Removal of tetracycline from aqueous solution by ultrasound and ultraviolet enhanced persulfate oxidation

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ABSTRACT

Tetracycline (TC) is the second most-consumed antibiotic and is produced worldwide. Environmental contamination with TC is considered as a serious concern in public health. Thus, many attempts have been made to discover new removal processes of TC. This study was conducted to evaluate the efficiency removal of TC from aqueous solution during combined ultrasonic (US), ultraviolet (UV) radiation, and persulfate (PS) process. The effect of various parameters including contact time (0–120 min), TC concentration (10–70 mg/L), pH (3–10), PS concentration (2–6 mM), and the input US power (100–500 W) were investigated in this process. At the end of each process, the remaining TC was measured by spectrophotometer (261 nm). The results implied that each of the UV and US processes alone did not have considerable removal efficiency of TC, as these values for UV and US processes were 41.69% and 12.36%, respectively. Additionally, the highest removal efficiency rate of TC was approximately 96.29% which was observed in combined UV/US/PS process during optimum conditions, including pH = 10, TC concentration = 10 mg/L, PS concentration = 4 mM, and input US power = 500 W. Our study supports the notion that UV/US/PS process can be applied to remove antibiotics such as TC or others with the same structure as well to optimize their biodegradation.

Keywords: Advanced oxidation processes (AOPs); Tetracycline; Persulfate, Ultrasonic, Ultraviolet

1. Introduction

The annual consumption of antibiotics in the world is estimated to be between 100,000 and 200,000 tons [1,2]. Antibiotics are rarely metabolized in the body after taking such that 30%–90% of them remain active after excretion [3,4]. Among various types of antibiotics, tetracycline (TC) is the second most abundant antibiotic in terms of production and consumption worldwide. TC is naturally obtained from the fermentation of some fungi or via semi-synthetic processes. Today, these antibiotics are used extensively for the treatment of various infectious diseases [5]. The occurrence of TC in the environments such as the aqueous medium would lead to various reactions from simple allergies to direct toxicity in some cases and development of antibiotic-resistant pathogens in the environment [4,6,7]. TC has been identified in various peripheral matrices including surface waters (0.07–1.34 µg/L) [8], soils

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(86.2–198.7 μg/kg) [9], liquid fertilizers (0.05–5.36 μg/kg) [9], and in 90% of the farmland pond (>3 μg/L) [10]. Therefore, it is essential to develop an alternative method to eliminate this compound and minimize its environmental risks [11]. Some methods like absorption with activated carbon and membranes do not eliminate pollutants; rather, they are transferred from one phase to another without degradation [6].

There are several leading processes to remove antibiotics including active sludge processes, microfiltration, and reverse osmosis. These processes need the revival or replacement of the substrate and the filtration of secondary wastewater [12]. New methods like advanced oxidation technologies (AOPs) generate hydroxyl radicals ($^•OH$) and sulfate radicals ($SO_4^{•-}$, SR) based on mineralization process, which eliminates toxic pollutants and converts them to lower toxicity products [6,13,14]. Hydroxyl radical ($^•OH$) – a radical with high redox potential (2.7 V under laboratory conditions) and non-selective oxidizer – reacts with organic pollutants [15]. The main properties of sulfate radical ($SO_4^{•-}$) include 2.5–3.1 V (under laboratory conditions) of redox standard and selectively reaction with organic pollutants [16,17]. Activation of some oxidants such as persulfate (PS) via UV irradiation and US waves (Eqs. (1) and (2)) leads to the generation of radicals such as sulfate and hydroxyl [18,19].

$$S_2O_8^{2-} + activator \rightarrow 2SO_4^{•-} \tag{1}$$

$$SO_4^{•-} + H_2O \rightarrow {}^•OH + SO_4^{2-} + H^+ \tag{2}$$
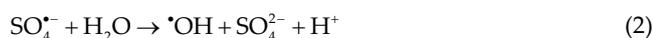
PS activation with UV and US waves compared to other methods is straightforward and easy to accomplish because of its unique advantages such as easy transportation and storage, high solubility in water, moderate stability, and high redox potential (2.1 V) [18–20]. Considering these advantages, recently, the PS combined with US and UV (based on the activation of the PS to form $SO_4^{•-}$) method has been used as an effective and green technology for the removal of various kinds toxic recalcitrant organics such as organic compound [13,21,22], pesticides [14,17], colors [23], and drugs [24] in polluted waters.

Additionally, since sulfate radical has less reaction potency with natural organic material, it is suitable for the removal of organic pollutants in the environment [16].

To the best of our knowledge, no laboratory studies have delineated the degradation of TC as a model organic pollutant via UV/US/PS system. Hence, the main objective of this study was to assess the degradation efficiency of TC by using UV and US separately. Next, it was tired to investigate the synergistic effect of a UV/US coupled system for the activation of PS (UV/US/PS) on TC degradation efficiency. Another purpose of this study was to optimize TC degradation. Finally, the effects of various variables such as PS dose, pH, US power on TC degradation were investigated.

2. Materials and methods

This experimental study was established under laboratory conditions. The removal efficiency of various concentrations of synthetic TC solution (purity of more than 95%) was assessed using the UV/US/PS process.

2.1. Materials

TC hydrochloride [$C_{22}H_{25}N_2O_8Cl$] (AR, 99%), was provided from Sigma-Aldrich, Merck. The chemical properties of TC hydrochloride are shown in Table 1. Sodium persulfate ($Na_2S_2O_8$, 98%) was provided from Sigma-Aldrich. Methanol (purity: 99.8%) and *tert*-butanol alcohol (TBA, purity: >99.0%), as radical scavenging compounds, were also purchased from Merck.

All other chemicals were analytical grades and used as received without any further modification or purification.

2.2. UV/US/PS reactor

Fig. 1 shows the designed reactor. The UV/US/PS reactor contains a 16 W UVC lamp with λ = 254 nm, coated with a quartz tube, and placed in the middle of the reactor. The whole system was wrapped in aluminum foil to prevent reflection. Ultrasonic generator at a constant frequency of 35 kHz and varied power (Elma, Singen, Germany). Circulating cooling water maintained sonicator temperature at 25°C ± 2°C.

2.3. Experiments procedure

Initially, TC solution (500 mg/L) was prepared freshly as stock and stored in the dark at 4°C. This stock was diluted to have an intended concentration of TC solution. The pH value was adjusted (Hanna Instruments, Japan) by adding chloride and sodium hydroxide (1 N) from 3 to 10. Based on previous studies, removal efficiency and mineralization of different concentrations of TC solution (10–70 mg/L), PS concentration (2–6 mM), and various pH (3,7, 10) were determined at 5 min intervals up to 120 min. The procedure involves preparing the intended concentration of TC solution, adjusting pH by NaOH and HCl, adding and completely mixing with intended PS concentration. Finally, this uniform sample was transferred to a designed reactor while exposed to UV/US. At the end of the process, residual TC was determined by a spectrophotometer (Shimadzu, Japan, 261 nm). According to the standard method, total organic carbon (TOC) was measured using a TOC Analyzer (TOC-L, Shimadzu model) [25].

TBA and Methanol were used to determine the scavenger factor of hydroxyl and sulfate radicals, respectively

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
pKa_1	3.2 ± 0.3
pKa_2	7.78 ± 0.05
pKa_3	9.6 ± 0.3
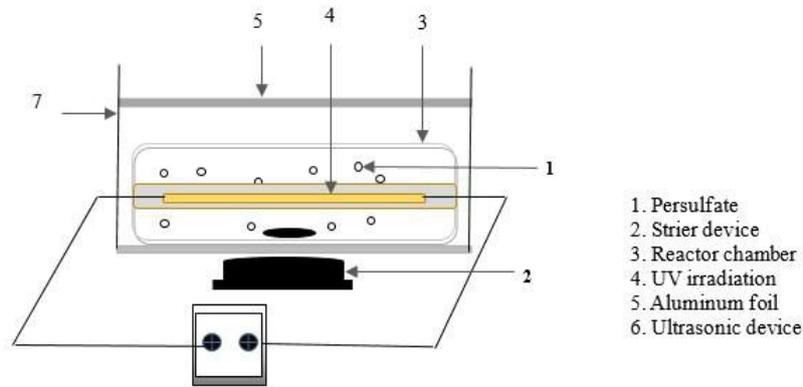
Fig. 1. Specifications of the used UV/US/PS reactor.

(1 g/L). Excel software was used for data analysis. The removal efficiency of TC was calculated by the flowing formula [26].

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

where C_0 and C_e represent initial and final concentrations of TC (mg/L), respectively. Additionally, R indicates the removal efficiency percentage of TC. The kinetic of the TC decomposition process was investigated under optimal conditions (PS concentration = 4 mM, pH = 10, and the initial TC concentration of 10 mg/L) at different time periods.

3. Results and discussion

3.1. pH effect on the UV/US/PS process

The effect of pH on the UV/US/PS process is given in Fig. 2. The average efficiency of TC removal was investigated at three pH values of 3, 7, and 10. The analyzed data revealed no difference in TC removal efficiency in various pH values. So, it could be concluded that pH is not a determinant factor in the removal efficiency of TC. The parallel conclusion was observed in recent studies performed by Lin et al. [27] and Asgari et al. [28]. Sulfate anion formation during the process is the cause of pH reduction. It has been reported that sulfuric acid and carboxylic acids were produced during the TC degradation process [29]. In this study, the final pH of the solution at initial pH values of 3, 7, and 10 are shifted toward lower pH values of 2.7, 2.8, and 2.8, respectively. The significant decrease in the final pH for all initial pH values indicates the high performance of the UV/US/PS process. As regards to almost similar final pH values, it could be concluded that initial pH value does not determine PS activation efficiency and following sulfate radicals generation. However, at alkaline pH (pH = 10) sulfate $SO_4^{\bullet-}$, superoxide $O_2^{\bullet-}$ and hydroxyl $^{\bullet}OH$ radicals were generated via alkaline-activated persulfate mechanism. Besides, under alkaline conditions, hydroxyl radicals ($^{\bullet}OH$) formed due to the reaction of sulfate radicals with hydroxyl anions. It is remarkable that by increasing pH values, the degradation rate of $S_2O_8^{2-}$ into $^{\bullet}OH$ and $SO_4^{\bullet-}$ was increased significantly [30]. Therefore, in our investigation, pH 10.0 was administered as optimum pH to perform subsequent experiments.

Almost similar findings have also been observed by Hou et al. [29] who employed the $US/NaS_2O_8/Fe_3O_4$ process at different pH levels to TC degradation.
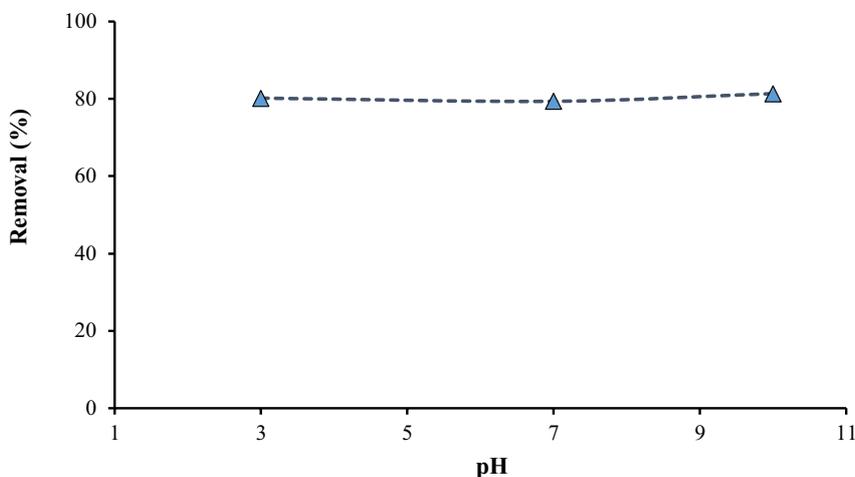
Fig. 2. Effect of pH on TC removal efficiency in UV/US/PS process (TC = 50 mg/L, PS = 4 mM, and time = 120 min).

3.2. Effect of initial TC concentration on UV/US/PS process

The effect of the initial concentration of TC in the UV/US/PS processes is demonstrated in Fig. 3. As can be seen, an increase in the initial concentration of TC would decrease the removal efficiency of TC. The total TC content in the aqueous solution increased with an increase in the initial concentration of TC, while the cavitation conditions and amount of •OH are constant; this might be the main cause of reducing TC degradation efficiency [31]. The higher TC concentrations would decrease the probability of collision and reaction between TC and radical hydroxyl molecules [32]. Also, due to increasing concentrations of intermediate products, hydroxyl radicals become the limiting reactant and so degradation rate of TC declined.

However, with increasing TC concentration in aqueous solutions, TC molecules have more tendency to enter the bubble cavitation and interphase bubbles. As a result, the total level of TC removal was increased [33]. These results are similar to those obtained by other researchers, including Klavarioti et al. [34] and Hoseini et al. [35].

3.3. Effect of initial PS concentration on UV/US/PS process

The initial PS concentration considers a fundamental parameter in the degradation of organic pollutants by the US/UV/PS process. The degradation percentage of TC was affected by PS dosage. Increasing PS concentration led to more sulfate anion formation that could enhance the degradation of TC before PS dosage reaching 4 mM. In this way, the amount of produced sulfate anion during the UV/US process has a linear relationship with a removal efficiency of TC before the optimal dosage. However, at a higher dosage of the optimal point, the removal efficiency was not noticeable [36].

Fig. 4 shows the effect of the initial concentration of PS during the UV/US/PS process. As can be seen, the increase in PS concentrations from 2 to 4 mM led to a significant rise in removal efficiency but exceeding the dosage of 4 mM point, the degradation rate will start to decline.

These results may be attributed to the generation of excess sulfate radicals due to the increase in the concentration of PS during the UV/US process, which led to the rapid decomposition of TC. The efficiency of TC removal
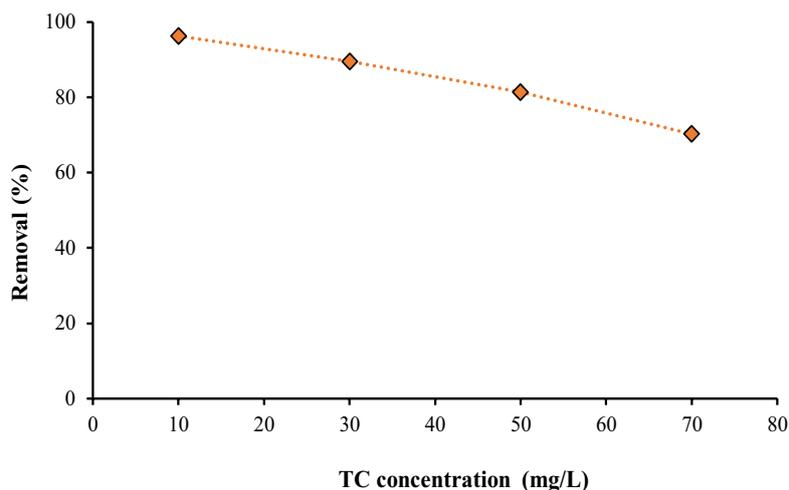
Fig. 3. Effect of initial TC concentration on TC removal efficiency in UV/US/PS process (pH = 10, PS = 4 mM, and time = 120 min).
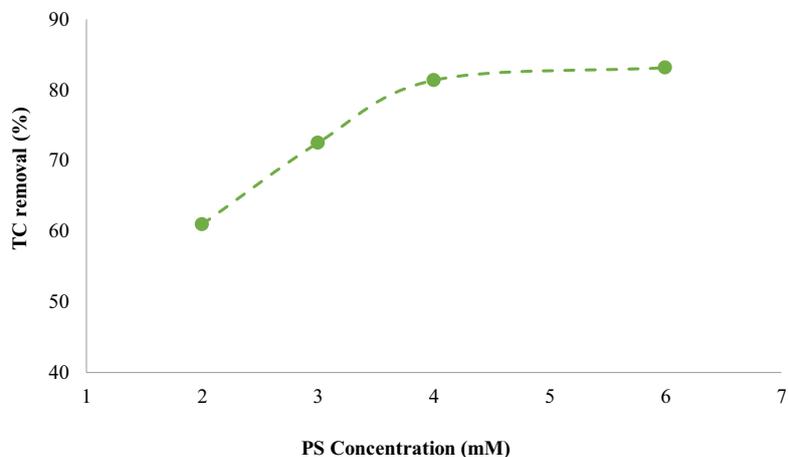
Fig. 4. Effect of initial PS concentration on TC removal efficiency in UV/US/PS process (TC = 10 mg/L, pH = 10, and time = 120 min).

was approximately the same at the PS concentrations of 4 and 6 mM. Therefore, to prevent the excessive consumption of PS, the concentration of 4 mM was considered as an optimum point. A similar conclusion was made in several previous studies [36–38].

PS is the generation source of sulfate radicals in the UV/US/PS process. Therefore, increasing the dosage of PS results in producing more sulfate radicals.

In an effort by Zhang et al. [39] to augment the process of reducing the toxicity of carbamazepine using the UV/PS process, it was observed that by increasing the concentration of PS, carbamazepine removal effect significantly increased. This might propose that there was an inhibition effect of a higher dosage of PS. It seems that there will be an optimum or inhibition point for oxidizing agent dosage. A possible explanation for the obtained results would be the interaction of hydroxyl radicals and sulfate radicals with excess PS leading to the reverse effect on removal efficiency [40,41].

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \tag{4}$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-} \tag{5}$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \tag{6}$$

3.4. Effect of US power on UV/US/PS process

The power of the US wave is a modulative factor that can determine the efficiency of the UV/US/PS process. This power was assessed in various power rates (100, 200, 300, and 500 W) under optimal conditions. Our results revealed a linear relationship between the increase in US power and the increase in the removal rate of TC. It could be concluded that the increase in US power leads to more degradation of $S_2O_8^2$. Following this step, the generated reactive species led to an increase in the TC degradation rate [19,20]. The collapse of cavitation bubbles from the US wave results in the generation of turbulence in solution, which caused enhancing the mass transfer rate of

contaminants by enhancing the US power. According to the maximum removal percentage, 500 W US power was employed as optimum power for the next experiments.

These results are in line with other recent studies that reported a similar relationship between US power and removal efficiency [42,43].

3.5. Kinetics of tetracycline degradation in UV/US/PS process

Fig. 5 shows the kinetics of TC degradation in the UV/US/PS process. Various kinetics of TC removal at different concentrations was examined to adjust and optimize the degradation rate of TC. Collected experiment data indicated that the removal of TC at all concentrations follows the first-order kinetics, as shown in Eq. (7). The reaction rate constant reduced as the initial TC concentration increased [3,36,44].

$$\text{Ln}\,\frac{C_0}{C_t} = -K_t \tag{7}$$

where K_0 is is the first-order reaction rate constant (min^{-1}), which could be calculated from the slope of a plot of $\ln(C_0/C_t)$. Safari et al. [33] suggest that TC degradation via a synthetic chemical process follows first-order kinetics.

3.6. Synergistic effect of the UV/US/PS process compared with the UV, US, and PS process

Fig. 6 depicts the synergistic effect of the UV/US/PS process compared to the UV, US, and PS alone processes. Our finding confirmed that the combination of these three processes at all concentrations of TC was synergistic vs. separate processes (UV, US, and PS). Moreover, the UV/US/PS process demonstrates more than five times removal efficiency compared to the separate processes. Thus, it means that this combined method has a higher potential for PS activation and subsequently more active free radicals production. The UV process had a negligible influence on the TC degradation rate. Therefore, it could be postulated that this rate is mainly due to the direct photolysis or hydrolysis of TC [39].

First Order

y = 0.0237x + 0.2875
R² = 0.9726

– Ln (Ct/C0) vs *Time(min)*
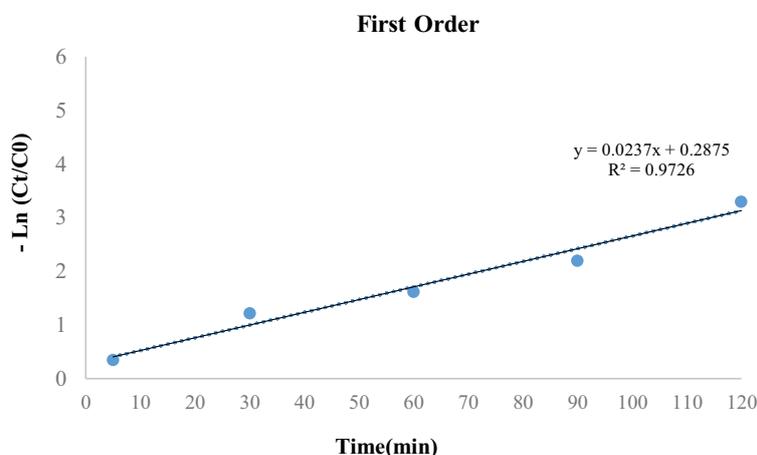
Fig. 5. First-order kinetic model of TC removal in UV/US/PS process (TC = 10 mg/L, pH = 10, PS = 4 mM, and time = 120 min).
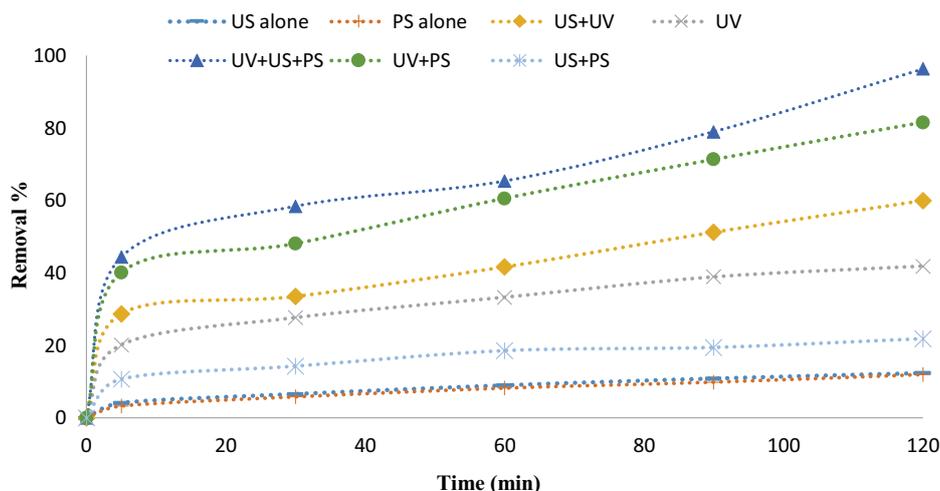
Fig. 6. Comparing different processes in optimal conditions.

When $S_2O_8^{2-}$ was combined with the US at ambient temperature, much faster degradation of TC was achieved. The results of this study show that the US process has more potential for activation of $S_2O_8^{2-}$. These results may be explained by the exacerbated cavitation under low temperatures, which leads to enhanced degradation and activation of $S_2O_8^{2-}$. Moreover, during the US process, degradation of $S_2O_8^{2-}$ to $SO_4^{\bullet-}$ radical was improved [27,45]. The only source of $^{\bullet}OH$ radical production in the presence of ultrasonic waves is water sonolysis. The amount of produced radicals during this process is negligible; the power to destroy and remove TC under these conditions is not significant.

Our work was following the previous study performed by Kim et al. [15] on the decomposition of clarithromycin, erythromycin, azithromycin, and TC by UV process. Furthermore, Hoseini et al. [46] found that the US process does not lead to a promising removal efficiency of the TC and such that its highest obtained efficiency was 20.3%.

3.7. Efficiency of UV/US/PS process in TC mineralization

Fig. 7 illustrates the efficiency of the UV/US/PS process in the TC mineralization. Chemical photoconductivity processes decompose organic pollutants and lead to the complete mineralization to CO_2 and H_2O [47]. However, due to their high stability, it is difficult to accomplish the complete mineralization of antibiotics. The results show that the removal of TOC follows first-order kinetics. Although the UV/US/PS process has a significant effect on TOC removal, the complete inactivation of TC by this process represents the formation of by-products due to TC decomposition during the process [48].

The incomplete mineralization suggests that TC was mainly transformed into products. However, further studies are required for the identification of the main byproducts of TC formed during sonochemical degradation.

3.8. Effect of radical scavenger on the average removal efficiency

As shown in Fig. 8, sulfate radicals were formed due to PS activation by UV/US process. The figure also depicts the performance diagram of the UV/US/PS process. In aqueous solutions, hydroxyl radicals generated following radical exchanges reaction of sulfate radicals. It was reported that both radicals and hydroxyl play an important role in the decomposition of organic pollutants during the UV/US/PS process. To investigate the effect of radical scavenger on TC removal efficiency and to determine the dominant of oxidizing species, two types of radical scavenger were used: *tert*-butanol as a scavenger of hydroxyl radical and methanol as a scavenger of both sulfate and hydroxyl radical [29].

According to Eqs. (21) and (22), the constant rate of TBA for $^{\bullet}OH$ radicals is 418–900 times more than $SO_4^{-\bullet}$ radical. Eqs. (8) and (11) show that the rate constant of MA for $^{\bullet}OH$ radical is nearly 300 times higher than $SO_4^{-\bullet}$ radical [20,45].

$$-BuOH + {^{\bullet}OH} \sim 3.8 - 7.6 \times 10^8 M^{-1}S^{-1} \tag{8}$$

$$t - BuOH + SO_4^{-\bullet} \sim 4 - 9.1 \times 10^5 M^{-1}S^{-1} \tag{9}$$

$$MA + {^{\bullet}OH} \sim 9.7 \times 10^8 M^{-1}S^{-1} \tag{10}$$

$$MA + SO_4^{-\bullet} \sim 3.2 \times 10^6 M^{-1}S^{-1} \tag{11}$$
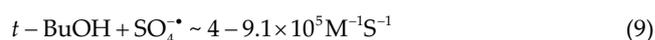
These data show that both sulfate and hydroxyl radicals play a crucial role in TC decomposition via the sonochemical process, whereas the sulfate radicals have a very important role in TC decomposition at all three levels of pH.

The catalytic process is based on the formation of strong oxidizing radicals that could eliminate most of the pollutants present in wastewater.

4. Conclusion

In the last decade, the development of new antibiotics removal methods of water and wastewater has attracted special attention. The purpose of this study was to determine the removal efficiency of TC via UV/US/PS process.

The results demonstrated that the US and UV processes alone cannot be used as effective methods to remove TC
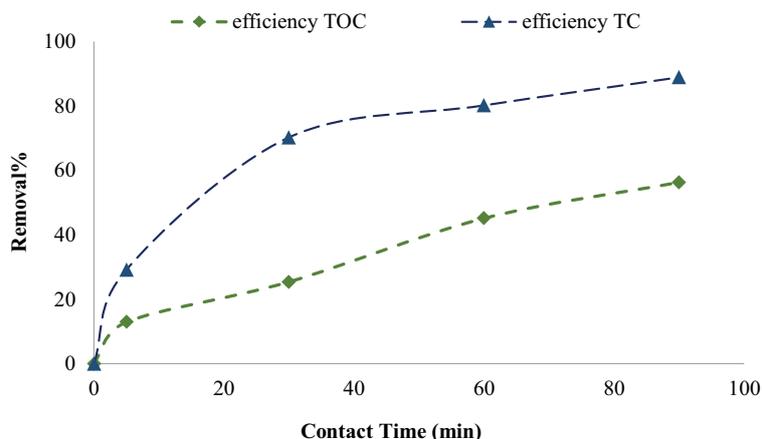
Fig. 7. TOC removal efficiency in UV/US/PS process at optimum condition (TC = 10 mg/L, pH = 10, PS = 4 mM, and time = 120 min).
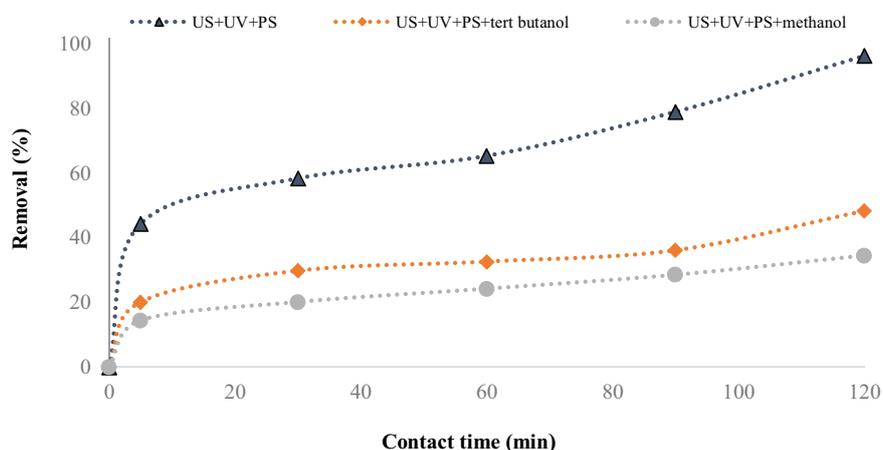
Fig. 8. Effect of radical scavenger on the TC removal efficiency in UV/US/PS process at optimum condition (TC = 10 mg/L, pH = 10, PS = 4 mM, and time = 120 min).

antibiotics from aqueous solutions. However, adding PS catalyst significantly increased the removal efficiency. The UV/US/PS process, one of best AOPs, exhibited more than 96.3% TC removal efficiency under the optimum conditions (i.e., PS concentration: 4 mM, pH: 10, TC concentration: 10 mg/L, and time: 120 min).

The UV/US/PS process has superior properties such as availability, eco-friendliness, and cost-effectiveness. According to the promising results of this study, this novel method has the potential of becoming an efficient process for the final treatment of wastewater or pre-treatment.

In conclusion, the obtained results revealed that the UV/US/PS process could be used as an effective process to remove the TC from aqueous solution.

Acknowledgments

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