Efficiency comparison of advanced oxidation processes for ciprofloxacin removal from aqueous solutions: Sonochemical, sono-nano-chemical and sono-nano-chemical/persulfate processes

Chinenye Adaobi Igwegbe[1], Shahin Ahmadi[2†], Somayeh Rahdar[2], Alireza Ramazani[3], Abdol Raufeh Mollazehi[2]

[1]Department of Chemical Engineering, NnamdiAzikiwe University, Awka, Nigeria
[2]Department of Environmental Health, Zabol University of Medical Sciences, Zabol, Iran
[3]Department of Environmental Health, Iranshahr University of Medical Sciences, Iranshahr, Iran

ABSTRACT

The aim of this study is to investigate the degradation of ciprofloxacin (CIP) from its aqueous solutions via different advanced oxidation processes (AOP). The effects of persulfate (PS) concentration, pH, zinc oxide nanoparticles (ZnO-NPs) dose, initial CIP concentration, and reaction time on the degradation of CIP were studied. It was found that the sonochemical (US) degradation is a less efficient process (with removal efficiency of 36%) compared to the sono-nano-chemical (US/ZnO) process which resulted in removal efficiency of 70%. Maximum removal of 99% was obtained using the sono-nano-chemical/PS (US/ZnO/PS) process at a frequency of 60 kHz, time of 10 min, pH of 7, initial CIP concentration of 25 mg/L, and PS concentration of 476.06 mg/L. The addition of PS and ZnO-NPs to the process enhanced the rate of US degradation of CIP. In addition, the kinetic parameters for the US/ZnO/PS process were obtained by fitting the kinetic data into the pseudo-first-order and pseudo-second-order kinetic models. The kinetic data was found to fit into the pseudo-first-order kinetic model than the pseudo-second-order model. The results showed that the AOP using US/ZnO/PS is a promising technique for the treatment of ciprofloxacin containing solutions.

Keywords: Advanced oxidation process, Aqueous solution, Ciprofloxacin, Nanoparticles, Persulfate

1. Introduction

Antibiotics along with sewage from veterinary clinics and hospitals, pharmaceutical industries' wastewaters, and agricultural products prominently enter into the water resources and environment [1, 2]. It was estimated that 100,000 to 300,000 tons of antibiotics have been consumed in the world [3]. They do not metabolize completely in the body and 30-90% of them are active after excretion. Therefore, it is clear that optimistically 3,000 tons and pessimistically 180,000 tons of active antibiotics have entered the environment annually [3, 4]. The department of environmental standards, USA specified that the concentration of antibiotics in sewage effluents must be less than 1 mg/L [5]. Fluoroquinolones are antibiotics that are irresolvable [6]. Ciprofloxacin (CIP) {1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-

(1-piperazinyl)-3 quinoline carboxylic acid}, which is of fluoroquinolone class is a synthetic broad-spectrum antibiotic against numerous bacteria including both gram-positive and gram-negative bacteria [7, 8]. CIP has been widely prescribed for the treatment of intra-abdominal infections, certain types of infectious diarrhea, respiratory tract infections and urinary tract infections [9]. High concentrations of fluoroquinolone in the ecosystem result in bacteria resistance to antibiotic treatment and chromosomal mutation [6, 9]. Antibiotics have a stable naphtol ring which is toxic to microorganisms, so they have been removed with great difficulty due to their stability in the environment [10].

Several methods have been introduced for antibiotics removal from aqueous environments which include nanofiltration [11], the use of nanotubes [12], electrocoagulation [13], adsorption [14, 15], photo catalysis [16], sonochemical (US) [17, 18] and other

processes. The advanced oxidation process (AOP) is one of the most commonly used methods for the removal of pollutants because of its simplicity, low cost and high efficiency [19]. The AOP is based on producing the strongest oxidants such as hydroxyl radical ($^{\bullet}$OH) in solution [20]. Sonolysis (that is, the use of ultrasound, US to degrade materials) of water produces $^{\bullet}$OH radicals and hydrogen atoms. The mechanism proposed for the production of OH$^{\bullet}$ and OOH$^{\bullet}$ by the use of the US is given as Eq. (1)-(6) [21]:

$$H_2O+)))[Ultra\ Sound] \longrightarrow HO + H \tag{1}$$

$$HO + H \longrightarrow H_2O \tag{2}$$

$$O_2))) \longrightarrow 2O \tag{3}$$

$$O+ H_2O \longrightarrow 2HO \tag{4}$$

$$H+ O_2 \longrightarrow OOH \tag{5}$$

$$2HO \longrightarrow H_2O_2 \tag{6}$$
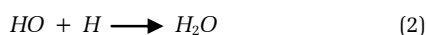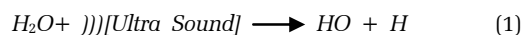
Although the use of advanced oxidation method alone is not effective, the addition of chemical materials such as persulfate (PS), nanoparticles (NPs) and catalytic particles could increase its efficiency [22]. Recently, PS (with oxidation-reduction potential of 2.01 V) oxidation has been commonly used due to its low cost, high solubility, high stability in producing radicals at different conditions and less dependency on organic compounds to remove resistant and toxic pollutants [23]. PS salts dissolve in water to produce peroxydisulfate ion ($S_2O_8^{2-}$) with less oxidative capacity. In order to increase the oxidative capacity and the production of sulfate radical ($SO_4^{\bullet-}$), this combination was used in different chemical and thermal reactions to produce active sulfate radical [24]. Ultraviolet waves, ultrasound waves, heat, and bicarbonate metals are among the most important activation factors for PS, which convert PS to free radicals such as sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals ($OH^{\bullet}$) (Eq. (7)-(10)) [25]:

$$S_2O_8^{2-}+))) \longrightarrow 2SO_4^{-} \tag{7}$$

$$S_2O_8^{2-}+heat/light \longrightarrow 2SO_4^{-} \tag{8}$$

$$2SO_4^{-}+H_2O \longrightarrow H^{+}+2SO_4^{2-}+OH \tag{9}$$

$$Fe^{2+}+S_2O_8^{2-} \longrightarrow Fe^{3+}+SO_4^{-}+SO_4^{2-} \tag{10}$$
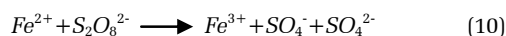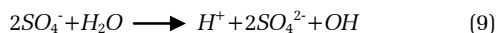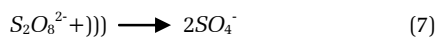
The presence of silica particles, active carbon, active alumina, copper, and zinc oxide nanoparticles (ZnO-NPs), for example, increases the cavitation effect and the rate of organic molecules decomposition [26]. NPs of metal oxides include F_2O_3, ZnO, and TiO_2. These NPs have provided unique optical, catalytic, semi conductive and piezoelectric properties that are developed technologically [27]. In order to remove pollutants that show low biodegradability, the sonochemical process in the presence of catalysts is more effective compared to the other AOPs, which is new in the area of sewage treatment. This process which has provided high catalytic capacity could be applied as an effective method [22]. Due to the ease of usage and non-production of toxic products in combination with other methods, the use of ultrasound has been considered. Therefore, in this study, the effect of activation via PS and ZnO-NPs on the US technique for the removal of CIP from its aqueous solution was examined. The effects of the parameters of operation such as pH, contact time, CIP concentration, PS concentration, and ZnO-NPs dose on CIP removal using AOPs (US, US/ZnO, and US/ZnO/PS)was also investigated.

2. Materials and Methods

2.1. Materials

CIP [Molecular mass: 385.8 g/mol, purity: 99.6% and molecular formula: $C_{17}H_{18}FN_3O_3HClH_2O$] and ZnO-NPs [99% purity, specific surface area: 90 m^2/g, particle size: 20 nm] of analytical grade were supplied by Sigma-Aldrich, USA. All reagents [sodium persulfate ($Na_2S_2O_8$, 99%), sodium hydroxide (NaOH, 98%), sulfuric acid (H_2SO_4, 99.99%)] were of analytical grade and were purchased from Merck (Germany). All solutions were prepared using de-ionized water.

2.2. Ultrasonic Procedure

The experiments were performed using a reactor of determined surface which includes a digital US appliance that is made of plexiglass with a piezoelectric transducer with diameter of 5 cm fixed at the bottom of the vessel, with samples of 100 mL each in the bath with US waves (model: Elma CD-Germany, 4820, input power: 500 W, input energy per unit: 2.5 W/cm^2, volume of reactor: 3.7 L and frequency: 60 kHz).

2.3. Analysis Procedure

Fourier transform infrared spectroscopy (FTIR, JASCO 640) was done on a plus machine (4,000-400 cm^{-1}). Scanning electron microscopy (SEM) of nanometer-sized particles was carried out using a Mira 3-XMU instrument. SEM was used to determine the morphology of the ZnO-NPs, and FTIR was used to determine the functional groups present in the NPs participating in the CIP degradation process.

2.4. Batch Experiments

The effects of different parameters such as pH (3, 5, 7 and 9), contact time (10, 20, 40, 60, 80 and 120 min), CIP concentration (25, 50, 100 and 150 mg/L), PS concentration (238.03, 476.06, 1,428.18, 1,904.24 and 2,380.03 mg/L) and ZnO-NPs dose (0.1, 0.15, 0.2 and 0.25 g/L) on the AOPs (US, US/ZnO, and US/ZnO/PS) for the removal of CIP were examined. The pH of the water samples was adjusted by adding 0.1 N HCl or 0.1 N NaOH solutions. At first, the optimum time and optimum CIP concentration were obtained under constant conditions of pH of 7, and frequency of 60 KHz. The optimum ZnO-NPs dose was obtained under constant conditions of pH 7, CIP concentration of 25 mg/L, and contact
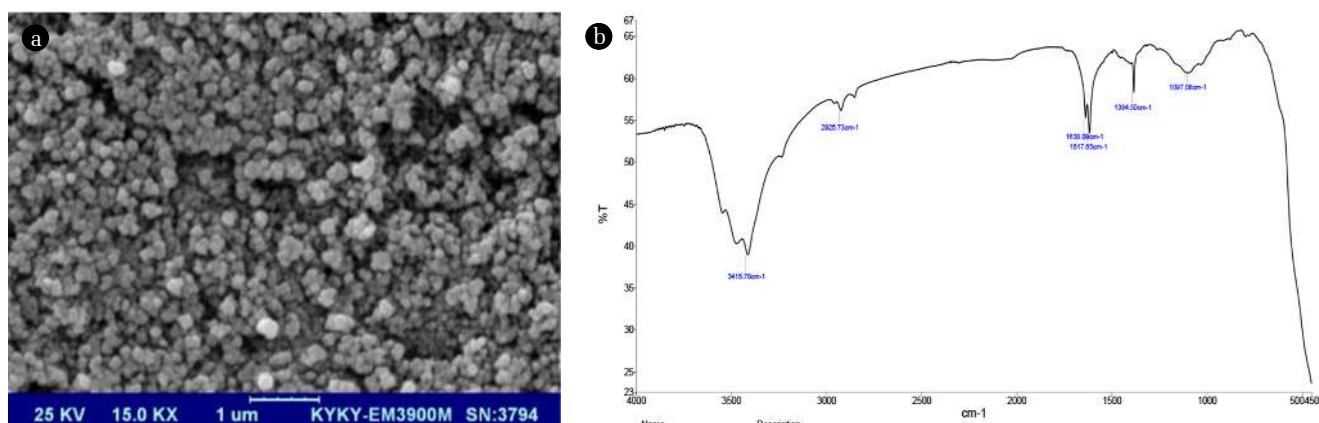
Fig. 1. (a) SEM image and (b) FTIR spectra of the ZnO-NPs.

time of 80 min using NP doses of 0.1, 0.15, 0.2, and 0.25 g/L. At last, the optimum PS concentration was determined at the optimum conditions obtained for the above-studied variables. All experiments were carried out according to the standard methods [18]. The initial and final CIP concentrations remaining in the solutions were analyzed by a UV-visible recording spectrophotometer (Shimadzu Model: CE-1021-UK). The CIP concentration was determined at a wavelength of maximum absorbance (λ_{max}): 275 nm [14]. The pH was measured using a MIT65 pH meter. The degradation efficiency (%R) was evaluated as follows:

$$\%R = \frac{(C_0 - C_f)}{C_0} \times 100 \qquad (11)$$

Where C_0 and C_f are the initial and residual CIP concentration, respectively.

3. Results and Discussion

3.1. SEM and FTIR Analysis on ZnO-NPs

The specific surface of the NPs was determined using the SEM method (Fig. 1(a)).The specific surface area of ZnO-NPs was determined as 90 m^2/g. This value implies that the ZnO-NPs possess a high surface area which will favor the CIP degradation process. The SEM image shows that the ZnO-NPs consist of lamellar-like structures. The infrared transmittance (%) was plotted against the wavelength (cm^{-1}) as seen in Fig. 1(b). The FTIR analysis on the ZnO-NPs indicates the presence of C-O stretch of alcohols, carboxylic acids, esters, ethers (1,097.08 cm^{-1}) and C-H rock of alkanes (1,384.50 cm^{-1}). The peaks 1,638.09 and 1,617.65 cm^{-1} depicts the presence of C-C stretch (in-ring) of aromatics. Peak 2,925.73 cm^{-1} indicates the presence of C-H stretch alkanes, which are strong, broad and multi-banded. The presence of O-H stretch, H-bonded of alcohols, phenols (3,415.78 cm^{-1}), which are also strong and broad bands [28] can be observed.These strong bands took part actively in the CIP degradation process.

3.2. Effect of Time and CIP Concentration on the Sonochemical (US) Process

The removal of CIP at a frequency of60 KHz and CIP concentrations of 25, 50, 100 and 150 mg/L at different time (10, 20, 40, 60, 80 and 120 min) is shown in Fig. 2. The low US removal rate is due to the fact that the formation of free radicals (OH) in the ultraviolet spectroscopy alone is insignificant. The only source of OH production in the US wave is the sonolysis of water according to the following equations [29]:

$$H_2 + US \longrightarrow H + OH \qquad (12)$$

$$2H + O_2 \longrightarrow 2HO \qquad (13)$$

Therefore, since the amount of radicals produced during this process is negligible, so its ability to reduce the antibiotics concentration is low. More investigations have shown that the higher the number of hydroxyl radicals and the higher the oxidation rate, the greater the number of OH radicals derived from the hybrid system than the US system, and the little effect pH changes have on this process. Therefore, a study of pH variations on this method is insignificant [30].
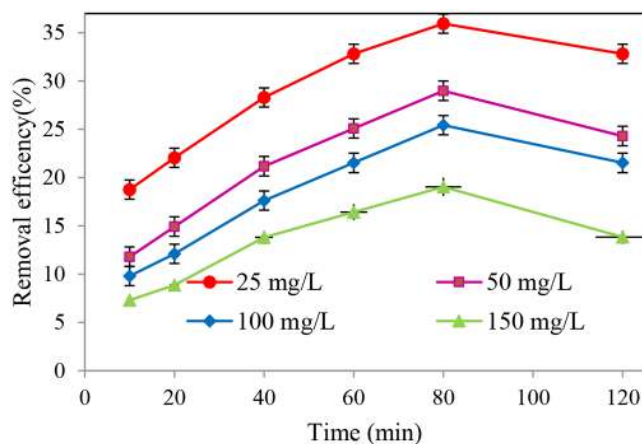

Fig. 2. Effect of time and CIP concentration on CIP removal efficiency using US process. (Frequency: 60 kHz and pH 7)

3.3. Effect of ZnO-NPs Dose, CIP Concentration and Reaction Time on the Sono-nano-chemical (US/ZnO) Process

The effect of ZnO-NPs dose on the removal of CIP was studied by varying the CIP concentrations from 0.1 to 0.25 g/L (Fig. 3(a)). In general, US was considered as the energy source to activate the NPs. NPs provide large surface and high energy which tends to accumulate [31]. When the ZnO-NPs particles were subjected to US waves, the orbit layer electrons were excited and then a positive charge was formed on the pores of the NPs. The positively charged pores reacted with $^\cdot OH$ and a chemical reaction was observed between the excited electrons and adsorbed O_2 on the ZnO-NPs [3]. Although US distribute the NPs, its strength is not enough to distribute them in high concentration. So, the efficiency of removal could be improved by adding NPs [30]. The results obtained were similar to the studies on the effect of different concentrations on the disintegration of organic pollutants using TiO_2 NPs in different AOPs [29, 31].
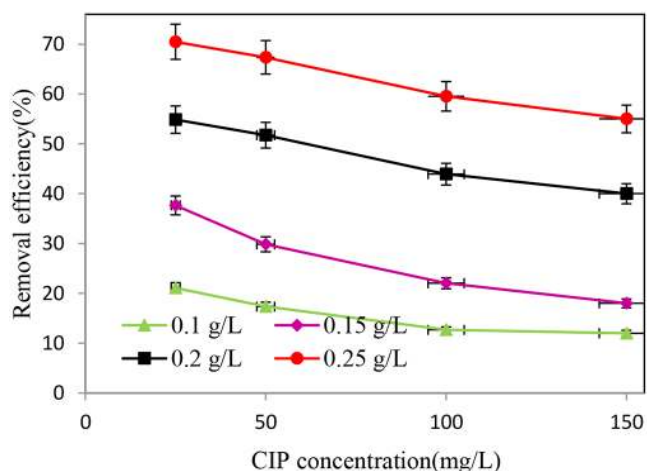

Fig. 3. (a) Effect of ZnO-NPs dose and CIP concentration on the removal efficiency of CIP using US/ZnO process. (Frequency: 60 kHz, pH: 7 and Time: 80 min).
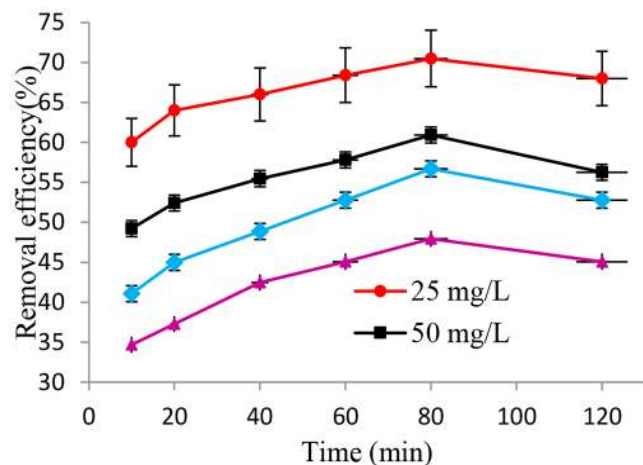

Fig. 3. (b) Effect of time and CIP concentration on the removal efficiency using US/ZnO process. (Frequency: 60 kHz, pH 7 and ZnO-NPs dose: 0.25 g/L).

The effect of reaction time and CIP concentration (Fig. 3(b)) on removal efficiency of CIP was investigated at different CIP concentrations (25, 50, 100 and 150 mg/L) and reaction time (10, 20, 40, 60, 80 and 120 min) at the optimum ZnO-NPs dose (0.25 g/L). The rate of removal increased rapidly during the time period of 10-80 min and then decreased. The efficiency of CIP decomposition was increased with decreasing initial CIP concentration at the same condition of NPs dose and free hydroxyl radical density. Therefore, CIP radical reaction with hydroxyl radicals would be increased at low CIP concentrations, which will result in increase in the CIP decomposition by the free radical [32].

3.4. Effect of Initial pH, Persulfate Concentration and Time on the Sono-nano-chemical/persulfate (US/ZnO/PS) Process
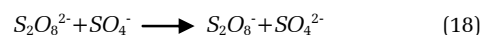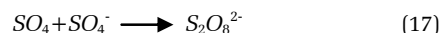
As seen in Fig. 4(a), higher efficiency was observed at a pH of 7using the US/ZnO/PS process. The most important cause of the effect of environmental phases on the synthesis of organic compounds is the type and amount of radicals produced by the AOP. During the use of PS as an oxidant, in addition to radical production of PSs, which have an important role in the production of organic compounds due to the higher oxidation potential of organic compounds. This reagent, as stated in Eq. (14), can affect the hydroxyl water molecules and convert them to hydroxyl radical, which can play a role in the acidic conditions of PS ions, which are converted into free radicals of PS [33].

$$SO_4^- + OH \longrightarrow SO_4^{2-} + OH \tag{14}$$
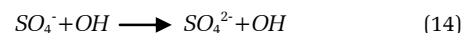
Therefore, these free radicals and hydroxyl radicals are dominant in acidic conditions. In neutral and basic pH, the $SO_4^{\cdot-}$ would be converted to $OH^\cdot$ according to Eq. (15) and (16), and this led to the increase in the oxidation and removal efficiency [34].

$$SO_4^- + OH^- \longrightarrow HSO_4^- + 0.5O_2 \tag{15}$$

$$SO_4^- + H_2O \longrightarrow SO_4^{2-} + OH + H^+ \tag{16}$$
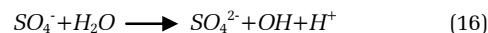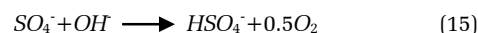
As seen in Fig. 4(b), increasing the PS concentration from 238.03 to 476.06 mg/L increased the removal of CIP, which decreased as the PS concentration was increased further from 1,428.18 to 2,380.3 mg/L. Eq. (17) and (18) described the PS behavior. At first, the PS was converted to sulfate radical (one of the strongest oxidizing substances) and it decomposed the resistive organic materials to water, CO_2 and non-organic acids [35]. PS radical reacted with water and hydroxyl ions indirectly to produce the hydroxyl radicals. Increasing the oxidizing substance, PS more than optimal level caused the PS radicals to act as a scavenger and converted sulfate radical to back to PS ($S_2O_8^{\cdot-}$). Therefore, the sulfate radicals were reduced [36].

$$SO_4 + SO_4^- \longrightarrow S_2O_8^{2-} \tag{17}$$

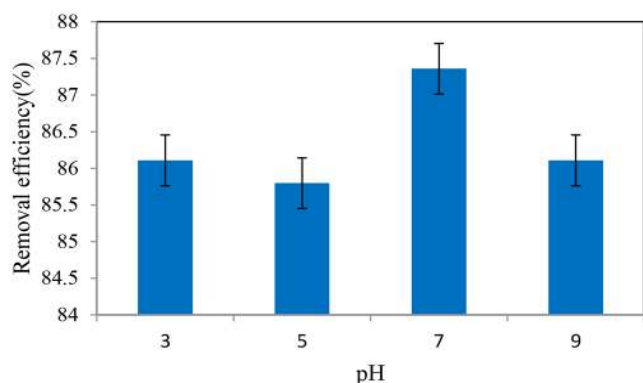$$S_2O_8^{2-} + SO_4^- \longrightarrow S_2O_8^- + SO_4^{2-} \tag{18}$$

Fig. 4. (a) Effect of pH on the removal of CIP using the US/ZnO/PS process. (Frequency: 60 kHz, time: 80 min, PS concentration: 476.06 mg/L and ZnO-NPs dose: 0.25 g/L).
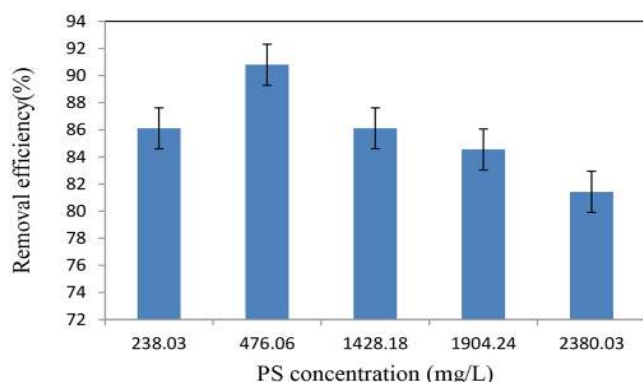

Fig. 4. (b) Effect of PS concentration on the removal of CIP using the US/ZnO/PS process. (Frequency: 60 kHz, time: 80 min, pH: 7 and ZnO-NPs dose: 0.25 g/L).
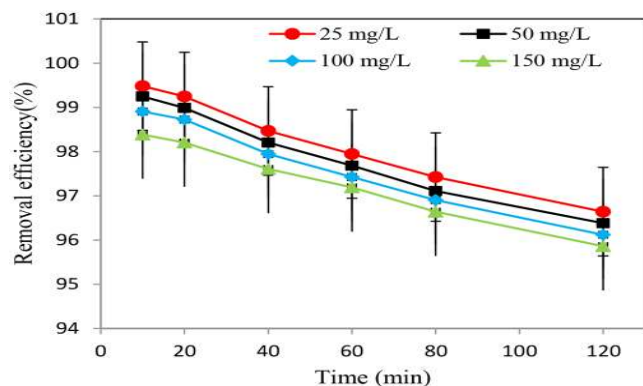

Fig. 4. (c) Effect of time and CIP concentration on CIP removal efficiency usingthe US/ZnO/PS process. (Frequency: 60 kHz, pH: 7 and ZnO-NPs: 0.25 g/L, PS concentration: 476.06 mg/L).

To evaluate the effect of initial CIP concentration and reaction time on the performance of the US/ZnO/PS) process, the experiments were carried out at different initial CIP concentrations of 25, 50, 100 and 150 mg/L at PS concentration of 476.06 mg/L and pH of 7. The results are presented in Fig. 4(c). CIP removal efficiency decreased after 10 min at concentrations of 25, 50, 100 and 150 mg/L. The highest removal efficiency was obtained at CIP concentration of 25 mg/L. The efficiency of removal at this concentration (25 mg/L) and the reaction time of 10 min was 96%. This may be due to the finite number of active sites present on the adsorbent that becomes saturated at high CIP concentration. In other words, at low CIP concentration and time, the availability of the adsorption sites was higher than at higher CIP concentrations and time [37].

3.5. Comparison of the Advanced Oxidation Processes (US, US/ZnO, and US/ZnO/PS)

The comparison of the processes studied and its simultaneous effect on the removal of the CIP antibiotics is shown in Fig. 5. The results showed that removal efficiency of 36% was obtained by applying only the US process. However, the removal of CIP was improved using the US/ZnO process (70%) and US/ZnO/PS process (99%). The result obtained is similar or even better than those reported by other authors (Table 1).
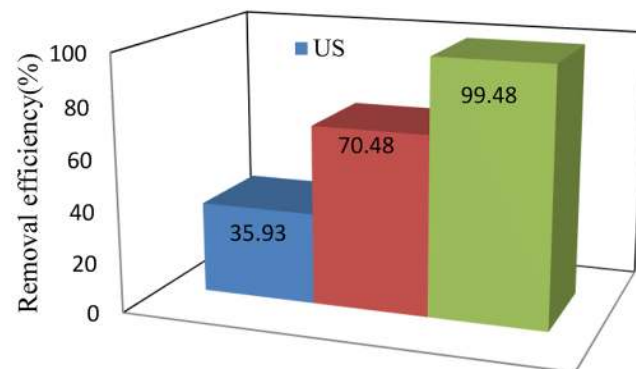

Fig. 5. Comparison of US, US/ZnO and US/ZnO/PS processes on CIP removal. (Frequency: 60 kHz, PS concentration: 476.06 mg/L, CIP concentration: 25 mg/L, ZnO-NPs dose: 0.25 g/L, pH: 7, Time: 10 min).

3.6. Kinetics Study

The kinetics study on the CIP degradation process using the US/ZnO/PS process was performed at the different CIP concentrations (25, 50, 100 and 100 mg/L) at the optimum conditions of contact time: 10 min, pH: 7, PS concentration: 476.06 mg/Land

Table 1. Removal Percentages of Antibiotics Reported by Different Authors with AOPs

Process	Catalysts used	Concentration of antibiotics (mg/L)	Persulfate concentration	Catalyst dosage (g/L)	Removal (%)	Reference
Nano/Persulfate	nZVI	Metronidazole: 25	1.85 mM	0.5 g/L	90.3	[38]
sono nanocatalytic	γ -Fe$_2$O$_3$	Penicilin: 10	-	0.3	95.5	[39]

NPs dose: 0.25 g/L). The pseudo-first-order and pseudo-second-order kinetic models were used to study the US/ZnO/PS process. The pseudo-first-order and pseudo-second-order model equations are given as Eq. (19) and (20), respectively [39, 40]:

$$\ln\left(\frac{C}{C_o}\right) = -k_1 t \qquad (19)$$

$$\frac{1}{C} - \frac{1}{C_o} = -k_2 t \qquad (20)$$

The slope of the straight line plot of $\ln\left(\frac{C}{C_o}\right)$ versus time, t (Fig. 6(a)) gives the value of the rate constant, k_1 (min⁻¹). The pseudo-second-order rate constant, k_2 was determined from the slope of the linear plot of $\left(\frac{1}{C} - \frac{1}{C_o}\right)$ versus t. C_o denotes the initial concentration in milligrams per liter, and C is the final concentration in milligrams per liter at time, t. The calculated results are shown in Table 2.

The correlation coefficients (R^2) for the pseudo-first-order and pseudo-second-order kinetic models were obtained as 0.923 and 0.715, respectively at the optimum CIP concentration of 25 mg/L; this implies that this study followed the pseudo-first-order kinetic model at all concentrations than the pseudo-second-order model. The rate of CIP decomposition was observed to be a function of time (Fig. 6(a) and 6(b)).The results were similar to the study by Wan et al. [40, 41], who analyzed the degradation of tetracycline in water using the US process.

Table 2. Kinetic Parameters for the CIP Degradation Using the US/ZnO/PS Process

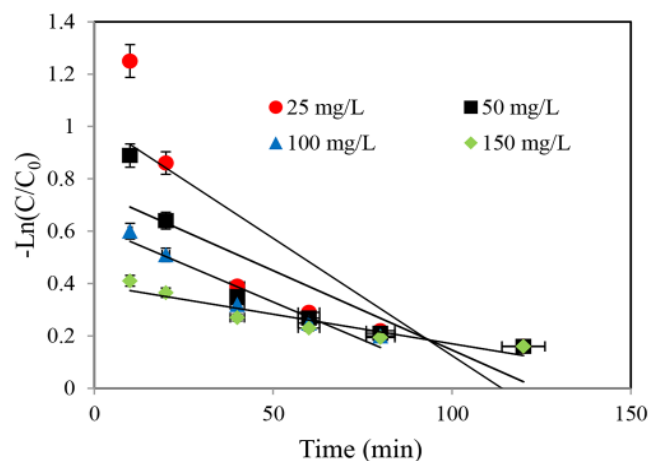| C_o (mg/L)	Pseudo-first order		Pseudo-second order	
	k_1	R^2	k_2	R^2
25	0.016	0.923	0.009	0.715
50	0.014	0.929	0.006	0.7534
100	0.012	0.934	0.0057	0.9178
150	0.008	0.958	0.0024	0.922

Fig. 6. (a) Pseudo-first-order plot for CIP degradation by US/ZnO/PS process.
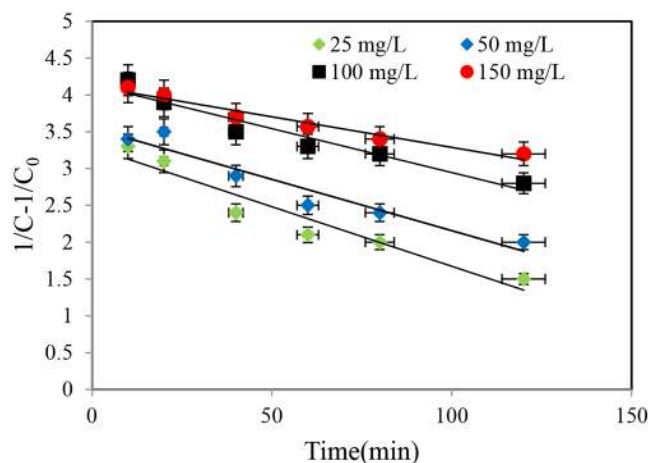

Fig. 6. (b) Pseudo-second-order plot for CIP degradation by US/ZnO/PS process.

4. Conclusions

The degradation of CIP using different AOPs, AOPs (US, US/ZnO, and US/ZnO/PS) was studied. The effects of pH, PS concentration, ZnO-NPs dose, initial CIP concentration, and reaction time on the degradation of CIP were examined. Optimum removal efficiency of 36% was obtained by applying only the US process. The sono-nano-chemical (US/ZnO) process resulted in an increase in the CIP removal efficiency to 70% but using sono-nano-chemical/persulfate (US/ZnO/PS) process, the efficiency was increased to 99% at the optimal conditions. Based on the results, it was found that the advanced oxidation using the US/ZnO/PS process is considered as a suitable method for CIP decomposition. The US process cannot be considered as an effective method for antibiotics removal. Addition of ZnO-NPs and PS significantly increased the removal efficiency. The kinetic data was found to follow the pseudo-first-order kinetic model.

Acknowledgments

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