Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.26435

208 (2020) 345–354
December

Biogenic nanosilver – assisted degradation of tetracycline in aqueous solutions via sulfate and hydroxyl radicals

Mohammad Malakootian[a,b], Seyedeh Nastaran Asadzadeh[b,c,*], Mehrdad Khatami[d]

[a]*Environmental Health Engineering Research Center, Kerman University of Medical Sciences, Kerman, Iran, email: m.malakootian@yahoo.com (M. Malakootian)*
[b]*Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Postal Code: 6719851351, Kerman, Iran, Tel. +98 (343) 2315700; Fax: +98 (343) 32315700; email: snasadzadeh3@gmail.com (S.N. Asadzadeh)*
[c]*Student Research Committee, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran*
[d]*Nanobioelectrochemistry Research Center, Bam University of Medical Sciences, Bam, Iran, email: mehrdad7khatami@gmail.com (M. Khatami)*

Received 5 January 2020; Accepted 4 August 2020

ABSTRACT

Tetracycline (TC), a widely used antibiotic in medicine and veterinary system around the world, is a major pollutant. Advanced oxidation processes based on radical sulfate and hydroxyl are widely applied due to the high oxidation potential for the degradation of recalcitrant organic pollutants in aqueous media. Herein, a strategy based on the green-synthesized biogenic nanosilver is described in conjunction with the deployment of peroxymonosulfate (PMS) and hydrogen peroxide which were activated by silver for the remediation of tetracycline in water. The effects of various parameters such as biogenic nanosilver dosage, the varying concentration of PMS and hydrogen peroxide, pH, and initial concentration of antibiotic in TC degradation were investigated; TC removal efficiency was over 85% within 90 min under optimal conditions: 15 mg/L TC, 50 mM PMS, 4 mM Ag nanoparticle, pH = 4, and 80 mM H_2O_2. The degradation of tetracycline in the PMS/H_2O_2/Ag NPs process followed the pseudo-first-kinetics.

Keywords: Tetracycline; Silver nanoparticles; Sulfate radical; Hydroxyl radical

1. Introduction

One of the major problems in today's healthcare system is the widespread administration or consumption of drugs, especially antibiotics which are of particular significance because of microbial resistance [1–4]. They are widely used in medicine and veterinary system to prevent and treat illnesses [5–8]. Antibiotics are introduced into the aquatic environment from various pathways such as agricultural runoff, direct discharge from urban wastewater, etc. [9,10] and thus have enduring effects on the environment [11]; ~30%–90% of antibiotics are not metabolized in the human and animal body and are excreted in the urine and feces as active compounds [12,13].

Tetracyclines (TC) are widely used among antibiotics and comprise oxytetracycline (OTC) tetracycline (TC), cholestracycline (CTC) among a large group of antibiotics used in animal husbandry [14].

The antibiotics and their metabolites have been detected in surface water, groundwater, wastewater, and drinking water at levels ranged from ng/L to µg/L [15]. The average concentration of TC, OTC, and CTC reported in United States surface water were 0.11, 1.34, and 0.15 µg/L, respectively [16,17].

Yazdanbakhsh et al. [4] illustrated that antibiotics were almost intact, and various antibiotics were found in groundwater, surface water, drinking water, and even soil.

---

* Corresponding author.

1944-3994/1944-3986

A study by Chen et al. [14] showed that the concentration of tetracycline in surface and underground waters, soil, liquid fertilizers, and wetlands were 0.15, 86–97, 4, and 3 µg/L, respectively [14]. The main processes of removing the antibiotics from water and wastewater include advanced oxidation processes (AOPs), biological purification of active sludge, membrane processes of microfiltration and ultrafiltration [18], and high-pressure separation technologies such as nanofiltration and reverse osmosis [19]. The use of ion exchange and membrane processes often involves the restoration, replacement, and treatment of produced saline waste [20]. In addition, microbial processes are generally slow and in some cases, in comparison with chemical degradation, are incomplete [21].

AOPs have been developed to degrade hazardous, persistent, and non-degradable organic pollutants in drinking water and industrial effluents [22,23], and most of the AOPs are based on the generation of hydroxyl radicals ($^\bullet OH$) [24,25], often via activation of H_2O_2 by a catalyst such as silver nanoparticles to yield the radical $^\bullet OH$ [26,27]. Sulfate radical ($SO_4^{\bullet-}$) – based AOPs, in which peroxymonosulfate (PMS) is used as an oxidant, has been a recent entry for the degradation of non-biodegradable contaminants [28,29]. PMS can be activated to generate $SO_4^{\bullet-}$ which iso a powerful oxidant that can oxidize most organics in wastewater [30,31].

The two peroxides mentioned above (derived from PMS and H_2O_2) are similar in structure and they all have an O–O bond [32,33]. One hydrogen atom in H_2O_2 is replaced by SO_3 to generate HSO_5^- and two hydrogen atoms in H_2O_2 are replaced by SO_3 to form $S_2O_8^{2-}$ [32]. Due to the influence of SO_3, the O–O bond is lengthened and the bond energy decreases. These peroxides are strong oxidizers, with standard oxidation–reduction potential (E_0) 1.82 V (PMS) and 1.776 V (H_2O_2), respectively [34]. They all possess limited ability to oxidize organics independently [33] but under metal (Ag^+, Fe^{2+}, Cu^+, etc.) activation conditions, these peroxides can generate free radicals $SO_4^{\bullet-}$ and $^\bullet OH$ [35–37].

Sulfate radicals are usually produced by the activation of oxidants such as PMS (HSO_5^-) or oxone (oxone, HSO_5^-) and a proxy dicarboxylic acid (PDS, $S_2O_8^{2-}$) or persulfate [PS ($S_2O_8^{2-}$)] with heat, ultraviolet radiation, ultrasonic waves, or deployment of catalysts (intermediate metal ions such as Fe^{2+}, Ag^+, etc.) at elevated pH [30,38–41].

Oxone or PMS is an asymmetric oxidant and, as a result, activates into radical hydroxyl and sulfate (Eqs. (1) and (2)) [41].

$$HSO_5^- \rightarrow SO_4^{\bullet-} + {}^\bullet OH \qquad (1)$$

$$SO_4^- + H_2O \rightarrow SO_4^{2-} + OH + H \qquad (2)$$

Silver nanoparticles are one of the intermediates, which, as a catalyst, transfer electrons through the process of decomposing oxone and hydrogen peroxide and producing sulfate and hydroxyl radicals [42,43]. They are uniquely suitable in view of size, optical structure, catalytic features, and electron-bearing properties [44].

The present study was undertaken for use of oxone as a source of sulfate radical and hydrogen peroxide as a source of hydroxyl radical and metal cations (silver) as an activator in the decomposition and removal of tetracycline antibiotics from aqueous environments.

Both these peroxides have a limited ability to oxidize organic compounds by themselves, but in presence of an activator, they can produce radicals that have the potential for oxidation and reduction; most of the organic pollutants could be oxidized and hence useful in water and wastewater treatment.

Hence, the main goal of this study was the assessment of tetracycline (TC) antibiotic removal from aqueous solution by Ag NPs/H_2O_2/PMS process. At first, nanoparticles were simply synthesized and their properties were determined. Influential factors, including pH, catalyst dosage, PMS concentration, and H_2O_2 concentration on antibiotic removal, were investigated next. The ideal goal of each chemical process for the elimination of organic compounds is the oxidation of parent molecule to its mineral compounds. Hence, chemical oxygen demand (COD) has been often determined for this purpose. In this way, COD removal was investigated to study the degree of mineralization.

2. Materials and methods

This experimental study was conducted at room temperature (23°C–26°C). All experiments were performed in a 500 mL reactor on 300 mL of synthetic wastewater containing various concentrations of tetracycline antibiotic with a purity of more than 95% using sulfate and hydroxyl radicals generated by the PMS/H_2O_2/Ag NPs process.

2.1. Materials

All chemicals in this study were of analytical grade and used without any further purification. All solutions were prepared with deionized water. Sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2, 30%), and sulfuric acid (H_2SO_4, 98%) were obtained from Merck and Co. Oxone ($2\ KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) was purchased from Sigma Inc., as the source of PMS. TC hydrochloride [$C_{22}H_{25}N_2O_8Cl$] (AR, 99%), was secured from Sigma–Aldrich. Chemical properties of TC hydrochloride are shown in Table 1 [14].

Table 1
Chemical properties of TC hydrochloride

Molecule	TC
Molecular weight (g/mol)	$C_{22}H_{24}O_8N_2$ HCl
Formula	480.9
Solubility (mol/L)	0.041
pKa1	3.2 ± 0.3
pKa2	7.78 ± 0.05
pKa3	9.6 ± 0.3

2.2. Greener synthesis and characterization of Ag nanoparticles

First, 10 g of rose petals were weighed using a sensitive scale (Keran and Gumby, D-72336) and washed twice with sterile deionized water to remove dust from the petals surface. Then they were added to the Erlenmeyer dishes containing 100 cc of boiling deionized water. The samples were boiled for 10 min and then cooled slowly to room temperature. Finally, the sample was filtered and petals were discarded and the supernatant was filtered using Whatman paper No. 40 to separate any insoluble particles. The filtered rose petal extract was used to synthesize silver nanoparticles.

2.3. Biosynthesis of silver nanoparticles

First, 50 mL of stock solution 0.1 mol of silver nitrate was prepared. One milliliter of silver nitrate was added to 25 mL of extracts. The reaction mixture (plant extract + silver nitrate) was stored in the dark and kept at 30°C.

2.4. Review of physical and chemical properties of nanoparticles

The absorbance of the sample was investigated using UV-visible spectrophotometry (Analytic Gena, Germany) at a wavelength between 200 and 700 nm. To determine the shape, distribution, and size of nanoparticles obtained from rose petals extract, a spectroscopic analysis was performed. To this end, a small drop of nanosilver suspension was added on a thin sheet of copper and dried at room temperature with no heat. The sample was then studied using an electron microscope (LEO912-AB LEO). To investigate the crystalline structure of the particles, 100 mL of silver nanoparticles suspension was centrifuged with a circle of 18,000 for 20 min (LADNET, America). Then the upper phase was removed and the deionized water was added to the depositional nanoparticles up to the previous volume (100 mL), which was repeated two times. Finally, the remaining sediments were analyzed after drying by X-ray diffraction (PAN analytical, XPERTPRO, and Holland).

2.5. Experiments procedure

In experimental studies, different doses of silver nanoparticles were added to the reactor, then varying amounts of the oxone and hydrogen peroxide were added to the system and the pH of the solution was adjusted by sulfuric acid. The reactor was then sampled and analyzed on a shaker at a speed of 200 rpm with specified intervals. A spectrophotometer with a wavelength of 261 nm was used to measure tetracycline and it was analyzed as soon as it was sampled. The experiments were repeated two times.

At first, the antibiotic tetracycline solution (500 mg/L) was prepared weekly and stored at 4°C.

Then, solutions of the desired concentration were made from an existing stock solution. Based on studies, the effects of silver nanoparticles (1, 2, 4, and 6 mM) and then PMS (2, 10, 20, 50, and 80 mM), H_2O_2 concentration (10, 30, 50, and 80 mM), TC concentration (15, 30, 45, and 60 mg/L), pH (4, 7, and 10), and finally mineralization at 90 min of contact were analyzed.

To determine the effect of hydroxyl and sulfate radicals, *tert*-butyl alcohol and methanol were used at a concentration of 1 g/L. Data was collected from different stages of the experiment and the results were analyzed using Excel software. For the TC removal efficiency, the following formula was used (Eq. (3)) [25].

$$\left(C_0 - \frac{C_e}{C_0}\right) \times 100 = R \tag{3}$$

where C_0 and C_e are the initial and final concentrations of tetracycline in mg/L, respectively. In order to evaluate the kinetic model, tetracycline was analyzed under optimum conditions (0–90 min).

2.6. Analytical methods

The pH of the solution was determined by a pH meter (Hanna Instruments, Japan). A UV spectrophotometer (Shimadzu, Japan) was used to measure the TC concentration in solution at $\lambda_{\max} = 261$ nm.

3. Results and discussion

3.1. Characterization of Ag NPs

Most of the chemical and physical processes that are normally used to synthesize nanoparticles require the use of harmful chemical compounds for the environment and humans and require the use of expensive equipment with possible high energy consumption. These methods can have irreparable risks to human health and the environment. The synthesis methods presented in this study, using rose petals (biological resources) in the production of stable nanoparticles, thus avoiding harmful methods. Developing this approach is a step towards greener chemistry and decreasing the use of harmful compounds and energy consumption in the process of producing nanoparticles.

Observing the color change of the reaction mixture of rose petals extract from a light cream to a reddish-brown is the first indication of the presence of silver nanoparticles in the sample (Fig. 1); visible sign with the naked eye can follow the synthesis of nanoparticles. The absorption peak in the sample blends at a range of 4,450 nm represents the synthesis of silver nanoparticles; observed absorption peak corresponds to the surface plasmon vibration (SPR) of the silver nanoparticles.

Transmission electron microscopy (TEM) images indicate that the synthesized silver nanoparticles using rose petals were less than 50 nm in size. The synthesis of silver nanoparticles is associated with a four-absorption peak at angels of 38, 44, 64, and 77 and crystalline plates of 111, 200, 220, and 311, respectively. These spectra confirm the existence of crystal silver in the reaction mixture. Observed crystalline plates indicate the presence of silver nanocrystals, which are crystallized in the structure of FCC (cubic crystalline cell centers) (Fig. 2).

3.2. Effects of important parameters on degradation of TC in Ag NPs/H_2O_2/PMS system

3.2.1. Effect of Ag NPs dosage

The effect of different concentrations of silver nanoparticles on tetracycline degradation was investigated and the results are shown in Fig. 3a. Increasing the concentration of silver nanoparticles has a positive effect on the efficiency of the removal due to the production of

Fig. 1. Color change of the extract after the formation of Ag NPs.

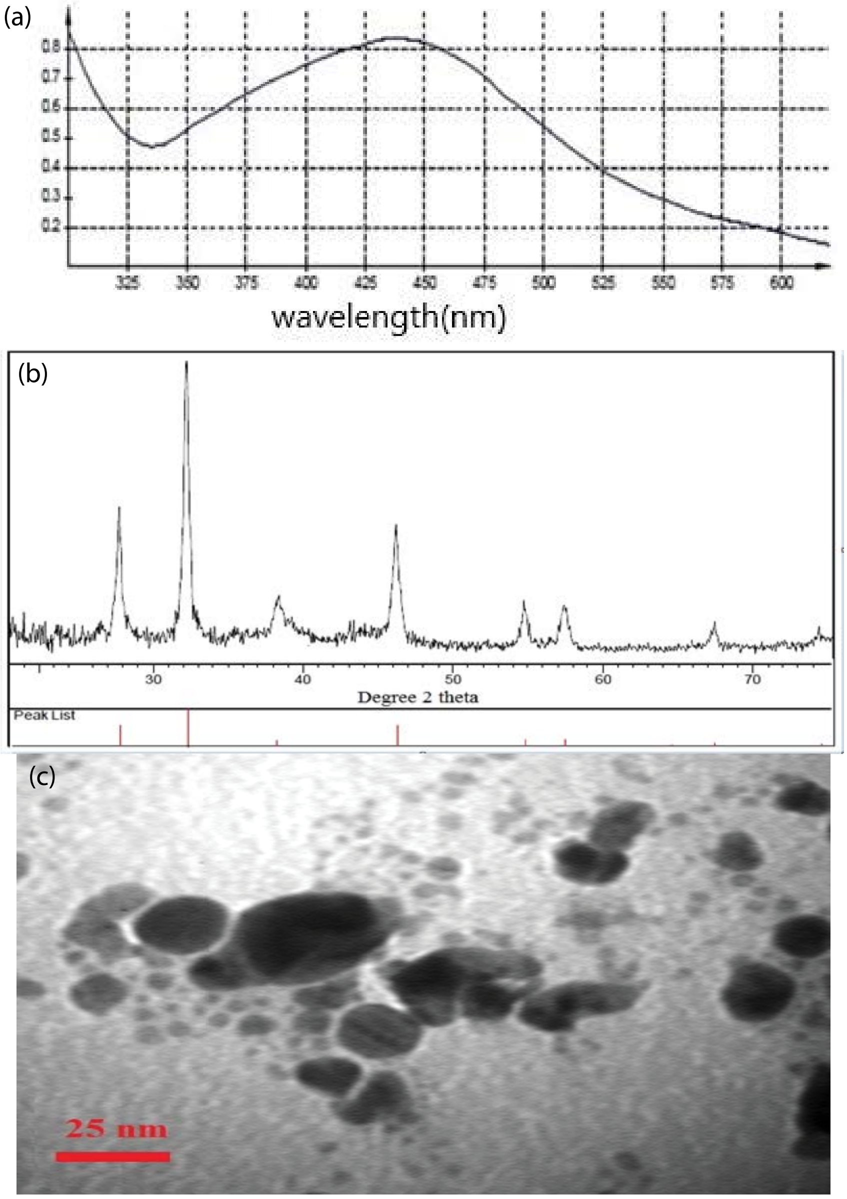

Fig. 2. Characterizations of the Ag nanoparticles (a) UV-vis absorption spectrum, (b) X-ray diffraction pattern, and (c) TEM images of the greener synthesized Ag NPs.

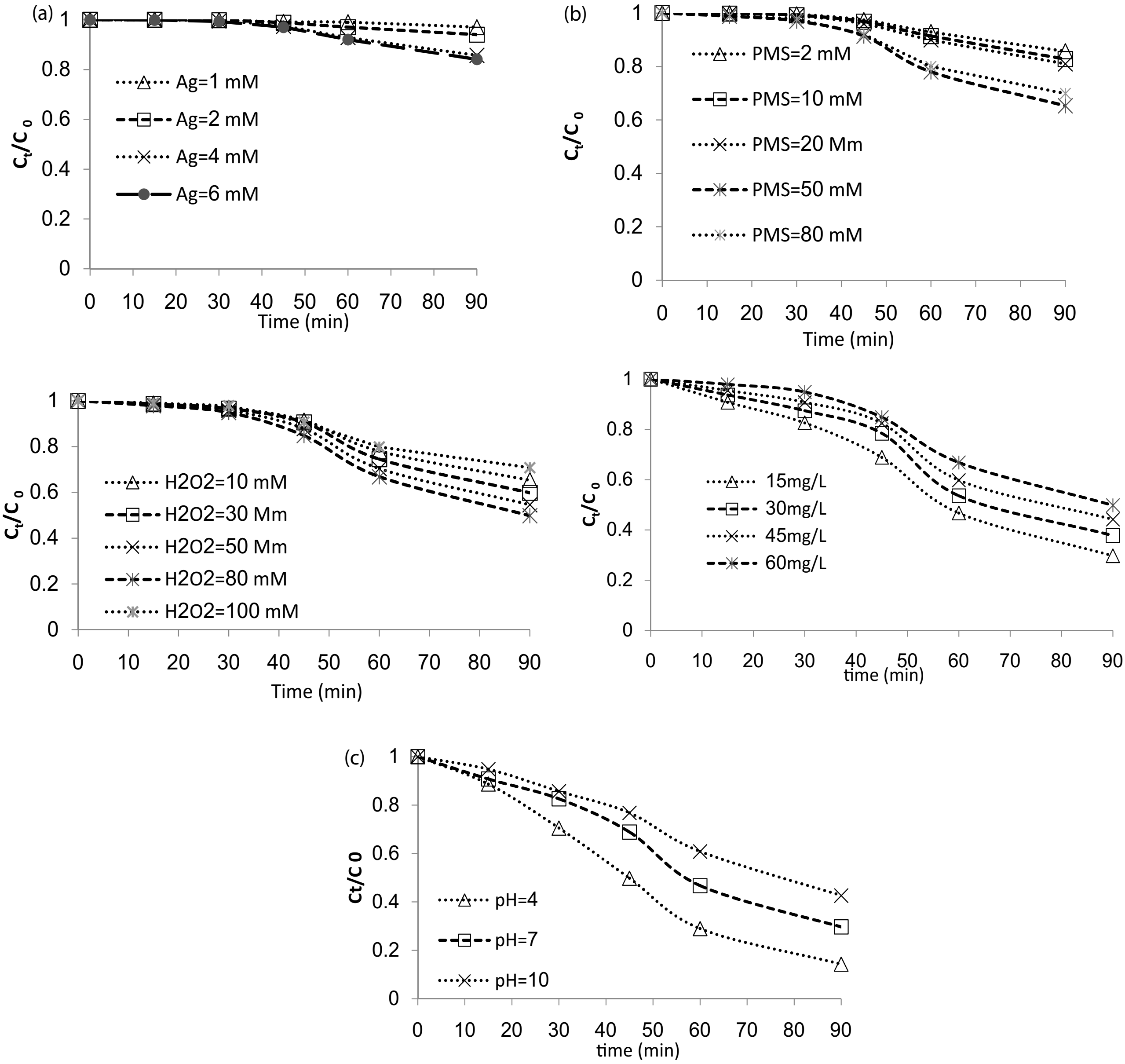

Fig. 3. Tetracycline degradation performance of the PMS/H_2O_2/Ag NPs system: (a) effect of Ag NPs dosage, (b) effect of PMS dosage, (c) effect of the H_2O_2 dosage, (d) effect of initial TC concentration, and (e) effect of pH solution conditions: Ag NPs = 0.15 mM, H_2O_2 = 80 mM, PMS = 20 mM, 15 mg/L TC; ambient temperature if not labeled).

more radical sulfate and hydroxyl as a result of the activation by silver nanoparticles; increased concentration of silver nanoparticles up to 4 mM causes a significant increase in the removal efficiency of tetracycline. At concentrations higher than 4 mM, the removal efficiency of tetracycline increases with a very small slope [45].

In a study by Eslami et al. [46] on the removal of tetracycline using the PS/US/Ag NPs process at various concentrations of silver sulfate from 0 to 6.5 mM, an optimal concentration of 3.5 mM was obtained. The addition of silver up to certain limits increases the activation of persulfates and the production of sulfate radicals and further eliminate tetracycline antibiotics.

3.2.2. Effect of PMS dosage

The effects of different concentrations of oxone from 2 to 80 mM on tetracycline degradation were investigated and the results are depicted in Fig. 3b. The increase of the concentration of oxone to 50 mM, the removal efficiency of tetracycline increases, but with the further increase in its concentration, the removal efficiency of tetracycline decreases. In fact, by increasing the concentration of the oxone, more sulfate radicals are produced, which enhances the efficiency of the tetracycline removal, but an increase in the concentration of the oxone has a negative effect on the efficiency of the removal process, which is due to two reasons: (1) higher concentrations of oxone causes the reaction sulfate radicals with each other according to Eq. (4) [47].

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8 + SO_4^{2-} \quad (4)$$

(2) controlling sulfate radicals by HSO_5^- and the formation of less active radicals of SO_5^- according to Eq. (5) [47].

$$HSO_5^- + SO_4^{\bullet-} \rightarrow SO_5^- + SO_4^{2-} + H^+ \quad (5)$$

In the related study for tetracycline remediation by Eslami et al. [46] was conducted via an enhanced sonochemical process with radical sulfate, TC degradation rates increased with the increase of the concentration of PS, varying from 71% to 83% for PS concentration of 2 and 70 mM, respectively [46].

Also, previous studies have shown that persulfate has a more optimal effect on the removal efficiency of pollutants, which may be due to the production of sulfate anions instead of radical sulfate and the reaction of radicals with each other radicals before their reaction with organics [48].

3.2.3. Effect of H_2O_2 dosage

In AOPs based on the presence of catalysts, the addition of hydrogen peroxide as a producer of free hydroxyl radicals in the suspension often results in an increase in catalytic proportions. In order to maintain the performance of added H_2O_2, it is appropriate to choose the H_2O_2 concentration according to the type and concentration of contaminants. Fig. 3c shows the efficiency of the removal of tetracycline against the concentration of hydrogen peroxide; the removal efficiency at all initial concentrations of tetracycline increases with increasing hydrogen peroxide concentration up to 80 mM, and then decreases. In other words, the higher amount of hydrogen peroxide has a deterrent effect on the production of hydroxyl radicals which reduces the efficiency of removal.

This can be attributed to the excessive reaction of H_2O_2 with $OH^\bullet$ according to the following reactions (Eqs. (6) and (7)) and the formation of HO_2, which, compared to the free radical of hydroxyl, has little or no radical scavenging oxidizing power [49–52].

$$H_2O_2 + H^+ \rightarrow H^+ + HO_2^\bullet \quad (6)$$

$$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O \quad (7)$$

In AOPs, the oxidation concentration is a major contributor to the degradation of organic matter. In Kakavandi et al. [53] study on the removal of tetracycline, an increase in H_2O_2 concentration from 1 to 5 mM led to an increased removal efficiency. The most degradation was obtained at a concentration of 5 mM H_2O_2.

3.2.4. Effect of initial TC concentration

The effect of the initial concentration of tetracycline on the process efficiency was also studied. The concentration of tetracycline was different at four concentrations of 15, 30, 45, and 60 mg/L in the solution. As shown in Fig. 3d, the process efficiency decreased at a higher concentration of the pollutant.

Since hydroxyl and sulfate radicals production remains constant in steady-state, it will be consumed by the increased amount of pollutants in the existing radical environment, and at higher concentrations of pollutants [54].

At higher concentrations of tetracycline, the probability of collision between the molecules of tetracycline and radicals is decreased. In addition, the intermediate products comprising tetracycline mineralization compete with the main pollutants in reaction with radical sulfate. Therefore, the process efficiency is decreased by the higher initial concentration of tetracycline [55].

At high concentrations, with the increase in antibiotics, there is the possibility of intermediate-competition with primary molecules, and this interference increases because of large amounts of intermediates (at high initial concentrations).

3.2.5. Effect of initial pH

To evaluate the effect of solution pH on the degradation of tetracycline antibiotic, pH values of 4, 7, and 10 were adjusted with hydrochloric acid and sodium hydroxide; pH level affects the production of hydroxyl and sulfate radicals and hence the oxidation efficiency. As shown in Fig. 3e, the degradation rate of tetracycline is increased at lower pH. The low removal efficiency at high pH can be due to different reasons, including (1) decreasing the radicals of sulfate by radical hydroxyl at higher pHs according to Eq. (8) [56].

$$SO_4^{\bullet-} + {}^\bullet OH \rightarrow HSO_4^- + 0.5O_2 \quad (8)$$

(2) the conversion of radical sulfate to radical hydroxyl with a lower oxidation potential in alkaline conditions according to Eq. (9) [57].

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^\bullet OH + H^+ \quad (9)$$

(3) the oxidizing properties of hydrogen peroxide are strongly decreased in alkaline pH range and converted to water [58]; AOPs in acidic environments will perform better than alkaline environments [59,60]. Also, an increase in the removal rate of tetracycline in acidic conditions can be attributed to the fact that tetracycline molecules have a positive charge under acidic conditions in a negative-charge bubble fluid interfacial; the concentration of active radicals and temperature is higher, and therefore, a higher removal rate occurs [61,62].

3.3. Mineralization of TC

The COD removal rate was evaluated under optimal conditions at 90 min after completion of the reaction (Fig. 4). The results of COD analysis showed that in the remediation of tetracycline antibiotic using the PMS/H_2O_2/Ag NPs process, the mineralization rate was about 50.2% after the

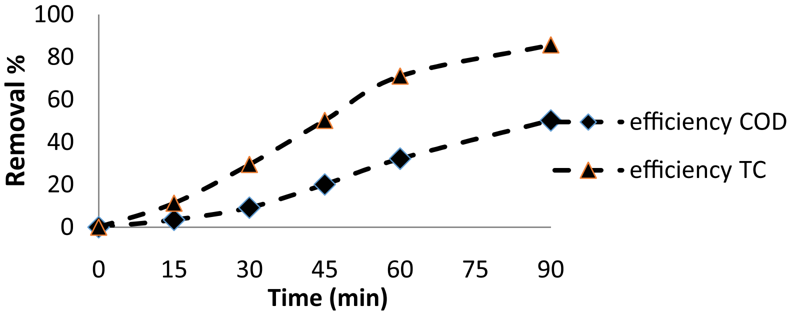

Fig. 4. COD removals from TC degradation (15 mg/L TC, 20 mM PMS, 0.15 Ag and pH = 4, and 80 mM H_2O_2)

end of the reaction. The results of COD removal under optimal conditions showed that the removal rate of COD was lower than the removal efficiency of tetracycline antibiotics. In fact, during the oxidation process, parts of the tetracycline antibiotic have not been fully decomposed, and as organic products have reduced the COD removal efficiency in comparison with the antibiotic removal efficiency. In other words, some antibiotics do not completely mineralize into the expected inorganic compounds of H_2O and CO_2, but to organic sub-products [63,64].

The higher the amount of contaminated mineralization, the lower the environmental hazard of wastewater drainage.

3.4. Degradation mechanism

The kinetic models including zero, first degree, and second-order-kinetics were investigated, and the results are presented in Fig. 5. The kinetics of tetracycline degradation is followed by a pseudo-first-kinetic, and the constant of the reaction speed is under optimal conditions (Eq. (10)). The criterion for choosing the most suitable and consistent model is the linear regression coefficient [65].

$$\text{Ln}\left(\frac{C_t}{C_0}\right) = -k_t \tag{10}$$

In this equation, C_t and C_0 are the concentration of tetracycline antibiotic at time t and time zero, and k is the reaction speed constant (1/min). Other studies that investigated the removal of tetracycline by using the AOP process behaved similarly. In a study, Oturan et al. [66] found to eliminate tetracycline using the electrochemical process and the destruction of TC follow pseudo-first-kinetics. In another study by Kakavandi et al. [53], the destruction of tetracycline by the UV-Fenton process followed the first-order-kinetics as well.

3.5. Comparison of various processes

The results of the comparative efficiency of tetracycline removal by Ag alone, PMS alone, H_2O_2 alone, and PMS/H_2O_2/Ag NPs processes under optimal conditions are secured (15 mg/L TC, 50 mM PMS, 4 mM Ag nanoparticle, pH = 4, and 80 mM H_2O_2) and depicted in Fig. 6. As the results indicate, the efficiency of removing tetracycline by the PMS/H_2O_2/Ag NPs hybrid process is higher than the Ag, PMS, and H_2O_2 processes alone. The removal efficiency for PMS from the H_2O_2 process is more than the silver nanoparticle process alone (Fig. 6) and are in the order

$$\text{PMS} / H_2O_2 / \text{Ag NPs} > \text{PMS} > H_2O_2 > \text{Ag NPs} \tag{11}$$

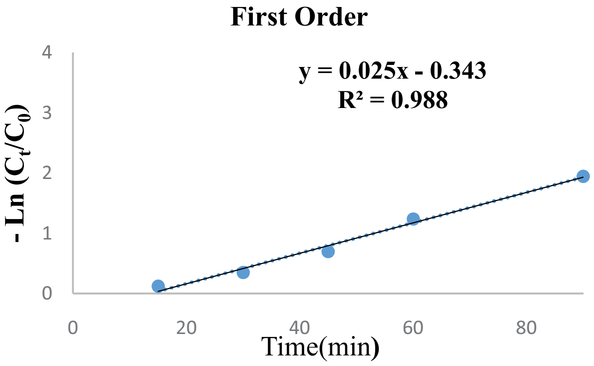

Fig. 5. First-order-kinetic model of TC removal in PMS/H_2O_2/Ag NPs system under condition: Ag NPs = 0.15 mM, H_2O_2 = 80 mM, PMS = 20 mM, and 15 mg/L TC.

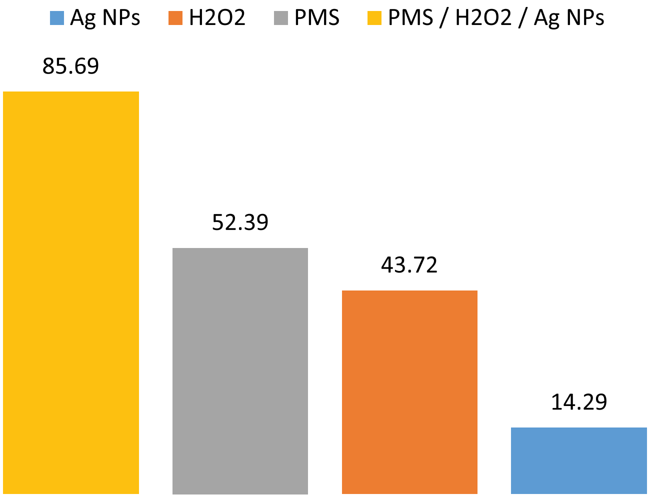

Fig. 6. Comparing different processes in optimal conditions (Ag NPs = 4 mM, H_2O_2 = 80 mM, PMS = 50 mM, 15 mg/L TC, and pH = 4).

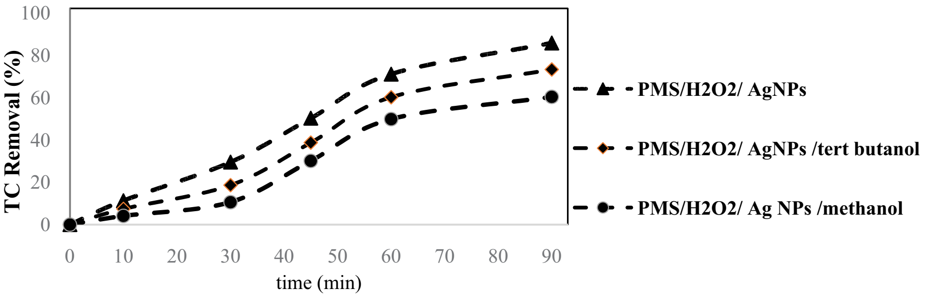

Fig. 7. Effect of radical scavenger on the TC removal efficiency in PMS/H_2O_2/Ag NPs system under condition: Ag NPs = 4 mM, H_2O_2 = 80 mM, PMS = 50 mM, 15 mg/L TC, and pH: 4.

3.6. Effect of radical scavenger on the average removal efficiency

To detect hydroxyl and sulfate radical production in the PMS/H_2O_2/Ag NPs process, *tert*-butanol alcohol (TBA) and methanol radicals scavenger were deployed. Methanol can scavenge both $^{\bullet}OH$ and $SO_4^{\bullet -}$ owing to both high reactivity toward two radicals resulting from the α-H in the alcohol molecular, whereas TBA is a quenching agent mainly effective for $^{\bullet}OH$ ($3.8–7.6 \times 10^8$/M/s) rather than $SO_4^{\bullet -}$ ($4.0–9.1 \times 10^5$/M/s).

It was noted that the reduction in the efficiency of tetracycline removal by *tert*-butanol, and methanol after the end of the reaction was 73.18% and 60.28% (Fig. 7). This compound is widely used in AOPs as a radical scavenger to determine the role of radical hydroxyl; *tertiary*-butanol has a high solubility in water and low absorption rates on catalysts and it reacts rapidly with free radicals of hydroxyl. Decreasing the efficiency of the removal of tetracycline in the PMS/H_2O_2/Ag NPs process by *tert*-butanol, suggests that hydroxyl and sulfate radicals play a major role in eliminating the tetracycline [43].

4. Conclusions

The results from this study revealed that the advanced technology based on oxidation by radical sulfate and hydroxyl to remove contaminants in aquatic environments is affected by several factors such as catalyst concentration (4 mM), oxidizing concentrations (oxone 50 mM and hydrogen peroxide 80 mM) and pH: 4, 15 mg/L initial concentration of contaminant and 90 min contact time. The study showed that the process is capable of decomposing and degrading recalcitrant organic pollutants such as tetracycline antibiotics from aqueous environments. In addition, this process can be deployed to remove antibiotics of the similar structure or enhance their biodegradability.

Acknowledgments

The authors express their gratitude for the support and assistance extended by the facilitators during the research.

References

[1] J. Zhang, L. Giorno, E. Drioli, Study of a hybrid process combining PACs and membrane operations for antibiotic wastewater treatment, Desalination, 194 (2006) 101–107.

[2] A.Y.-C. Lin, T.-H. Yu, C.-F. Lin, Pharmaceutical contamination in residential, industrial, and agricultural waste streams: risk to aqueous environments in Taiwan, Chemosphere, 74 (2008) 131–141.

[3] S.N. Muchohi, N. Thuo, J. Karisa, A. Muturi, G.O. Kokwaro, K. Maitland, Determination of ciprofloxacin in human plasma using high-performance liquid chromatography coupled with fluorescence detection: application to a population pharmacokinetics study in children with severe malnutrition, J. Chromatogr. B, 879 (2011) 146–152.

[4] A.R. Yazdanbakhsh, M. Manshouri, A. Sheikhmohammadi, M. Sardar, Investigation the efficiency of combined coagulation and advanced oxidation by fenton process in the removal of clarithromycin antibiotic COD, Water Wastewater, 23 (2012) 22–29.

[5] E. Zuccato, S. Castiglioni, R. Bagnati, M. Melis, R. Fanelli, Source, occurrence and fate of antibiotics in the Italian aquatic environment, J. Hazard. Mater., 179 (2010) 1042–1048.

[6] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters, Water Res., 41 (2007) 1013–1021.

[7] S. Kurwadkar, V. Sicking, B. Lambert, A. McFarland, F. Mitchell, Preliminary studies on occurrence of monensin antibiotic in Bosque River Watershed, J. Environ. Sci., 25 (2013) 268–273.

[8] A. Murata, H. Takada, K. Mutoh, H. Hosoda, A. Harada, N. Nakada, Nationwide monitoring of selected antibiotics: distribution and sources of sulfonamides, trimethoprim, and macrolides in Japanese rivers, Sci. Total Environ., 409 (2011) 5305–5312.

[9] 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.

[10] Y. Kitazono, I. Ihara, G. Yoshida, K. Toyoda, K. Umetsu, Selective degradation of tetracycline antibiotics present in raw milk by electrochemical method, J. Hazard. Mater., 243 (2012) 112–116.

[11] M. Hadi, R. Shokoohi, A. Ebrahimzadeh Namvar, M. Karimi, M. Solaimany Aminabad, Antibiotic resistance of isolated bacteria from urban and hospital wastewaters in Hamadan City, Iran. J. Health Saf. Environ., 4 (2011) 105–114.

[12] A. Sheikhmohammadi, M. Sardar, The removal of penicillin G from aqueous solutions using chestnut shell modified with H_2SO_4: isotherm and kinetic study, Iran. J. Health Environ., 2013 (2013) 497–508.

[13] J. Muhammad, S. Khan, J.Q. Su, A.E.-L. Hesham, A. Ditta, J. Nawab, A. Ali, Antibiotics in poultry manure and their associated health issues: a systematic review, J. Soils Sediments, 20 (2020) 486–497.

[14] H. Chen, H. Luo, Y. Lan, T. Dong, B. Hu, Y. Wang, Removal of tetracycline from aqueous solutions using polyvinylpyrrolidone (PVP-K30) modified nanoscale zero valent iron, J. Hazard. Mater., 192 (2011) 44–53.

[15] L. Tong, P. Li, Y. Wang, K. Zhu, Analysis of veterinary antibiotic residues in swine wastewater and environmental water samples

using optimized SPE-LC/MS/MS, Chemosphere, 74 (2009) 1090–1097.
[16] G. Safari, M. Hoseini, M. Seyedsalehi, H. Kamani, J. Jaafari, A. Mahvi, Photocatalytic degradation of tetracycline using nanosized titanium dioxide in aqueous solution, Int. J. Environ. Sci. Technol., 12 (2015) 603–616.
[17] R. Daghrir, P. Drogui, Tetracycline antibiotics in the environment: a review, Environ. Chem. Lett., 11 (2013) 209–227.
[18] E. Sahar, R. Messalem, H. Cikurel, A. Aharoni, A. Brenner, M. Godehardt, M. Jekel, M. Ernst, Fate of antibiotics in activated sludge followed by ultrafiltration (CAS-UF) and in a membrane bioreactor (MBR), Water Res., 45 (2011) 4827–4836.
[19] K. Košutić, D. Dolar, D. Ašperger, B. Kunst, Removal of antibiotics from a model wastewater by RO/NF membranes, Sep. Purif. Technol., 53 (2007) 244–249.
[20] W.L. Ang, A.W. Mohammad, N. Hilal, C.P. Leo, A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants, Desalination, 363 (2015) 2–18.
[21] M.A. Zazouli, R. Dianatitilaki, M. Safarpour, Nitrate removal from water by nano zero valent iron in the presence and absence of ultraviolet light, J. Mazandaran Univ. Med. Sci., 24 (2014) 151–161.
[22] S. Sharma, J. Ruparelia, M.L. Patel, A General Review on Advanced Oxidation Processes for Waste Water Treatment, Vol. 481, Institute of Technology, Nirma University, Ahmedabad, 2011, pp. 08–10.
[23] M. Oturan, OP3, Electrochemical Advanced Oxidation Processes for Efficient Removal of Persistent Organic Micropollutants from Wastewater. Application to Elimination of Pharmaceutical Pollutants, The Jubilee Conference on Applied Chemistry, 2011.
[24] Y. Deng, R. Zhao, Advanced oxidation processes (AOPs) in wastewater treatment, Curr. Pollut. Rep., 1 (2015) 167–176.
[25] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: a review, Chem. Eng. J., 284 (2016) 582–598.
[26] R.T. Paulsen, D.S. Kilin, Silver nanoparticles for catalysis of hydrogen peroxide decomposition: atomistic modeling, MRS Online Proc. Lib. Arch., 1787 (2015) 21–25.
[27] M.A Bhosale, B.M Bhanage, Silver nanoparticles: synthesis, characterization and their application as a sustainable catalyst for organic transformations, Curr. Org. Chem., 19 (2015) 708–727.
[28] J. Sharma, I. Mishra, D.D. Dionysiou, V. Kumar, Oxidative removal of Bisphenol A by UV-C/peroxymonosulfate (PMS): kinetics, influence of co-existing chemicals and degradation pathway, Chem. Eng. J., 276 (2015) 193–204.
[29] Y.-H. Guan, J. Ma, Y.-M. Ren, Y.-L. Liu, J.-Y. Xiao, L.-q. Lin, C. Zhang, Efficient degradation of atrazine by magnetic porous copper ferrite catalyzed peroxymonosulfate oxidation via the formation of hydroxyl and sulfate radicals, Water Res., 47 (2013) 5431–5438.
[30] F. Ghanbari, M. Moradi, Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants, Chem. Eng. J., 310 (2017) 41–62.
[31] Y. Rao, F. Han, Q. Chen, D. Wang, D. Xue, H. Wang, S. Pu, Efficient degradation of diclofenac by $LaFeO_3$-catalyzed peroxymonosulfate oxidation-kinetics and toxicity assessment, Chemosphere, 218 (2019) 299–307.
[32] Y. Liu, Y. Wang, Gaseous elemental mercury removal using combined metal ions and heat activated peroxymonosulfate/H_2O_2 solutions, AIChE J., 65 (2019) 161–174.
[33] S. Esmaeili, M. Dehvari, A. Babaei, Degradation of Acid Orange 7 dye with PMS and H_2O_2 activated by $CoFe_2O_4$/PAC nanocomposite, Arch. Hyg. Sci., 8 (2019) 35–45.
[34] A.B. Kurukutla, P.S.S. Kumar, S. Anandan, T. Sivasankar, Sonochemical degradation of rhodamine b using oxidants, hydrogen peroxide/peroxydisulfate/peroxymonosulfate, with Fe^{2+} ion: proposed pathway and kinetics, Environ. Eng. Sci., 32 (2015) 129–140.
[35] J. Wang, S. Wang, Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants, Chem. Eng. J., 334 (2018) 1502–1517.
[36] Y. Feng, J. Liu, D. Wu, Z. Zhou, Y. Deng, T. Zhang, K. Shih, Efficient degradation of sulfamethazine with $CuCo_2O_4$ spinel nanocatalysts for peroxymonosulfate activation, Chem. Eng. J., 280 (2015) 514–524.
[37] Y. Wang, X. Zhao, D. Cao, Y. Wang, Y. Zhu, Peroxymonosulfate enhanced visible light photocatalytic degradation bisphenol A by single-atom dispersed Ag mesoporous g-C_3N_4 hybrid, Appl. Catal., B, 211 (2017) 79–88.
[38] M.M. Ahmed, S. Barbati, P. Doumenq, S. Chiron, Sulfate radical anion oxidation of diclofenac and sulfamethoxazole for water decontamination, Chem. Eng. J., 197 (2012) 440–447.
[39] Y.-q. Gao, N.-y. Gao, Y. Deng, Y.-q. Yang, Y. Ma, Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water, Chem. Eng. J., 195 (2012) 248–253.
[40] R. Xiao, Z. Luo, Z. Wei, S. Luo, R. Spinney, W. Yang, D.D. Dionysiou, Activation of peroxymonosulfate/persulfate by nanomaterials for sulfate radical-based advanced oxidation technologies, Curr. Opin. Chem. Eng., 19 (2018) 51–58.
[41] C. Qi, X. Liu, J. Ma, C. Lin, X. Li, H. Zhang, Activation of peroxymonosulfate by base: implications for the degradation of organic pollutants, Chemosphere, 151 (2016) 280–288.
[42] C. Zhang, Z. Hu, P. Li, S. Gajaraj, Governing factors affecting the impacts of silver nanoparticles on wastewater treatment, Sci. Total Environ., 572 (2016) 852–873.
[43] Y.-Y. Ahn, E.-T. Yun, J.-W. Seo, C. Lee, S.H. Kim, J.-H. Kim, J. Lee, Activation of peroxymonosulfate by surface-loaded noble metal nanoparticles for oxidative degradation of organic compounds, Environ. Sci. Technol., 50 (2016) 10187–10197.
[44] V. Thamilselvi, K. Radha, A review on the diverse application of silver nanoparticle, IOSR J. Pharm., 7 (2017) 21–27.
[45] L. Hou, H. Zhang, X. Xue, Ultrasound enhanced heterogeneous activation of peroxydisulfate by magnetite catalyst for the degradation of tetracycline in water, Sep. Purif. Technol., 84 (2012) 147–152.
[46] A. Eslami, H. Bahrami, A. Asadi, A. Alinejad, Enhanced sonochemical degradation of tetracycline by sulfate radicals, Water Sci. Technol., 73 (2016) 1293–1300.
[47] B. Li, L. Li, K. Lin, W. Zhang, S. Lu, Q. Luo, Removal of 1, 1, 1-trichloroethane from aqueous solution by a sono-activated persulfate process, Ultrason. Sonochem., 20 (2013) 855–863.
[48] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int., 35 (2009) 402–417.
[49] E.S. Elmolla, M. Chaudhuri, Comparison of different advanced oxidation processes for treatment of antibiotic aqueous solution, Desalination, 256 (2010) 43–47.
[50] V. Homem, L. Santos, Degradation and removal methods of antibiotics from aqueous matrices–a review, J. Environ. Manage., 92 (2011) 2304–2347.
[51] 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.
[52] 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.
[53] 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.
[54] R. Lindberg, P.-Å. Jarnheimer, B. Olsen, M. Johansson, M. Tysklind, Determination of antibiotic substances in hospital sewage water using solid phase extraction and liquid chromatography/mass spectrometry and group analogue internal standards, Chemosphere, 57 (2004) 1479–1488.
[55] F. Rivas, O. Gimeno, T. Borallho, Aqueous pharmaceutical compounds removal by potassium monopersulfate. Uncatalyzed

and catalyzed semicontinuous experiments, Chem. Eng. J., 192 (2012) 326–333.

[56] F. Ghanbari, M. Moradi, F. Gohari, Degradation of 2, 4, 6-trichlorophenol in aqueous solutions using peroxymonosulfate/activated carbon/UV process via sulfate and hydroxyl radicals, J. Water Process Eng., 9 (2016) 22–28.

[57] P. Nfodzo, H. Choi, Triclosan decomposition by sulfate radicals: effects of oxidant and metal doses, Chem. Eng. J., 174 (2011) 629–634.

[58] S. Parsons, Advanced Oxidation Processes for Water and Wastewater Treatment, IWA Publishing, London, 2004.

[59] A.H. Lau, N.P. Lam, S.C. Piscitelli, L. Wilkes, L.H. Danziger, Clinical pharmacokinetics of metronidazole and other nitroimidazole anti-infectives, Clin. Pharmacokinet., 23 (1992) 328–364.

[60] B. Dhandapani, S. Rasheed, P. Ramakrishna, A. Pradesh, Method development and validation for the simultaneous estimation of ofloxacin and ornidazole in tablet dosage form by RP-HPLC, Int. J. Pharma Sci. Res., 1 (2010) 78–83.

[61] M. Hoseini, G.H. Safari, H. Kamani, J. Jaafari, M. Ghanbarain, A.H. Mahvi, Sonocatalytic degradation of tetracycline antibiotic in aqueous solution by sonocatalysis, Toxicol. Environ. Chem., 95 (2013) 1680–1689.

[62] E. De Bel, J. Dewulf, B. De Witte, H. Van Langenhove, C. Janssen, Influence of pH on the sonolysis of ciprofloxacin: biodegradability, ecotoxicity and antibiotic activity of its degradation products, Chemosphere, 77 (2009) 291–295.

[63] 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.

[64] I.R. Bautitz, R.F.P. Nogueira, Degradation of tetracycline by photo-Fenton process—solar irradiation and matrix effects, J. Photochem. Photobiol., A, 187 (2007) 33–39.

[65] L. Yu, Z. Ye, J. Li, C. Ma, C. Ma, X. Liu, H. Wang, L. Tang, P. Huo, Y. Yan, Photocatalytic degradation mechanism of tetracycline by Ag@ZnO/C core–shell plasmonic photocatalyst under visible light, Nano, 13 (2018) 1850065, doi: 10.1142/S1793292018500650.

[66] N. Oturan, J. Wu, H. Zhang, V.K. Sharma, M.A. Oturan, Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: effect of electrode materials, Appl. Catal., B, 140 (2013) 92–97.