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Degradation of sulfamethoxazole antibacterial by sono-Fenton process using nano-zero valent iron: influence factors, kinetic and toxicity bioassay

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ABSTRACT

This study investigated the efficiency of sono-nano Fenton process in the degradation of sulfamethoxazole (SMX) antibacterial in aqueous solution. The effect of ultrasonic frequency, initial pH, the dose of nZVI, SMX concentration and hydrogen peroxide concentration are investigated. The results show that the oxidation power of Fenton system increases by ultrasonic irradiation. The optimum degradation efficiency of SMX was achieved in the condition of 1 mM H_2O_2, 80 kHz frequency, 1 g/L nZVI, and pH: 3 after 60 min contact with US/Fenton (about 95%). Also, the degradation kinetics and toxicity test for effluent of US/ nZVI /H_2O_2 system in optimal condition were studied. It was shown that degradation of SMX could be described by a first-order kinetic model and the toxicity of treated SMX solution decreases with treatment by sono Fenton system. This study shows that US/Fenton can be used as an effective method for the treatment of polluted water and wastewater with SMX.

Keywords: Ultrasound; nZVI; H_2O_2; Fenton; Sulfamethoxazole; Toxicity test

1. Introduction

In recent years, pharmaceutical, especially antibiotics have become the subject of great interest to environmental researchers worldwide [1]. The studies have shown the existence of a variety of drugs such as antimicrobials (including erythromycin, ciprofloxacin, sulfamethazine and tetracycline), analgesics (e.g., ibuprofen), β-blockers (such as propanol), endocrine disruptors (for example, ethynylestradiol) at both of the surface and groundwater [2–6].

Sulfonamides, a group of antibacterial drugs, are widely used for the treatment of bacterial, protozoal and fungal infections in human therapy, livestock production and aquaculture [7]. Sulfamethoxazole (SMX) is a bacteriostatic antibacterial sulfonamide which is commonly used in the treatment of urinary tract infections [8].

Several physicochemical and biological methods are used to remove drugs [9–12]. According to the inability of conventional treatment processes for the removal of these compounds from the environment, it is essential to find effective and reliable methods. Studies have shown that advanced oxidation process (AOPs) has a high efficiency in the destruction of pharmaceutical contaminants in aquatic environments. Recently, the use of ultrasound as an effective and easy method has attracted a great attention [13]. Attributed mechanisms for degradations of organic materials by this process

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are: oxidation by OH radicals, decomposition pyrolytic and supercritical water oxidation [14].

The techniques which use ultrasonic waves with catalysts have a high ability to degradation of aromatic organic pollutants [15]. In the ultrasound system, cavitation phenomena occur due to the sound irradiation and hydrolysis of water that results in producing OH radicals. In Fenton system, the production of OH radicals arises from the iron reaction with hydrogen peroxide. The OH radicals cause the oxidation of organic contaminants. However, in the Fenton system, there are steps with low kinetics rate which produce Fe $(OOH)^{2+}$ (Eq. (5)) and $Fe(OH)^{2+}$ complexes (Eq. (7)). Ultrasonic irradiation accelerates releasing ferrous iron and the formation of hydroperoxy radical •OOH (Eq. (6)) and •OH (Eq. (8))[16]. Ferrous iron and hydroperoxy radical can participate as a factor in the redox reactions (Eqs. (3), (4) and (9)).

$$Fe^0 + 2H^+ + US \rightarrow Fe^{2+} + H_2 \text{ (in acidic solution)} \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad (2)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (3)$$

$$^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \quad (4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe \ldots OOH^{2+} + H^+ \quad (5)$$

$$Fe \ldots OOH^{2+} + US \rightarrow {}^{\bullet}O_2H + Fe^{2+} \quad (6)$$

$$Fe^{3+} + H_2O \rightarrow [Fe(OH)^{2+}] + H^+ \quad (7)$$

$$[Fe(OH)^{2+}] +))) \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (8)$$

$$Fe^{3+} + {}^{\bullet}O_2H \rightarrow Fe^{2+} + H^+ + O_2 \quad (9)$$

In the reactions illustrated above, there is possibility for the produced ferrous ions (Eq. (2)) to react with additional hydrogen peroxide (Eq. (5)), water (Eq. (7)), oxidized species (Eq. (10)) or metallic ions (Eq. (11)) and convert to ferrous iron species and again come back to the reaction cycle.

$$R^{\bullet} + Fe^{3+} \rightarrow R^+ + Fe^{2+} \quad (10)$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \quad (11)$$

According to the earlier explanation, it can be found that Fenton reaction can be influenced by created metal cations, and this may restrict the reaction. In low acid pH condition, another function of sound irradiation in the Fenton process improves the dissolution of iron particles in solution. Sonicated sulfamethoxazole solution causes the oxidation and mineralization of SMX in the presence of nZVI (production of Fe^{2+} and Fe^{3+}) and hydrogen peroxide (production of OH radicals).

Several studies have used the US/Fenton process for removal of organic pollutants from the aqueous solutions such as 1-alkyl-3-methylimidazolium [17], azo dye Acid black 1 [18], phenol, 2-chlorophenol and 3,4-dichlorophenol [19], C.I. Acid Orange 7 [20], carcinogenic polycyclic aromatic hydrocarbons [21] and sodium alginate [22].

This study has evaluated the performance of Sono-nano-catalytic process in degradation of a type sulfonamide antibacterial using nZVI. The general characteristics of SMXwere shown in Table 1. Also, the toxicity of effluent Sono nano-catalytic process was investigated by the microbial toxicity test.

2. Experimental setup

2.1. Materials

Standard SMX ($C_9H_9N_3O_2S_2$) purchased from Sigma Aldrich. $FeSO_4.7H_2O$ (Sigma–Aldrich, > 99.0%) was applied to make the nZVI and 30% hydrogen peroxide (H_2O_2, DUKSAN) was employed. Methanol (HPLC grade), ethanol (99.7%), Sulphuric acid, sodium hydroxide and $NaBH_4$ were supplied by Merck Company, Germany.

2.2. Preparation of nZVI particles

Preparation of nZVI was done by the reaction of $FeSO_4.7H_2O$ with $NaBH_4$ in the aqueous phase. In this reaction, Fe^{2+} was reduced to Fe^0 according to the reaction (Eq. (12)) and Polyvinylpyrrolidone was used as dispersion agent [23].

$$Fe(H_2O)_6^{2+} + 2BH_4^- \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \uparrow \quad (12)$$

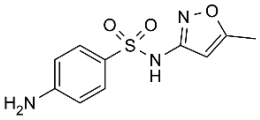
For preparing the nZVI, first, $FeSO_4{\cdot}7H_2O$ was added to the ethanol/water with stirring, then $NaBH_4$ quickly added under nitrogen and mixed well to make a dark color solution. After that, the nZVI was separated from the solution by magnetic procedure and washed with deionized water and ethanol. The produced nZVI stored in ethanol [24].

To determine the surface morphology of the nZVI a scanning electron microscope (SEM) equipped with an energy dispersive X-ray microanalysis (LEO-1,430 VP) was used. X-ray diffraction methods (Philips XRD 3,100 diffractometer) systematic were applied to investigate the characterization of the nZVI.

2.3. Experimental procedure

Experiments were carried out in a batch reactor at the room temperature. For the preparation of different concentrations of SMX a stock solution of 1 g/L was used. The nZVI

Table 1
General characteristics of the antibiotic Sulfamethoxazole

Molecular structure	
Chemical structure	$C_{10}H_{11}N_3O_3S$
Molecular weight	253.28 g/mol
Solubility in water	610 g/lit
pk_{a1}	1.6
pk_{a2}	5.7
melting point	169 °C (336 °F)

dose (0.5–2 g/L), H_2O_2 concentration (10–150 mM), frequency of ultrasonic (20–80 kHz), initial solution pH (3–9) and SMX concentration (5–150 mg/L) were investigated. Sulphuric acid and sodium hydroxide were used to adjust the pH of solution. Prepared samples were stored at 4°C. The volume of the reaction solution was 100 mL containing SMX, nZVI and hydrogen peroxide which were under influence of ultrasonic waves. During the contact of SMX with sound radiation, vials containing the reaction were immersed in the water of ultrasonic device. After contact time, some of the samples were taken and after filtering, the remaining amount of drugs was determined with HPLC. Each experiment was performed in duplicate. Following equation was used for calculating the removal percentage:

$$\text{Removal efficiency (\%)} = (1 - C_t/C_0) \times 100 \quad (13)$$

where C_t and C_0 are the concentrations (mg/L) of SMX at reaction time t and prior to sonication, respectively.

2.4. Test toxicity

In this study, bacterial toxicity test was used to evaluate the performance of the sono-nano Fenton process for inactivation of SMX. We compared the amount of bacterial growth in both untreated and treated samples with sonocatalytic process. The inhibitory growth of three gram-negative bacterial strains (*Escherichia coli* ATCC 25,922, *Pseudomonas aeruginosa* ATCC 9,027 and *Salmonella enterica* ATCC 19,430) and three gram-positive bacterial strains (*Staphylococcus aureus* ATCC 6,538, *Streptococcus pneumoniae* ATCC 49,619 and *Bacillus* subtilis ATCC 6,633) were used. At first, each bacterium was cultivated separately in nutrient broth media to reach the OD_{600} of 0.1. Then output samples of sonoreactor and untreated samples containing SMX were added to medium and incubated at 37°C. To obtain changes in bacterial growth, OD_{600} was recorded every 2 h for a 10-h period. A Medium containing bacteria without sulfonamide was incubated as a control. Finally, the percentage of growth inhibition (GI%) was calculated using the following equation [25]:

$$\text{GI (\%)} = 1 - \frac{D_{600S}}{D_{600C}} \quad (14)$$

where OD_{600S} is OD_{600} of the sample and OD_{600C} is OD_{600} of the control. In this test, to prevent the effects of nanoparticles and peroxides on the growth of bacteria, the nanoparticles were first separated by magnet and then passed through a filter to completely remove the solution. Also, to prevent the interference H_2O_2, after contacting SMX with the US/nZVI/H_2O_2 process, immediately, afterward the potassium permanganate was added to the samples. All experiments were performed in triplicate.

2.5. Analysis of sulfamethoxazole

The concentration of SMX in the samples was detected with a high-performance liquid chromatography apparatus (HPLC, CECIL 4,100, Cambridge, UK) equipped with a UV-visible diode array detector set at 254 nm. Chromatographic separation was achieved on a Perfect Sil C18 reverse phase column (C18, 25 cm × 0.46 cm i.d., 20 mM particle size) from MZ-Analysentechnik (GmbH, Germany) at a flow rate of 1 mL/min and 20 μL injections. The mobile phase was composed of a mixture of acetic acid (50 mM) and methanol (50:50 v/v). Retention time for SMX was obtained 8 min [26,27].

3. Results and discussion

3.1. Characterization of nZVI particles

Surface morphology and composition of nZVI particles were studied by SEM-EDX before and after the heterogeneous sono-Fenton reaction. As shown in Fig. 1(a), these particles were spherical and most of their sizes were between 10–100 nm. After contacting the nanoparticle with sulfamethoxazole, the particles lost their spherical shape and pores decreased, which resulted in the contact surface of the nanoparticle reduction (Fig. 1(b)).

Fig. 2 depicts the powder XRD pattern of nZVI samples under ambient conditions. The broad peak reveals the

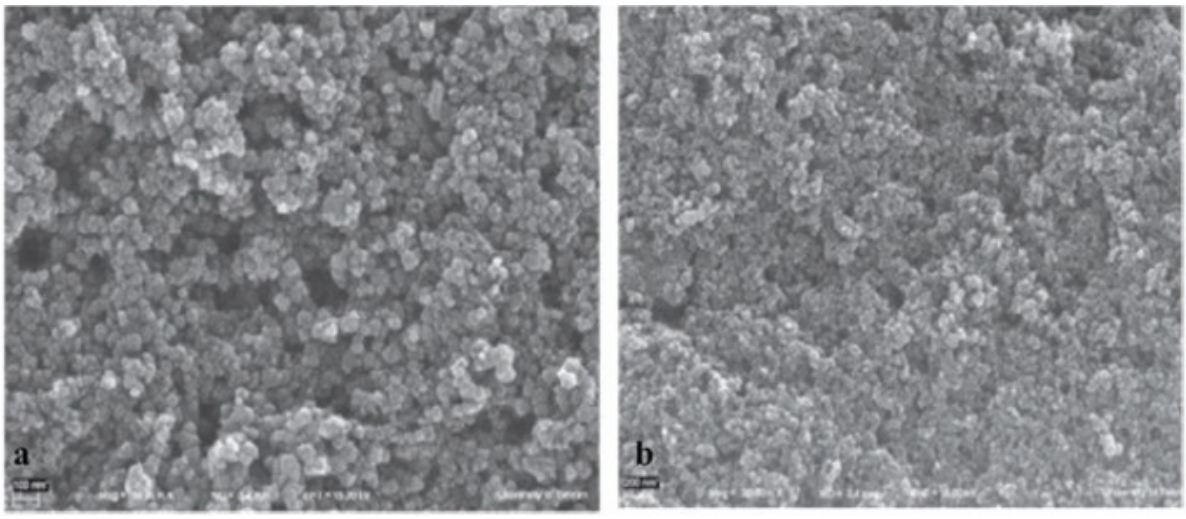


Fig. 1. SEM micrographs of then nZVI: before (a) and after (b) reaction.

existence of an amorphous phase of iron. The characteristic broad peak at 2θ of 45º indicates that the zero valent iron is predominantly present in the sample.

3.2. Effect of initial pH

The pH is an important factor which can have a great impact on sono-catalytic processes. For this purpose, the pH ranges of 3–9 were selected. The relationship between the removal efficiency and initial pH values in sulfonamide solution are shown in Fig. 3. The results showed that with the increase in pH, the efficiency of the process was decreased and higher removal efficiency was observed in acidic condition. Acidic conditions and irradiation of ultrasonic increase concentration of Fe^{2+} that results in increasing the production of OH radicals (Eqs. (15) and (16)) [28,29]:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (15)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (16)$$

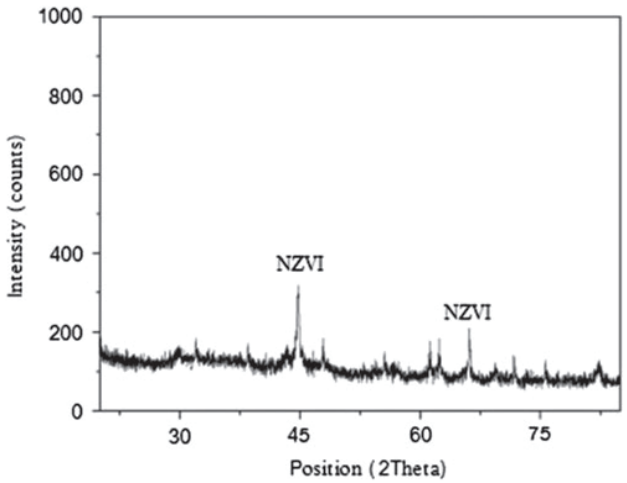


Fig. 2. XRD patterns of synthesized nZVI.

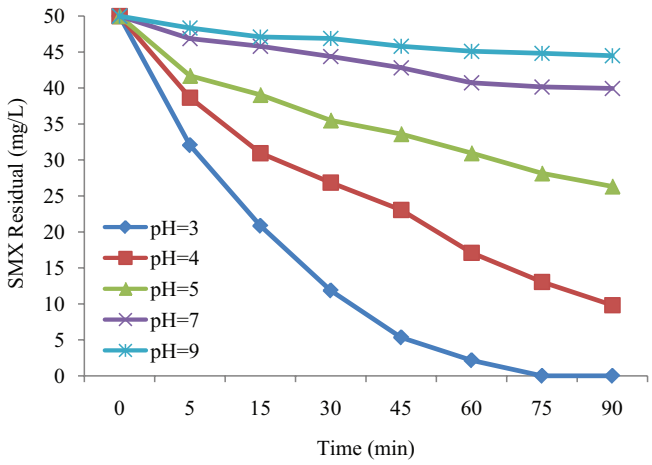


Fig. 3. Effect of reaction time on SMX degradation at different initial pH (experimental conditions: nZVI: 1 g/L, H_2O_2: 50 mM, US: 80 kHz and SMX: 50 mg/l).

On the other hands, in high pH and alkaline environments, destruction of hydrogen peroxide increases, which results in effectively reduction of the oxidation reaction [30–32]. These conditions increase the formation of fe^{3+}-hydroxo complexes, which prevent the production of OH radicals [19]. Similar results can be observed in the study by Fang et al., [24].

3.3. Effects of H_2O_2 concentration

Four concentrations of 10, 30, 50, 100 and 150 mM were used for investigating the effect of H_2O_2 concentration. Results were observed under the condition of pH: 3, nZVI: 1 g/L, US: 80 kHz and SMX: 50 mg/L (Fig. 4). In the H_2O_2 concentrations of 10 to 50 mM, there was an increasing trend in the removal of SMX and optimum removal obtained in the H_2O_2 concentration of 50 mM (95% in 60 min). At H_2O_2 concentrations higher than 50 mM, a significant increase in removal of SMX was not observed. According to Eq. (2), hydrogen peroxide in presence of Fe^0 generates OH radicals. Thus, at lower concentrations of hydrogen peroxide, OH radical's production was reduced and resulted in a less degradation efficiency. But in higher H_2O_2 concentration, •OH may be consumed through several approaches such as scavenging effects of H_2O_2 and recombination of •OH (Eqs. (17) and (18)) [33].

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}OOH + H_2O \quad (17)$$

$${}^{\bullet}OOH + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (18)$$

$$2{}^{\bullet}OH \rightarrow H_2O_2 \quad (19)$$

This can cause a lack of significant increase in the efficiency of the process, due to the negligible activity of produced radicals compared with the OH radical [30,34–36]. To apply this process for degradation of carbamazepine, the amounts of 50, 100, 150 and 200 µL of H_2O_2 were used and the optimum performance was obtained at 100 µL [37].

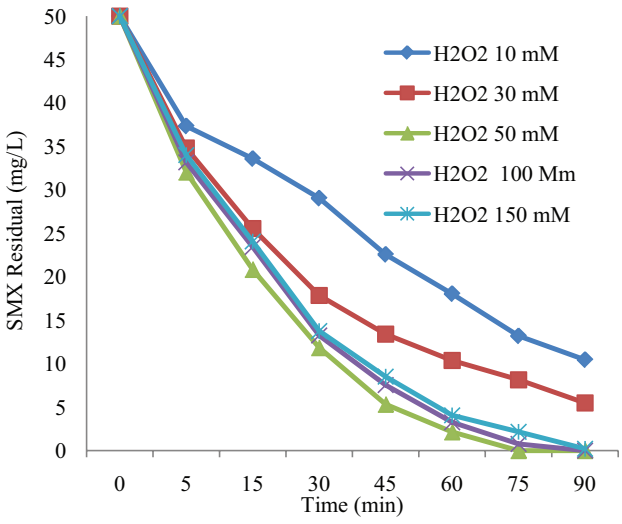


Fig. 4. Effect of reaction time on SMX degradation at the different initial concentration of H_2O_2 (experimental conditions: nZVI: 1 g/L, pH: 3, SMX: 50 mg/l and the US: 80 kHz).

After completion of the reaction time, the remaining hydrogen peroxide in the sample can be destroyed by heating after adjusting with alkalinity [38]. Similar results have been obtained in other studies [39,40].

3.4. Effects of nZVI dose

The effect of nZVI dose is shown in Fig. 5 with optimized conditions of other parameters. The results showed that with increasing in nZVI dosage the removal efficiency was increased, so that in the contact time of 60 min, removal efficiency in the dose of 0.5 g/L nZVI was 50 % and in the dose of 1 g/L was 95 %. At higher concentration of 0.5 g/L, there was no significant increase in removal efficiency. With increasing the doses of iron nanoparticles, the free surface area increases and as a result more active site adsorption orders to degradation of hydrogen peroxide which led to the production of more reactive oxidants such as •OH [35]. Considering that the concentration of hydrogen peroxide is fixed; in higher than the certain concentration of nanoparticles is not observed any increase in the degradation of SMX. As a result, in the higher concentration of nZVI does not appear significant increase in the efficiency of the process. Therefore, the concentration of 1 g/L was considered as the optimal dose of nZVI for these conditions. Similar results can be observed in the study by Zhou et al., [38].

3.5. Effects of ultrasonic irradiation

In order to study the effect of ultrasonic irradiation on the degradation of SMX, degradation experiments were carried out using frequencies of 20, 40 and 80 kHz at a fixed condition (nZVI: 1 g/L, H_2O_2: 50 mM, SMX: 50 mg/L, pH: 3). Also, in this condition, one sample tested without any irradiation. As given in Fig. 6, the results showed that with increasing the frequency, the oxidation rate of sulfonamides was increased. So that, in conditions of without ultrasonic waves, the removal efficiency in the contact time of 60 min was only 31.85%, while at the same time in the frequencies of 20, 40 and 80 kHz, the removal efficiency was about 58%, 63% and 95%, respectively. Ultrasonic waves in the water produce active cavitation bubbles, as a result, OH radicals and hydrogen peroxide are generated. Li et al., (2013) [41] obtained similar results in the removal of trichloroethane by a sono-activated persulfate process. In the study of Eren and Ince, the low frequencies were ineffective at the removal of dyes by ultrasonic irradiation, while high frequencies with more production of OH radicals had a great influence on the oxidation of dyes [42].

3.6. Effects of initial sulfamethoxazole concentration

To investigate the effect of initial SMX concentration in the removal process, four concentrations (5, 25, 50, 100 and 150 mg/L) were used in the constant conditions of nZVI: 1 g/L, H_2O_2: 50 mM, US irradiation: 80 kHz and pH: 3. As seen in Fig 7, with increasing of SMX concentration the degradation

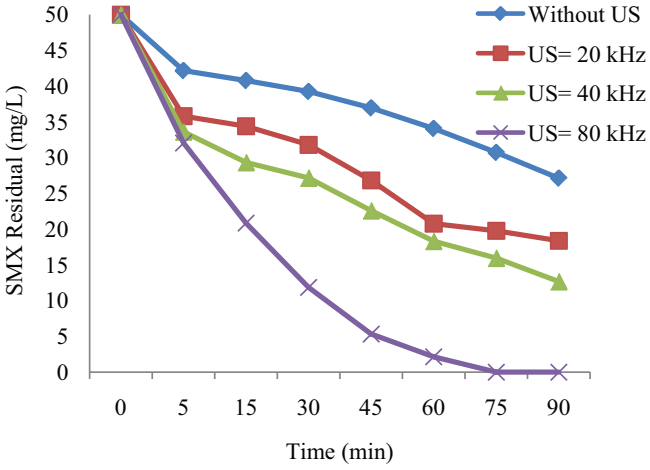


Fig. 6. Effect of reaction time on SMX degradation at the different frequency of US (experimental conditions: nZVI: 1 g/L, H_2O_2: 50 mM, pH: 3 and SMX: 50 mg/l).

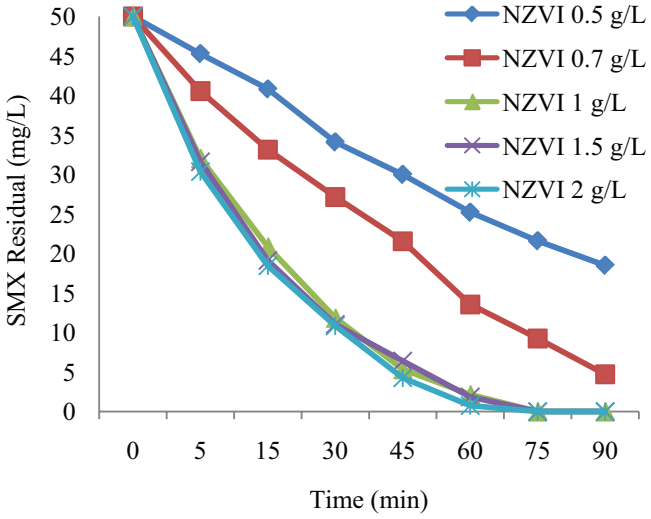


Fig. 5. Effect of reaction time on SMX degradation at the different initial concentration of nZVI (experimental conditions: H_2O_2: 50 mM, pH: 3, SMX: 50 mg/l and the US: 80 kHz).

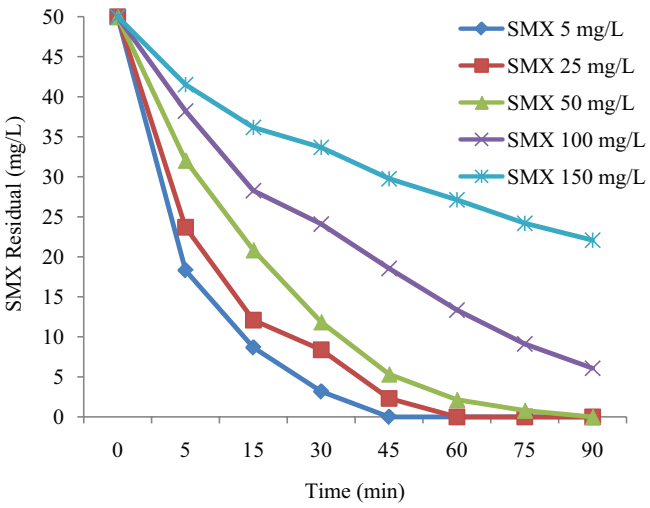


Fig. 7. Effect of reaction time on SMX degradation at the different initial concentration of SMX (experimental conditions: nZVI: 1 g/L, H_2O_2: 50 mM, pH: 3 and US: 80 kHz).

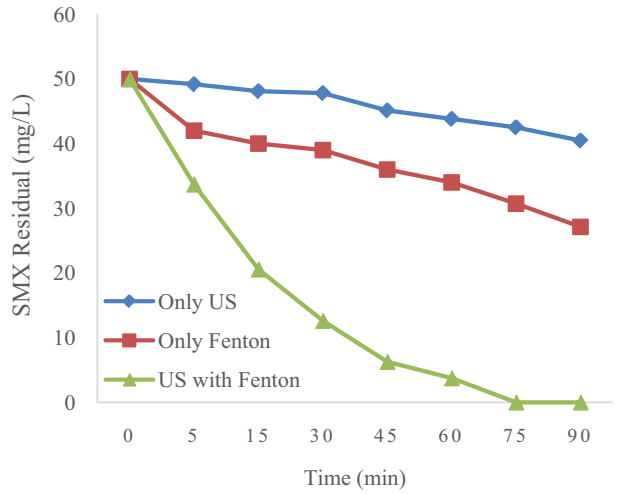


Fig. 8. Comparison of US/nZVI/H_2O_2, nZVI/H_2O_2 and US process in degradation of SMX (experimental conditions: nZVI: 1 g/L, H_2O_2: 50 mM, pH: 3 and US: 80 kHz).

rate decreases. This usually occurred in advanced oxidation processes [43]. With fixing of hydrogen peroxide concentration, nZVI dose and US irradiation, production of radical hydroxyl is fixed. The increase of SMX concentration would decrease the reaction of SMX with radical hydroxyl. The inverse relationship between the removal efficiency and concentration of pollutants can be seen in the studies of the oxidation of dyes. [44–46].

3.7. Comparison of US/Fenton process with Fenton and ultrasonic

To compare the efficiency of the US/Fenton process with Fenton and ultrasonic, a sample containing 50 mg / L of SMX was contacted with each of them in the optimal conditions (pH=3, nZVI=1g/L, US=80 kHz and H_2O_2 =5 mM). At first, the samples containing SMX were contacted with ultrasonic waves alone (80 kHz) and as seen in Fig. 8, the results showed no significant effect on oxidation of SMX, so that at the contact time of 90 min the removal was only 20%. Then, the samples containing SMX were contacted with the Fenton process under the conditions of pH=3 nZVI=1g/L and H_2O_2 =5 mM. The highest efficiency of this process was at 90 min with removal efficiency of about 45%. In the case of the combination of Fenton and ultrasonic methods together, it shows a good performance in the removal of SMX. In the US/Fenton process, the ability to complete the removal of SMX from aqueous solutions was observed at 75 min.

3.8. Kinetics of the reaction

Kinetics reaction for oxidation of SMX by the sono-nano-catalytic process was studied in the concentration of 50 mg/L under the optimized condition of nZVI: 1 g/L, H2O2: 50 mM, pH: 3, US: 80 kHz. As seen in Fig. 9, the results show that the oxidation of SMX by US/nZVI/H2O2 can be expressed by the first-order kinetic model according to the following equation:

$$\ln\frac{C_0}{C} = kt \quad (20)$$

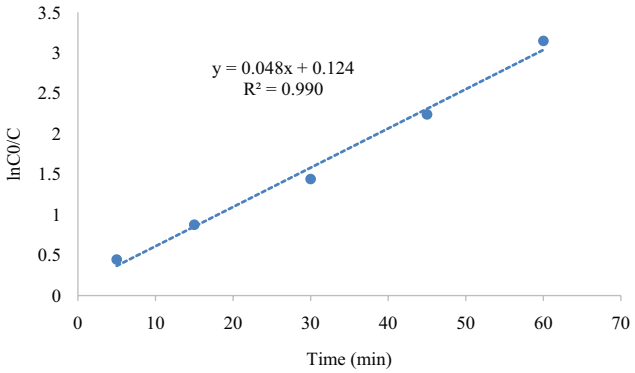


Fig. 9. Kinetic reaction of SMX under optimized conditions (experimental conditions: nZVI: 1 g/L, H_2O_2: 50 mM, pH: 3 and US: 80 kHz).

Table 2
Growth inhibition percentage (GI%) of untreated and treated SMX against six bacterial strains. Values are averages of three replicates ± standard deviation

Microorganism	SMX	
	Un-treated[a]	Treated[b]
E. coli	90.7±0.5	38.5.3±0.1
P. aeroginosa	88.3±0.3	47.8±0.5
S. typhi	89.4±0.1	35.8±0.2
B. subtilis	82.5±0.2	27.9±0.9
S. aureus	91.7±0.6	41.2±0.5
S. pneumoniae	83±0.3	33.9±0.8

[a]GI% in presence of untreated SMX solution (50 mg/L).
[b]GI% in presence of treated SMX solution assisted by nZVI/H_2O_2/US (nZVI: 1g/L, H_2O_2: 50 mM, US: 80 kHz, pH:3).

where C_0 is the initial concentration and C is the concentration at any time, t. The semilogarithmic plots of the SMX concentration vs. time obtained a straight line.

3.9. Microtoxicity study

Potential of different chemical and physical methods for the production of toxic metabolites after treatment of pollutants encourages researchers to evaluate the effects of formed toxic metabolites [47]. The growth Inhibition of standard microbial (for example, Bacillus megaterium, E. coli and Saccaromyces cerevisiae) is one of the most commonly used methods which has developed for such assessments [48]. In this study, 3 gram-positive and 3 gram-negative bacteria were used to evaluate the ability of bacterial growth inhibition of effluent. The results of this test showed that the process is well oxide sulfonamides in water or with the product of intermediate compounds; these compounds are not toxic to the environment (Table 2). This decreasing of inhibition was different for bacterial species tested; so that the highest percentage of inhibition was observed for E. coli as 94.8% and lowest at 82.5% for Bacillus in untreated sulfonamides. Investigations of Cytotoxicity and microtoxicity by Younes et al., (2012) [49] have shown a decreased toxicity in final degraded products. Although the study by Mendes et al.,

(2011) [49, 50] was performed for investigation of the oxidizing dyes by the enzyme, the results showed that the toxicity of some dyes was increased after oxidation.

4. Conclusions

Sono-nanocatalytic degradation of SMX in aqueous solution was investigated by ultrasound/Fe^0/H_2O_2 treatment. The effect of parameters such as pH, radiation intensity, concentration of hydrogen peroxide, nanoparticle dose and concentration of SMX was studied. The results showed that US/Fenton process can oxidize 95% of SMX after 60 min under the optimum condition. Kinetics study indicated that the degradation kinetics of SMX followes the first-order kinetics model. The inhibitory growth bacterial test with using the culture of 3 Gram-positive and 3 Gram-negative bacteria was applied to evaluate the toxicity of the effluent. The Result of toxicity test shown that the ability of inhibitory bacterial growth of SMX decreases after oxidation with Sono-nanocatalytic process. This study showed that the degradation of SMX is strongly accelerated using the ultrasonic irradiation. The concentration of H_2O_2 was one of the most effective parameters in US/Fenton which played an important role in determining of optimal conditions. So that, at a concentration range of 10–150 mM hydrogen peroxide, the optimal concentration was 50 mM.

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