

*Original Article***The Removal of Amoxicillin with ZnO Nanoparticles in Combination with US-H₂O₂ Advanced Oxidation Processes from Aqueous Solutions**Somayeh Rahdar¹ Shahin Ahmadi^{1*}

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Abstract

Background and purpose: The aim of this study was to evaluate the efficiency of zinc oxidenanoparticles (ZnO NPs) in combination with US-H₂O₂ advanced oxidation processes (AOPs) for the removal of antibiotic amoxicillin (AMO) from aquatic environment.

Materials and Methods: This experimental study was conducted in a batch reactor system. The effect of the parameters, such as pH (3-8), the dose of nanoparticles (0.01-0.08 g/L), reaction time (10-100 min), the initial concentration of the AMO (150-250 mg/L) and H₂O₂ (0.1 – 5Mol/L) on the removal efficiency were studied in ultrasonic reactor. The residual AMO concentrations were measured at 190 nm using a UV/Vis spectrophotometer.

Results: The results showed that the US-H₂O₂ advanced oxidation processes using ZnO NPs can effectively lead to the removal of AMO from the wastewater. The optimal conditions for this process were pH 3, 0.1 M of H₂O₂ and the dose ZnO NPs 0.05 g/L and time of 60 minutes. In the current study, it was found that the removal efficiency dropped with the increasing concentrations of AMO. Under optimal conditions with 150 mg/L of AMO and contact time of 60 min, the efficiency removal was also equal to 92.47%.

Conclusion: The results of this study showed that AOP was a very effective method that can be used for the removal of AMO antibiotic from aqueous solutions.

Keywords: ZnO Nanoparticles; Advanced Oxidation Processes; Amoxicillin, Removal.

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1. Introduction

The pollution of surface and groundwater has caused many health problems where antibiotics have been one of the main pollutants (1). The antibiotics have a special position in the human and veterinary treatment, and incidental entry of different types of antibiotics to sewage as well as effluent was known as one of the sources of antibiotic in the environment (2). Among the antibiotics, the Beta-lactam compounds which include amoxicillin (AMO) have been the most common drugs (3).

The Beta-lactam compounds consist of agents that contain a beta-lactam ring in their molecular structures which provides antimicrobial properties against positive and negative gram bacteria (4). The AMO, C₆H₁₉N₃O₅S is semi-synthetic penicillin with B-lactam ring with a molecular weight of 4.365 g/mol, showing high solubility in water and preventing resistance cell wall in bacteria (4, 5). AMO properties cause many unwanted effects including low biological decomposition ability, high toxicity, carcinogenesis, and mutagenesis effects, damaging the DNA and lymphocytes, increasing the allergic reactions, and providing drug resistance (6).

The introduction of effluents containing antibiotics result in serious and hazardous consequences for the environment, so efficient and effective techniques are necessary to remove the pollutants (7). The chemical and physical methods for purification of water polluted with different types of antibiotics include: chemical oxidation, biological decomposition, and physical purification (8, 9). However, biological purification of antibiotics is difficult as antibiotics have naphthol stable ring (main structure), and are toxic to microorganisms (8). Recently, Advanced

Oxidation Process (AOP) has been introduced as a new method for purifying the effluents containing antibiotics (9). The oxidation process is one of the common methods in removing the pollutants because of simplicity, low costs, and high efficiency (8). The advanced oxidation process is also based on producing the strongest oxidants, such as hydroxyl radical in solution (8, 9). Using ultrasonic in AOP among the methods that produce hydroxyl radical is novel (10).

The water molecules are broken, and the products are hydroxyl radical and free hydrogen (11). The reaction generates and further destructs gaseous bubbles yielding in high pressure and temperature (10, 11). Therefore, the soluble organic compounds are destructed thermally producing free radicals, such as (O[•], OH[•], and H[•]), or some oxidants, such as hydrogen peroxide, that react with organic compounds (12). Hydrogen peroxide (H₂O₂) is a well-known oxidant which is stronger than chlorine, chlorine dioxide, and potassium permanganate (13). This compound produces OOH[•] and OH[•] radicals, which can oxidize organic compounds once diffused into water (13, 14). One of the advantages of this process is the lack of production of carcinogenic side effects. There is no need for the use and storage of hazardous chemicals, and just a small space is required for the installation of an ultrasonic unit (14). The presence of silica particles, active carbon, active alumina, copper and zinc oxides (ZnO), for example, increase the cavitation effect and the decomposition rate of organic molecules (15, 16). Nanoparticles (NPs) of metal oxides include F₂O₃, ZnO, and TiO₂ which possess unique optical, catalytic, semiconductor, and piezoelectric properties that are developed technologically (17).

The aim of this study was to evaluate the efficiency of zinc oxidenanoparticles (ZnO NPs) in combination with US-H₂O₂ advanced oxidation processes for the removal of antibiotic amoxicillin from aquatic environments.

2. Materials and Methods

2.1. Materials

Amoxicillin (AMO) was supplied by Sigma–Aldrich (US). Its pK_a value is 2.7,

7.5, and 9.63 (8). The chemical structure of AMO is as shown below (Figure 1). All reagents [sodium hydroxide (NaOH, 98%), and sulfuric acid (H₂SO₄, 99.99%)] were of analytical grade and purchased from Merck (Germany). All solutions were prepared by using de-ionized water. The pH of the solution was also adjusted by adding HCl or NaOH 0.1 N solutions.

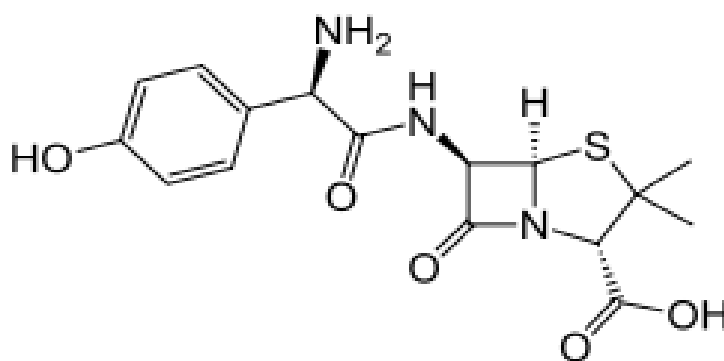


Figure 1. The chemical structure of AMO (8)

2.2. Pilot ultrasonic reactor

The reactor used for the study had a determined surface area containing digital ultrasonic (Elma CD-Germany, 4820), appliance made of Plexiglas with volumes of 3.7L, input energy per unit 2.5 W/cm², and input power 500 W with 100 mL samples in bath with US waves.

2.3. Experimental methods

The stock solution of AMO was prepared with a concentration of 1000 mg/L in double distilled water. The sample water pH was adjusted to given values using 0.1 N HCl or 0.1 N NaOH. Four process variables have been studied in the current study, which include: the initial pH of solution (3, 5, 7 and 8), concentration of zinc oxidenanoparticles (ZnO NPs) (0.01, 0.02, 0.03, 0.04, 0.05 and 0.08 g/L), contact

time (10, 20, 45, 60 and 100 min), concentration of H₂O₂ (0.1, 0.5, 0.7, 5 Mol/L), and the initial concentrations of AMO (50, 150, 200 and 250 mg/L). After measuring the final, fixed pH (by means of MIT65 pH meter), the samples were poured into 250 mL Erlenmeyer flasks, and ZnO NPs was added inside the ultrasonic apparatus and treated under ultrasound waves (60 kHz) according to the set different contact times. The residual concentrations of AMO were measured using a UV/Vis spectrophotometer (Shimadzu Model: CE-1021-UK) at λ=190 nm (18). The removal efficiency: R (%) was calculated based on the following formula (19, 20):

$$\%R = \frac{(C_0 - C_f)}{C_0} 100 \quad (1)$$

Where, C₀ and C_f is the initial and equilibrium liquid phase concentration of AMO (mg/L), respectively.

The sample standard deviation of the metabolic rate for the female fulmars is calculated as follows (21).

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$$

$$SD = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \mu)^2} \quad (2)$$

where (x₁, x₂, ..., x_N) are the observed values of the sample items, μ is the mean value of

these observations, and N is the number of observations in the sample.

3. Results

3.1. Effect of the initial pH on US/H₂O₂/ZnO reactions

As is illustrated in Figure 2, under time contact of 30 min, the concentration of hydrogen peroxide was equal to 0.5 Mol/L, and the concentration of AMO of 100 mg/L for the tested pH range was optimally pH= 3. As there can be observed, the process efficiency rate was 98.98% under these conditions.

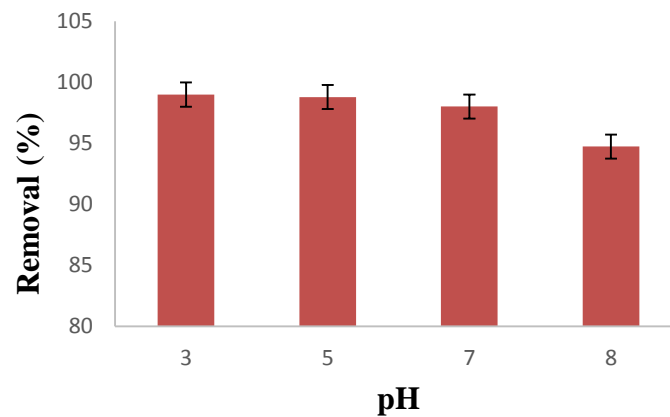


Figure 2. Effect of pH on removal efficiency of AMO (US frequency: 60 kHz, H₂O₂ concentration: 0.5 mol/L, C₀:100 mg/L and ZnO NPs: 0.05 g/L)

3.2. Effect of the initial concentrations of ZnO NPs

To determine the optimal dose of ZnO NPs in the ultrasound-hydrogen peroxide process, the concentrations of 0.02, 0.03, 0.04, 0.05, and 0.08 g/L nanoparticles were investigated. A solution of 100 mg/L AMO and hydrogen peroxide with a

concentration of 0.5 Mol/L at pH 3 was prepared, and nanoparticles were exposed to contact, as demonstrated in Figure 3. It was also observed that the dose of ZnO NPs above 0.05 g/L caused much higher removal efficiency (99.98%) in comparison to concentration of 0.02 g/L (97.5%).

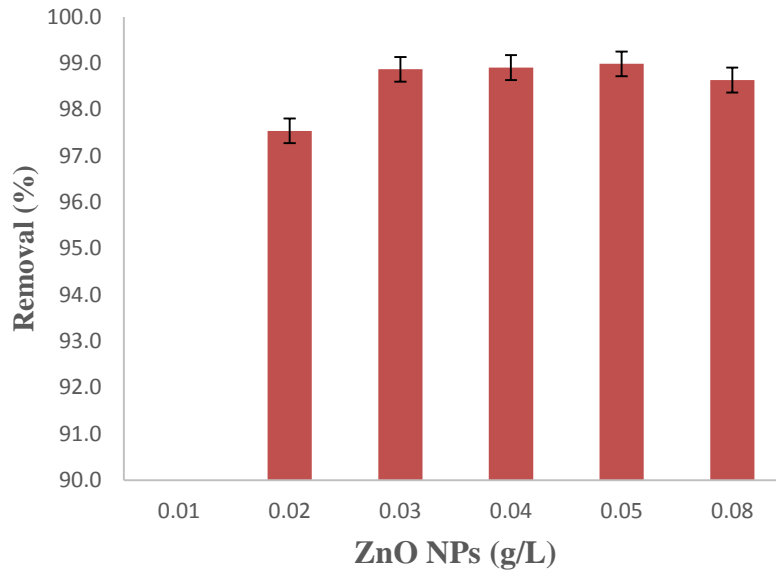


Figure 3. Effect of concentration of ZnO NPs on the removal efficiency of AMO (US frequency: 60 KHz, H₂O₂ concentration: 0.5 Mol/L and C₀:100 mg/L)

3.3. Effects of the initial concentration of hydrogen peroxide

The effects of hydrogen peroxide on the removal of AMO were determined for the

concentration of 100 mg/L of AMO (Figure 4). The maximum removal efficiency was obtained at the concentration of H₂O₂ equal to 0.1 Mol/L.

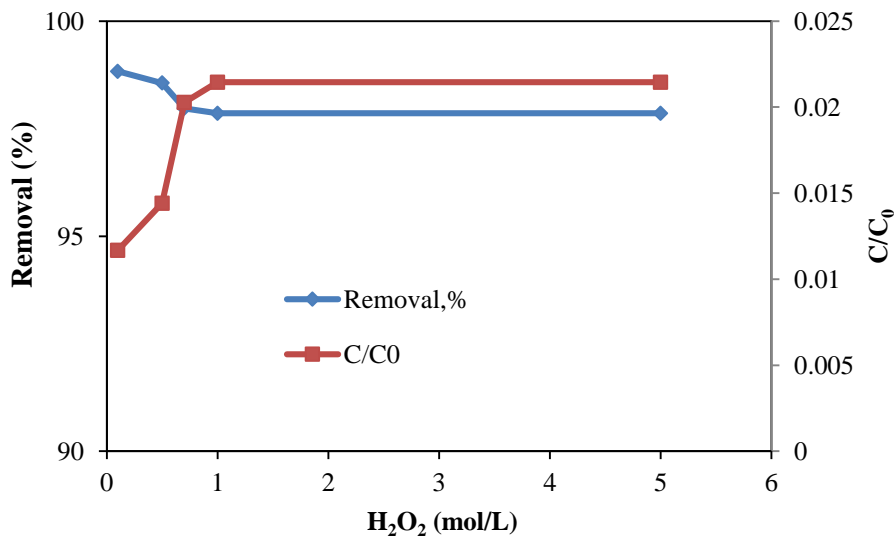


Figure 4. Effect of the concentration of H₂O₂ on the removal efficiency of AMO (US frequency 60 kHz, pH: 3 and C₀:100 mg/L)

3.4. Effects of Time and AMO concentration

In the current study, the effect of increasing bleaching concentration on the efficiency of the ultrasonic process in combination with ZnO NPs and hydrogen peroxide was investigated. The concentrations of 150,

200 and 250 mg/L were prepared and tested in the above process. As can be seen (Figure 5), the mentioned efficiency rates for AMO at the mentioned concentrations at 60 min were 90.17%, 86.9% and 88%, respectively.

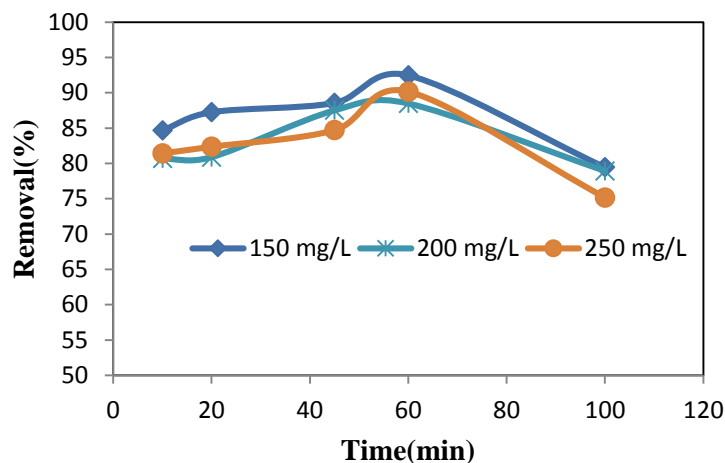


Figure 5. Effect of Time on removal efficiency of AMO (US frequency 60 KHz, H₂O₂ concentration 0.2 mol/L and pH: 3)

3.5. Kinetic studies of AMO degradation

The kinetic model of the pseudo first order reaction was used. The kinetics constants of AMO are shown in Table 1. The results showed that for the different values of the

correlation coefficient achieved for the three concentration forms (Table 1 and Figure 6), pseudo-second-order kinetic showed the best correlation coefficient ($R^2=0.95$ at $C_0=150$ mg/L).

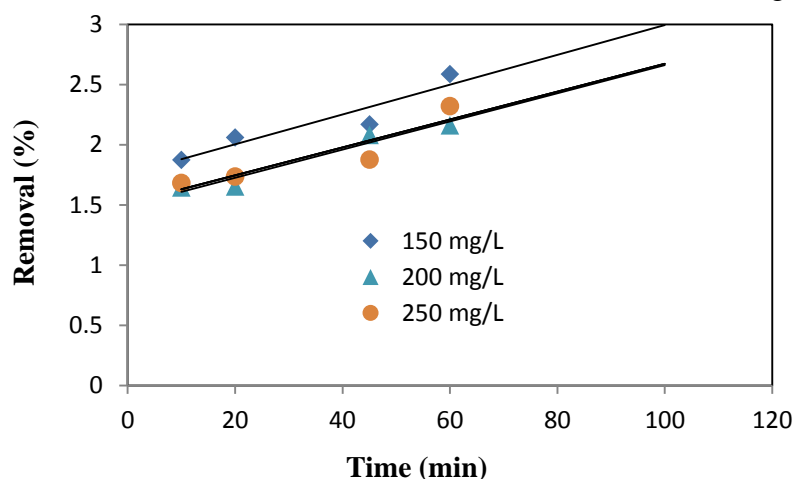


Figure 6. Pseudo-first-order, plot of AMO

Table 1. Pseudo first order kinetic for the AMO degradation process

C ₀	K ₀ (min ⁻¹)	R ²	SD
150	0.0124	0.95	0.81
200	0.0117	0.883	0.9
250	0.0116	0.8401	1.1

4. Discussion

Effect of pH (Figure 2) was an important parameter in these reactions. Solution pH affected the velocity of the reactions that occur on the surface of semiconductor particles by influencing the properties of the surface charge (21, 22). The highest removal rate was observed at PH 3. Kamani et al. (date of publication) used various pH to decompose erythromycin and metronidazole, and the results showed that the son-nanocatalyst process had maximum decomposition power under acidic conditions. The removal efficiency rate of erythromycin and metronidazole pH 3 was 95% (23). As is shown in Figure 3, it was observed that the dose of zinc oxidenanoparticles (ZnO NPs) above 0.02 g/L caused much higher removal efficiency (99%). The higher doses did not change the efficiency. However, in some studies, the positive effect of nanoparticle concentration (as a catalyst) has been mentioned. Masombaigi et al. (date of publication) reported that improved catalyst performance at higher concentrations was related to more active places on the catalyst surface and possibly the stronger ultraviolet radiation effect on it. In this study, as mentioned earlier, removal efficiency was increased with increased concentrations of nanoparticles to 0.05g/L (21, 23). The frequency of collision of the substrate and antibiotic molecules has increased with

increasing the concentration of hydrogen peroxide, so the removal efficiency was increased by using more concentrated H₂O₂. In addition, higher concentration of hydrogen peroxide resulted in increased generation of hydroxyl radicals due to stronger interactions of ultrasounds with hydrogen peroxide molecules. The radicals oxidized antibiotic molecules and thus decreased their concentrations. Initially, the removal velocity was high, followed by a decrease (24). However, this phenomenon was not observed in the present study. The results are shown in Figure 5. As can be seen, the mentioned efficiency rates for the AMO at the mentioned concentrations at 60 min were 90.17%; by increasing the initial AMO concentration, the removal efficiency was decreasing. At the beginning, the AMO concentration was high, and the possibility of collision between AMO molecules and free radicals of hydroxyl has increased. After a while, with decreasing the AMO concentration, the free radicals of hydroxyl in pilot oxidized the AMO metabolites. Therefore, the removal process showed lower velocity (25, 26). The study results showed that ZnO-H₂O₂-US followed pseudo first order kinetics. The result obtained was found similar or even better than those reported by other authors (Table 2).

Table 2. Removal percentages of antibiotics reported by different authors with time of reaction, catalyst type, and antibiotics concentrations

AOP	antibiotics	Operational condition	results	reference
Nano/Persulfate Process	Metronidazole	- Initial antibiotic concentration = 25 mg/L	removal efficiency =90.3%	(27)
		- Catalyst dosage(nZVI) = 0.5 g/L		
		- Reaction time = 30 min		
		- Persulfate= 1.85 Mm		
nano-sonocatalytic	tetracycline	- pH=3	removal efficiency =94%	(28)
		- Initial antibiotic concentration = 27 mg/L		
		- Catalyst dosage (TiO ₂)= 25 mg/L		
		- pH = 4		
H ₂ O ₂ / ZnO	Ceftriaxone	- Irradiation time = 60 min	removal efficiency =92%	(29)
		- Frequency=35 kHz		
		- hydrogen peroxide= 100 mg/l		
		- Initial antibiotic concentration = 5 mg/L		
		- H ₂ O ₂ / ZnO molar ratio= 1.5		
		- time = 90 min		
		- pH=11		

5. Conclusions

In the present study, the advanced oxidation process (AOP) removal of amoxicillin (AMO) from aqueous solutions was investigated. The effect of oxidation process parameters, pH, dosage, concentration of hydrogen peroxide, initial concentration of AMO, and contact time were investigated. Optimum conditions of pH 3, contact time of 60 min, AMO concentration of 150 mg/L, and zinc oxidenanoparticles (ZnO NPs) of 0.02 g/L, and concentration of hydrogen peroxide 0.1 Mol/L were obtained, which gave AMO removal efficiency of 90.17%. The results revealed that the experimental data fit the pseudo-first-order kinetic ($R^2 = 0.95$ at 150 mg/L AMO concentrations). From the study, it was deduced that the SD can be used for the optimization of the process parameters for AMO removal from aqueous solutions and the advanced oxidation process.

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Conflict of interest

The Authors have no conflict of interest.

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