water. The solution was stirred up to achieve the desired concentration. All test solutions used in the experiments were prepared by reducing the concentration of this stock solution (Ghollasi, 2021).

Fig. 1 Batch reactor in the laboratory

2.4 Photocatalytic Experiments for Doxycycline

Degradation Experiments have been conducted in a 250 ml batch reactor (Fig. 1). Experimental Setup: Doxycycline solutions with initial concentrations of (10, 15, 25, 30, 50, and 60 mg/l) were prepared. Catalyst doses were adapted within the range of (0.1, 0.25, 0.5, 0.75, and 1 g/l). pH values were set

at (3, 5, 7, 9, and 11). The reaction time was tested at (10, 30, 60, 90, and 120 min). Light Source and Reaction Process: A 9-watt UV-C lamp was used as the light source. A vacuum pump has been used to guarantee appropriate mixing during the experiments. Moreover, samples were collected at specified intervals and centrifuged at 5500 rpm for 10 min to separate the catalyst from the solution. The degradation efficiency was measured using a UV-Vis spectrophotometer at a maximum absorption wavelength of 360 nm.

The removal efficiency was calculated using Eq. 1:

$$R = \left[\frac{c_0 - c_f}{c_0}\right] \times 100 \tag{1}$$

where, R is the percentage of catalyst removal, C_0 is the initial concentration of the pollutant solution in mg/l, and C_f is the final concentration of the pollutant solution in mg/l.

2.5. Pollutant photocatalytic removal kinetic studies

Kinetic analysis of the reaction was conducted to examine the degradation of Doxycycline medicine by the photocatalytic process using Excel software. To perform this analysis, Eq. 2

was used, and by integrating Eq. 2, Eq. 3 was derived (Ahmadpour et al., 2020):

$$\frac{dc}{dt} = -kC \tag{2}$$

$$ln\left(\frac{c}{c_0}\right) = -kt \tag{3}$$

where, k and t represent the reaction rate constant and time, respectively. C and C_0 are the concentrations of the reactant at times t = t and t = 0 (Ahmadpour et al., 2020).

3. Results and Discussion
3.1 Characterization results
3.1.1 XRD analysis

The X-ray diffraction pattern of the ZnO@g-C$_3$N$_4$ nanocomposite is shown in Fig. 2. The ZnO nanoparticles are distributed on the GCN substrate. The structure of the nanoparticles was identified in the spectral range between 10 and 80°. The ZnO@g-C$_3$N$_4$ nanocomposite aligns with the reference code 0451–230-96. This has a hexagonal crystal structure. To examine and identify the formed phases, the High Score Plus X'Pert software was used.

Fig. 2 X-ray diffraction pattern of ZnO@g-C$_3$N$_4$ Nanocomposite
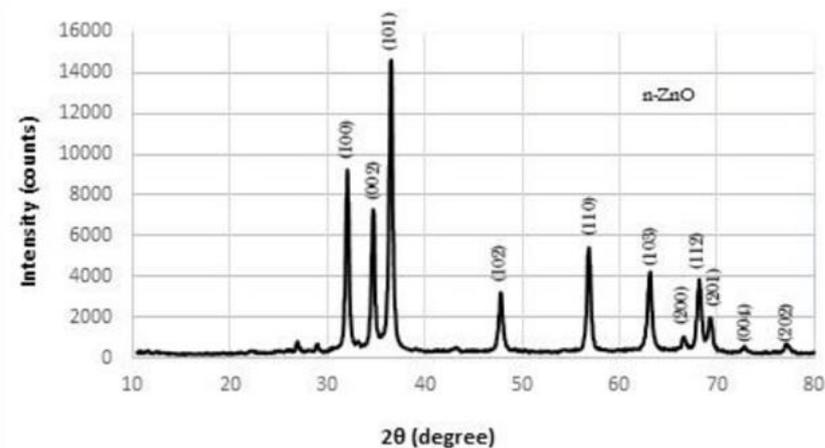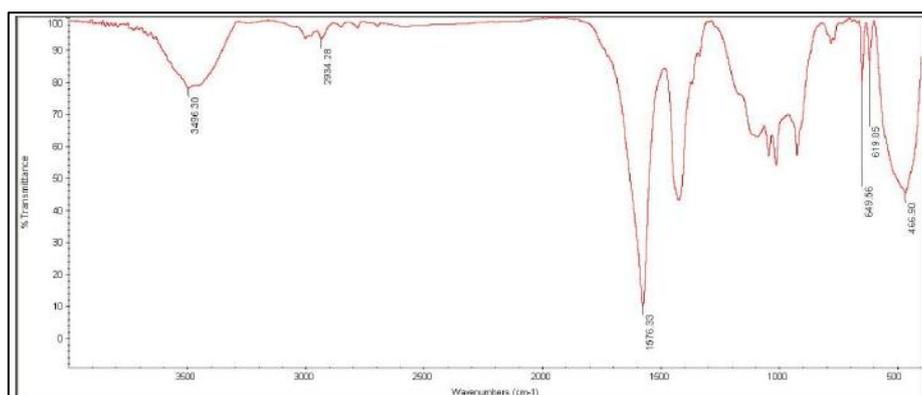

Fig. 3 FTIR Spectrum of ZnO@g-C$_3$N$_4$ Nanocomposite

3.1.2 Fourier transform infrared spectroscopy

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum of the ZnO@g-C$_3$N$_4$ nanocomposite was shown in the range of 400–4000 cm^{-1}. A peak at 3496 cm^{-1} corresponds to O-H stretching vibrations, the peak at 2934 cm^{-1} is related to C-H vibrations, the peak at 1576 cm^{-1} corresponds to C=O stretching, and the peaks at 649, 619, and 466 cm^{-1} are

associated with Zinc oxide vibrations (Fig. 3) (Handore et al., 2014; Bragaru et al., 2012; Perito et al., 2012; Sirvastava et al., 2013). The results indicate proper synthesis and correct functionality of the desired nanocomposite.

3.1.3 Photoluminescence analysis

The wavelength near 300 nm is associated with the presence of small amounts of carbon in the nanocomposite substrate,

i.e., g-C$_3$N$_4$ (Yadav et al., 2020). This may be due to the fact that electrons transfer in the carbon-carbon bonds. After that, a decrease is observed, followed by an increase in peak intensity in the range of 390 to 485 nm. According to similar studies (Saikia et al., 2015; Raj and Sadayandi, 2016), this shows the presence of the combination of free excitons due to the exciton-exciton interaction process in the Zinc oxide semiconductor. The reason behind is that when a photon is absorbed by a semiconductor, it may generate an exciton. The

created peaks gradually increase and then narrow into a thin line at their highest point, which may be due to the fact that electron transfer from the localized surface to the valence band. Similarly, the confinement of crystal size and the surface effects that the nanoparticle powder has on optical transitions in luminescence (Raj and Sadayandi, 2016). The Photoluminescence analysis (PL) test results, similar to the XRD analysis results, proved the presence of small amounts of carbon and high amounts of Zinc oxide (Fig. 4).

**Fig. 4** PL Spectrum of ZnO@g-C$_3$N$_4$ Nanocomposite
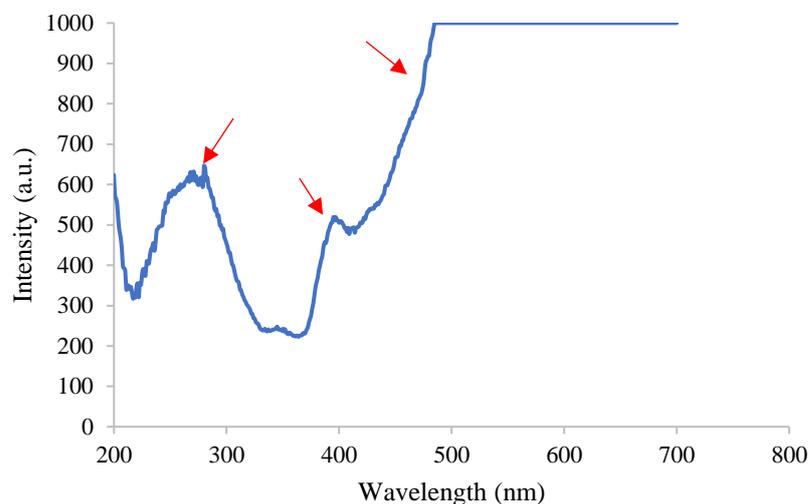
3.1.4 Thermogravimetric analysis

The Thermogravimetric Analysis (TGA) thermogram (Fig. 5) indicated that the nanocomposite was thermally stable up to 390 °C. A weight loss of 12.67 % occurred between 390–708

°C according to similar articles (Aghazadeh et al., 2022; Arora et al., 2014; Rakati et al., 2019), corresponding to the release of absorbed water molecules in the composite. These results successfully verified high thermal stability, which makes the composite suitable for photocatalytic applications.

Fig. 5 TGA Thermogram of ZnO@g-C$_3$N$_4$ Nanocomposite
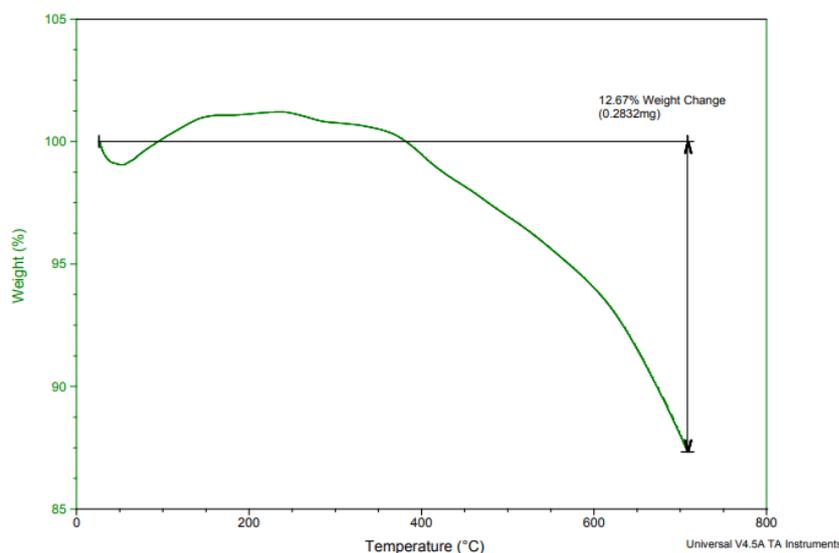
3.1.5 Scanning electron microscopy

The Zinc oxide nanoparticles have uniform sizes and a polyhedral structure. The hexagonal structure that forms these plates is consistent with the XRD analysis. The particle size of the Zinc oxide nanoparticles indicates that the largest particle

has a size of 85.60 nm, while the smallest particle measures 33.49 *nm*, as shown in Fig. 6(a).

3.1.6 Energy-Dispersive X-ray Spectroscopy

The percentage of Zinc oxide is higher compared with other components, indicating that the nanocomposite has been

Environ. Water Eng.

successfully produced and the Zinc oxide nanoparticles are well deposited on the GCN nanoparticles, which serve as the substrate. Based on this analysis, the composition includes

84.3 % zinc, 14.2 % oxygen, and 1.5 % carbon, as shown in Fig. 6(b).

Fig. 6: a) SEM image and b) EDAX analysis of ZnO@g-C₃N₄ nanocomposite
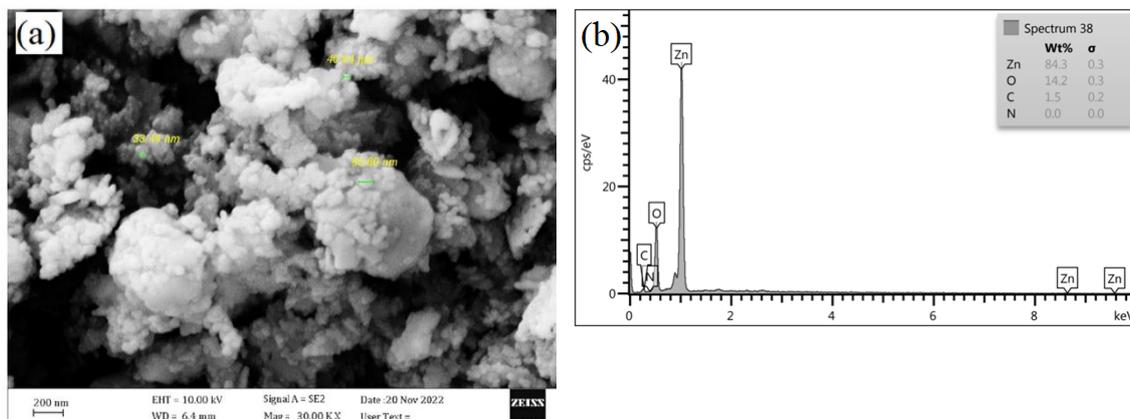
3.2 Photodegradation Results
3.2.1 Effect of pH on Doxycycline Removal

The present study evaluated the effect of different pH values (3, 5, 7, 9, and 11) on the photocatalytic degradation of the pharmaceutical pollutant Doxycycline using the ZnO/GCN nanocomposite over various time intervals (10-120 min). As shown in Fig. 8(a), the highest pollutant removal rate can be observed in the acidic pH range. In other words, the maximum removal percentage of the pollutant was observed at pH 5, considering a removal rate of 62.01 %. Simultaneously with the increase in the pH from 3 to 11, the removal and degradation efficiency of the pollutant decreased between 30% and 62.01%. Therefore, as the pH range increases, the removal efficiency significantly decreases. Following obtaining this result, pH 5 was considered the optimal pH for further experiments. The photocatalytic degradation process is considered an activity that occurs on the surface of the material. Therefore, it can be concluded that the greater the tendency for pollutant molecules to adsorb onto the catalyst surface, the greater the degradation might be expected. In general, pH is a parameter affecting various parameters including the surface charge of the catalyst, the ionization degree of different pollutants, the dissociation of functional groups on sites and active areas of the catalyst, the rate and mechanism of hydroxyl radical production, the molecular structure of the pollutant, and other chemical and physical properties of the system. Consequently, it plays a crucial role in the degradation of organic pollutants by semiconductor oxides (Zainudin et al., 2010; Ghasemi et al., 2016). Jorfi et al. (2018) conducted a study aiming at the photocatalytic degradation of azo dye from textile wastewater. They used the TiO₂ nanocomposite, under optimal conditions, including an initial concentration of 20 mg/l, pH 3, and a nanocomposite dose of 2 g/l, a degradation efficiency of 91 % was reported (Jorfi et al., 2018).

3.2.1 Effect of Doxycycline antibiotic concentration on photocatalytic removal

The pollutant solution was studied at concentrations of (10, 15, 25, 30, 50, and 60 mg/l) to study the effect of the removal and degradation of the Doxycycline antibiotic as a target pollutant by the synthesized photocatalyst (Fig. 8b). Following an increase in the concentration, the catalyst's efficiency in degrading the pollutant increased up to a certain point. However, beyond this concentration, the efficiency started to decrease. The reason behind this can be the saturation of the catalyst's surface sites by the pollutant. In these conditions, light cannot sufficiently reach the catalyst's surface which leads to a decrease in its performance. Additionally, the pollutant itself absorbs light at higher concentrations and prevents it from reaching the catalyst surface. In other words, when the pollutant solution exceeds a certain concentration, the photon energy is absorbed by the pollutant molecules prior to reaching the catalyst surface. Therefore, while the pollutant concentration is increasing, the molecules absorb the emitted photons and prevent them from reaching the UV source or the catalyst surface. According to the results obtained in this study, the optimal concentration for the photocatalytic degradation of doxycycline antibiotic under experimental conditions is 50 mg/l, with a removal efficiency of 67.23%.

3.2.2 Effect of nanocomposite dose on Doxycycline antibiotic removal

By increasing the dose of the nanocatalyst, more active sites are formed. This can speed up the removal and degradation of the pollutant. Therefore, increasing the amount and range of the nanocatalyst up to a certain limit can significantly improve the degradation and removal efficiency. However, if the nanocatalyst dose exceeds a certain threshold, it may lead to increased turbidity and sometimes it may interfere with light penetration into the solution. In these conditions, the removal and degradation of the pollutant occur more slowly and they follow a downward trend. On the other hand, increasing the nanocatalyst dose beyond the optimal concentration ends in the expansion of the catalyst's active surface which results in

positive changes in the production of hydroxyl radicals and other oxidative radicals.

Fig. 8 Diagrams of photocatalytic analysis: a) pH effect diagram, b) Doxycycline antibiotic concentration effect diagram, c) ZnO@g-C₃N₄ nanocomposite concentration effect diagram, and d) Time effect diagram
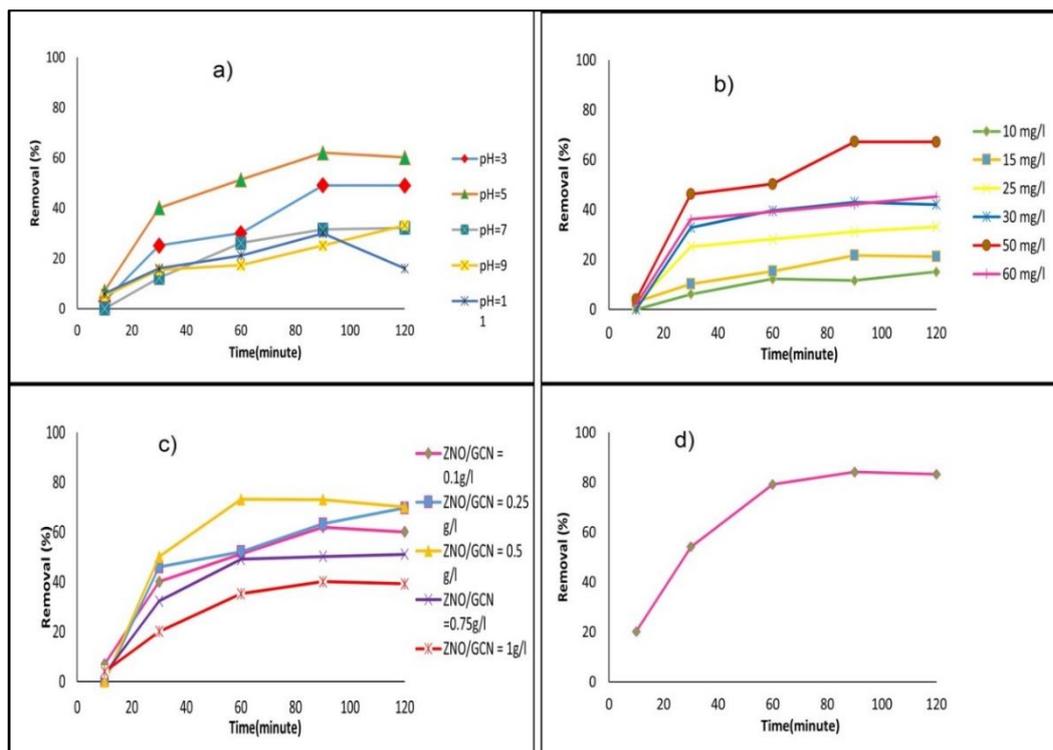
According to Fig. 8(c), the influence of different nanocatalyst doses on pollutant removal was examined in the range of (0.1, 0.25, 0.5, 0.75, and 1 g/l). The results showed that the removal of the pollutant increased significantly with the increase in nanocatalyst dose, demonstrating a direct relationship between them. In optimal conditions, including pH 5, a pollutant concentration of 50 mg/l, and a catalyst dose of 0.5 g/l, the removal percentage was 73.14 %. Therefore, a nanocatalyst dose of 0.5 g/l was considered optimal, and at higher doses, due to doses from 0.1–1 g/l were tested (Fig. 8c). The optimal dose was 0.5 g/l, which can achieve 73.14 % degradation. Higher doses cause turbidity, and they reduce light penetration and efficiency.

Further analysis showed that at 90 min, the pollutant removal rate was 84.14v%. Therefore, as the processing time increases, the pollutant removal efficiency also shows an upward trend. The reason behind is that, over time, the pollutant molecules have more chances to interact with the active sites on the surface of the nanocatalyst. However, after the active sites on the nanocatalyst surface become saturated or fully utilized, the degradation efficiency levels off. When it further increases in time, and does not significantly improve the removal rate (Fig. 8d).

3.3 Pollutant photocatalytic removal kinetic studies

The first-order and second-order equations are based on Eqs. 2 and 3, were examined for different pH values of 3, 5, 7, 9, and 11 at various times of 10, 30, 60, 90, and 120 min. The results are presented in Table 1.

Table 1 Comparison of first and second-order kinetics

Type of Equation	PH	3	5	7	9	11
First order Equation	K	0.0059	0.0075	0.0036	0.0029	0.0035
	R^2	0.9084	0.8278	0.8877	0.9594	0.9738
	SS	37.91536	198.3702	21.22797	10.88152	97.8212
Second order Equation	K	0.0088	0.0134	0.0045	0.004	0.0043
	R^2	0.9124	0.8435	0.5269	0.959	0.3159
	SS	23.42398	63.95009	14.54366	7.451909	88.63798

Based on the results obtained from Table 1, the second-order kinetics is better than the first-order kinetics, and the best k value was obtained at pH = 5.

4. Conclusion

The main purpose of this research was to analyze the photocatalytic removal of Doxycycline antibiotics by using ZnO-GCN nanocomposite. The effects of catalyst dosage,

initial pollutant concentration, temperature, pH, and reaction time on Doxycycline removal were also studied.

1. In this study, the ZnO@g-C₃N₄ nanocomposite was successfully synthesized for the removal of Doxycycline antibiotics from aqueous environments. The nanocomposite was characterized and evaluated using techniques such as XRD, FTIR, SEM, PL, TGA, and EDAX.

2. Key parameters affecting the photocatalytic process, such as pH, pollutant concentration, catalyst dose, and time, were examined. The results of these experiments showed that the best removal and degradation efficiency of Doxycycline as a pollutant in aqueous environments was achieved under optimal conditions with pH = 5, pollutant concentration of 50 mg/l, catalyst dose of 0.5 g/l, and a reaction time of 90 min, resulting in a removal rate of 84.14 %.

3. The kinetic degradation tests indicated that the process follows a second-order kinetic model.

4. Based on the results obtained from this study, the ZnO@g-C₃N₄ nanocomposite can be introduced as an effective, environmentally friendly catalyst for the degradation of pharmaceutical pollutants. To enhance and build upon the findings of this research, the following suggestions are proposed:

Investigating the effect of the ZnO@g-C₃N₄ nanocomposite on a larger scale, such as hospital wastewater, due to the use of the antibiotic Doxycycline, and assessing the ability to degrade other antibiotics that are considered pollutants using ZnO@g-C₃N₄ nanocomposite.

Acknowledgment

Statements and Declarations
Data availability

The data used in this research are provided in the text of the article.

Conflicts of interest

The author of this paper declared no conflict of interest regarding the authorship or publication of this paper.

Author contribution

Sh. Forghani Darmiyan: Experiments, Data Collection, Writing– original draft, M. R. Rezaei: Supervisor, Writing – review and editing, Results Analysis and Research Management, and M. H. Sayadi Anari: Advisor, Writing – review and editing, Results Analysis and Research Management.

References

Aghazadeh, M., Hasani, A., & Borghei, M. (2022). Optimization of catalytic sono-praxone hybrid process in the presence of iron oxide-zinc oxide catalyst for the treatment of petroleum wastewater by centralcomposite design. *Iran. J. Health Environ.*. *15*(3):419-40. DOI: 20.1001.1.20082029.1401.15.3.3.6 [In Persian]

Ahmadpour, N., Sayadi, M. H., & Homaeigohar, S. (2020). A hierarchical Ca/TiO₂/NH₂-MIL-125 nanocomposite photocatalyst for solar visible light induced photodegradation of organic dye pollutants in water. *RSC Adv.*, *10*(50), 29808-29820. DOI: 10.13005/ojc/300427.

Arora, A. K., Devi, S., Jaswal, V. S., Singh, J., Kinger, M., & Gupta, V. D. (2014). Synthesis and characterization of ZnO nanoparticles. *Orient. J. Chem*, *30*(4), 1671-1679. DOI: 10.13005/ojc/300427.

Bajpai, S. K., Bajpai, M., & Rai, N. (2012). Sorptive removal of ciprofloxacin hydrochloride from simulated wastewater using sawdust: Kinetic study and effect of pH. *Water Sa*, *38*(5), 673-682, DOI: 10.4314/wsa.v38i5.4.

Esrafili, A., Salimi, M., Gholami, M., & Farzadkia, M. (2018). Photocatalytic Removal of Metronidazole from Aquatic Environment Using g-C₃N₄-TiO₂. *J. Health. Syst. .Res., 14*(3), 403-409, DOI: 10.22122/jhsr.v14i3.3413 [In Persian].

Ghasemi, Z., Younesi, H., & Zinatizadeh, A. (2016). Efficiency of immobilized nano TiO₂ on Fe-ZSM-5 zeolite in organic pollutants removal from petroleum refinery wastewater. *J. Water Wastewater, 27*(2), 22-33. [In Persian].

Ghazi Tabatabai, Z., Shekari, R., Eimani, Sh., & Skori, Sh., (2018). Investigating the efficiency of Graphene nano oxide coated with Zinc oxide nanoparticles in removing Tetracycline antibiotics. *The 5th National Conference on New Researches in Chemistry and Chemical Engineering*, Iran, Theran.[In Persian].

Ghollasi nezhad, M. (2021). Evaluation of the efficiency of copper oxide reinforced magnetic carbon nanotubes in the removal of cationic and anionic dyes. MSc Thesis**.** University of Birjand. Bijand. Iran [In Persian].

Handore, K., Bhavsar, S., Horne, A., Chhattise, P., Mohite, K., Ambekar, J., Pande,N., & Chabukswar, V. (2014). Novel green route of synthesis of ZnO nanoparticles by using natural biodegradable polymer and its application as a catalyst for oxidation of aldehydes. *J Macromol. Sci., Part A*, *51*(12), 941-947, DOI: 10.1080/10601325.2014.967078

Jafari, K., Khadir, A., Hoseinzadeh, E., Fathabad, A. E., & Rahmanian, O. (2020). Methods for removal of antibiotics from aqueous solution: A review. *Hozan J. Environ.Sci; 4*(2), 12-42.[In Persian].

Jorfi, S., Mirali, S., Mostoufi, A., & Ahmadi, M. (2018). Visible light photocatalytic degradation of azo dye and a real textile wastewater using Mn, Mo, La/TiO₂/AC nanocomposite. *Chim. Biochem. Eng. Q*, *32(2),* 215-227, DOI : 10.15255/CABEQ.2017.1261.

Kümmerer, K., Al-Ahmad, A., & Mersch-Sundermann, V. (2000). Biodegradability of some antibiotics, elimination of the genotoxicity and affection of wastewater bacteria in a simple test. *Chemosphere*, *40*(7), 701-710, DOI: 10.1016/S0045-6535(99)00439-7.

Moosavi, F., Cheng, C., Gheinani, T. T., Traore, M., Kanaev, A., & Nikravech, M. (2019). Photocatalytic destruction of amoxicillin in a pilot sunlight reactor with supported titania nano-photocatalyst. *Chem. Eng. Trans.*, *79*, 175-180. DOI: 10.3303/CET1973030

Moosavi, F., Tavakoli, T., Nikravech, M., Khley, C., & Kanaev, A. (2019). Investigation of removal of amoxicillin antibiotic from water by photocatalyst in different operating conditions. *J. Nat. Environ.*, *72*(3), 379-388, DOI: 10.22059/jne.2019.271472.1592 [In Persian].

Prieto-Rod]riguez, L., Miralles-Cuevas, S., Oller, I., Agüera, A., Puma, G. L., & Malato, S. (2012). Treatment of emerging contaminants in wastewater treatment plants (WWTP) effluents by solar photocatalysis using low TiO_2 concentrations. *J. Hazard. Mater.*, *211*, 131-137, DOI: 10.1016/j.jhazmat.2011.09.008.

Raj, K. P., & Sadayandi, K. (2016). Effect of temperature on structural, optical and photoluminescence studies on ZnO nanoparticles synthesized by the standard co-precipitation method. *Physica B: Condensed Matter*, *487*, 1-7. DOI: 10.1016/j.physb.2016.01.020.

Rakati, K. K., Mirzaei, M., Maghsoodi, S., & Shahbazi, A. (2019). Preparation and characterization of poly aniline modified chitosan embedded with $ZnO-Fe_3O_4$ for Cu(II) removal from aqueous solution. *Int. J. Biol. Macromol*, *130*, 1025-1045. DOI: 10.1016/j.ijbiomac.2019.02.033.

Saikia, L., Bhuyan, D., Saikia, M., Malakar, B., Dutta, D. K., & Sengupta, P. (2015). Photocatalytic performance of ZnO nanomaterials for self sensitized degradation of malachite green dye under solar light. *Appl. Catal. A: General*, *490*, 42-49. DOI: 10.1016/j.apcata.2014.10.053.

Shan, W., Hu, Y., Bai, Z., Zheng, M., & Wei, C. (2016). In situ preparation of g-C_3N_4/bismuth-based oxide nanocomposites with enhanced photocatalytic activity. *Appl. Catal. B: Environ.*, *188*, *1-12*, DOI: 10.1016/j.apcatb.2016.01.058

Shokri, M., Akbari Shorgoli, A., & Doudkanlouye Milan, V. (2020). Investigation of photocatalytic degradation of doxycycline antibiotic in aqueous solutions using immobilized zinc oxide nanoparticles on glass: influence of operational parameters and kinetic studies. *Iran. J. Chem.*, *3*(1), 95-107. DOI: 10.22036/IJC.2019.183978.1077 [In Persian].

Srivastava, V., Gusain, D., & Sharma, Y. C. (2013). Synthesis, characterization and application of zinc oxide nanoparticles (n-ZnO). *Ceram. Int.*, *39*(8), 9803-9808. DOI: 10.1016/j.ceramint.2013.04.110.

Yadav, R. M., Kumar, R., Aliyan, A., Dobal, P. S., Biradar, S., Vajtai, R., Singh, D. D., Marti,A. A., & Ajayan, P. M. (2020). Facile synthesis of highly fluorescent free-standing films comprising graphitic carbon nitride (gC 3 N 4) nanolayers. *New J. Chem.*, *44*(6), 2644-2651, DOI: 10.1039/C9NJ05108B

Zainudin, N. F., Abdullah, A. Z., & Mohamed, A. R. (2010). Characteristics of supported nano-TiO_2/ZSM-5/silica gel (SNTZS): photocatalytic degradation of phenol. *J. Hazard. Mater.*74(1-3), 299-306*, DOI: 10.1016/j.jhazmat.2009.09.051