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Photocatalytic degradation of amoxicillin, cephalexin, and tetracycline from aqueous solution: comparison of efficiency in the usage of TiO_2, ZnO, or GO-Fe_3O_4 nanoparticles

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ABSTRACT

In this study, effects of a number of parameters such as pH of the solution (3–11), the adsorbent quantity (0.2–4 g L^{-1}), contact time (0–60 min), initial concentration of antibiotics (1–100 mg L^{-1}) and the power of lamp (6 and 18 W) on the removal efficiency of antibiotics with different nanoparticles were compared. After carrying out the incumbent experiments and analyses, it was determined that pH adjustment had no effect on the UV/GO-Fe_3O_4 system efficiency. In one hand, it was indicated that the optimal contact times were achieved at 15, 45, and 45 min and the amounts of catalysts were evaluated at 2, 4, and 4 g L^{-1} for tetracycline, amoxicillin, and cephalexin, respectively. On the other hand, the optimal conditions in the UV-TiO_2/ZnO processes were obtained as the 'catalysts value of 2 g L^{-1}', 'antibiotics concentration of 15 mg L^{-1}', 'radiation intensity of 18 W', 'pH of 5, 7, and 5', 'contact time of 15, 45, and 45 min' for amoxicillin, cephalexin, and tetracycline, respectively. The optimum initial concentration for all three antibiotics was 15 mg L^{-1} and the maximum removal efficiency occurred at 18 W of ultraviolet radiation. In addition, degradation of tetracycline, a complete removal percentage was achieved for all mentioned catalysts, however, considering amoxicillin and cephalexin, the obtained values were variable and making use of GO-Fe_3O_4 for amoxicillin and ZnO for tetracycline removal had the maximum removal efficiency (87.1% and 81.8%, respectively). Finally, it was noteworthy to mention that a multitudinous of experiments were conducted to determine the most effective catalysts in the photocatalytic degradation of three types of prevalent antibiotics.

Keywords: Graphene oxide; Titanium dioxide; Zinc oxide; Amoxicillin; Cephalexin; Tetracycline

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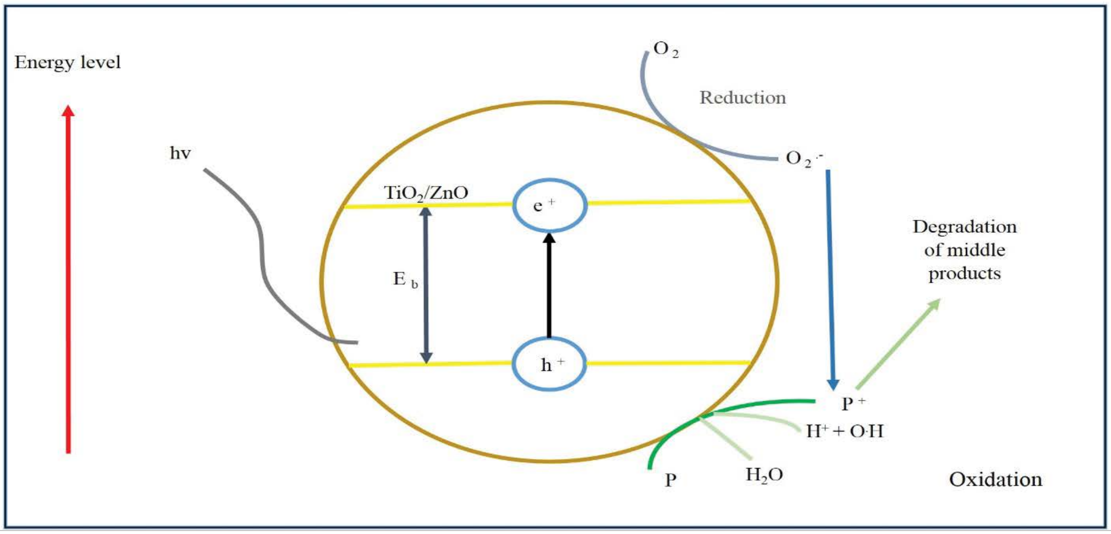
1. Introduction

Today, metropolises are experiencing marked progresses and this has caused many issues. Mismanagement of water resources, the growing competition for using freshwater and decaying resources caused by pollutants also incline the depth of these issues. Restriction of water resources and incidence of drought as well as the devastating effects of human activity on the environment have contributed to serious challenges on the way to benefiting from freshwater resources. Inappropriate distribution of precipitation, the mismatch between demand and time of precipitation, the dire need for investing in the storages, monitoring and protection sectors of water resources further complicate the dimensions of water challenge. Moreover, freshwater resources are considered as renewable resources and renewability process of these resources follows water cycle in nature; however,



the amount of water that emerges through this way across the earth or in any geographical region is constant and specific regardless of year-round variations. Strict protection of water resources against any contamination and reusing it are very significant [1]. Therefore, these days one of the main concerns of human beings is the entrance of pharmaceutical compounds into water resources. Unless it is controlled, it might result in irrecoverable damages [2,3].

Among the pharmaceutical compounds which cause water pollution, antibiotics have always been playing a significant role due to their high degrees of usage in medicine and veterinary. The annual consumption of antibiotics in the world is estimated between 100,000 and 200,000 tons. Antibiotics are rarely metabolized in the body after they are consumed from 30% to 90% of them remain active after excretion. Hence, it can be concluded that in the best condition, 30,000 tons year^{-1}, and in the worst condition, 180,000 tons of active antibiotics enter the environment.

Generally, advanced oxidation process is the most efficient technology for the decomposition and removal of persistent organic pollutants, resistant and non-degradable organic pollutants in aquatic environments and therefore it has played a major role in water and wastewater treatment over the past decades. The main mechanism of these processes is based on the production of hydroxyl radicals which are almost capable of oxidizing many organic compounds [4].

- Semiconductor + hv $\rightarrow e^- + h^+$
- $h^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH$
- $h^+ + OH^- \rightarrow {}^{\bullet}OH$
- $e^- + O_2 \rightarrow {}^{\bullet}O_2^-$
- ${}^{\bullet}O_2^- + H_2O + H^+ \rightarrow H_2O_2 + OH^-$
- $H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^-$
- OH + Organic matter (OM) → degradation of OM
- h^+ + OM → OM$^{\bullet+}$ → oxidation of OM

Among the various processes of advanced oxidation, photocatalytic processes comprise a promising technology for the removal of antibiotics from aqueous solutions. The recombination rate of the photo-generated electron–hole pairs in ZnO is usually faster than that of surface redox reactions, which seriously restricts its practical applications, especially in photocatalytic degradation of organic compounds. In addition, TiO_2 has been investigated as a potential photocatalyst. Practical applications of TiO_2 photocatalyst is dependent highly on the stable immobilization of catalyst powder on a support in such a way as to afford a reasonably high surface area and accessibility of the immobilized catalyst [5,6]. The main advantages of these processes are lack of limitation of mass transfer, environmental exploitation, availability of crystalline commercial forms and various particle characteristics, high chemical stability in a wide range of pH, high resistance to chemical failure and optical corrosion [7]. For this aim, the materials selected as pollutants in this study include amoxicillin, cephalexin, and tetracycline, which have been defined as follows.

Amoxicillin includes a broad range of penicillin antibiotic and activated against many gram-positive and gram-negative bacteria. The molecular formula for this antibiotic is $C_{16}H_{19}N_3O_5S{\cdot}3H_2O$ and its molecular weight is 419.45; the molecular structure (Fig. 1) of amoxicillin is as follows [8].

Cephalexin is a type of oral medication which comes from the first generation of antibacterial cephalosporin. The molecular formula for this antibiotic is $C_{16}H_{17}N_3O_4S$ with water and its molecular weight is 365.4; its molecular structure is shown in Fig. 2 [8].

Tetracycline is a family of bacterio-static antibiotics activating against gram-negative and gram-positive bacteria,

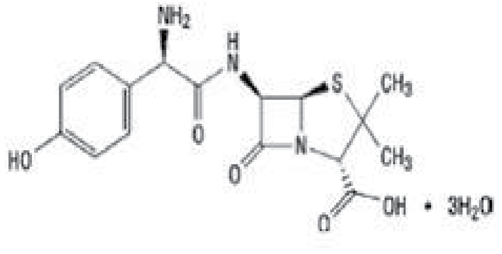


Fig. 1. Chemical structure of amoxicillin [8].

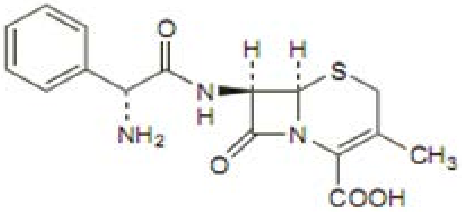


Fig. 2. Chemical structure of cephalexin [8].

namely Mycoplasma, chlamydia, and rectasia. The chemical formula of this antibiotic is $C_{22}H_{24}N_2O_8$; its molecular weight is 444.44 and the molecular structure of this antibiotic is shown in Fig. 3 [8].

The consumed nanoparticles include titanium dioxide, zinc oxide, and magnetized graphene oxide, which structurally comprise of three types: rutile, anatase, and brookite. Titanium dioxide is known as titanium (IV) oxide or titania, with the chemical formula of TiO_2. It is worth noting that, when it is used as a dye, it is known as white titanium, white dye, and CI77891 [9].

Zinc oxide has the chemical formula of ZnO, which is a significant semiconductor with a high band gap (37.3 eV) and excitation energy (60 meV) at room temperature. In recent years, zinc oxide has attracted a great deal of attention mainly due to its unique optical, electronic, and piezoelectric properties. It also has found various applications including solar cells, blue-light-emitting diodes, sensors, and reducers [10].

Graphene is a layer of graphite and as a two-dimensional allotrope of carbon with a grid plate structure looks similar to a vespiary. It has the chemical formula of GO [11].

Wenjie et al. [12] studied preparation of attapulgite/TiO_2/graphene composite and its application for the photocatalytic degradation of chlortetracycline. They found that ATP could improve the dispersity of TiO_2 nanoparticles and that RGO can decrease the band gap of TiO_2 and the degradation rate could reach up to more than 90% with the UV light irradiation. Furthermore, it was indicated that the highest removal rate could be achieved when the initial concentration of CTC was 20 mg L^{-1} and the catalyst dosage was 0.4 g L^{-1}. h^+ and $^{\bullet}O_2^-$ plays a significant role in the photocatalytic process. The composite also showed both high reusability and stability, providing a good application prospect in photocatalysis field [12].

In the same line of research, Jain et al. [13] investigated the removal of rifabutin antibiotic using titanium dioxide nanoparticles in the presence of ultraviolet radiation. They employed hydrogen peroxide as an auxiliary oxidizer. After obtaining the optimal conditions (contaminant concentration = 0.4 mg L^{-1}, pH = 10.5, and catalyst concentration = 0.06 g L^{-1}), they aimed to remove 85% of this antibiotic from aqueous environments [13].

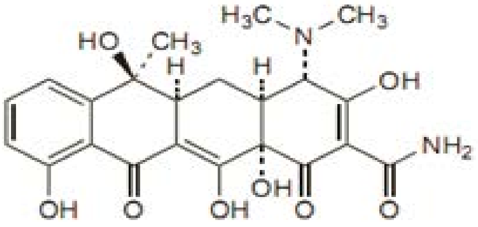


Fig. 3. Chemical structure of tetracycline [8].

Similarly, Yazdani et al. [14] investigated performance evaluation of combined ultrasonic/UV process in the removal of tetracycline antibiotic from aqueous solutions using response surface methodology. This experimental study was performed by the ultrasonic bath associated with ultraviolet radiation. The results of this study showed that the removal efficiency of UV and ultrasonic processes was 16% and 32% in optimum conditions, respectively. While in ultrasonic/UV process, the removal efficiency increased. The best removal efficiency (72%) was observed in pH of 4.5, antibiotic concentration of 10 mg L^{-1}, the input power of 240 W and contact time of 50 min [14].

In 2016, Mostafapour [15] conducted an investigation on the photocatalytic degradation of ciprofloxacin using copper oxide in aqueous environments. At first, they measured the concentration of the antibiotic using the spectrophotometer device at the maximum wavelength of 276 nm. Then, they considered pH = 7, nanoparticles dose of 0.07 g L^{-1}, and time of 60 min as the optimal values. With the elevation of the antibiotic concentration within the optimal time, they observed the maximum efficiency of the system as 73% [15].

Furthermore, Xinjiang et al. [16] examined the efficient removal of tetracycline from aqueous media with a Fe_3O_4 nanoparticles@graphene oxide nanosheets assembly. In this investigation, a readily separated composite was prepared via direct assembly of Fe_3O_4 magnetic nanoparticles onto the surface of graphene oxide (GO) (labeled as Fe_3O_4@GO) and used as an adsorbent for the removal of tetracycline (TC) from wastewater. The results obtained using the two-compartment model showed that when the initial adsorption concentration was 10 or 50 mg L^{-1}, the fast adsorption process dominated TC adsorption. Additionally, when the initial concentration was 100 mg L^{-1}, the slow adsorption process dominated. During adsorption, film diffusion and intraparticle diffusion occurred simultaneously and film diffusion was the adsorption rate-limiting step. The isotherm experimental data were consistent with the Langmuir model and the adsorption reaction was an endothermic process. Fe_3O_4@GO had a high adsorption capacity even after four cycles of adsorption, indicating that it had an excellent regeneration performance [16].

Regarding the above-mentioned studies, the main objective of this research is to investigate the performance of titanium dioxide and zinc oxide nanoparticles in removing antibiotics from the wastewater produced by pharmaceutical industries.

For this aim, a comparison is made between the performance of photocatalytic process by different nanoparticles in the degradation of mentioned antibiotics from aqueous solution.

2. Materials and methods

2.1. Chemicals

This study is empirical, and the following chemicals were used: amoxicillin trihydrate, cephalexin monohydrate, and tetracycline with a purity greater than 95% which were taken from the pharmaceutical company Jaber Ibn Hayan and Razak (Tehran, Iran). Graphene oxide with 99% purity and particle size 3, 4 up to 7 nm and a special surface area from 100 to 300 m^2 g^{-1}, titanium dioxide (Code US3490, anatase type, with a purity of +99.5% and particle size of 10–25 nm), zinc oxide nanoparticles (Code US3590, anatase type, with a purity of +99.5% and particle size of 10–30 nm) were purchased from US-Research Nanomaterials (Houston, Texas, USA) [11]. Other chemicals which were used for the aim of carrying out this research were iron (III) hexahydrate and iron (II) chloride tetrahydrate acetonitrile, triethylamine, methanol, acetic acid, phosphoric acid, boric acid, and sodium hydroxide, made by Merck (Darmstadt, Germany).

2.2. Apparatuses

In order to measure pH, an experimental pH-meter (BASIC20, Switzerland) was used, while a spectrophotometer device (Hach DR5000, Germany) and an HPLC device (KNAUER, Germany) were used along with UV detector and C18 column (4.6 × 250 mL) to evaluate the residual antibiotics concentration.

The mobile phases characteristics which were employed to measure the residual of antibiotic concentrations are as follows: acetonitrile with KH_2PO_4 0.225 molar (30%:70%) for amoxicillin, 225 mL distilled water, 24.6 mL acetonitrile, 12.3 mL methanol, and 3.7 mL of triethylamine for cephalexin, and acetonitrile 0.01 molar and oxalic acid solution (70%:30%). The flow rate was 1 mL min^{-1}, which ultimately evaluated the amoxicillin, cephalexin, and tetracycline residues at wavelengths 228, 261, and 357 nm.

3. Procedure of the experiment

This investigation was conducted on laboratory and sampling method was manual and daily. First of all, 100 mg L^{-1} of each antibiotic solution was made with distilled water on a stirrer at 700 rpm and at a constant temperature for 3 h. Second, samples with concentrations of 1, 5, 10, 15, 20, 50, and 100 mg L^{-1} were prepared from the first solution made. Next, the considered pH (3, 5, 7, 9, and 11) by acetic, phosphoric, boric acid and 2 mol caustic soda were adjusted. Furthermore, samples were poured into 250 mL beakers and then in order to combine the solution with the various quantity of nanoparticles (0.2, 1, 4/1, 2, 3, and 4 g L^{-1}), samples were put on a shaker placed inside an ultraviolet pilot. After that, the combination was vibrated considering time (3, 5, 15, 30, 45, and 60 min) at 25°C at 350 rpm and a radiation power of 6 W. Last of all, they were filtered by syringe filter (0.22 µm) and all the experiments were repeated once again in a radiation power of 18 W. At each step, by changing one parameter and keeping other parameters constant, the removal percentage of antibiotics was calculated by a spectrophotometer. Finally, for the accuracy of the obtained results, all the specimens were measured under optimal conditions with a chromatography liquid device (HPLC).

3.1. Magnetic modification of graphene oxide

For preparing magnetized graphene oxide (Fig. 4), 6.8 g of iron (III) chloride hexahydrate, 3.5 g of iron (II) chloride tetrahydrate and 1.0 g of graphene oxide were dissolved by an ultrasonic mixer in 250 mL of distilled water at 353 K for 30 min. After mixing uniformly, the mixture was transferred to a round-bottomed balloon with two spans. Then, 10 mL of ammonia 32% was poured into a separatory funnel and was gradually added to the contents of the round balloon for 15 min. This action was carried out under reflux conditions at 353 K and continuous stirring. In this step, the nitrogen gas bubbles came out of the solution with a color of dark brown. When ammonia was over, the separatory funnel faucet was closed and the rest of the 60 min reflux continued at the same temperature. Then, the balloon span was completely closed and the solution was stirred at room temperature for 24 h. In the end, the nanosized composites were washed for several times with distilled water and twice with ethanol, separated by a cubic magnet (Fig. 5), stored at an Arlene at a temperature of 323 K and then they were dried for further use in a desiccator.

3.2. Characteristics of magnetized graphene oxide

The prepared graphene oxide and magnetic graphene oxide were identified and analyzed by IR spectroscopy, X-ray diffraction, and scanning electron microscopy (SEM) image. Comparison of IR spectra of graphene oxide and magnetized graphene oxide is depicted in Fig. 6. As shown in Fig. 6a, oxygen-carbon bonds including hydroxyl, epoxy, carbonyl, and carboxyl groups appear in the oxidation process of vibration. Two tensile vibration strains related to the C–O bond were perceived in 1,126 cm^{-1} regions and 1,214 cm^{-1}. They belonged to the carbon and bonded to the hydroxyl and carboxyl groups. The C=O bond of the carboxyl group was observed in the 1,632 cm^{-1} region. Finally, a strong vibration in the 3,441 cm^{-1} related to the O–H graft was also evident. In Fig. 6b, the FTIR analysis of magnetic graphene oxide noticed a peak in 671 cm^{-1} which it was related to the Fe–O band. The broad peak of 3,420 cm^{-1} corresponds to the hydroxyl group in the absorbent structure. The produced peaks in 1,739 and 1,548 cm^{-1} represented asymmetric tensile vibrations for the C=O group and the second type of amine group, respectively.

In the X-ray diffraction pattern of graphene oxide (Fig. 7), a high-intensity peak in the region of $2\theta = 12.2°$ and a very low peak in the region of $2\theta = 42°$ are indicated which there were a trivial amount of unoxidized graphite in the environment. Altering the interlayer space illustrated the presence of oxygenated groups and increased in the thickness of carbon plates.

Figs. 8a and b demonstrate images of SEM for graphene oxide and magnetic composite graphene oxide, respectively. These analyses were performed in order to investigate the morphology and the properties surface of graphene and optimized graphene in 15 kV. In Fig. 8a, it was observed that graphene oxide had a proper sheet-shaped porosity, which would expand the level of contaminant contact with adsorbent and consequently expand the absorption efficiency. As it can be seen in Fig. 8b, iron oxide nanoparticles have been scattered in the form of polygonal and asymmetric graphene oxide. In the above-mentioned forms, it was seen that the synthesized absorbent had a size of 10–15 µm and it was uniform in the form of porosity at the surface.

The obtained results from SEM and XRD for titanium dioxide nanoparticles and SEM images of zinc oxide nanoparticles (Figs. 9 and 10) were also provided from the website of the manufacturer of the nanoparticles (US Research Nanomaterials Company, Houston, Texas, USA).

3.3. Calculations

Initially, using a spectrophotometer, the maximum absorbed wavelengths were obtained at 228, 261, and 357 nm for amoxicillin, cephalexin, and tetracycline. Thereafter, the calibration curves for antibiotics were plotted in Excel by using the absorption numbers of discrepant concentrations of the antibiotics.

The removal percentage formula (E) for all antibiotics was measured as follows:

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

Here, C_0 and C_e were the initial and final equilibrium concentration of amoxicillin, cephalexin, or tetracycline (mg L^{-1}) in aqueous solution, respectively [18].

In these calculations, first, the percentage of degraded antibiotics was calculated by the spectrophotometer device but in the end, for analyzing the accuracy of the obtained results, the samples were measured by liquid chromatography (HPLC) under optimal conditions.

4. Results

4.1. Effect of pH

The obtained results from investigating the pH alteration on the removal efficiency of antibiotics have been illustrated in Fig. 11. As shown in this chart, when MGO was used as a catalyst, the pH adjustment was not an effective parameter in antibiotics degradation. Meanwhile, in an acidic or near-neutral environment, the removal of tetracycline was better. On the other hand, the suitable pH for the removal of amoxicillin by TiO_2 and ZnO nanoparticles was achieved at pH 5. Considering cephalexin, it became obvious that with increasing pH from 3 to 7, the removal percentage inclined in both catalysts, with the most suitable pH being the neutral pH; increasing pH from 7 to 11 led to the decline in the extent of removal. For efficiently removing tetracycline, the suitable pH of the solution was equal to 5.

In their investigation to remove tetracycline from the aqueous by graphene oxide, Yuan et al. [18] concluded that the optimum condition for the medium and low initial concentrations of absorption capacity could be reached at pH 8 and 14, respectively [18]. Similarly, Yan-Bo et al. [21] investigated the separation of sulfonamide antibiotics from aqueous media by magnetic graphene oxide. They showed that the

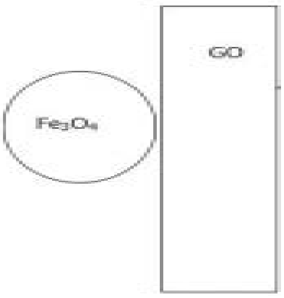


Fig. 4. Schematic of magnetized graphene oxide.

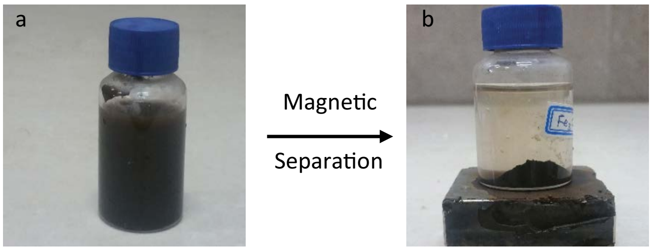


Fig. 5. Photographs of magnetic nano-adsorbent without (a) and with (b) external magnetic field.

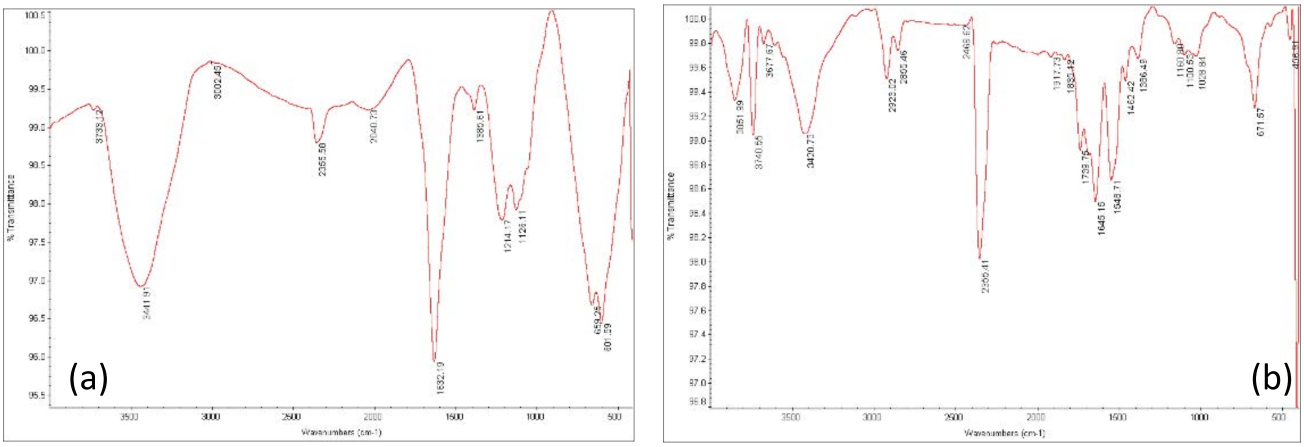


Fig. 6. FTIR spectrum of graphene oxide (a) and magnetized graphene oxide (b).

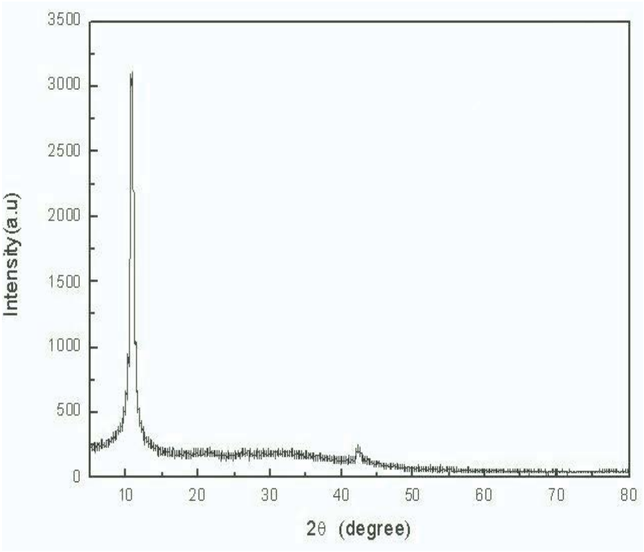


Fig. 7. XRD of graphene oxide.

highest isolation capacity for these antibiotics was obtained at pH 3 [22]. In another study by Yuexin et al. (2013), it was found that pH had a very weak effect on the reaction between tetracycline and magnetic graphene oxide [23]. Also, Chen et al. (2014), in a research addressed the removal of sulfamethoxazole and ciprofloxacin from aqueous solution by graphene oxide. It became evident that ciprofloxacin was adsorbed only at pH 2 [24]. Mostafapour [15] obtained the optimal pH as 7. Jain et al. [13] obtained the pH of 10.5 as the optimal pH in removing rifabutin antibiotic using titanium dioxide nanoparticles in the presence of ultraviolet radiation. Akbari et al. [19] obtained the maximum removal efficiency for doxycycline as 90.24% using titanium dioxide nanoparticles at the pH of 6.5. In addition, Dimitrakopoulou et al. (2012), concluded that pH was not an influential factor in the removal efficiency [25]. Using a nano-sonochemical process, Hosseini et al. [4] obtained the best removal efficiency (94.3%) at pH of 4. Motlagh et al. [23] indicated the maximum removal efficiency for tetracycline using titanium dioxide nanoparticles at the pH of 5. Rodrigo et al. (2009), obtained optimal pH equal to 8.7, and 11 titanium zinc oxide nanoparticles, respectively [27]. Safari et al. (2015), concluded that pH had no significant role in the removal of antibiotic tetracycline in UV/TiO_2 process [28].

Considering the comparison between this investigation and other articles results, pH adjustment could have positive or neutral effects on the antibiotics removal from aqueous solutions and it is depended on the antibiotics structures. Hence, this test must be taken in order to determine whether pH adjustment plays a significant role or not.

4.2. Effect of contact time

The results of the effect of time have been presented in Fig. 12. As can be seen in this chart, when MGO was used, the elimination process of tetracycline, amoxicillin and cephalexin was increased till 15, 45, and 45 min. Thereafter, the degradation process of maintenance was either steady or declined. Under other conditions, when TiO_2 or ZnO were used, the removal of amoxicillin ascended until 15 min. Next, this trend descended from 15 to 60 min. Contrarily, considering cephalexin and tetracycline, until 45 min, the removal percentage increased whereby the removal percentage reached a peak. After that, a trivial descending trend was observed in cephalexin degradation until 60 min.

In their study to remove tetracycline from the aqueous environment by graphene oxide, Yuan et al. [18] came to the conclusion that the contact time for the adsorption of tetracycline from the aqueous media was 90 min. In a study by Yuexin et al. (2013), it was obtained that a 10 min time was the appropriate contact time in order to remove antibiotics [23]. Chen et al. (2014) concluded an optimum time of 3 min for the removal of sulfamethoxazole and ciprofloxacin

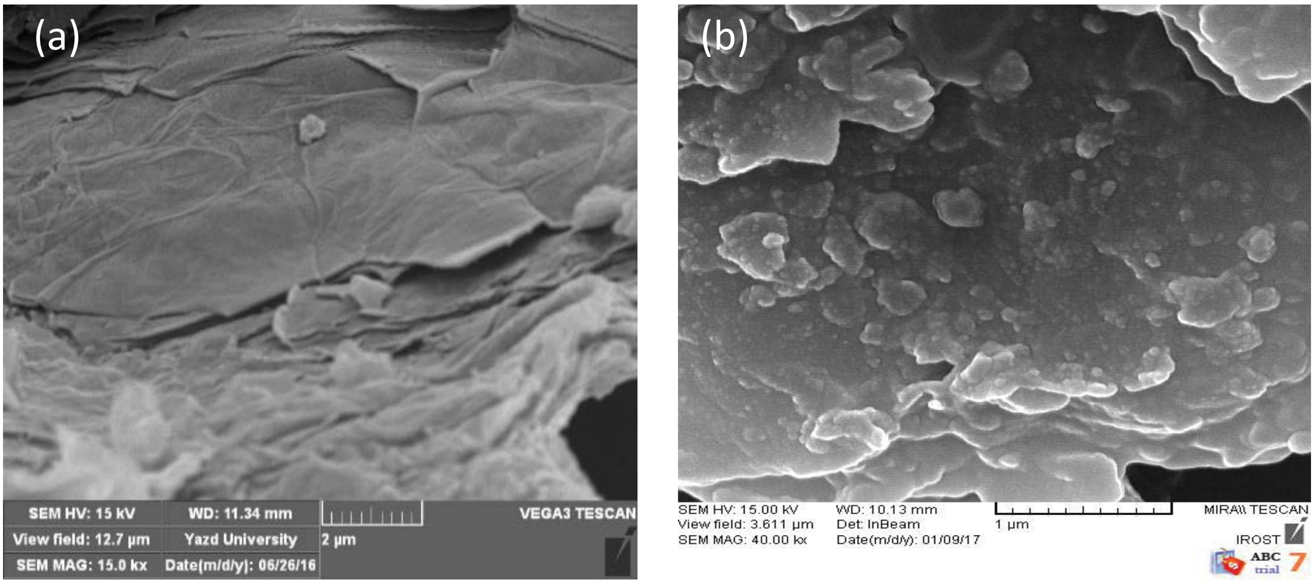


Fig. 8. SEM image of graphene oxide (a) and magnetized graphene oxide (b) [17].

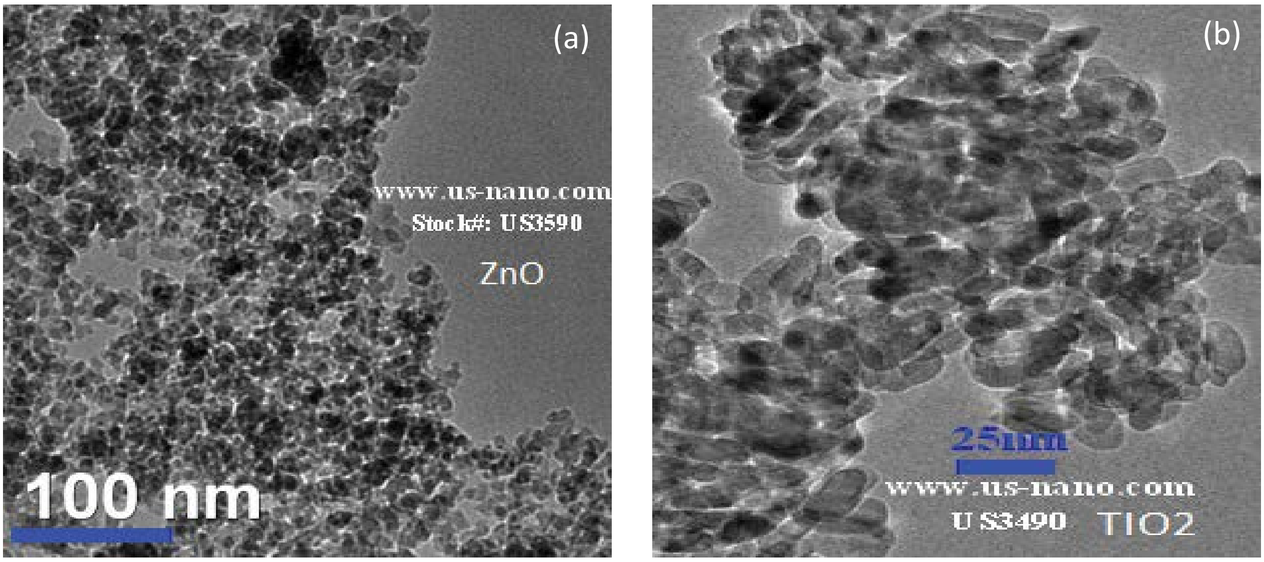


Fig. 9. SEM images of zinc oxide (a) and titanium dioxide nanoparticles (b) [17].

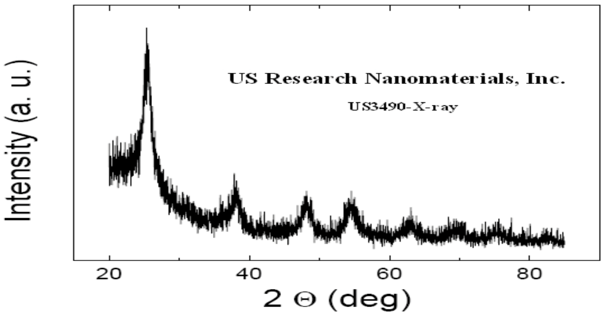


Fig. 10. XRD image of titanium dioxide nanoparticle [17].

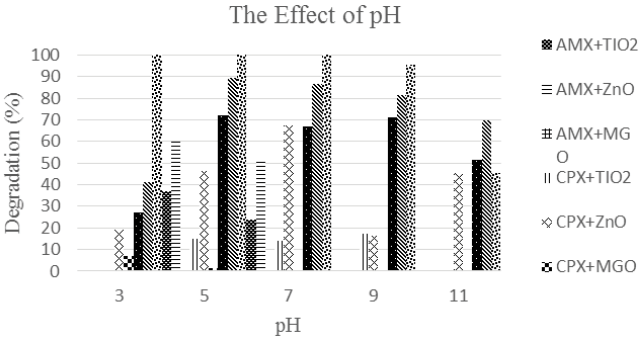


Fig. 11. Effect of pH on the degradation efficiency of AMX, CPX, and TCN under UV-ZnO, TiO_2, or GO-Fe_3O_4 processes. Time = 20 min, Ads = 1 g L^{-1}, antibiotics concentration = 5 mg L^{-1}, radiation intensity = 6 W, pH = 3, 5, 7, 9, and 11.

from aqueous solution by graphene oxide [24]. Mostafapour [15] reported 60 min as the optimal time in photocatalytic degradation of ciprofloxacin using copper oxide from aqueous environments. Najafi et al. [20] obtained 180 min for removing metronidazole using TiO_2 exposed to ultraviolet radiation as the optimal contact time. Dimitrakopoulou et al. (2012) stated 25 and 90 min as the reaction time for the optimal values of 10 and 250 mg L^{-1} of titanium dioxide catalyst in removing amoxicillin, respectively [25]. Hosseini et al. [4] claimed 60 min as the best removal efficiency of Tetracycline by adding hydrogen peroxide to the UV/TiO_2 process. Motlagh et al. [23] reported the optimal contact time of 100 min [26]. Rodrigo et al., (2009), as well as Reyes et al. [26], succeeded to remove 50% of the initial concentration of tetracycline after 10 min of exposure to UV light [27,29]. Safari et al. [7,25] reached 91.4% elimination after 90 min of UV radiation [28]. Chung et al. (2016) calculated 240 min for the optimal contact time [30].

Making a comparison between results of this paper and all above-mentioned achievements, it can be concluded that the length of contact time is variable and has an indirect correlation with many factors such as radiation intensity.

4.3. Effect of catalyst quantity

The results of the effect of catalyst quantity are depicted in Fig. 13. As can be viewed in this diagram, with appending the quantity of MGO up to 4 g L^{-1}, the percentage of antibiotic degradation was increased. However, there was no significant degradation after 2 g L^{-1}. In case of using TiO_2 and ZnO, with the elevation of the amount of TiO_2 or ZnO until 1 g L^{-1}, the removal percentage of amoxicillin and cephalexin was increased, while at 1.4 g L^{-1}, a minor reduction of removal was observed. Thereafter, from 1.4 to 3 g L^{-1}, the removal percentage was climbed and reached a climax. Next, until 4 g L^{-1}, this trend was descended. However, it was a little different from tetracycline, where with the elevation of the amount of catalysts to 4 g L^{-1}, the removal percentage of tetracycline increased; but there was no significant removal rate from 2 g L^{-1} and values higher than that.

In a study, Yuexin et al. (2013) found that when the amount of magnetic graphene oxide was 10 mg L^{-1}, it could eliminate 86% of tetracycline and 98% of that when the amount of adsorbent was 30 mg [23]. According to Chen

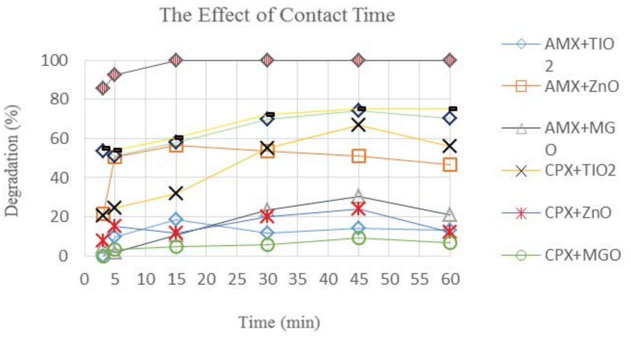


Fig. 12. Effect of contact time on the degradation efficiency of AMX, CPX, and TCN under UV-ZnO, TiO_2, or GO-Fe_3O_4 processes (pH (AMX, CPX, TCN with GO-Fe_3O_4) = unset, pH (AMX, CPX, TCN with TiO_2 or ZnO) = 5, 7, 5, catalysts quantity = 1 g L^{-1}, antibiotics concentration = 5 mg L^{-1}, radiation intensity = 6 W, time = 3, 5, 15, 30, 45, and 60 min).

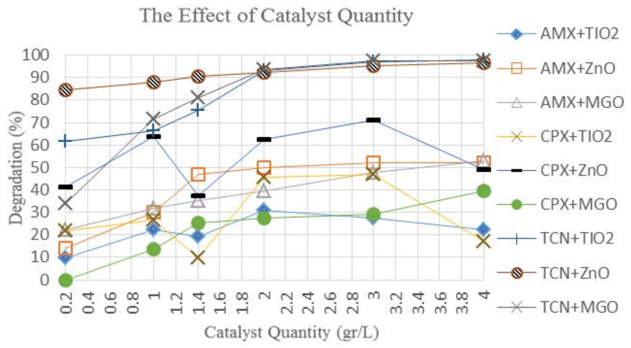


Fig. 13. Effect of catalyst quantity on the degradation efficiency of AMX, CPX, and TCN under UV-ZnO, TiO_2, or GO-Fe_3O_4 processes. pH (AMX, CPX, TCN with GO-Fe_3O_4) = unset, pH (AMX, CPX, TCN with TiO_2, or ZnO) = 5, 7, 5, time (AMX, CPX, and TCN/MGO) = 45, 45, 15 min, time (AMX, CPX, and TCN/TiO_2, or ZnO) = 15, 45, 45 min, antibiotic concentration = 5 mg L^{-1}, radiation intensity = 6 W, catalyst quantity = 0.2, 1, 1.4, 2, 3, and 4 g L^{-1}.

et al. (2014) who studied the removal of sulfamethoxazole and ciprofloxacin from aqueous solution by graphene oxide, the researchers achieved 0.3 mg of magnetized graphene as an optimal amount in order to remove antibiotics [24]. Jain et al. [13] aimed to remove 85% of rifabutin antibiotic from aqueous environments using titanium dioxide nanoparticles in the presence of ultraviolet radiation at the optimal value of 0.06 g L^{-1}. Furthermore, Mostafapour [15] observed the maximum efficiency of the system as 73% for photocatalytic degradation of ciprofloxacin, using copper oxide at the optimal value of 0.07 g L^{-1}. Dimitrakopoulou et al. (2012) obtained 10 and 250 mg L^{-1} as the optimal absorbent values for titanium dioxide [25]. Hosseini et al., (2014) achieved a Tetracycline removal of 94.3% by adding 100 mg L^{-1} of hydrogen peroxide to the UV/TiO_2 process [4]. Motlagh et al. [23] also observed an optimum catalytic dose of 0.2 grams per liter for the removal of tetracycline [26]. Reyes et al. (2006) observed that the maximum efficiency of the system for photocatalytic degradation of tetracycline, using copper TiO_2, for the optimal value of 0.5 g L^{-1} [29].

Considering the above-mentioned results, it can be concluded that with increasing the quantity of catalysts from a specific amount, the removal percentage of antibiotics from aqueous solutions declines.

4.4. Effect of antibiotics concentration

The obtained results from investigating the effect of antibiotics concentration have been presented in Fig. 14. As can be noticed in this diagram, antibiotics removal efficiency with MGO, TiO_2, or ZnO catalysts increased from 1 to 15 mg L^{-1}, after which it diminished at higher concentrations. However, it was not true about tetracycline by TiO_2 or ZnO. With growing the concentration of antibiotic (more than 15 mg L^{-1}), the extent of removal decreased and the complete elimination did not occur.

Jain et al. [13] attempted to remove 85% of rifabutin antibiotic using titanium dioxide nanoparticles in the presence of ultraviolet radiation at the optimal concentration of 0.4 mg L^{-1}. Akbari et al. [19] calculated doxycycline removal percentage as 90.24% at the initial concentration of 20 mg L^{-1}. Najafi et al. [20] obtained the optimal concentration of metronidazole using TiO_2 under ultraviolet radiation as 20 mg L^{-1}. Motlagh et al. [23] obtained the optimal concentration of tetracycline using TiO_2 under ultraviolet radiation as 10 mg L^{-1}. Moreover, Safari et al. obtained an optimal tetracycline concentration of 27 mg L^{-1} [13–19–20–24–26].

Taking a glance to the above results, it is obvious that, the concentration of antibiotics which is degradable with photocatalytic processes is limited. It means that, with raising the concentration of antibiotics, the removal percentage of antibiotics goes down.

4.5. Effect of radiation intensity

The obtained results from investigating the impact of radiation intensity have been demonstrated in Fig. 15. As can be observed, antibiotics elimination had been higher at the

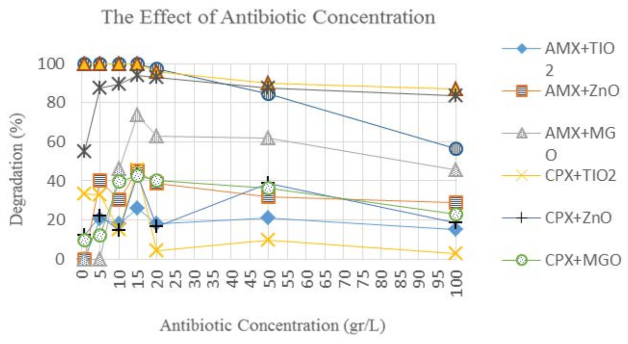


Fig. 14. Effect of catalyst quantity on the degradation efficiency of AMX, CPX, and TCN under UV-ZnO, TiO_2, or GO-Fe_3O_4 processes. pH (AMX, CPX, TCN with GO-Fe_3O_4) = unset, pH (AMX, CPX, TCN, with TiO_2 or ZnO) = 5, 7, 5, Time (AMX, CPX, and TCN/MGO) = 45, 45, 15 min, Time (AMX, CPX, and TCN/TiO_2 or ZnO) = 15, 45, 45 min, MGO quantity (with AMX, CPX, or TCN) = 4, 4, 2 g L^{-1}, TiO_2 or ZnO quantity (with AMX, CPX, or TCN) = 2, 2, 2 g L^{-1}, radiation intensity = 6 W, Antibiotics concentration = 1, 5, 10, 15, 20, 50, and 100 mg L^{-1}.

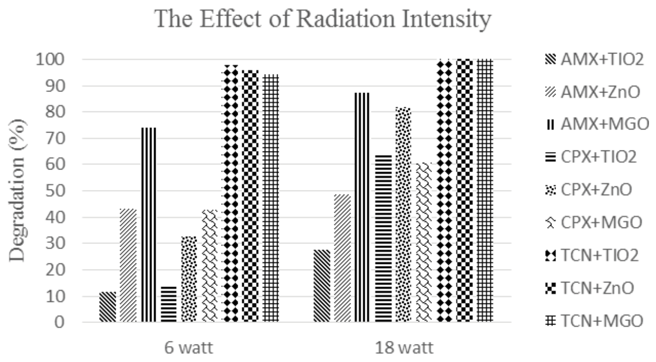


Fig. 15. Effect of catalyst quantity on the degradation efficiency of AMX, CPX, and TCN under UV-ZnO, TiO_2, or GO-Fe_3O_4 processes (pH (AMX, CPX, TCN with GO-Fe_3O_4) = unset, pH (AMX, CPX, TCN with TiO_2 or ZnO) = 5, 7, 5, time (AMX, CPX, and TCN/MGO) = 45, 45, 15 min, time (AMX, CPX, and TCN/TiO_2 or ZnO) = 15, 45, 45 min, MGO quantity (with AMX, CPX, or TCN) = 4, 4, 2 g L^{-1}, TiO_2 or ZnO quantity (with AMX, CPX, or TCN) = 2, 2, 2 g L^{-1}, antibiotics concentration = 15 mg L^{-1}, radiation intensity = 6 and 18 W).

Table 1
Maximum efficiency of antibiotics removal under the optimal conditions (%)

Nanoparticles	Antibiotics (Maximum efficiency of antibiotics removal under the optimal conditions (%))		
	Amoxicillin	Cephalexin	Tetracycline
TiO_2	27.6	63.5	100
ZnO	48.6	81.8	100
GO-Fe_3O_4	87.1	60.5	100

luminescence of 18 W, compared to 6 W by all the three catalysts. Akbari et al. revealed the removal percentage as 90.24 with radiation intensity of 17 W [19]. Due to the results of this investigation and other papers achievements, it is crystal clear that with increasing the intensity of radiation, the percentage of antibiotics degradation reaches a climax as well.

4.6. Maximum efficiency of antibiotics removal under the optimal conditions

Table 1 demonstrates the maximum removal efficiency of antibiotics under the optimal conditions. With a glance, considering amoxicillin degradation, it is evident that the performance of GO-Fe_3O_4, in comparison with ZnO or TiO_2 nanoparticles was much higher (87.1%). When it comes to cephalexin, the best removal percentage was related to ZnO (81.8%). However, to eliminate tetracycline, all three types of nanoparticles acted similar to each other and a complete removal percentage was achieved.

5. Conclusions

In this investigation, magnetized graphene oxide, titanium dioxide, and zinc oxide nanoparticles were used for the removal of amoxicillin, cephalexin, and tetracycline from aqueous. The optimal conditions for enhancing the efficiency of degradation in the UV/GO-Fe_3O_4 processes were included. The parameters were pH with no effect, the contact time of 15, 45, and 45 min and the amount of catalyst of 2, 4, and 4 g L^{-1} for tetracycline, amoxicillin and cephalexin, respectively. The maximum removal efficiency of 18 W ultraviolet radiation for amoxicillin, cephalexin, and tetracycline was also 87.8%, 60.5%, and 100%, respectively. On the other hand, the optimal conditions in the UV-TiO_2/ZnO processes were obtained: the catalysts value of 2 g L^{-1}, antibiotics concentration of 15 mg L^{-1}, radiation intensity of 18 W, pH of 5, 7, and 5, contact time of 15, 45, and 45 min for amoxicillin, cephalexin, and tetracycline, respectively. The results revealed that the zinc oxide proved a better performance than titanium dioxide nanoparticle in the removal extension and the maximum removal efficiency under optimal conditions. For amoxicillin with titanium dioxide and zinc oxide nanoparticles was 27.6% and 48.6%, respectively. Considering cephalexin, the respective values were 63.5%, 81.8% but in the case of degrading tetracycline, a complete removal percentage was achieved for both of the mentioned catalysts.

As it was shown in the results, the pH adjustment was not effective in the degrading antibiotics by graphene oxide, but in the case of using titanium dioxide or zinc oxide, the removal rate was higher in acidic or near neutral conditions; This can be attributed to the tendency for positive charge adsorption by antibiotics at lower pH. It was shown that, in these conditions, the positive charge of the environment increased and due to changes in the structure of antibiotics, they could be eliminated. In addition, catalysts tend to agglomerate in the aquatic environment, which depended on ionic tension, pH, and suspension. In an acidic environment, it tended to be less agglomerate than neutral whereby the specific surface area of the catalyst grew. With a higher specific surface area, the amount of absorption of pollutants would raise as well.

According to the contact time diagram, it can be concluded that the extent of removal increased over time until it reached a specific point, which after a descending trend occurred in the removal processes. It can be attributed to sorption and desorption and incomplete solubility of nanoparticles.

In a large amount of catalysts, no significant reduction was observed. It can be due to reduced light penetration, light dispersion or the accumulation and deposition of the fact that the rate of antibiotic degradation decreases gradually at high concentrations is because of the reaction rate. At low concentrations, the reaction rate was higher due to the low absorption of antibiotics on the active catalyst sites and at high concentrations due to the site's occupation. All the active catalyst sites were limited in mass transfer and elimination rates.

Destruction of the pharmaceutical compounds in the presence of photocatalyst mainly depended on the active form (hydroxyl radical, hole, superoxide ion) in the process. According to the results of this research, radical hydroxyl production was higher at 18 W of lamp power and, consequently, the removal efficiency was higher too.

Based on the obtained results, suggesting the high performance of UV-TIO_2/ZnO photocatalytic processes, it is recommended that the efficiency of this method be investigated using strong oxidants such as hydrogen peroxide along with the main catalysts in these experiments. Furthermore, the temperature and dissolved oxygen could also be taken into account as parameters in the experiments.

To conclude, according to the results of this paper, if there would not be an economical controversy, the application of UV-GO-Fe_3O_4 could be strongly recommended due to their yield of elimination in comparison with UV-TIO_2/ZnO processes.

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