

Photocatalytic degradation of metronidazole (MNZ) antibiotic in aqueous media using copper oxide nanoparticles activated by H₂O₂/UV process: biodegradability and kinetic studies

Abdolmotalleb Seid-Mohammadi^a, Zeinab Ghorbanian^b, Ghorban Asgari^a,
Abdollah Dargahi^{c,d,e,*}

^a*Social Determinants of Health Research Center (SDHRC), Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran, Tel. +989183729180; email: sidmohammadi@umsha.ac.ir (A. Seid-Mohammadi), Tel. +989123609313; email: asgari@umsha.ac.ir (G. Asgari)*

^b*M.Sc. of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran, Tel. +989186067993; email: zeinab.ghorbanian1003@gmail.com (Z. Ghorbanian)*

^c*Department of Environmental Health Engineering, School of Public Health, Ardabil University of Medical Sciences, Ardabil, Iran, Tel. +989141597607; email: a.dargahi29@yahoo.com (A. Dargahi)*

^d*Social Determinants of Health Research Center, School of Health, Ardabil University of Medical Sciences, Ardabil, Iran*

^e*Environmental and Occupational Health Research Center Research Center, School of Health, Ardabil University of Medical Sciences, Ardabil, Iran*

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ABSTRACT

Metronidazole (MNZ) has identified as a remarkable environmental pollutant since it is highly consumed and is resistant to biological degradation. This study was accomplished to assess the photocatalytic degradation of MNZ in aqueous media using copper oxide nanoparticles (CuO-NPs) activated by H₂O₂ in the presence of UV irradiation (UV/H₂O₂/CuO-NPs process). For this purpose, the laboratory-scale experiments were carried out in the 2.5 L batch reactor. The effect of operational parameters, that is, initial pH (3–11), the concentration of MNZ (25–100 mg/L), the concentration of H₂O₂ (10–40 mg/L), the concentration of CuO-NPs (2–8 mg/L), and reaction time (0–60 min) were also assessed. The results of this study clarified that under optimum conditions (pH = 3, H₂O₂ = 10 mg/L, [MNZ]₀ = 50 mg/L, CuO-NPs = 8 mg/L, and reaction time = 60 min), the removal efficiencies of MNZ, chemical oxygen demand (COD), and total organic carbon (TOC) using the UV/H₂O₂/CuO-NPs process were 98.36%, 73.0%, and 56.52%, respectively. According to the results, by increasing reaction time from 0 to 60 min, the AOS in the effluent was increased from 1.39 to 2.38, and the COD/TOC ratio was decreased from 1.74 to 0.8. The results related to parameters of the kinetics showed that the removal of MNZ antibiotic using the studied system conforms to the pseudo-first-order kinetics ($R^2 = 0.983$), and kinetics rate constant (k) was 0.0624 min⁻¹. This study provides UV/H₂O₂/CuO-NPs process as an innovative method to degrade the MNZ antibiotic and enhance its biodegradability. We concluded that the studied process can be used as an effective and eco-friendly method in the removal of MNZ antibiotics.

Keywords: Advanced oxidation processes (AOPs); Metronidazole antibiotic; Copper oxide nanoparticles; Hydrogen peroxide; Kinetic studies; Biodegradability

* Corresponding author.

1. Introduction

Antibiotics are a group of strong drugs, which are used to treat infectious diseases of humans and animals and consist of 15% of the world's total drug consumption. They are slightly metabolized after consumption results in the release of a remarkable part of them into the environment [1].

Metronidazole (MNZ), a kind of nitroimidazole antibiotic, has antibacterial and anti-inflammatory properties. This antibiotic has extensively applied for treating infectious diseases such as *Giardia lamblia* and *Trichomonas vaginalis* [2]. It is also used as an additive in poultry and fish feed for destroying the parasites, which leads to the accumulation of MNZ in animals' body, fish farm water, and effluents of meat industries [3]. US National Institutes of Health has declared that MNZ is associated with several problematic harmful effects such as headache, gastrointestinal disorders, and hypersensitivity reactions [4]. These harmful effects on human health and aquatic organisms are due to the toxicity, potential mutagenicity, and carcinogenicity of MNZ [5,6]. Due to MNZ low biodegradability and high solubility in water which results in accumulation in the aquatic environment, its removal by the traditional methods is challenging. [7] and it leads to the threatening consequences to the environment and human health [8]. Thus, using appropriate methods for the elimination of this antibiotic is essential. In this case, several techniques such as advanced oxidation process (AOPs) [9–13], adsorption [5,14–16], and biological methods have been studied and reported [17].

Nevertheless, among the mentioned methods, the AOPs have recently identified as the spectacular methods for the antibiotics removal. The basis of AOPs is the production of strong oxidative radicals, for example, hydroxyl, sulfate, and superoxide radicals; these radicals have excellent potential for the degradation of various chemicals such as antibiotics [18]. The hydroxyl radicals are unstable and extremely active and are generated through the chemical or photochemical reactions *in situ* [19]. Free radicals have identified as strong oxidizing agents, they can attack the organic molecules and separate a hydrogen atom from the organic material structures [18,20]. These processes develop through the combination of oxidizing agents, the addition of catalysts, and the incorporation of activating methods (ultrasound and UV irradiation). H_2O_2 is an eco-friendly oxidant, and the UV/ H_2O_2 process has excellent properties, for example, a lack of sludge production, simplicity of operation, and low cost [21].

Photocatalytic processes are among the AOPs using metal oxides, which have recently found special attention for the removal of organic pollutants and microbial agents due to its low environmental problems. The mechanism of this process is the UV radiation to a semi-conductor material and, consequently, the electron excitation and its emission from the valence band to the conduction band. The electron excitation leads to the production of active hydroxyl radical ($\cdot OH$), which has a significant role in oxidizing organic pollutants [22]. The copper oxide nanoparticles (CuO-NPs), which are of the semi-conductors, have been identified to be highly efficient because of the most effective surface area and quantum size compared to the masses of copper [23].

It has been mentioned that CuO-NPs have a narrow bandgap, ranging from 1.2 to 2.9 eV, and have the potential to work as a visible-light photocatalyst, however, these

nanoparticles have not widely studied as photocatalyst for degradation of organic pollutants [24]. However, there are a few studies about employing CuO-NPs as a photocatalyst, which further degradation of organic pollutants by CuO-NPs required UV light exposure [25]. Considering the advantages and specific features of AOPs and UV in the degradation of organic compounds, especially antibiotics, and the lack of sufficient information about the role different oxidants such as H_2O_2 activated by CuO catalyzer, the present study aimed to the investigation of the photocatalytic degradation of MNZ antibiotic from aqueous solutions using CuO-NPs activated by hydrogen peroxide in the presence of ultraviolet irradiation (UV/ H_2O_2 /CuO process). In addition, this study evaluated the biodegradability and kinetics of the process under optimal conditions.

2. Materials and methods

2.1. Chemicals and instruments

Chemicals were used in analytical grade and were applied without further purification. MNZ antibiotic with the formula of $C_6H_9N_3O_3$ (the purity of >99%) was purchased from Merck Co., (Germany); the characteristics of MNZ were summarized in Table 1. CuO-NPs, sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and hydrogen peroxide (H_2O_2) 30% w/w were provided from Sigma-Aldrich. The adjustment of the solution pH was done using 1 M sulfuric acid (H_2SO_4) and 1 M sodium hydroxide (NaOH). A pH meter (HACH-Ha-USA), centrifuge machine (Sigma), TOC analyzer (Elementar, Germany), and spectrophotometer (DR 6000, HACH, USA) were the instruments and devices used in this study. In all steps, the preparation of suspensions and solutions was performed by double distilled water. The inductively coupled plasma-optical emission spectroscopy (Optima-8300) was utilized to measure the leaching of copper (Cu) after the complete treatment of the MNZ in the studied process.

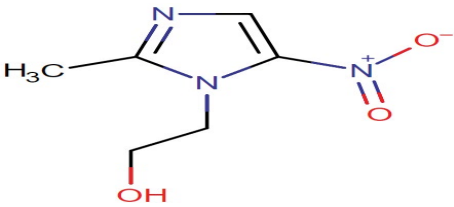
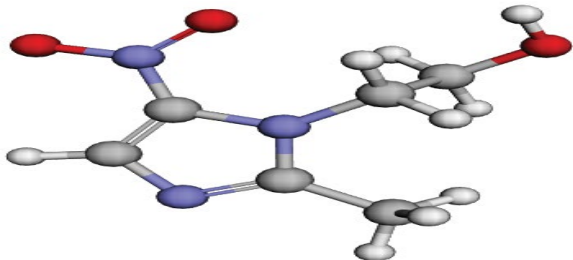
2.2. Photocatalytic reactor

This study was performed in a laboratory-scale batch reactor (a cylindrical photochemical reaction chamber made of stainless steel with an efficient volume of 2.5 L consisting of a low-pressure mercury lamp with radiation power of 55 W). The schematic of this reactor was represented in Fig. 1. Furthermore, Table 2 shows the characteristics of the ultraviolet reactor used in this experiment. The reaction was performed at the space between the quartz membrane around the lamp and the stainless steel 304 (SS304) chamber. The samples used in the present study were synthetic wastewater, which was prepared in the laboratory in different and certain concentrations of MNZ. The studied parameters affecting the performance of the studied system were initial pH (3–11), H_2O_2 concentration (10–40 mg/L), CuO-NPs (2–8 mg/L), MNZ concentration (25–100 mg/L), and reaction time (60 min). The transformer was used as a power supply with a characteristic of 210–240 V.

2.3. Analytical methods

To determine the residual concentrations of the MNZ in the solutions, after collecting the samples at predetermined

Table 1
Properties and chemical structure of the MNZ antibiotic

Component	Information/schematic/value
Molecular (chemical) formula	$C_6H_9N_3O_3$
2D structure	
3D structure	
Molar mass	171.156 g/mol
Melting point	159°C–163°C (318–325°F)
Solubility in water	9.5 g/L
LD ₅₀	500 mg/kg/d (orally in rat)
Half-life	6–8 h
pK _a	2.55

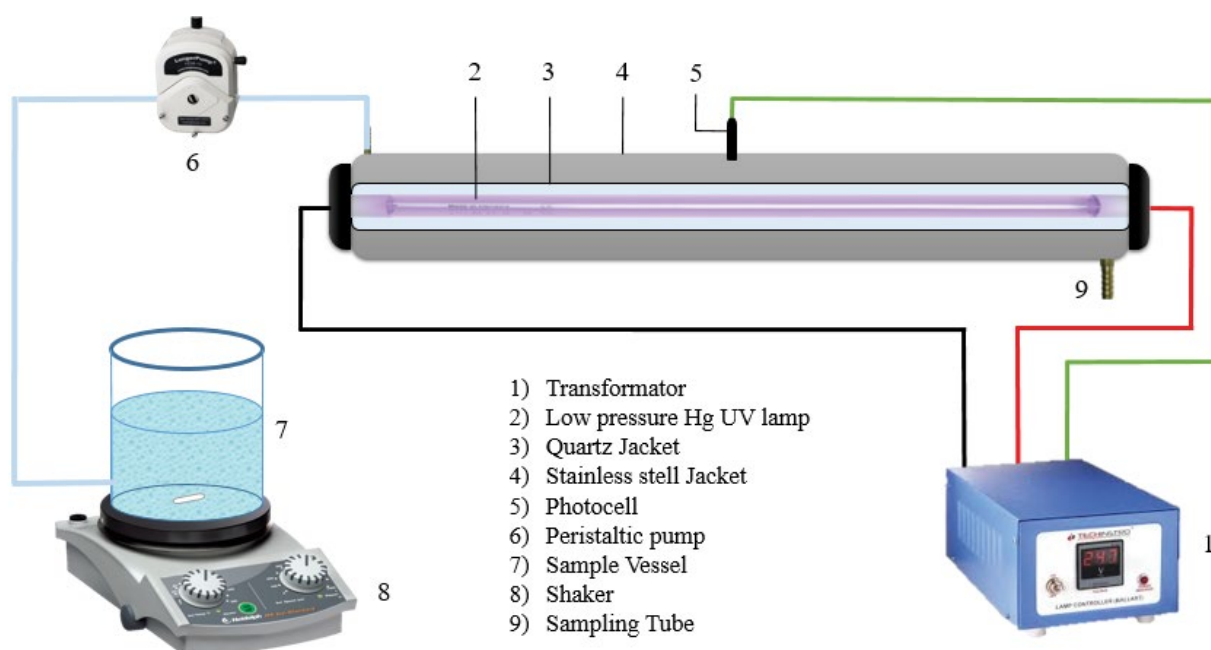


Fig. 1. Schematic of the studied reactor.

time intervals and filtration through 0.45 μm membrane filter, a spectrophotometer (DR 6000, HACH, USA) at a wavelength of 320 nm was used. Moreover, the chemical oxygen demand (COD) was estimated by COD ampoules (HACH

Chemical) using a spectrophotometer (DR 6000, HACH, USA). The measurement of the total organic carbon (TOC) content of the MNZ antibiotic was determined using the TOC analyzer (Elementar, Germany). Subtracting the amount of

Table 2
Ultraviolet reactor characteristics

Parameter	Property
Light color	White
Lamp power (W)	55
Copacity (GPM)	12
Connectors size (Inch)	3/4
Dimensions of UV chamber (mm)	910 × 310 × 310
Company	OSRAM
Manufacturer country	Germany
Frequency (Hz)	50–60
Intensity of radiation (μws/cm)	50,000

inorganic carbon (IC) from total carbon (TC) was carried out to calculate the TOC that existed in the samples.

In addition, Eqs. (1)–(3) were applied to calculate the MNZ antibiotic removal efficiency and the COD removal efficiency and TOC removal efficiency by UV/H₂O₂/CuO process, respectively.

$$\text{MNZ degradation (\%)} = \frac{[\text{MNZ}]_0 - [\text{MNZ}]_t}{[\text{MNZ}]_0} \times 100 \quad (1)$$

$$\text{COD removal (\%)} = \frac{[\text{COD}]_0 - [\text{COD}]_t}{[\text{COD}]_0} \times 100 \quad (2)$$

$$\text{TOC removal (\%)} = \frac{[\text{TOC}]_0 - [\text{TOC}]_t}{[\text{TOC}]_0} \times 100 \quad (3)$$

where [MNZ]₀ and [MNZ]_t corresponds to the initial concentration of MNZ at the time 0 and the concentration of MNZ at time *t*, respectively. [COD]₀ and [COD]_t represents the COD before and after treatment, respectively. Furthermore, [TOC]₀ and [TOC]_t indicates the TOC before and after treatment, respectively. The COD and TOC evolution were estimated at the beginning of the process (0 min) and after 60 min (the end of the treatment). To determine the effect of the photocatalytic process in biodegradability of the aqueous media contaminated by MNZ, the average oxidation state and COD/TOC ratio were used.

The average oxidation state (AOS) [26] was calculated by Eq. (4):

$$\text{AOS} = 4 - 1.5 \frac{\text{COD}}{\text{TOC}} \quad (4)$$

where TOC and COD are expressed in “moles of C per liter” and “moles of O₂ per liter”, respectively. The maximum value of +4 is related to the most oxidized state of carbon, CO₂, and the minimum value of −4 indicates the most reduced state of carbon, CH₄. All experiments were carried out three times based on the standard methods of water and wastewater experiments, the 21st ed. [27]. All experiments were

accomplished at a temperature of 22°C ± 3°C in the batch system.

3. Results and discussion

3.1. Comparison of different techniques in MNZ degradation

In the experiments, a comparative study was defined to evaluate the efficiency of the degradation techniques, including UV/H₂O₂/CuO, UV/H₂O₂, UV/CuO, H₂O₂/CuO, UV, H₂O₂, and CuO. Fig. 2 revealed the degradation efficiency of MNZ in different processes at 60 min; As observed in Fig 2, the fastest degradation of MNZ antibiotic (with 98.36% degradation efficiency) was achieved by UV/H₂O₂/CuO process. Degradation of MNZ was also observed to be efficient (89.62%) in the UV/H₂O₂ oxidation process. Unlike, the efficiencies of CuO-NPs (5.3%) and H₂O₂ (15.07%) treatments alone were low, and these systems provided insignificant degradation efficiency. Thus, it can be expressed that MNZ degradation can occur at a relatively high reaction rate in the UV/H₂O₂/CuO process. The increase in •OH radical generation resulted from the coupling of UV irradiation and H₂O₂ may be the reason for this event. In general, based on the observed results related to the MNZ degradation rate, the order of efficiencies of the processes used can be reported as follows:

UV/H₂O₂/CuO < UV/H₂O₂ < UV/CuO < UV < H₂O₂/CuO < H₂O₂ < CuO. The results suggested that the UV/H₂O₂/CuO process was an apt approach for the degradation of MNZ.

3.2. Effect of initial pH of a solution

Since solution pH is a vital factor and influences the contaminant degradation mechanism during an oxidation process, it is imperative to estimate the effect of this parameter on the photocatalytic degradation of the MNZ antibiotic. In AOPs, the production of various radicals such as the production of hydroxyl radicals is led to pH changes, which affect the oxidation of organic matter [10]. Therefore, in the present study, the acidic (pH = 3), neutral (pH = 7), and basic (pH = 11) conditions were applied to discover the effect of pH on the removal of MNZ at the H₂O₂ concentration of 10 mg/L, MNZ concentration of 50 mg/L, and CuO nanoparticles (CuO-NPs) concentration of 2.0 mg/L. Fig. 3 shows the degradation percentages of MNZ, as a function of initial pH in the studied process. The Fig 3 illuminates that the degradation efficiency was decreased by increasing the solution pH from 3 to 11; so that increasing the solution pH from 3 to 11 was led to diminishing the degradation of MNZ from 95.06% to 69.3%. The results of this work are in agreement with the results of the studies conducted by Zarei et al. [28]. Zarei et al. [28] have studied the potential of the UV/S₂O₈²⁻ process in the removal of the MNZ antibiotic from aqueous solutions and observed that the degradation efficiency showed an increasing trend by decreasing the pH from 11 to 3. The higher efficiency at lower pH values could be ascribed to the high redox potential of •OH. Previous reports illuminated that the redox potential of •OH reduced by increasing pH when pH was below 7.0 [29,30]. When pH was adjusted to 11.0, the degradation

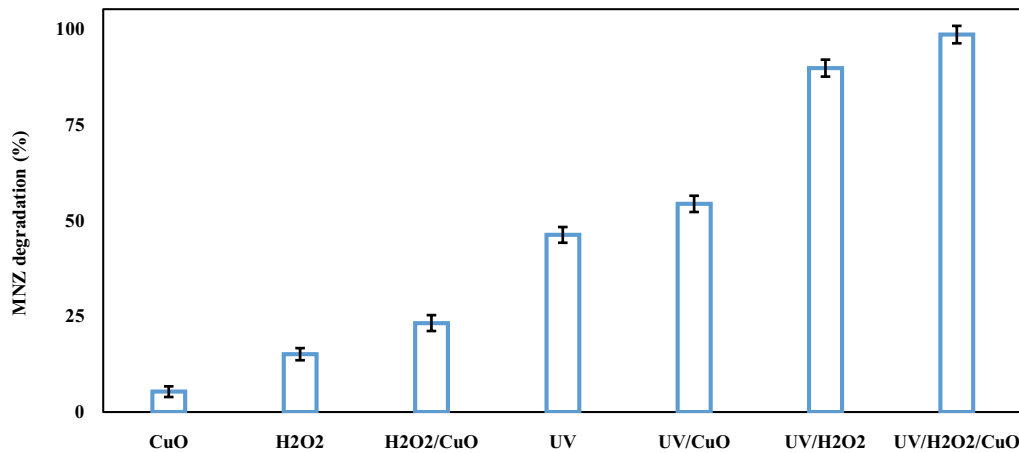


Fig. 2. Comparison of the efficiency of different techniques in MNZ degradation under optimal conditions (pH, 3; H₂O₂, 10 mg/L; [MNZ]₀, 50 mg/L; CuO-NPs, 8 mg/L; reaction time, 60 min).

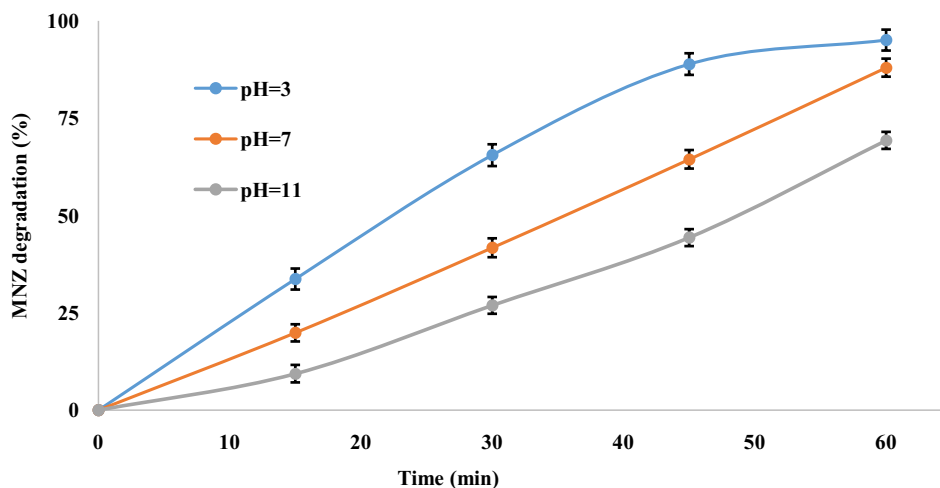


Fig. 3. Effect of initial pH changes on the efficiency of UV/H₂O₂/CuO process in degradation of MNZ antibiotic (H₂O₂, 10 mg/L; [MNZ]₀, 50 mg/L; CuO-NPs, 2.0 mg/L).

efficiency of MNZ was dramatically declined because of the decomposition of H₂O₂ in alkaline conditions. Furthermore, the degradation of MNZ by CuO-NPs was enhanced only in the presence of H₂O₂. Therefore, it may be surmised that H₂O₂ played the role of an oxidizing agent to facilitate the photocatalytic process mechanism, which can be attributed to the possible reduction of Cu²⁺ to Cu⁺ at the surface of the CuO-NPs by photogenerated electrons. Then, H₂O₂ can react with Cu⁺ to form [•]OH and Cu²⁺ for completing the Cu²⁺/Cu⁺ cycle [31]. Furthermore, to further understand the impact of pH on the UV/H₂O₂/CuO process, the leaching of metal ion (Cu) were monitored along with the change of pH. The largest leaching concentration of Cu (0.03 mg/L) was measured at the pH value of 3.0. The concentration of Cu ion was decreased by increasing pH. As pH was controlled at 11.0, Cu was not detected. The results of this work are in agreement with the results of the study conducted by Yao et al. [29].

3.3. Effect of initial concentration of H₂O₂

One of the factors affecting the performance of the AOPs is the type and concentration of the used oxidizing agent [32]. The effect of initial Hydrogen peroxide (H₂O₂) concentration on the efficiency of MNZ degradation by UV/H₂O₂/CuO hybrid process was studied at H₂O₂ concentrations of 10–40 mg/L and its results were brought in Fig. 4. As shown in Fig. 3, the initial concentration of H₂O₂ is effective in the degradation process; so that, the degradation efficiency was partially decreased by an increase in the initial concentration of H₂O₂. According to this Fig. 3, a further increase in the initial concentration of H₂O₂ reduces the degradation of MNZ; at higher concentrations of H₂O₂, H₂O₂ itself acts as an important receptor for hydroxyl radical in the environment, and consequently decreasing the degradation efficiency [33]. Actually, at higher concentrations of H₂O₂, [•]OH radicals

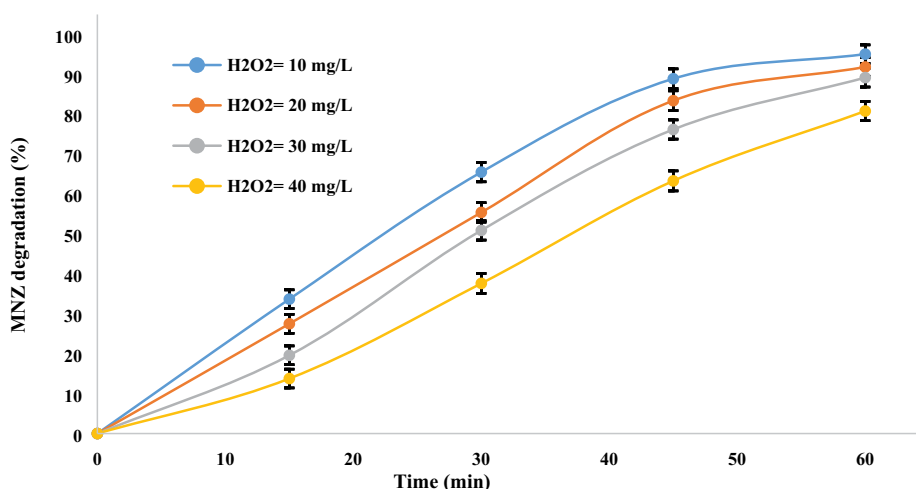
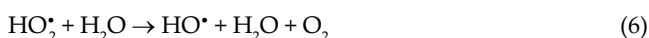


Fig. 4. Effect of initial H_2O_2 changes on the efficiency of UV/ H_2O_2 /CuO process in the degradation of MNZ antibiotic (pH, 3; $[\text{MNZ}]_0$, 50 mg/L; CuO-NPs, 2.0 mg/L).

may be produced through other reactions, that is, the radical reactivity effect of H_2O_2 and the recombination of the radicals of OH, based on following reactions [Eqs. (5)–(8)] [18].



According to Eq. (5), HO_2^\bullet radicals are produced, the reactivity of this radical is much less than that of radical hydroxyl. Therefore, the determination of the optimal concentration of hydrogen peroxide, which depends on the concentration and chemical nature of the pollutants in the sewage, is necessary to prevent the increase of additional amounts and delay in the degradation of MNZ [34].

Hence, the time needed for complete degradation of MNZ at a higher concentration of H_2O_2 will be longer, and the H_2O_2 level in the degradation of MNZ has great importance and should be controlled, this is agreed with the results of the studies by Seid-Mohammad et al. [18] and Malani et al. [35]. Seid-Mohammad et al. [18] have reported that increasing H_2O_2 concentration up to a certain level (from 10 to 40 mL/L) decreases the cephalexin (CEX) antibiotic removal percentage. These results were indicative of this fact that by increasing the hydrogen peroxide concentration to the values higher than 30 mg/L, the extra H_2O_2 acts as $\bullet\text{OH}$ radical scavenger and leads to reducing the process efficiency.

Additionally, Babuponnusami and Muthukumar [36] declared that the phenol removal efficiency was initially boosted by increasing H_2O_2 concentration, and a further increase in H_2O_2 concentration is led to decreasing the efficiency, based on the results of this study, excessive production of hydroxyl radicals is the reason for this phenomenon.

3.4. Effect of CuO nanoparticles (CuO-NPs) concentration

The effect of changes in the concentration of CuO-NPs in the degradation of MNZ by the UV/ H_2O_2 /CuO process is presented in Fig. 5. According to Fig. 5, with a rise in CuO-NPs concentration, MNZ degradation was slightly increased. So that increasing the CuO-NPs from 2 to 8 mg/L is led to enhance the MNZ degradation rate from 95.24% to 98.36%. Increasing the degradation efficiency by increasing the concentration of CuO-NPs can be due to the more activation of H_2O_2 by these nanoparticles and the generation of hydroxyl radicals for the removal of greater amounts of the pollutants. Increasing the concentration of nanoparticles in the reaction medium leads to increasing the adsorbent surface, which increases the active sites for photocatalytic reactions and improves UV absorption by the Cu catalyst; this ultimately offers more free radicals for degradation of the pollutants and increases efficiency, which is consistent with the results of Khoshnamvand et al. [37]. Khoshnamvand et al. [37] have also observed an increase in the ciprofloxacin (CIP) degradation rate by increasing the CuO-NPs concentration. Also, El-Sayed et al. [38] have conducted a study for evaluation of photocatalytic degradation of MNZ using CuO-NPs, and have identified that the MNZ removal efficiency was increased by increasing CuO-NPs concentration and contact time, in their study, increasing the concentration of CuO-NPs from 0.05 to 0.3 g/L increased the MNZ degradation rate from 60% to 85%.

3.5. Effect of the initial concentration of MNZ

The concentrations of actual industrial pollutants vary with the wastewater flow rate. Thus, evaluation of the effect of the initial concentration of MNZ on the degradation of pollutants has a practical significance. The results related to the evaluation of the effect of this parameter on the MNZ degradation rate using the UV/ H_2O_2 /CuO hybrid processes are represented in Fig. 6. The result showed that increasing the initial concentration of MNZ from 25 to 100 mg/L

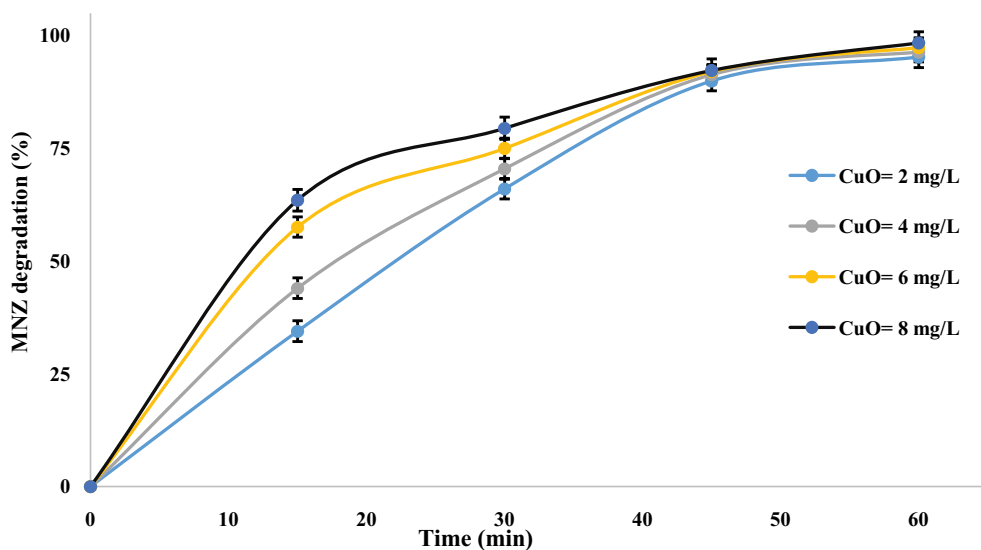


Fig. 5. Effect of initial CuO changes on the efficiency of UV/H₂O₂/CuO process in the degradation of MNZ antibiotic (pH, 3; H₂O₂, 10 mg/L; [MNZ]₀, 50 mg/L).

has resulted in a decrease in MNZ degradation from 99.96% to 91.91%, similar results have been reported by Dai et al. [39] and Seid-Mohammad et al. [10]. Seid-Mohammad et al. applied the US/O₃/S₂O₈²⁻ process for degradation of the MNZ antibiotic from aqueous solutions and reported that the antibiotic degradation efficiency showed an increasing trend by decreasing the initial concentration antibiotic from 30 to 5 mg/L. It is clear that increasing the concentration of pollutants in the environment will lead to more consumption of oxidants such as hydroxyl radicals and a reduction in removal efficiency. Moreover, an increase in the concentration of antibiotics will lead to increasing the level of irradiated matter, which will increase the time needed for the degradation of studied pollutants. This

matter will act as a filter and will reduce the penetration of UV radiation; thus, an increase in antibiotic concentration increases the process efficiency [40].

3.6. Kinetics studies

The studies related to kinetic models are carried out to assess the speed of chemical reactions. The estimation of the reaction rate for gases and liquids is carried out in terms of concentration in unit time. The basis of the explanation of the speed of reaction is a decrease in the concentration of reactive material in the time unit or an increase in the concentration of a product in the time unit [1]. The kinetics of the process were estimated by pseudo-first-order and

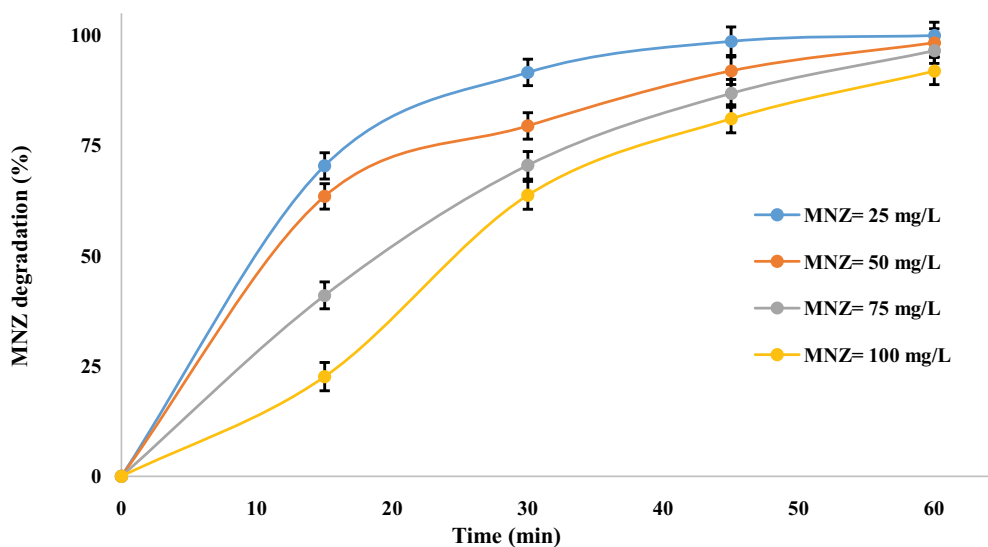


Fig. 6. Effect of initial MNZ concentration changes on the efficiency of UV/H₂O₂/CuO process in the degradation of MNZ antibiotic (pH, 3; H₂O₂, 10 mg/L; CuO-NPs, 8 mg/L).

pseudo-second-order kinetic models at the optimum condition achieved in previous stages.

The pseudo-first-order and the pseudo-second-order models for MNZ degradation were calculated using Eqs. (9) and (10).

$$\ln\left(\frac{[\text{MNZ}]_0}{[\text{MNZ}]_e}\right) = kt \quad (9)$$

$$\frac{1}{[\text{MNZ}]_e} - \frac{1}{[\text{MNZ}]_0} = -kt \quad (10)$$

where $[\text{MNZ}]_0$ and $[\text{MNZ}]_e$ show the initial and final concentrations of MNZ antibiotic, respectively, and k represents the constant of removal value; the calculation of rate constants (k) was carried out by plotting $\ln([\text{MNZ}]_0/[\text{MNZ}]_t)$ vs. electrolysis time (t). Moreover, the half-life ($t_{1/2}$) was determined by Eq. (11).

$$t_{1/2} = \frac{0.693}{k} \quad (11)$$

In the present study, the evaluation of the MNZ antibiotic degradation in optimum conditions was carried out by first- and second-order kinetic's models, and the results are shown in Fig. 7 and Tables 3 and 4. According to the results, the regression coefficients (R^2) of the first-order and the second-order kinetic models were estimated to be 0.98 and 0.67, respectively. Based on this, pseudo-first-order model (with a higher coefficient of correlation (R^2)) was found to be the best model to fit the data of MNZ degradation. These results are in accordance with the results of the studies conducted by El-Sayed et al. [38], Farzadkia et al. [41], and Ammar [42].

The parameters of the kinetics (Table 3) demonstrate that there is a good linear relationship. Moreover, the degradation of MNZ on the UV/ H_2O_2 /CuO process obeys pseudo-first-order kinetic, which is indicative of the excellent

potential of the system for the degradation of MNZ. The rate constant (k) obtained for MNZ degradation using the photo-degradation process for the pseudo-first-order model was 0.0624 min^{-1} , however, it was 0.0176 min^{-1} for pseudo-second-order model. As can be seen, it is approximately 3.54 times higher for the pseudo-first-order model compared to the pseudo-second-order model. In addition, the half-life ($t_{1/2}$) of antibiotic removal in the studied system was 11.1 min (Table 3).

3.7. Biodegradability and mineralization

In order to determine the effective role of the UV/ H_2O_2 /CuO process in degradation and mineralization of MNZ, the removal efficiencies of MNZ, TOC, and COD were evaluated in optimal condition (Fig. 8a). The results showed that with an increase in reaction time, the antibiotic degradation rate was increased. So that the MNZ antibiotic degradation rate by the UV/ H_2O_2 /CuO process was increased to 98.36% by increasing the reaction time from 0 to 60 min. Furthermore, the TOC and COD removal rates were obtained to be 56.52% and 73%, respectively.

Generally, decreasing the COD engages chemical oxidation of the desired compound and, consequently, the modification of its chemical structure, which is led to increasing its biodegradability. On the other hand, limited mineralization is needed to guarantee sufficient residual organic carbon for following biologic treatment. As a result, a desirable trend is a reduction in the COD/TOC ratio [43]. The COD values for the non-treated target compound was decreased

Table 3
Kinetics for the removal of MNZ antibiotic by UV/ H_2O_2 /CuO process (reaction time, 60 min; pH, 3; H_2O_2 , 10 mL/L; $[\text{MNZ}]_0$, 50 mg/L; CuO-NPs, 2.0 mg/L)

Kinetics	k (min^{-1})	R^2	$t_{1/2}$ (min)
Pseudo-first-order model	0.0624	0.983	11.10
Pseudo-second-order model	0.0176	0.6744	39.37

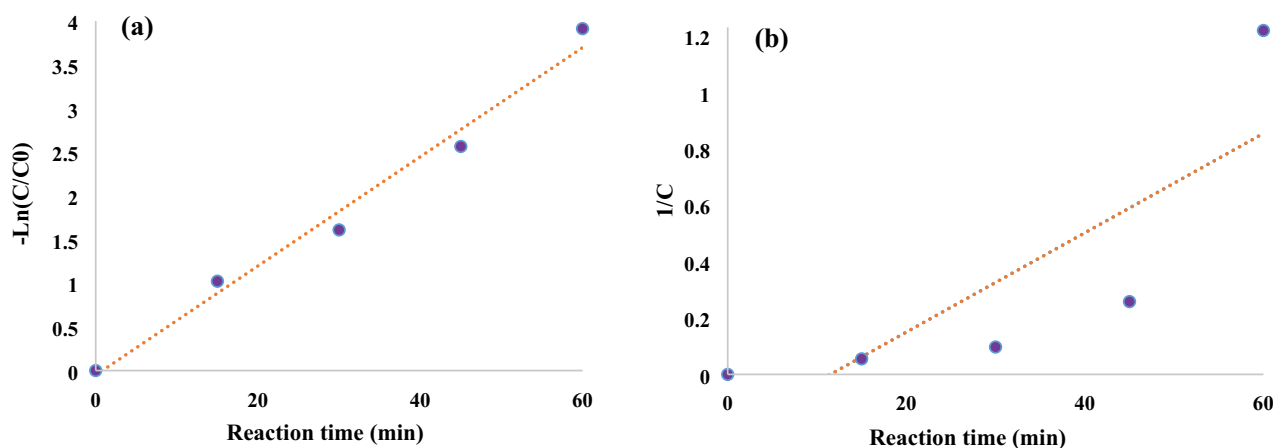


Fig. 7. Kinetics of MNZ antibiotic degradation at the optimum conditions (reaction time, 60 min; pH, 3; H_2O_2 , 10 mg/L; $[\text{MNZ}]_0$, 50 mg/L; CuO-NPs, 8.0 mg/L). (a) Pseudo-first-order model and (b) pseudo-second-order model.

Table 4

Kinetic coefficients related to UV/H₂O₂/CuO process in degradation of MNZ antibiotic (reaction time, 60 min; pH, 3; H₂O₂, 10 mL/L; CuO-NPs, 2.0 mg/L)

Time (min)	[MNZ] ₀ (mg/L)	[MNZ] _t (mg/L)	[MNZ]/[MNZ] ₀	Ln([MNZ]/[MNZ] ₀)	1/[MNZ] _t
0	0	0	0	0	0
15	50	18.26	0.36	-1.022	0.055
30	50	10.27	0.20	-1.609	0.097
45	50	3.87	0.077	-2.564	0.258
60	50	0.82	0.02	-3.912	1.219

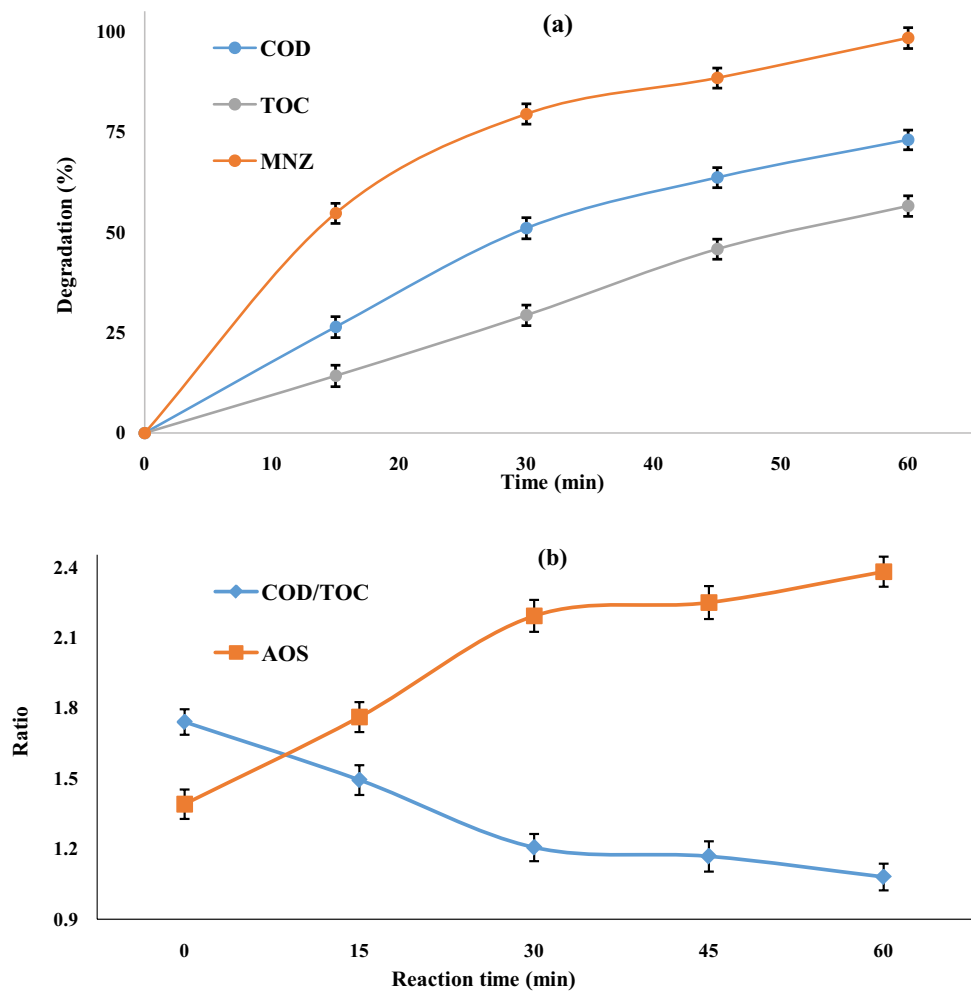


Fig. 8. (a) Performance of UV/H₂O₂/CuO process in the removal of MNZ antibiotic, COD, and TOC and (b) average oxidation state (AOS) and COD/TOC of MNZ antibiotic in the UV/H₂O₂/CuO process at the optimum conditions (reaction time, 60 min; pH, 3; H₂O₂, 10 mg/L; [MNZ]₀, 50 mg/L; CuO-NPs, 8.0 mg/L; COD₀, 68.7 mg/L; TOC₀, 39.5 mg/L).

from 68.7 mg O₂/L to 50.58, 33.66, 25.01, and 18.54 mg O₂/L at reaction times of 15, 30, 45, and 60 min, respectively (Fig. 8). Moreover, Fig. 8 shows the normalized TOC degradation by the UV/H₂O₂/CuO process. The mineralization or oxidation profile, defined by the TOC, was remarkably reduced during the optimum conditions, and the removal efficiencies were achieved to be 14.21%, 29.3%, 45.78%, and 56.52% after 15, 30, 45, and 60 min of reaction time, respectively.

To determine the biodegradability of MNZ in the effluent released from the UV/H₂O₂/CuO process, COD/TOC and AOS ratios were evaluated. The results showed that increasing reaction time from 0 to 60 min is led to develop the AOS ratio in the effluent released from the photocatalyst process from 1.39 to 2.76 (Fig. 8b). Moreover, by increasing the reaction time, the ratio of COD/TOC in the effluent of the UV/H₂O₂/CuO process was reduced from 1.74 to 1.8.

The evolution of the COD/TOC ratio was favorable since the COD/TOC was decreased (Fig. 8b). This decrease reflects the biological resolution of MNZ antibiotics by this process, which is consistent with the study by Ferrag-Siagh et al. [26]. In the study by Ferrag-Siagh et al. [26], the electro-Fenton process was applied as a pre-treatment for the biological process to treat the resistant pollutant of Tylosin tartrate. In this study, COD/TOC and AOS ratio parameters in the effluent released from the electro-Fenton process were investigated to determine the biodegradability of the pre-treatment process. The results showed that the AOS parameter in the outlet effluent was increased, and the COD/TOC ratio was decreased, which is indicative of the biodegradability of the process. The AOS parameter in the outlet effluent of the electro-Fenton process was increased from 0.25 to 2.9, and the COD/TOC ratio was decreased from 2.32 to 0.73.

3.8. Comparison of degradation of MNZ antibiotic using other methods

Table 5 compares the results of the present study with the results of the previous studies. Based on previous studies, it was observed that a variety of the methods, for example, US/O₃/S₂O₈²⁻ (PS) process [10], nano/persulfate (nZVI/PS)

process [44], electro/Fenton process [45], catalytic ozonation process [46], sono-Fenton process [11], photocatalytic process [47], photo-Fenton processes [48], poly(acrylic acid) (PAA)/poly(vinylidene fluoride) (PVDF) hybrids [49], catalytic ozonation process [50], and photocatalytic degradation process [38] have been used for the removal of MNZ antibiotic. In Table 5, the comparison of the studied process with the mentioned processes was carried out based on various factors, including initial pH, reaction time, initial H₂O₂, initial MNZ concentration, MNZ, and COD removal efficiency. The results of this comparison revealed that the obtained results in the present study were comparatively better than the results of the mentioned studies. It should be noted that in all of the methods mentioned, the highest efficiency of MNZ antibiotic degradation was found in acidic pH, the lowest concentration of MNZ and the highest reaction time.

4. Conclusion

This study was carried out to estimate the potential of the UV/H₂O₂/CuO process in the degradation of MNZ. The obtained results demonstrated that the studied system has exceptional potential in the degradation and mineralization of MNZ. Moreover, it was observed that

Table 5
Comparison of degradation of MNZ antibiotic using other methods

Type of process	Parameters	Degradation (%)	COD (%)	References
US/O ₃ /S ₂ O ₈ ²⁻ (PS) process	Conc. MNZ (5–30 mg/L), conc. PS (100–1,000 mg/L), conc. CaCl ₂ (0.13–1.03 g/L), reaction time (0–90 min), and pH (3–11)	90	56	[10]
Nano/persulfate (nZVI/PS) process	Conc. MNZ (1–120 mg/L), conc. nZVI (0.0025–2 g/L), conc. PS (0.1–3.33 mM), reaction time (5–150 min), and pH (3–11)	90.3	*	[38]
Electro/Fenton process	Conc. MNZ (10–50 mg/L), conc. H ₂ O ₂ (0–0.02 M/L), current density (30 V), reaction time (5–40 min), and pH (3–11)	92	*	[39]
Catalytic ozonation process	Conc. MNZ (1–40 mg/L), conc. catalyst (0.25–2 g/L), conc. PS (60 mM/L), reaction time (5–60 min), and pH (3–12)	95	*	[40]
Sono-Fenton process	Conc. Fe ²⁺ (3 mM/L), conc. H ₂ O ₂ (0–0.02 mM/L), temperature: (30°C–60°C), reaction time (180 min), and pH (3)	98	*	[11]
Photocatalytic process	Conc. MNZ (5–25 mg/L), reaction time (30–150 min), and UV light intensity (12.2–47.2)	93	70	[41]
Photo-Fenton processes	Conc. MNZ (6 μM/L), conc. Fe ²⁺ (2.94–11.76 μM/L), conc. H ₂ O ₂ (0–50 mg/L), reaction time (0–300 s), and pH (2–4)	94	*	[42]
PAA/PVDF–NZVI hybrids	Conc. MNZ (43.10–75.83 mg/L), temperature: (298–313 K), reaction time (5–120 min), and pH (3–11)	91.22	*	[43]
Catalytic ozonation process	Conc. MNZ (1–40 mg/L), conc. MgO (0.25–4 g/L), reaction time (0–35 min), and pH (3–12)	98	*	[44]
Photocatalytic degradation process	Conc. MNZ (1–8 mg/L), conc. CuO-NPs (0.05–0.3 g/L), reaction time (0–120 min), and pH (2)	85.5	*	[32]
UV/H ₂ O ₂ /CuO hybrid process	Conc. MNZ (25–100 mg/L), conc. H ₂ O ₂ (10–40 mL/L), conc. CuO-NPs (2–8 mg/L), reaction time (0–60 min), and pH (3–12)	98.36	73	Present study

*Not considered.

decreasing initial MNZ concentration, pH solution, H_2O_2 concentration, and increasing reaction time have led to accelerating the degradation of MNZ. Furthermore, in this study, the optimum laboratory conditions for degradation of MNZ were as follows: pH solution of 3, reaction time of 60 min, initial MNZ antibiotic concentration of 50 mg/L, H_2O_2 concentration of 10 mg/L, and CuO-NPs of 8 mg/L. Under optimum conditions, the removal efficiencies of MNZ, COD, and TOC were 98.36%, 73%, and 56.52%, respectively. Based on the results, it can be concluded that the UV/ H_2O_2 /CuO process can be utilized as a complete or pretreatment system for wastewaters containing MNZ. Furthermore, since it can improve the biodegradability of MNZ containing solutions, it may be used as post-treatment in a bioreactor.

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