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Oxidative removal of tetracycline by sono Fenton-like oxidation process in aqueous media

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ABSTRACT

In the present study, the removal of tetracycline antibiotic was investigated using the Sono Fenton like oxidation and using magnetic nanoparticles Fe_3O_4 (MNPs) was prepared. By using X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy techniques, we tried to characterize the catalyst. Experimental parameters such as Fe_3O_4 MNP dose, initial solution pH, and H_2O_2 concentration, initial antibiotic concentration, and ultrasonic power were evaluated by one factor at a time method. The maximum removal of tetracycline was under the optimal conditions, including pH = 3, concentration of hydrogen peroxide = 5 mM, catalyst dosage = 500 mg/L, ultrasonic power = 500 watt and reaction time = 120 min. The results showed that TC and TOC removal efficiencies of 88.36% and 32.3%. Furthermore, Fe_3O_4 nanoparticles retained its activity and degradation efficiency remained even after four concessive cycles of use. According to the findings of this study, the advanced ultrasound/Fe_3O_4/H_2O_2 oxidation process has high potency in removing tetracycline antibiotics from aqueous solutions and real hospital wastewater.

Keywords: Ultrasound (US); Fe_3O_4 nanoparticles; Sono Fenton-like oxidation; Tetracycline; Water treatment

1. Introduction

The presence of antibiotics in the environment seriously threatens the health of humans and animals [1]. These compounds are not completely metabolized in the body and are usually transferred to the environment by urine and feces after use, digestion, and metabolism. Tetracycline (TC) is the second most commonly used antibiotic group worldwide in terms of production and usage, and is naturally derived from the fermentation of some fungi or by the use of semi-synthetic drugs, and is frequently used for treating infectious diseases. Absorption of TC is extremely weak, irregular and variable, and non-absorbed TC (50%–80%) is transmitted to urban sewage as non-metabolized compounds, ultimately polluting the environment and resources. In addition, TC has entered the environment and water resources by the sewage of pharmaceutical factories, the removal of unused and expired products, and the leakage of animal and agricultural waste [2–4]. The presence of medicinal compounds in the environment potentially damages the ecosystem and human health, and therefore, an efficient system is required to remove these compounds from aquatic environments [5].

So far, different techniques have been proposed for TC removal, such as adsorption [6,7], electrochemical treatments [8], biological treatments [9,10], and membrane processes [11]. However, their low removal efficiency or high costs often limit their application.

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Advanced oxidation is a major process for the decomposition and removal of hazardous, resistant, and non-biodegradable pollutants in aquatic environments that have been widely used over the last decade and play an important role in water and sewage treatment [2,3,12]. The main mechanism of these processes is based on hydroxyl radical production, in which these radicals are capable of oxidizing many organic compounds quickly and non-selectively [13].

Hydroxyl radical is usually produced by activating oxidants such as hydrogen peroxide and by using heat, ultraviolet (UV) radiation, ultrasonic waves, intermediate metal ions, and high pH [14,15]. Hydroxyl radical is the most reactive compound after fluorine, with a relative oxidation of 2.8, and acts as an initial radical [16].

The Fenton process has been regarded as a highly advanced oxidation process due to its simplicity and high oxidation potential. In a common Fenton reaction, radical hydroxyl and ionic ferric are produced [17,18]. The use of ultrasonic waves is another advanced oxidation technique for the decomposition of chemical compounds that are used alone or in combination with other methods, including Fenton. The ultrasound (US) irradiation technique plays a critical role in the activation and/or decomposition of oxidants (Eq. (1)) [19].

Ultrasonic waves destroy the organic materials based on the production of small bubbles through the cavitation that occurs during the low-pressure section of sound. The high temperature and pressure, which are 2 µs and 200 µm, are caused by the fall and collapse of bubbles, which leads to the pyrolysis of natural materials and the production of highly reactive radicals such as $HO_2^{\bullet}$, $^{\bullet}OH$, and $H^{\bullet}$ (Eqs. (2) and (3)) that are ultimately involved in chain reactions and decomposition of organic materials [20,21].

The sono-Fenton process is a combination of the Fenton process and ultrasonic waves that promote the removal and formation of organic compounds. Therefore, a sono-catalytic process is an efficient process for the removal of bio-decomposable waste materials by using highly activated catalysts [22].

$$H_2O_2 + \text{US wave}\left(f > 20\text{ KHz}\right) \rightarrow 2^{\bullet}OH \tag{1}$$

$$Fe^{3+} + H_2O_2 + \text{US waves} \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \tag{2}$$

$$Fe^{3+} + H_2O + \text{US waves} \rightarrow Fe^{2+} + {}^{\bullet}OH + H^{+} \tag{3}$$

Magnetic nanoparticles (MNPs) increase the rate of hydroxyl radical production due to having octahedral sites in their structure, including iron ions (Fe^{2+}). They are also the most effectual heterogeneous Fenton reagent catalysts. In the Fenton reaction, hydrogen peroxide decomposition and hydroxyl radical production occur by MNPs (Eqs. (4) and (5)). Other benefits of MNPs include their high stability, biocompatibility, and ease of preparation and separation and in-situ application [23,24].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\bullet} + H^{+} \tag{5}$$

The main objective of the present study was to synthesize and determine the characteristics of the magnetic nanoparticle (by using scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDS) techniques) and to investigate the efficiency of the combined processes of ultrasonic waves and hydrogen peroxide and a catalyst for the removal of TC from aqueous environments. The effect of various operational parameters on the removal efficiency of TC by Fe_3O_4 MNPs was also assessed. Moreover, the kinetics of TC removal, as well as the stability and reusability of the catalyst, were evaluated.

2. Materials and methods

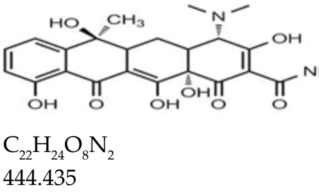
2.1. Materials

Tetracycline hydrochloride [$C_{22}H_{25}N_2O_8Cl$] (AR, 99%), was prepared from Sigma-Aldrich, Agilent. The chemical properties of tetracycline hydrochloride are presented in Table 1 [1]. All the other chemicals were of analytical grade and were utilized without further purification. H_2O_2 (30%), $FeCl_2{\cdot}4H_2O$ (99.9%), $FeCl_3{\cdot}6H_2O$ (98%), H_2SO_4 (98%), NaOH, acetonitrile, and methanol were also purchased from Merck Co., Germany. Catalyst separation was performed using a magnet.

2.2. Preparation and characterization of Fe_3O_4 nanoparticles

MNPs of Fe_3O_4 were synthesized based on a coherent method at room temperature (25°C ± 1°C). To this end, 0.04 mol of iron chloride with six molecules of water ($FeCl_3{\cdot}6H_2O$) and 0.2 mol of iron chloride with four molecules of water ($FeCl_2{\cdot}4H_2O$) were dissolved in 50 mL of normal chloride acid 0.5%. At the same time, 500 mL of 1.5 M sodium hydroxide solutions were added dropwise at 80°C and bubbled through nitrogen gas. After 60 min, the iron nanoparticles were separated by placing an external magnet at the edge of the flask. Finally, the magnetic Fe_3O_4 nanoparticles were washed several times with distilled water and ethanol and dried under vacuum conditions [25]. After preparing the nanoparticles, their physical and structural properties were determined using SEM and EDS electron

Table 1
Chemical properties of tetracycline hydrochloride (TC)

Properties	Tetracycline hydrochloride
Structure	
Chemical formula	$C_{22}H_{24}O_8N_2$
Molecular weight (g/mol)	444.435
λ_{max}	261 nm
Solubility (mol/L)	10 mg/mL

microscopy. EDS and SEM techniques were applied respectively for the determination of the chemical composition and nanostructure of the synthesized nanoparticles. The crystalline phase of the nanoparticles was determined using an X-ray diffractometer (X'Pert MPD, Philips, The Netherlands) employing Cu Ka radiation.

2.3. Sono-Fenton-like oxidation

Laboratory tests were conducted to determine the optimal conditions for the removal of TC at room temperature (25°C ± 1°C). Initially, tetracycline hydrochloride salt was dissolved in distilled water with a purity of >95% ($C_{22}H_{24}N_2O_8 \cdot HCl$). A TC solution (200 mg/L) was prepared weekly and stored in the dark at 4°C. Sulfuric acid ($H_2SO_4 \cdot 1N$) and sodium hydroxide ($NaOH \cdot 1N$) were used with a pH meter (HANNA, Romania) to adjust the pH of the solution. US waves were used by an ultrasonic apparatus with variable power and constant frequency of 60 Hz (Elma, Singen, Germany) at room temperature (25°C ± 1°C). Then, solutions with the desired concentrations were provided in a glass container of 200 mL using a stock solution. In order to determine the effect of independent variables on the dose of MNPs (100, 300, 500, and 1,000 mg/L), hydrogen peroxide (1, 3, 5, 10 mM), contact time (120 min), the initial antibiotic concentration (20, 30, 40, 50, 60 mg/L), and power of ultrasonic waves (100, 300, 500 W) were analyzed on the dependent variable of TC concentration. At the selected time intervals, the catalyst was separated from the solution by a magnet, and residual TC concentration was measured. Prior to analysis by high-performance liquid chromatography (HPLC), the samples were filtered using 0.22 mm syringe filters [26]. Each experimental stage was repeated three times, and the corresponding mean and standard deviation (SD) of the values were used to compute the final results.

2.4. Analytical methods

An HPLC (Agilent 1200 Infinity Series) equipped with a UV detector was employed to measure the concentration of TC in the solution (wavelength of 261 nm). Removal efficiency was determined using Eq. (6).

$$\text{Removal}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{6}$$

where C_0 and C_t are the initial concentrations and the remaining concentration of TC, respectively. Based on total organic carbon (TOC), the mineralization degree was determined using a TOC analyzer (Shimadzu VCHS/CSN, Japan) [27]. In order to assess catalyst stability, the quantity of leached Fe was determined via an atomic absorption spectrophotometer instrument (Analytikjena Vario 6, Germany) [28]. The pH of the solution was measured by a pH meter (HANNA model, Romania). In addition, scales (Shimadzu-Libror model, Japan) were used to weigh the materials.

The chemical characteristics of wastewater samples, such as total suspended solids (TSS), total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and pH were measured based on the standard methods for evaluating water and wastewater [27].

3. Results and discussion

3.1. Characterization of synthesized MNPs

Fe_3O_4 nanoparticles are a strong absorbent for water purification. A magnetic nanoparticle is an iron compound with a cubic structure whose electrical and magnetic properties cause the transfer of Fe^{2+} and Fe^{3+} electrons in its octagonal structure. It also has non-toxic, hydrophilic, chemically stable, and magnetic properties. The Fe_3O_4 magnetic nanoparticle is easily collected using a magnet and can be reused frequently. Fe_3O_4 is an effective catalyst compared to other iron oxides due to Fe^{2+} in its structure, which can increase the rate of hydroxyl radical production [29,30]. In Fig. 1a, the results of the XRD analysis using Cu Ka radiation indicate that the peaks are formed at the angles of 21.2°, 35.1°, 41.4°, 50.6°, 63.2°, 67.4°, and 74.3° according to the 190629-NO, JCPDS (JCPDS – Joint Committee on Powder Diffraction Standards) standard for cubic Fe_3O_4 crystals. Fig. 1b illustrates the SEM images of a nanoparticle with a spherical structure. The average magnetic particle size is about 27.64 nm. Furthermore, the findings of EDS analysis, based on Fig. 1c, revealed only two peaks of Fe (72.15%) and O (20.8%) in the structure of synthesized MNPs, thus confirming its high structural purity.

3.1.1. Effect of dosage of magnetite nanoparticles

One of the most important parameters influencing the yield of the hybrid process is the nanoparticle dosage used in the sono-Fenton-like process. In this study, the effects of magnetic nanoparticle concentrations of 0.1 to 1 g/L were investigated. Fig. 2a depicts the interaction between the dose of the magnetic nanoparticle and the antibiotic removal of TC, which increases with an increase in the dose of nanoparticles from 0.1 to 0.5 g/L of antibiotic decomposition. Lower yields at higher concentrations of nanoparticles (>0.5 g/L) are due to less hydroxyl radical production. Also, the increase of Fe^{2+} ions due to the combination of this ion with hydroxyl radicals and the availability of hydroxyl radicals prevents the removal of antibiotics by the hydroxyl radical [31].

The presence of MNPs in the sono-catalytic process provides nuclei and additional levels for cavitation, which will increase the number of bubbles and radicals. In other words, the presence of nanoparticles leads to an increase in the decomposition of the produced H_2O_2 during the cavitation process, resulting in an increase in free radicals produced in aqueous environments (Eqs. (7)–(9)). The increased removal efficiency as a result of increasing the dose of nanoparticles is probably due to the presence of more active agents at the catalyst level and the possibility of greater contact between antibiotics with Fe_3O_4 nanoparticles [32–34].

The results of a study by Katsumata et al. [33] conducted using the photo-Fenton and ultrasonic process for the decomposition of linuron herbicide, showed that the removal efficiency of the photo-Fenton/ultrasonic process increased by increasing Fe^{2+} concentration from 0.05 to 1 mM; however, after this, the efficiency was reduced. In a study by Zou et al. [34] on antibiotic removal using the Fenton method, it was observed that Fe^{2+} concentration increased the removal efficiency to a specified concentration, and then the efficiency decreased.

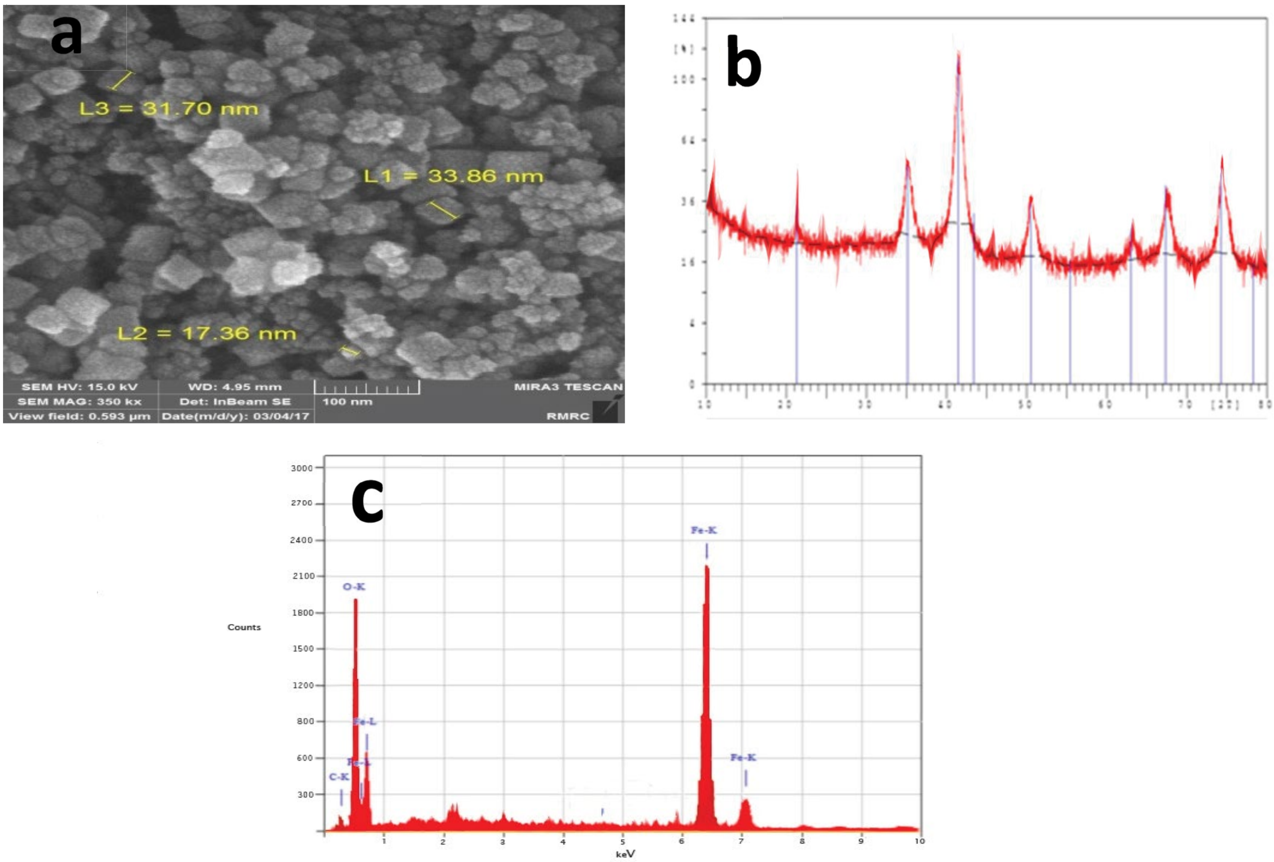


Fig. 1. (a) XRD images of synthesized MNPs, (b) FE-SEM spectrum, and (c) EDS spectrum.

$$Fe^{3+} + H_2O_2 \rightarrow Fe-O_2H^{2+} + H^+ \quad (7)$$

$$Fe-O_2H^{2+} + \text{US waves} \rightarrow Fe^{2+} + {}^{\bullet}OOH \quad (8)$$

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

3.1.2. Effect of initial H_2O_2 concentration

A significant parameter affecting oxidation processes is oxidizing radicals. In the sono-Fenton-like oxidation process, hydrogen peroxide is a source of hydroxyl radical and reacts with iron ions (Fe^{2+}) to produce hydroxyl radical, which has a high oxidation and reduction. As shown in Fig. 2b, increasing the concentration of hydrogen peroxide to a certain extent increases the production of hydroxyl radical and, as a result, enhances process efficiency. In addition, the results revealed that an excessive concentration of hydrogen peroxide would reduce the efficiency of the sono-Fenton-like oxidation process [35]. In fact, the hydrogen peroxide acts as a hydroxyl radical scavenger at high concentrations and will affect the hydroxyl radical concentration. Also, at high concentrations of hydrogen peroxide, two hydroxyl radical molecules react with each other to produce hydrogen peroxide [36,37]. Hydroperoxyl radical ($HO_2^{\bullet}$) is an intermediate substance produced by hydrogen peroxide decomposition when excessive hydrogen peroxide is added (Eq. (10)). This intermediate has a reaction rate and oxidation power less than the hydroxyl radical [38–40].

Monteagudo et al. [41] utilized the photo-Fenton process to purify the sewage of pharmaceutical industries. The results showed that increasing the concentration of hydrogen peroxide to a specific concentration would first increase and then decrease the removal efficiency. Furthermore, Chen et al. [42] studied the use of the photo-Fenton process for the removal of reactive brilliant orange and observed that increasing the concentration of hydrogen peroxide from 0.8 to 1.94 mM increases the process efficiency; after this point, however, the efficiency decreases with increasing the concentration.

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (10)$$

3.1.3. Effect of initial TC concentration

The results of changes in the initial concentration of TC are given in Fig. 2c. At this stage, the antibiotic concentrations (20, 30, 40, 50, and 60 mg/L) were tested, and the efficacy of the removal process was investigated. As shown in Fig. 2c, with increasing TC concentration, the removal efficacy decreases. At the concentration of 20 mg/L of TC,

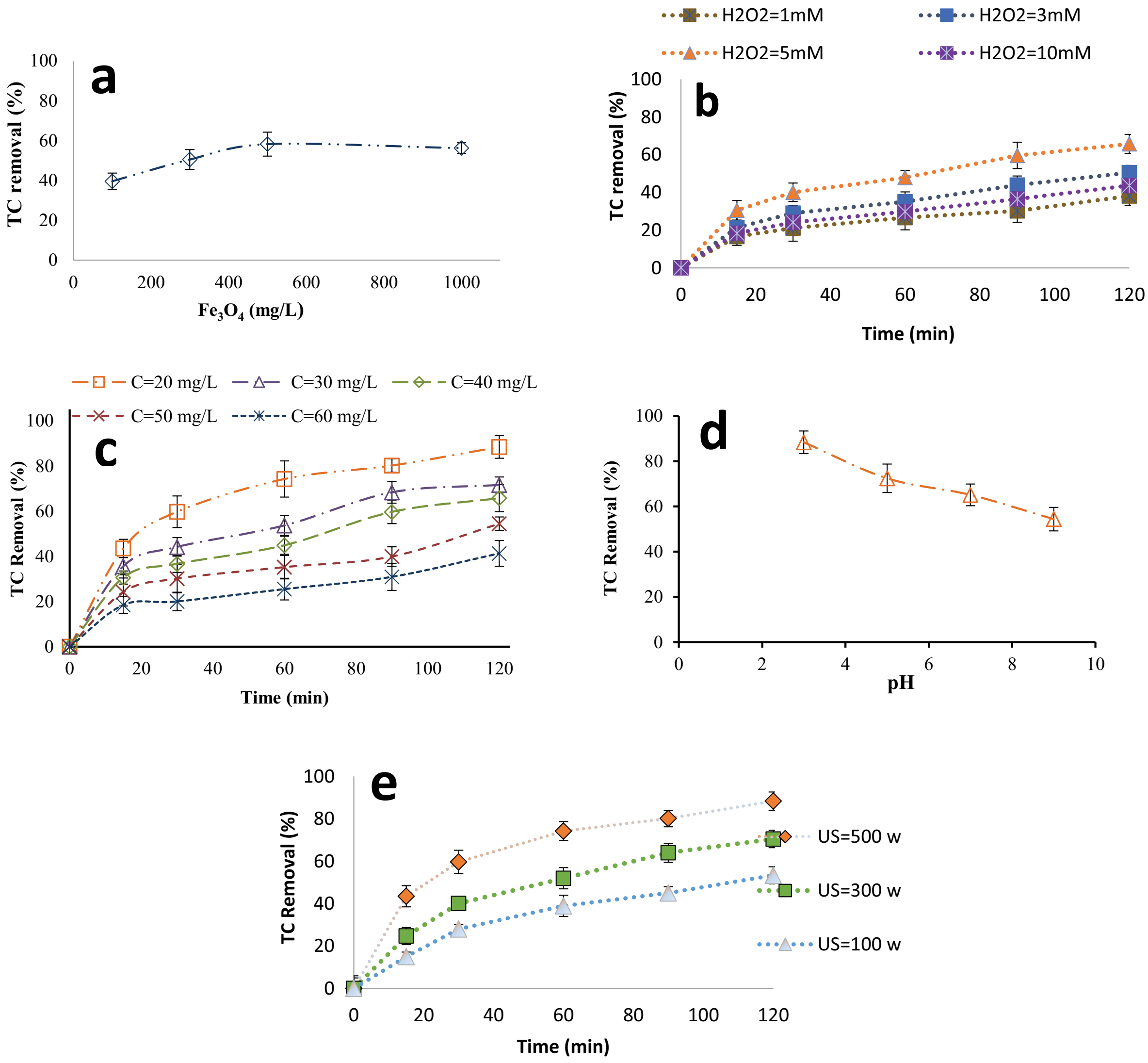


Fig. 2. Effect of experimental parameters on the degradation of TC under conditions contact time of 120 min, $T = 25°C \pm 1°C$, initial pH of 3, H_2O_2 concentration of 3 mM, TC = 40 mg/L, MNPs dosage of 0.5 g/L, US power of 500 W. (a) Effect of catalyst dosage, (b) effect of H_2O_2 concentration, (c) effect of initial TC concentration, (d) effect of pH, and (e) effect of ultrasonic power.

the maximum removal efficiency for 120 min was 88.36%, and with an increase in TC concentration to 60 mg/L, the removal efficiency of the process dropped to 41.48%.

By increasing the number of pollutants, the competitive use of hydroxyl radicals increased with intermediate products, which led to a decrease in removal efficiency [43,44]. Jiao et al. [43] studied TC using UV rays and concluded that decomposition rate depends on the initial concentration of TC; thus, with an increase in the initial concentration of TC, the decomposition rate is significantly decreased.

3.1.4. Effect of initial pH

The results of the effect of pH on the removal of TC are shown in Fig. 2d. Accordingly, the highest efficacy in the removal of TC was at pH = 3, which was equal to 88.36%. The results showed that with increasing the pH of solution samples, the removal efficiency is significantly decreased. Based on the results of previous studies, the initial pH of the solution is one of the most influential environmental factors on the removal of pollutants using chemical processes. In advanced oxidation processes, pH has a direct impact on the durability of hydrogen peroxide, hydroxyl radical production, and the determination of the species and state of the iron present in the solution. An increase in environment pH and the alkaline condition reduce the solubility of Fe, and iron is produced in the form of colloid, which leads to the production of ferric species that can rapidly decompose hydrogen peroxide into oxygen and water. Therefore, a decrease in hydroxyl radical production will decrease removal efficiency [45,46].

It has been reported that the conventional Fenton process has high catalytic activity under acidic conditions with pH in the range of 2–4. At acidic conditions, there are a more dissolved fraction of iron species which could increase the oxidation rate of TC [28].

In the Fenton-like process, at pHs > 5, H_2O_2 rapidly decomposes into water due to the instability of the structure. In addition, an increase in pH leads to a decrease in the potential of hydroxyl radical oxidation, so increasing the pH greatly decreases the efficiency of the Fenton-like process and other processes [28].

In a study conducted by Golash and Gogate [46] to analyze dichlorvos by the sono-Fenton process, it was revealed that this process can remove dichlorvos from the acidic pH up to 100%. Elmolla and Chaudhuri [5] also reported that at a lower pH, hydrogen peroxide was more stable due to the formation of oxonium ions, and that elm ions improved H_2O_2 stability.

3.1.5. Effect of US power

The effect of intensity of US irradiation on TC degradation rate by a US/H_2O_2/Fe_3O_4 system as another effective operational factor was evaluated at the powers of 100, 300, and 500 W at optimal conditions. The TC removal efficiency was significantly decreased upon decreasing ultrasonic irradiation (Fig. 2e). Increasing the ultrasonic power increases the energy of cavitation, decreases the threshold limit of cavitation, and enhances the quality of cavitation bubbles [47].

Based on the maximum removal percentage, 500 W US power was employed as an optimal intensity for further experiments. With an increase in ultrasonic power from 100 to 500 W, the TC degradation rate increased from 53.4% to 88.36%. It is evident that the increase in US intensity to a specific high level promoted the degradation of H_2O_2 and the generation of reactive species, consequently increasing the rate of TC degradation.

3.2. Kinetic studies

The kinetics of the reaction was determined in order to analyze the removal rate of TC at different concentrations and to compare them with each other (Fig. 3). Kinetic reactions are reaction rates. Theoretically, the reaction rate expresses the rate of reactant reduction or the rate of product growth and is proportionate to the concentration of reactive substances that have reached various potentials. Reaction speed is determined by measuring the concentration of the primary material or a product during the completion of the process. There are different degrees of reaction in the sewage treatment process (zero, first-degree, and second-degree). The results of the experiments indicated that the removal of TC at all concentrations follows first-order kinetics. First-order reactions are reactions in which the reaction rate is only a function of the concentration of a substance [48–50]. A study by Safari et al. [51] on TC analysis using a sonochemical process showed that the kinetics of the TC decomposition reaction was first-order.

3.3. Comparison of the efficiency of alternative processes for TC degradation

In order to verify the efficiency of the process of MNPs/H_2O_2/US against the US alone, H_2O_2 alone, MNPs alone, H_2O_2/US, MNPs/US, and MNPs/H_2O_2 processes were tested for TC removal under similar conditions (temperature: 25°C ± 1°C and TC = 20 mg/L) (Fig. 4). The results demonstrated that the use of the US alone and H_2O_2 alone had little effect on TC removal (respectively 4.1% and 7.63%), which could be due to the absence of hydroxyl radical production. Using MNPs alone yielded a 40.2% removal of TC after 120 min, which was mainly due to surface adsorption. However, the US irradiation/H_2O_2 process provided a higher degradation of TC compared with H_2O_2 and US alone (removal efficiency MNPs alone >US/H_2O_2). This can be explained by the dissociation of H_2O_2 (Eq. (1)) by US irradiation, which produced $^\bullet$OH.

In the Fenton-like system (MNPs/H_2O_2) without US irradiation, the degradation efficiency was 60.3% which is a relatively high removal rate and can be ascribed to the intrinsic peroxidase mimetic activity and the reactive surface of MNPs.

The highest removal efficiency was associated with the process of MNPs/H_2O_2/US with a removal efficiency of 88.36%, which is due to the direct effect of the reaction between Fenton factors and ultrasonic waves, which results in the production of very large amounts of hydroxyl

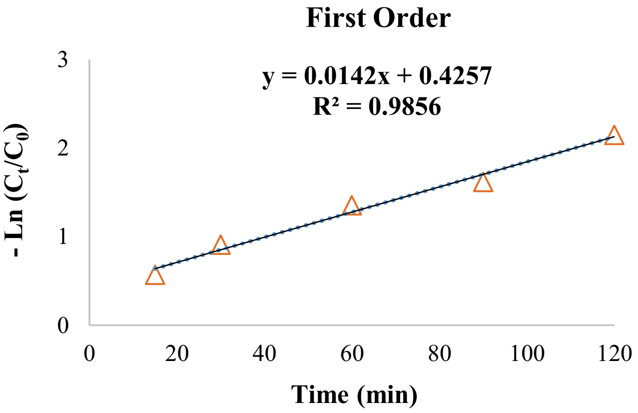


Fig. 3. First-order kinetic model of TC removal in US/MNPs/H_2O_2 process, pH = 3, MNPs dosage of 0.5 g/L, H_2O_2 concentration of 5 mM, TC concentration = 20 mg/L, US power of 500 W, and *T* = 25°C ± 1°C.

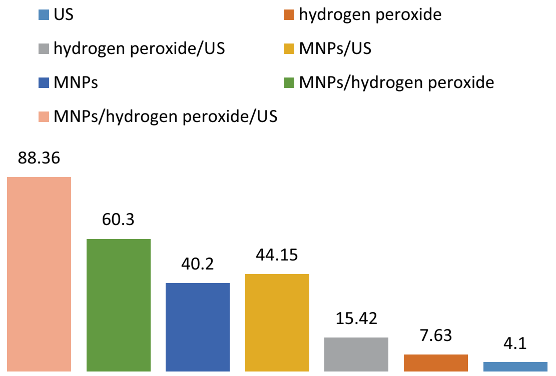


Fig. 4. TC degradation in the different system at pH of 3, MNPs dosage of 0.5 g/L, H_2O_2 concentration of 5 mM, TC concentration of 20 mg/L, US power of 500 W, contact time of 120 min, and *T* = 25°C ± 1°C.

radicals [31]. In the US/MNPs/H_2O_2 process, the active radicals are produced through two simultaneous mechanisms of heterogeneous (MNPs/H_2O_2) and homogeneous (US/H_2O_2) catalysis [52].

Another reason for the high efficiency of the US/MNPs/H_2O_2 system can be the fact that the US irradiation contributed to a synergistic effect on the catalyst surface, H_2O_2 and regeneration of Fe(II) for the effective generation of hydroxyl radical. It is worthwhile to emphasize that US irradiation can clean the surface of MNPs and thus make larger available surface areas for MNPs catalyst.

In a study by Khataee et al. [36] the sono-Fenton-like process on the color of textile industry sewage was performed under optimal conditions (catalyst dosage of 4 g/L, initial dye concentration of 10 mg/L, pH of 5, and US power of 300 W), and achieved a removal efficiency of 93.7% [35].

3.4. Mineralization

The changes of TOC to determine the level of mineralization of TC by the process of US/MNPs/H_2O_2 under optimal conditions (pH = 3, MNPs dosage of 0.5 g/L, H_2O_2 concentration of 5 mM, TC concentration of 20 mg/L, US power of 500 W, and reaction time of 120 min) are shown in Fig. 5. The results showed that with the TC removal of >88%, the TOC removal rate was about 72.1% which indicates that the TC composition during the process is not completely converted to minerals (carbon dioxide and water) [10,53]. Therefore, according to the results of other studies, the advanced oxidation process completely converts the organic compounds into the mineral or converts the organic composition into a structure with the least resistance to biological decomposition [54]. In a study conducted by Bremner et al. [55] on the efficacy of removing 2,4-chlorofenoxy acetic acid by ultrasonic and Fenton processes, the TOC removal efficiency by the ultrasonic process after 60 min was 11%. Nevertheless, when the combined ultrasonic/Fenton process was used, the efficiency increased to 64%.

3.5. Reusability and stability of as-prepared MNPs

Two parameters of recyclability and durability are important for economic evaluation and reusability of the catalyst [56]. To investigate the reusability of the catalyst in the sono-Fenton process, the synthesized MNPs were employed in four oxidation cycles under optimum conditions. After the end of each process, the nanoparticles were collected by a magnet, washed several times with deionized water, and reused [57].

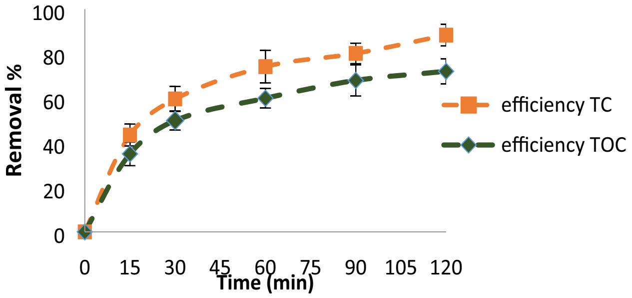


Fig. 5. Mineralization and degradation of TC in US/MNPs/H2O2 system.

Fig. 6 shows that the removal efficiency of TC in the sono-Fenton process was almost unchanged (77.1%) after four re-uses of the catalyst, and decreased by only 11% compared to the first cycle. This decrease in removal efficiency may be due to the loss of part of the mass of the nanoparticle or the difficulty of completely removing the product from the active site of the catalyst during washing and drying. On the other hand, after four times of using the nanoparticles in the cycle, a small amount of Fe^{2+} ion was lost due to the stable physicochemical properties of the synthesized nanoparticles.

Durability tests indicated that the leaching quantity of Iron was negligible (<0.25 mg/L) for all studied cycles, demonstrating a high physicochemical stability for Fe_3O_4 NPs [57]. Because of the excellent performance of MNP regeneration during the sono-Fenton process, it can be concluded that these nanoparticles are cost-effective catalysts for TC removal.

3.6. Effect of radical scavengers on TC removal

Tert-butanol radical is utilized in advanced oxidation processes as a hydroxyl radical trap. It has a high solubility in water and a low absorption rate in the catalysts and reacts rapidly with free hydroxyl radicals [58]. The reaction rate constant of *tert*-butanol with hydroxyl radicals (6×10^8 M^{-1} S^{-1}) is much higher than the reaction rate constant with hydrogen peroxide (2×10^7 M^{-1} S^{-1}), and therefore this compound is a carrier hydroxyl radical [58,59].

Tert-butanol radicals were used to detect hydroxyl radical production in the sono-Fenton process. The results showed that the TC reduction efficiency with *tert*-butanol (1 gr/L) in the sono-Fenton process was 58.2% (Fig. 7). In other words, *tert*-butanol reacts with hydroxyl and reduces the amount of hydroxyl radicals. The results indicated that the Fe_3O_4 NPs catalyzed H_2O_2 to form $^{\bullet}OH$ radicals which were mainly responsible for the degradation of TC.

3.7. Removal of TC from hospital wastewater

To investigate the effect of intervening materials, experiments were conducted under optimal conditions and were

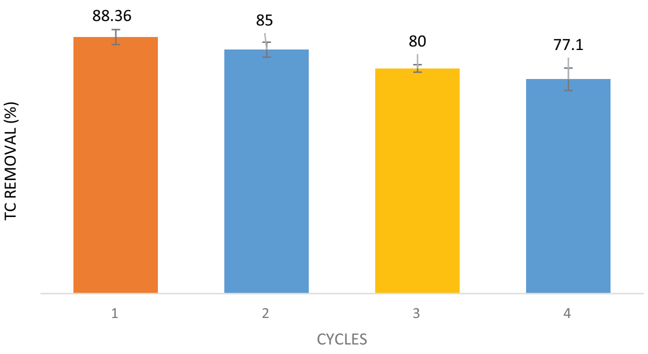


Fig. 6. Reusability of MNPs after four consecutive cycles at pH of 3, MNPs dosage of 0.5 g/L, H_2O_2 concentration of 5 mM, TC concentration of 20 mg/L, US power of 500 W, contact time of 120 min, and *T* = 25°C ± 1°C.

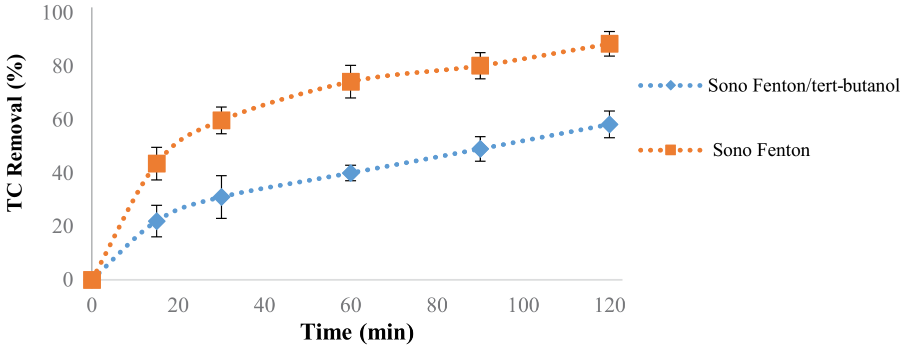


Fig. 7. Effects of OH scavengers (*tert*-butanol) on the degradation of TC at pH of 3, MNPs dosage of 0.5 g/L, H_2O_2 concentration of 5 mM, TC concentration of 20 mg/L, US power of 500 W, contact time of 120 min, and $T = 25°C \pm 1°C$.

repeated using hospital wastewater. The real samples were collected from Kerman Hospital. The features of the raw wastewater according to the hospital report are shown in Table 2. The removal efficiency was then compared with the synthetic condition.

The removal efficiency under optimum conditions (pH: 3, contact time: 120 min, MNP dosage: 0.5 g/L, H_2O_2 dosage: 5 mM, initial concentration of TC: 20 mg/L) was 88.36% for the synthetic samples. TC and TOC removal from hospital wastewater under optimal conditions was 81.29% and 52.6%, respectively. Intervening factors (e.g., TSS and COD) increased turbidity in the solution, which prevented the penetration of U.S. irradiation and decreased the rate of sonocatalytic degradation of the TC. Competitive consumption with organic matter in real wastewater with oxidative species and the occupation of adsorption sites on the surface of the solid catalyst appeared to decrease the degradation efficiency of TC.

4. Conclusion

Fe_3O_4 nanoparticles were synthesized using the co-precipitation method and utilized as a catalyst in a sono-Fenton-like process of TC degradation and real hospital wastewater. Fe_3O_4 nano-catalyst was prepared as an active catalyst to remove TC from aqueous solutions. The optimal conditions for the test were pH: 3, hydrogen peroxide concentration: 5 mM, catalyst concentration: 0.5 g/L, ultrasonic power: 500 W, reaction time: 120 min, and antibiotic concentration of TC: 20 mg/L. A comparison of the ultrasonic, Fenton-like, and sono-Fenton-like processes showed that the combination of sono-Fenton-like has a higher removal efficiency. Fe_3O_4 nanoparticles showed good stability and activity even after four recycles, indicating that the catalyst had a high re-use value. The TOC removal for synthetic wastewater and real hospital wastewater equaled 66.8% and 58.6%, respectively, after 120 min in the same conditions. Additionally, the kinetic analysis, based on the experimental data, suggested that oxidation can be better described by a first-order kinetic model. Therefore, according to the increasing number of antibiotics in aqueous solutions and the existing concerns, this method can be adopted as a new and cost-effective method for purifying environments polluted with medicinal sewage.

Table 2
Chemical and physical characteristics of hospital wastewater

Parameter	Amount
TSS	147 (mg/L)
TDS	512 (mg/L)
pH	7.6
BOD_5	254 (mg/L)
COD	536 (mg/L)

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References

[1] J. Jeong, W. Song, W.J. Cooper, J. Jung, J. Greaves, Degradation of tetracycline antibiotics: mechanisms and kinetic studies for advanced oxidation/reduction processes, Chemosphere, 78 (2010) 533–540.
[2] M.A. Gilliver, M. Bennett, M. Begon, S.M. Hazel, C.A. Hart, Enterobacteria: antibiotic resistance found in wild rodents, Nature, 401 (1999) 233–234.
[3] A.K. Sarmah, M.T. Meyer, A.B. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere, 65 (2006) 725–759.
[4] A.B. Boxall, D.W. Kolpin, B. Halling-Sørensen, J. Tolls, Peer reviewed: are veterinary medicines causing environmental risks?, Environ. Sci. Technol., 37 (2003) 286–296.
[5] E.S. Elmolla, M. Chaudhuri, Comparison of different advanced oxidation processes for treatment of antibiotic aqueous solution, Desalination, 256 (2010) 43–47.
[6] W. Khanday, B. Hameed, Zeolite-hydroxyapatite-activated oil palm ash composite for antibiotic tetracycline adsorption, Fuel, 215 (2018) 499–505.
[7] W. Xiong, G. Zeng, Z. Yang, Y. Zhou, C. Zhang, M. Cheng, Y. Liu, L. Hu, J. Wan, C. Zhou, Adsorption of tetracycline antibiotics from aqueous solutions on nanocomposite multi-walled carbon nanotube functionalized MIL-53 (Fe) as new adsorbent, Sci. Total Environ., 627 (2018) 235–244.
[8] K.N. Parra, S. Gul, J.M. Aquino, D.W. Miwa, A.J. Motheo, Electrochemical degradation of tetracycline in artificial urine medium, J. Solid State Electrochem., 20 (2016) 1001–1009.
[9] H. Xiong, S. Dong, J. Zhang, D. Zhou, B.E. Rittmann, Roles of an easily biodegradable co-substrate in enhancing tetracycline

treatment in an intimately coupled photocatalytic-biological reactor, Water Res., 136 (2018) 75–83.

[10] F. Ferrag-Siagh, F. Fourcade, I. Soutrel, H. Aït-Amar, H. Djelal, A. Amrane, Tetracycline degradation and mineralization by the coupling of an electro-Fenton pretreatment and a biological process, J. Chem. Technol. Biotechnol., 88 (2013) 1380–1386.

[11] N. Prado, J. Ochoa, A. Amrane, Biodegradation by activated sludge and toxicity of tetracycline into a semi-industrial membrane bioreactor, Bioresour. Technol., 100 (2009) 3769–3774.

[12] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance, Environ. Sci. Technol., 36 (2002) 1202–1211.

[13] S. Yang, P. Wang, X. Yang, L. Shan, W. Zhang, X. Shao, R. Niu, Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: persulfate, peroxymonosulfate and hydrogen peroxide, J. Hazard. Mater., 179 (2010) 552–558.

[14] A.A. Babaei, K. Ahmadi, I. Kazeminezhad, S.N. Alavi, A. Takdastan, Synthesis and application of magnetic hydroxyapatite for removal of tetracycline from aqueous solutions, J. Mazandaran Univ. Med. Sci., 26 (2016) 146–159.

[15] J.J. López-Peñalver, M. Sánchez-Polo, C.V. Gómez-Pacheco, J. Rivera-Utrilla, Photo degradation of tetracyclines in aqueous solution by using UV and UV/H_2O_2 oxidation processes, J. Chem. Technol. Biotechnol., 85 (2010) 1325–1333.

[16] E. Yamal-Turbay, E. Jaén, M. Graells, M. Pérez-Moya, Enhanced photo-Fenton process for tetracycline degradation using efficient hydrogen peroxide dosage, J. Photochem. Photobiol., A, 267 (2013) 11–16.

[17] Y. Ghaffari, A. Mahvi, M. Alimohammadi, R. Nabizadeh, A. Mesdaghinia, L. Kazemiza, Evaluation of Fenton process efficiency in removal of tetracycline from synthetic wastewater, J. Mazandaran Univ. Med. Sci., 27 (2017) 291–305.

[18] S. Dehghani, J.A. Jonidi, M. Farzadkia, M. Gholami, Investigation of the efficiency of Fenton's advanced oxidation process in sulfadiazine antibiotic removal from aqueous solutions, Arak Med. Univ. J., 15 (2012) 19–29.

[19] B. Kakavandi, M. Ahmadi, Efficient treatment of saline recalcitrant petrochemical wastewater using heterogeneous UV-assisted sono-Fenton process, Ultrason. Sonochem., 56 (2019) 25–36.

[20] I. Michael, L. Rizzo, C. McArdell, C. Manaia, C. Merlin, T. Schwartz, C. Dagot, D. Fatta-Kassinos, Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: a review, Water Res., 47 (2013) 957–995.

[21] R.J. Emery, M. Papadaki, L.M.F. Dos Santos, D. Mantzavinos, Extent of sonochemical degradation and change of toxicity of a pharmaceutical precursor (triphenylphosphine oxide) in water as a function of treatment conditions, Environ. Int., 31 (2005) 207–211.

[22] O. Acisli, A. Khataee, S. Karaca, A. Karimi, E. Dogan, Combination of ultrasonic and Fenton processes in the presence of magnetite nanostructures prepared by high energy planetary ball mill, Ultrason. Sonochem., 34 (2017) 754–762.

[23] B. Kakavandi, A. Takdastan, S. Pourfadakari, M. Ahmadmoazzam, S. Jorfi, Heterogeneous catalytic degradation of organic compounds using nanoscale zero-valent iron supported on kaolinite: mechanism, kinetic and feasibility studies, J. Taiwan Inst. Chem. Eng., 96 (2019) 329–340.

[24] A.A. Babaei, B. Kakavandi, M. Rafiee, F. Kalantarhormizi, I. Purkaram, E. Ahmadi, S. Esmaeili, Comparative treatment of textile wastewater by adsorption, Fenton, UV-Fenton and US-Fenton using magnetic nanoparticles-functionalized carbon (MNPs@C), J. Ind. Eng. Chem., 56 (2017) 163–174.

[25] J. Wang, S. Zheng, Y. Shao, J. Liu, Z. Xu, D. Zhu, Amino-functionalized Fe_3O_4@SiO_2 core–shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal, J. Colloid Interface Sci., 349 (2010) 293–299.

[26] A.J. Jafari, B. Kakavandi, N. Jaafarzadeh, R.R. Kalantary, M. Ahmadi, A.A. Babaei, Fenton-like catalytic oxidation of tetracycline by AC@Fe_3O_4 as a heterogeneous persulfate activator: adsorption and degradation studies, J. Ind. Eng. Chem., 45 (2017) 323–333.

[27] W.E. Federation, A.P.H. Association, Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), Washington, DC, USA, 2005.

[28] B. Kakavandi, A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei, A. Azari, Application of Fe_3O_4@C catalyzing heterogeneous UV-Fenton system for tetracycline removal with a focus on optimization by a response surface method, J. Photochem. Photobiol., A, 314 (2016) 178–188.

[29] B. Hou, H. Han, S. Jia, H. Zhuang, P. Xu, D. Wang, Heterogeneous electro-Fenton oxidation of catechol catalyzed by nano-Fe_3O_4: kinetics with the Fermi's equation, J. Taiwan Inst. Chem. Eng., 56 (2015) 138–147.

[30] H. Wei, D. Hu, J. Su, K. Li, Intensification of levofloxacin sono-degradation in a US/H_2O_2 system with Fe_3O_4 magnetic nano particles, Chin. J. Chem. Eng., 23 (2015) 296–302.

[31] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, J. Environ. Chem. Eng., 4 (2016) 762–787.

[32] C. Özdemir, M.K. Öden, S. Şahinkaya, D. Güçlü, The sonochemical decolorisation of textile azo dye CI Reactive Orange 127, Color. Technol., 127 (2011) 268–273.

[33] H. Katsumata, T. Kobayashi, S. Kaneco, T. Suzuki, K. Ohta, Degradation of linuron by ultrasound combined with photo-Fenton treatment, Chem. Eng. J., 166 (2011) 468–473.

[34] X. Zou, T. Zhou, J. Mao, X. Wu, Synergistic degradation of antibiotic sulfadiazine in a heterogeneous ultrasound-enhanced Fe^0/persulfate Fenton-like system, Chem. Eng. J., 257 (2014) 36–44.

[35] N. Wang, L. Zhu, M. Wang, D. Wang, H. Tang, Sono-enhanced degradation of dye pollutants with the use of H_2O_2 activated by Fe_3O_4 magnetic nanoparticles as peroxidase mimetic, Ultrason. Sonochem., 17 (2010) 78–83.

[36] A. Khataee, P. Gholami, B. Vahid, Heterogeneous sono-Fenton-like process using nanostructured pyrite prepared by Ar glow discharge plasma for treatment of a textile dye, Ultrason. Sonochem., 29 (2016) 213–225.

[37] M.R. Heidari, R.S. Varma, M. Ahmadian, M. Pourkhosravani, S.N. Asadzadeh, P. Karimi, M. Khatami, Photo-Fenton like catalyst system: activated carbon/$CoFe_2O_4$ nanocomposite for reactive dye removal from textile wastewater, Appl. Sci., 9 (2019) 963.

[38] M. Malakootian, M. Khatami, M. Ahmadian, S.N. Asadzadeh, Biogenic silver nanoparticles/hydrogen peroxide/ozone: efficient degradation of Reactive Blue 19, BioNanoscience, 10 (2019) 1–8.

[39] M. Munoz, Z.M. De Pedro, J.A. Casas, J.J. Rodriguez, Preparation of magnetite-based catalysts and their application in heterogeneous Fenton oxidation–a review, Appl. Catal., B, 176 (2015) 249–265.

[40] Z. Zhang, H. Zheng, Optimization for decolorization of azo dye acid green 20 by ultrasound and H_2O_2 using response surface methodology, J. Hazard. Mater., 172 (2009) 1388–1393.

[41] J. Monteagudo, A. Durán, I. San Martín, Mineralization of wastewater from the pharmaceutical industry containing chloride ions by UV photolysis of H_2O_2/Fe(II) and ultrasonic irradiation, J. Environ. Manage., 141 (2014) 61–69.

[42] Q. Chen, P. Wu, Y. Li, N. Zhu, Z. Dang, Heterogeneous photo-Fenton photo degradation of reactive brilliant orange X-GN over iron-pillared montmorillonite under visible irradiation, J. Hazard. Mater., 168 (2009) 901–908.

[43] S. Jiao, S. Zheng, D. Yin, L. Wang, L. Chen, Aqueous oxytetracycline degradation and the toxicity change of degradation compounds in photo irradiation process, J. Environ. Sci., 20 (2008) 806–813.

[44] M.A. Seid, A.H. Movahedian, p-Chlorophenol oxidation in industrial effluent by ultrasonic/Fenton technology, Water Wastewater, 22 (2011) 43–49.

[45] S. Curteanu, K. Godini, C.G. Piuleac, G. Azarian, A.R. Rahmani, C. Butnariu, Electro-oxidation method applied for activated sludge treatment: experiment and simulation based on supervised machine learning methods, Ind. Eng. Chem. Res., 53 (2014) 4902–4912.

[46] N. Golash, P.R. Gogate, Degradation of dichlorvos containing wastewaters using sonochemical reactors, Ultrason. Sonochem., 19 (2012) 1051–1060.

[47] M. Malakotian, S.N. Asadzadeh, M. Khatami, M. Ahmadian, M.R. Heidari, P. Karimi, N. Firouzeh, R.S. Varma, Protocol encompassing ultrasound/Fe_3O_4 nanoparticles/persulfate for the removal of tetracycline antibiotics from aqueous environments, Clean Technol. Environ. Policy, 21 (2019) 1665–1674.

[48] K. Tyrovola, E. Peroulaki, N.P. Nikolaidis, Modeling of arsenic immobilization by zero valent iron, Eur. J. Soil Biol., 43 (2007) 356–367.

[49] Q. Wang, S. Snyder, J. Kim, H. Choi, Aqueous ethanol modified nanoscale zerovalent iron in bromate reduction: synthesis, characterization, and reactivity, Environ. Sci. Technol., 43 (2009) 3292–3299.

[50] H. Remini, C. Mertz, A. Belbahi, N. Achir, M. Dornier, K. Madani, Degradation kinetic modelling of ascorbic acid and colour intensity in pasteurised blood orange juice during storage, Food Chem., 173 (2015) 665–673.

[51] G.H. Safari, S. Nasseri, A.H. Mahvi, K. Yaghmaeian, R. Nabizadeh, M. Alimohammadi, Optimization of sonochemical degradation of tetracycline in aqueous solution using sono-activated persulfate process, J. Environ. Health Sci. Eng., 13 (2015) 76.

[52] N. Jaafarzadeh, A. Takdastan, S. Jorfi, F. Ghanbari, M. Ahmadi, G. Barzegar, The performance study on ultrasonic/Fe_3O_4/H_2O_2 for degradation of azo dye and real textile wastewater treatment, J. Mol. Liq., 256 (2018) 462–470.

[53] M. Hoseini, G.H. Safari, H. Kamani, J. Jaafari, A. Mahvi, Survey on removal of tetracycline antibiotic from aqueous solutions by nano-sonochemical process and evaluation of the influencing parameters, Iran. J. Health Environ., 8 (2015) 141–152.

[54] T.D. Nguyen, N.H. Phan, M.H. Do, K.T. Ngo, Magnetic Fe_2MO_4 (M:Fe, Mn) activated carbons: fabrication, characterization and heterogeneous Fenton oxidation of methyl orange, J. Hazard. Mater., 185 (2011) 653–661.

[55] D.H. Bremner, S. Di Carlo, A.G. Chakinala, G. Cravotto, Mineralisation of 2,4-dichlorophenoxyacetic acid by acoustic or hydrodynamic cavitation in conjunction with the advanced Fenton process, Ultrason. Sonochem., 15 (2008) 416–419.

[56] N. Jaafarzadeh, B. Kakavandi, A. Takdastan, R.R. Kalantary, M. Azizi, S. Jorfi, Powder activated carbon/Fe_3O_4 hybrid composite as a highly efficient heterogeneous catalyst for Fenton oxidation of tetracycline: degradation mechanism and kinetic, RSC Adv., 5 (2015) 84718–84728.

[57] L. Xu, J. Wang, Fenton-like degradation of 2,4-dichlorophenol using Fe_3O_4 magnetic nanoparticles, Appl. Catal., B, 123 (2012) 117–126.

[58] I. Gültekin, G. Tezcanli-Güyer, N.H. Ince, Sonochemical decay of CI Acid Orange 8: effects of CCl_4 and *t*-butyl alcohol, Ultrason. Sonochem., 16 (2009) 577–581.

[59] F. Chen, S. Xie, X. Huang, X. Qiu, Ionothermal synthesis of Fe_3O_4 magnetic nanoparticles as efficient heterogeneous Fenton-like catalysts for degradation of organic pollutants with H_2O_2, J. Hazard. Mater., 322 (2017) 152–162.