

Degradation of tetracycline by heat/peroxymonosulfate and ultrasound/peroxymonosulfate systems: performance and kinetics

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ABSTRACT

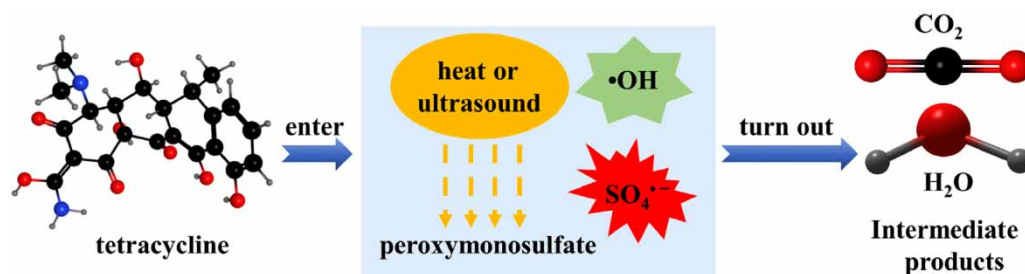
In recent decades, water pollution caused by emerging contaminants such as pharmaceuticals, has attracted much attention. Antibiotics are commonly used pharmaceuticals, and their residue in water may accelerate the development of antibiotic resistance genes, which can produce resistance to the treatment of diseases. In this study, two energy-based systems, heat/peroxymonosulfate (PMS) and ultrasound (US)/PMS were chosen to treat the typical antibiotic tetracycline (TC) in water. The influencing factors and kinetic equations of TC degradation by heat/PMS and US/PMS were investigated and the rates of TC degradation by the two systems were compared. The results showed that the optimal PMS concentration required for TC degradation in both systems was 0.3 mM, and neither system was affected by solution pH. The power of the US in the US/PMS system was as important as the temperature in the heat/PMS system because they provided activation energy. Both heat and US could activate PMS to degrade TC, and US was slightly superior with 80% TC removal under the conditions of [TC] = 20 mg/L, [PMS] = 0.3 mM, pH = 6.4, T = 20 °C, and US power = 550 W. US is considered to be more advantageous in activating PMS to degrade TC.

Key words: heat, peroxymonosulfate, sulfate radicals, tetracycline, ultrasound

HIGHLIGHTS

- Heat/peroxymonosulfate and ultrasound/peroxymonosulfate systems were compared toward tetracycline degradation.
- The influencing factors of tetracycline degradation in both systems were studied.
- The kinetic equations for tetracycline degradation were modeled.
- Tetracycline degradation was mainly caused by hydroxyl radicals and sulfate radicals.

GRAPHICAL ABSTRACT



1. INTRODUCTION

In recent decades, advanced oxidation processes (AOPs) based on sulfate radicals (SO₄•⁻, $E^0 = 2.5\text{--}3.1\text{ V}$) have been extensively studied to treat recalcitrant organic contaminants in water with remarkable efficiencies (Oh *et al.* 2016).

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The oxidants persulfate (PS, $S_2O_8^{2-}$, $E^0 = 1.96$ V) and peroxymonosulfate (PMS, HSO_5^- , $E^0 = 1.75$ V) are two precursors capable of generating $SO_4^{\bullet-}$ (Ushani *et al.* 2020). PS and PMS have limited abilities to oxidize organic contaminants when employed alone at room temperature, while they can be activated to form $SO_4^{\bullet-}$ by different energies, transition metals, or carbon materials (Zhang *et al.* 2015; Ma *et al.* 2017; Gao *et al.* 2018; Zhang *et al.* 2021). Compared to heterogeneous activation methods such as carbon materials and transition metals activation, no additional chemicals are required and no secondary water contamination occurs during the energy activation process. External energies available include heat (Milh *et al.* 2021; Arvaniti *et al.* 2022), microwaves (MWs) (Hu *et al.* 2020; Bose & Kumar 2022), ultrasound (US) waves (Yin *et al.* 2018; Malakootian & Asadzadeh 2020), etc. Although these methods consume energy, they save on chemical costs. The activation of energies toward PS and PMS is very suitable for the treatment of small volumes of recalcitrant organic contaminants in water.

The chemical structures of both PS and PMS include the O–O bond with a bond energy of 140–213.3 kJ/mol (Wang & Wang 2017). When external energy above this bond energy is fed into the aqueous solution containing PS or PMS, the O–O bond breaks, and thus, $SO_4^{\bullet-}$ is formed (Equations (1) and (2)) (Qi *et al.* 2014; Milh *et al.* 2020; Ulucan-Altuntas *et al.* 2022). For heat activation, the energy input by high temperature can cause fission of the O–O bond (Fan *et al.* 2015). Heat activation uses traditional forms of heating, such as heating water in a container electrically or in a water bath. Microwave activation is based on the same principle as conventional heat activation, except that the heating time of the microwave is short and energy is saved (Gao *et al.* 2020). The ultrasonic activation is due to the collapse of the cavitation bubble generating a local high temperature (5,000 K), which can activate PS and PMS (Yang *et al.* 2019). Also, we note that, in contrast to PS, PMS has an asymmetric structure, which makes it easier to be activated (Milh *et al.* 2020). In addition, a PMS molecule activated by transition metals, carbon materials, and different energies can produce $SO_4^{\bullet-}$ and a hydroxyl radical (HO^{\bullet} , $E^0 = 2.8$ V) as shown in Equation (2) (Chen *et al.* 2018). The hydroxyl radicals are not selective for organic matter, while the sulfate radicals are selective, so the simultaneous appearance of both radicals is more beneficial for the synergistic degradation of organic contaminants (Scaria & Nidheesh 2022).



In recent years, the treatment of antibiotic contaminants in water has received widespread attention as antibiotics in the environment can contribute to the production of resistant strains of bacteria and resistance genes, affecting the action of antibiotic-based pharmaceuticals against human infectious diseases (Gheraout & Elboughdiri 2022). Some approaches based on PS or PMS activated via energies for the treatment of different antibiotics have been reported. Heat was used to activate PS or PMS to eliminate sulfamethoxazole (Milh *et al.* 2021), oxytetracycline (Ulucan-Altuntas *et al.* 2022), sulfamethazine (Fan *et al.* 2015), sulfachloropyridazine (Liu *et al.* 2018), and penicillin G (Norzaee *et al.* 2018) from water, and the process parameters, degradation efficiencies, reaction kinetics, and mechanisms were investigated. The MW/PS process performed well by controlling microwave power to oxidize antibiotics sulfamethoxazole (Qi *et al.* 2014) and tetracycline hydrochloride (Gao *et al.* 2020). US was applied to active or assist transition metals to activate PS/PMS in removing antibiotics such as sulfamethazine (Yin *et al.* 2018; Zhang *et al.* 2020), tetracycline (Malakootian & Asadzadeh 2020), amoxicillin (Su *et al.* 2012), and ciprofloxacin (Kyzas *et al.* 2022), and worked well. From the above, it is clear that energies/PS (PMS) processes are outstanding in antibiotics remediation given the short reaction times, high efficiencies, and simple operation. However, few studies focus on diverse energies-based activation methods in activating PMS to degrade antibiotics. Moreover, the energy/PMS process has not yet been practically applied in antibiotics remediation and nonstop effort is required for commercial applications.

In this study, tetracycline (TC), a typical antibiotic, was chosen as the target contaminant, and energies (heat, US) based activation methods were utilized to catalyze PMS for the degradation of TC. The TC removal efficiency, influencing factors, and degradation kinetics were examined in three systems (heat/PMS, US/PMS) in terms of batch experiments. In addition, the mechanisms of PMS activation in different systems were discussed.

2. METHODOLOGY

2.1. Chemicals

All chemical reagents (at least analytical grade) involved in this study are summarized in Table 1. The solutions used in the experiments were prepared with ultrapure water from an ultrapure water machine (Momecular 1810D, Newlong Life Technology Co., Ltd, Shanghai, China).

2.2. Degradation of TC

In the heat/PMS/TC experiment, 250-mL conical flasks were used as reactors containing a reaction solution of 100 mL (including 20 mg/L of TC). A water bath thermostatic oscillator (THZ-82A, Coricolin Industrial System Integration Co., Ltd, Tianjin, China) was applied to raise the temperature of the TC solution to design values (20–60 °C), and a certain dose of PMS (0.1–0.3 mM) was added to the conical flask to initiate chemical reactions. The TC solution was sampled every 10 min to test the remaining TC concentration via a UV-visible spectrophotometer (T-U9, Youke Instrument Co., Ltd, Shanghai, China) at 357 nm. Importantly, the sample vial needed to be filled with 0.5 mL of methanol to quench the reaction, after which the TC concentration was analyzed. In addition, if the initial pH needed to be adjusted during the reaction, H₂SO₄ and NaOH would be employed to achieve a pH varying from 5.0 to 9.0. A pH meter (pH_S-3C, Yidian Scientific Instrument Co., Ltd, Shanghai, China) was utilized to monitor the pH values.

In the US/PMS/TC experiment, the heating of the water samples was realized in an ultrasonic device (KQ-2200B, Ruibang Xingye Technology Co. Ltd, Beijing, China). A 250-mL conical flask was filled with 100 mL of the reaction solution, placed in the ultrasonic reaction cell with water, and the temperature of the water was controlled at the temperature required for the experiment, in order to be consistent with the temperature conditions of the heat/PMS/TC experiment. The knob on the ultrasonic device was adjusted to set the ultrasonic power, and thus, the oxidation reaction was initiated. The TC solution was sampled every 10 min to test the remaining TC concentration. Specific sampling and analytical methods were the same as the heat/PMS process. In the influence factor experiments, the concentration ranges of the factors were as follows: [PMS] = 0.1–0.3 mM, pH = 5–9, and US power = 350–550 W.

In the radical scavenger experiment, methanol (MeOH) and tert-butanol (TBA) were utilized to identify the free radicals formed in reaction for TC degradation in the three systems.

2.3. Detection of TC

The concentration of TC in the solution was determined by UV-visible spectrophotometry with an optimal absorption wavelength of 357 nm. The relationship between TC concentration and absorbance was experimentally determined to be $\text{absorbance} = 0.0327 \text{ TC (mg/L)} + 0.005$ ($R^2 = 0.9994$), where the concentration of TC is applicable in the range of 5–50 mg/L. Six copies of 2-mL TC standard solution were sucked up precisely and six parallel replicates were performed. The standard deviation was calculated to be 0.208%, and the RSD of the relative standard deviation was 0.504% ($n = 6$), which indicated that the precision of the instrument was very high. The removal rate of TC was calculated by Equation (3), where R refers to the TC removal rate, and C_0 and C_t indicate the initial concentration of TC and TC concentration at the t moment, respectively.

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (3)$$

Table 1 | Chemicals used in this study

Chemicals	Molecular formulas	Providers
Tetracycline	C ₂₂ H ₂₄ N ₂ O ₈	Yuanye Biotechnology Co., Ltd (Shanghai, China)
Tert-butanol	C ₄ H ₁₀ O	Maclean Biochemical Technology Co., Ltd (Shanghai, China)
Potassium monopersulfate triple salt	K ₅ H ₃ S ₄ O ₁₈ (42–46% KHSO ₅ basis)	
Methanol	CH ₄ O	Kelong Chemical Reagent Factory (Chengdu, China)
Sodium hydroxide	NaOH	Bohao Chemical Co. Ltd (Leping, China)
Sulfuric acid	H ₂ SO ₄	Beijing Chemical Reagent Factory (Beijing, China)

3. RESULTS AND DISCUSSIONS

3.1. Effect of temperature in the heat/PMS process

In the heat/PMS process, as temperature acts as an activation means, its change significantly affects the degradation efficiency of pollutants. For this reason, five temperatures (20, 30, 40, 50, and 60 °C) were adopted to survey their effects on TC decomposition via the heat/PMS process. Based on Figure 1(a) and Table 2, as the temperature of the TC solution elevates from 20 to 60 °C, the removal rate of TC by the heat/PMS process increases from 31.1 to 80.4% after 60 min of reaction. The results indicate that a greater thermal energy has a stronger activation ability to PMS, which could cause the decomposition of PMS to generate more SO_4^- and HO^\cdot , thereby oxidizing more TC (Chen *et al.* 2017). In addition, high temperatures intensify the thermal movement of molecules and enhance the collision between reactive radicals and organic substrates, accelerating the reaction rate (Yin *et al.* 2022). Previous studies (Waldemer *et al.* 2007; Milh *et al.* 2020; Ulucan-Altuntas *et al.* 2022) have also reached similar conclusions about the role of temperature in heat/PS(PMS) systems. Figure 1(b) and Table 2 exhibit the kinetic profiles and the kinetic constants of TC degradation at different temperatures, which testify that the degradation of TC is consistent with the pseudo-first-order kinetic model with high R^2 (0.95306–0.99771).

To study the thermodynamic laws of TC degradation, Equation (4) is utilized to analyze the relationship between K_{obs} and T (Li *et al.* 2022). In Equation (4), K_{obs} is the apparent rate constant for TC degradation, A refers to the pre-exponential factor, E_a represents the apparent global activation energy ($\text{J}\cdot\text{mol}^{-1}$), and R and T are the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and the absolute temperature (K), respectively. According to Figure 2, $\ln k$ is linearly correlated with $1/T$ and a high R^2 value is obtained. After calculations, the E_a value was $290.5 \text{ kJ}\cdot\text{mol}^{-1}$ and $\ln A$ was 6.31 min^{-1} at 20–60 °C.

$$\ln k_{\text{obs}} = \ln A - \frac{E_a}{RT} \quad (4)$$

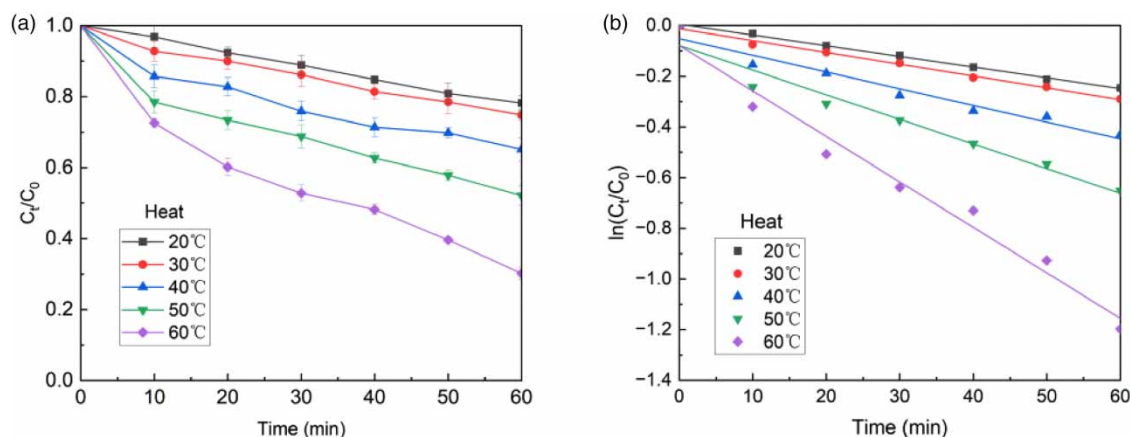


Figure 1 | (a) The effect of temperature in the heat/PMS system; (b) kinetics of TC degradation in the heat/PMS system. Conditions: [TC] = 20 mg/L, [PMS] = 0.2 mM, pH = 6.4.

Table 2 | Kinetic parameters at different temperatures

Temperature	20 °C	30 °C	40 °C	50 °C	60 °C
k	−0.00423	−0.00466	−0.00659	−0.00972	−0.01795
Intercept	0.00535	−0.01245	−0.05139	−0.07840	−0.07856
R^2	0.99771	0.99223	0.95306	0.95551	0.97403

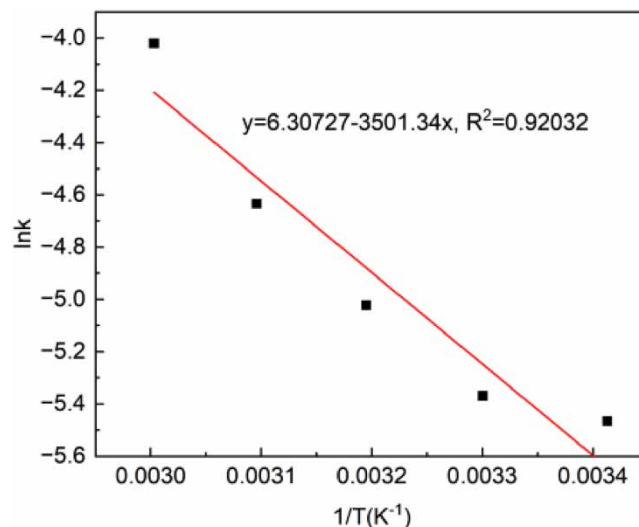


Figure 2 | The relationship between $\ln K_{\text{obs}}$ and $1/T$.

3.2. Effect of PMS concentration in the heat/PMS process and the US/PMS process

The effect of different initial PMS concentrations on TC removal in the heat/PMS process was examined, and the corresponding results are shown in Figure 3(a). Figure 3(a) indicates that as the PMS concentration increases from 0.10 to 0.30 mM, TC removal shows an upward trend after 60 min of reaction. It is known that PMS, as an oxidant, has the role of providing free radicals when thermally activated in the heat/PMS system, so the concentration of PMS is very important for the reaction. Generally, an increase in the concentration of PMS promotes the generation of more free radicals in the degradation of organics. However, a higher PMS concentration may inhibit the degradation of organic pollutants. Too much PMS more than the system needs would generate two side reactions, i.e., the reaction of PMS with the free radicals (Equations (5) and (6)) and the merger reaction between the free radicals (Equation (7)), both of which would lead to a reduction of the free radicals in the reaction, and thus, inhibiting the degradation of TC. In the study of Yin *et al.* (2022), the enhancement of PMS concentration was not observed to inhibit the degradation of pentachlorophenol in a heat/PMS system, probably owing to inadequate PMS dosage. A similar finding was obtained by Wang *et al.* (Milh *et al.* 2021) in the degradation of sulfamethoxazole via a heat/PMS system. Figure 3(b) and Table 3 display the kinetic profiles and the kinetic constants of TC degradation at different PMS concentrations. TC degradation satisfies the pseudo-first-order kinetic model ($\ln(C_t/C_0) = K_{\text{obs}} \cdot \text{Time} + \text{Intercept}$) with R^2

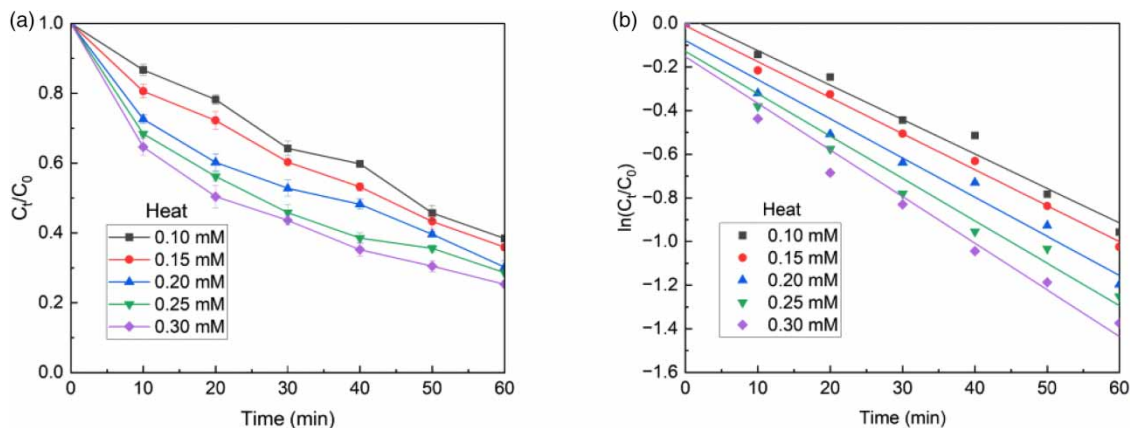
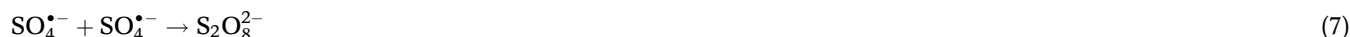


Figure 3 | (a) The effect of PMS concentration in the heat/PMS system and (b) kinetics of TC degradation in the heat/PMS system. Conditions: $[\text{TC}] = 20 \text{ mg/L}$, $T = 60 \text{ }^\circ\text{C}$, $\text{pH} = 6.4$.

Table 3 | Kinetic parameters at different PMS concentrations

PMS	0.10 mM	0.15 mM	0.20 mM	0.25 mM	0.30 mM
k	-0.01579	-0.0165	-0.01795	-0.01943	-0.02137
Intercept	0.03273	-0.01054	-0.07856	-0.12805	-0.15299
R^2	0.98249	0.99469	0.97403	0.96636	0.96469

higher than 0.96496 at various PMS concentrations.



The effect of PMS concentration on TC removal in the US/PMS system is shown in Figure 4. It is found from Figure 4(a) that when the PMS concentration increased from 0.10 to 0.3 mM, the C_t/C_0 value decreased from 0.631 to 0.315 at 60 min, indicating that the increase in PMS concentration promoted the TC degradation rate. The high concentration of PMS facilitates the provision of more precursors for the production of free radicals ($\text{SO}_4^{\bullet-}$ and HO^\bullet) (Equation (2)), which promotes the production of a large number of free radicals. In addition, the mechanism of ultrasonic activation of PMS is a bit more complicated than the heating activation of PMS. US not only activates PMS to generate $\text{SO}_4^{\bullet-}$ and HO^\bullet , but also decomposes water into HO^\bullet and H^\bullet (Equation (8)) (Xu *et al.* 2020), increasing the concentration of HO^\bullet in the solution. The reason why US can activate water and PMS is due to the extreme conditions ($>5,000^\circ\text{C}$, $>100\text{ MPa}$) that occur when the bubbles created in the system eventually collapse (Kermani *et al.* 2020; Xu *et al.* 2020). The kinetic equations and apparent rate constants of TC degradation at different PMS concentrations are displayed in Figure 4(b) and Table 4. The TC degradation data at several PMS concentrations were well fitted to the pseudo-first-order kinetic equation with high correlation coefficients.



It is found that the pattern of the effect of PMS concentration on the heat/PMS process and the US/PMS process was basically similar, after comparing Figures 3 and 4. Increased PMS concentrations (0.10–0.30 mM) were able to promote more TC degradation at higher reaction rates in both the heat/PMS process and the US/PMS process. Heat and US belong to the same energy-based activation method, and their main activation mechanisms are similar, relying on the activation of PMS by molecular heat energy to generate free radicals ($\text{SO}_4^{\bullet-}$ and HO^\bullet), thus degrading organic matter. Higher PMS provided more

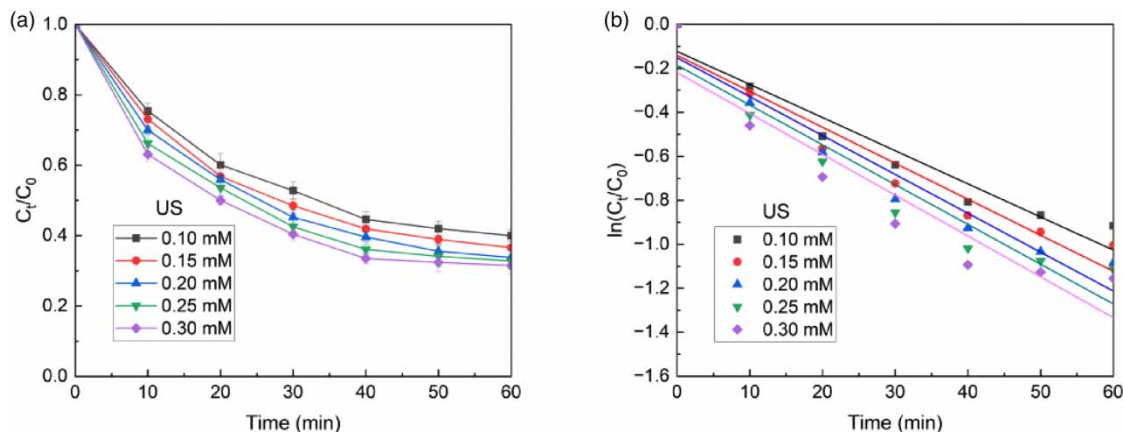


Figure 4 | (a) The effect of PMS concentration in the US/PMS system and (b) kinetics of TC degradation in the US/PMS system. Conditions: $[\text{TC}] = 20\text{ mg/L}$, $T = 20^\circ\text{C}$, $\text{pH} = 6.4$, US power = 450 W.

Table 4 | Kinetic parameters at different PMS concentrations

PMS	0.10 mM	0.15 mM	0.20 mM	0.25 mM	0.30 mM
k	-0.01560	-0.01636	-0.01768	-0.01809	-0.01857
Intercept	-0.12262	-0.14083	-0.15184	-0.18594	-0.21948
R^2	0.93320	0.92882	0.93282	0.90588	0.88287

precursors that could generate free radicals, and there was no excess of PMS in the designed concentration range (0.10–0.30 mM), in both processes.

3.3. Effect of initial pH in heat/PMS process and US/PMS process

The influence of pH on TC degradation was conducted under five initial pH values (5.0, 6.0, 7.0, 8.0, and 9.0) in the heat/PMS/TC system. The result (Figure 5(a)) shows that the removal rate of TC is almost unaffected by the changes in pH. It was found during the experiment that TC solutions with preconfigured initial pH values decreased to 3.0–7.0 when PMS was added to initiate the reaction. For example, a solution with an initial pH of 9.0 dropped to 7.0 when PMS was added. This meant that the pH of the solution dropped below 7.0 in the actual reaction. TC is an amphoteric chemical, and the overall charge of TC would be positive ($\text{pH} < 3.3$), neutral ($3.3 < \text{pH} < 7.7$), or negative ($\text{pH} > 7.7$) (Chao *et al.* 2017). In the pH range of this experiment, TC was neutral, so no protonation occurred and the pH had little effect on its degradation. Also, the main principle of thermally activated PMS is that heat in excess of the O–O bond energy opens the bond and generates free radicals, with little effect on pH. As can be seen from Figure 5(a), the best treatment result is achieved at a pH of 6.0. This value is close to the original pH 6.4 of the TC solution, so no additional procedures make the process effective and cheaper in operation. The kinetic curves of TC degradation at different pH values and the relevant constants are shown in Figure 5(b) and Table 5. The kinetic constants of the curves (Figure 5(b)) do not differ much from each other and match the trend of Figure 5(a).

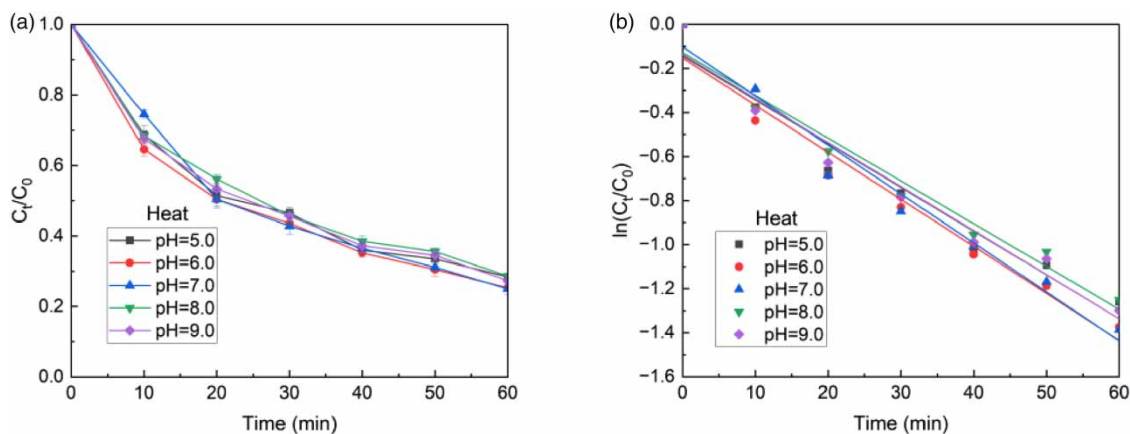


Figure 5 | (a) The effect of pH in the heat/PMS system and (b) kinetics of TC degradation in the heat/PMS system. Conditions: [TC] = 20 mg/L, [PMS] = 0.3 mM, $T = 60^\circ\text{C}$.

Table 5 | Kinetic parameters at different pH values

pH	5.0	6.0	7.0	8.0	9.0
k	-0.01990	-0.02137	-0.02226	-0.01941	-0.02001
Intercept	-0.14295	-0.15299	-0.10220	-0.12804	-0.13633
R^2	0.95504	0.96469	0.96497	0.95963	0.95692

TC removal for different pH scenarios is given in Figure 6(a). The effect of pH on TC degradation in the US/PMS system is similar to that in the heat/PMS system. That is, the effect of pH on the degradation of TC in the US/PMS system is very small and negligible. With the same energy-based activation method, no external chemical reagents were introduced into the two systems (heat/PMS and US/PMS), which had little effect on the change of solution pH. In addition, as mentioned earlier, the pH_{pzc} (the pH of TC with a surface charge of zero) value of TC has no effect on the electrical properties of TC within the experimental pH range. Therefore, the degradation of TC was not affected by pH. The degradation kinetic equations and rate constants for several pH conditions (pH = 5.0–9.0) were very close to each other and satisfied the pseudo-first-order kinetic equation ($R^2 > 0.90$) (see Figure 6(b) and Table 6).

In both the heat/PMS process and the US/PMS process, the changing pH showed very little effect on them. Since the two systems were energetically activated, they mainly relied on the external energy provided to induce the breaking of the O–O bond of PMS to produce free radicals, and thus, pH did not play a role in this activation. In addition, since TC exists in a neutral range of isoelectric points ($3.3 < \text{pH} < 7.7$), this pH range is large, in which TC is not charged in solution, and thus, the morphology of TC itself has less influence on TC degradation. Excluding the above two effects, the activation effect of energies (heat and US) on PMS was very stable under different pH conditions. Since the pH of the original TC solution is 6.4, it is recommended that no pH adjustment is required in the actual treatment process, which saves on chemical costs.

3.4. Effect of US power in the US/PMS process

The power of an ultrasonic device, as the energy used to generate US, plays a crucial role in the US/PMS system. The role of the five powers (350, 400, 450, 500, 550 W) was examined in the degradation of TC in the US/PMS system. As observed in Figure 7(a), as the ultrasonic power increased from 350 to 550 W, the C_t/C_0 value declined from 0.581 to 0.205. This means that the TC removal rate increased with increasing US power. The high power can turn a large amount of water into bubbles, which is conducive to the generation of a transient high temperature and high pressure, which in turn, promotes the generation of free radicals (Kermani *et al.* 2020). The fitted kinetic equations for different power conditions are presented in

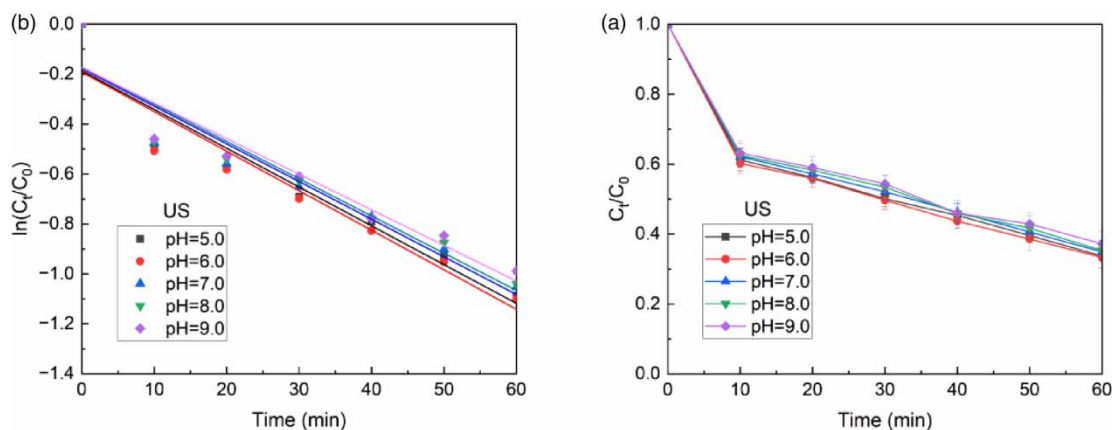


Figure 6 | (a) The effect of pH in the US/PMS system and (b) kinetics of TC degradation in the US/PMS system. Conditions: $[\text{TC}] = 20 \text{ mg/L}$, $T = 20 \text{ }^\circ\text{C}$, $[\text{PMS}] = 0.3 \text{ mM}$, US power = 450 W.

Table 6 | Kinetic parameters at different pH values

pH	5.0	6.0	7.0	8.0	9.0
k	-0.01553	-0.01584	-0.01508	-0.01490	-0.01425
Intercept	-0.18605	-0.19174	-0.17751	-0.17176	-0.17346
R^2	0.90935	0.90848	0.91169	0.91304	0.90515

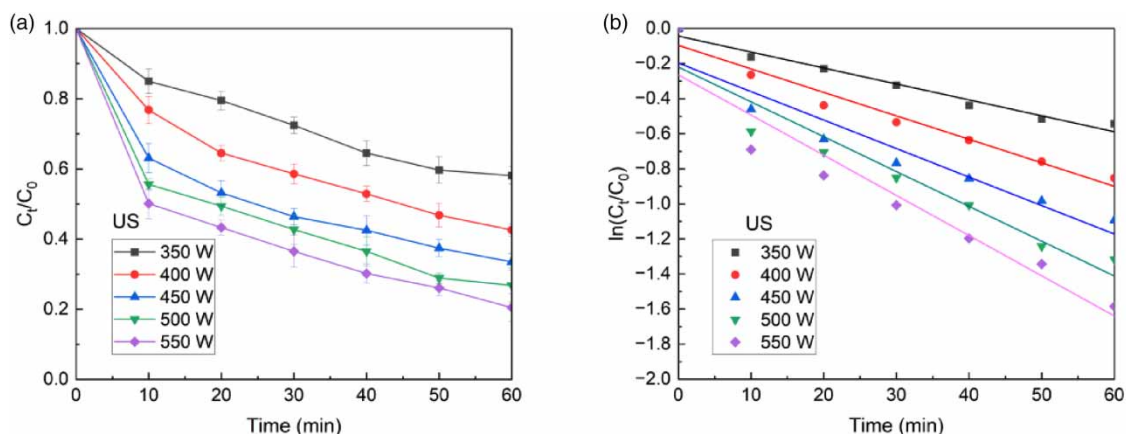


Figure 7 | (a) The effect of US power in the US/PMS system and (b) kinetics of TC degradation in the US/PMS system. Conditions: [TC] = 20 mg/L, $T = 20^\circ\text{C}$, $\text{pH} = 6.4$, [PMS] = 0.3 mM.

Figure 7(b) and Table 7. The kinetic constant for TC degradation increased from 0.00909 to 0.02292 min^{-1} as the power enhanced from 350 to 550 W. TC degradation at various powers fitted the pseudo-first-order kinetic equation ($R^2 > 0.90$).

3.5. Identification of free radicals in the heat/PMS process and the US/PMS process

In order to deeply analyze the mechanism in the heat/PMS process, free radical quenchers (TBA and MeOH) were added to the system to investigate the changes in TC degradation. TBA (without α -hydrogen) was used to identify HO^\cdot owing to its high reaction rate with HO^\cdot ($3.8\text{--}7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) (Song *et al.* 2019). MeOH (containing α -hydrogen) reacted at a comparable rate with HO^\cdot ($1.2 \times 2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and $\text{SO}_4^{\cdot-}$ ($1.6\text{--}7.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$), thus was used to scavenge both HO^\cdot and $\text{SO}_4^{\cdot-}$ (Qian *et al.* 2015). It can be seen from Figure 8(a) that TBA in the heat/PMS system inhibited the degradation of TC, and the TC removal rate decreased from 74.7 to 30.0%, proving that HO^\cdot was generated in the system. When MeOH was put into the system, the TC removal rate decreased rapidly to 9.7%, which testified the generation of $\text{SO}_4^{\cdot-}$. Thus, in the heat/PMS system, heat-activated PMS produced $\text{SO}_4^{\cdot-}$ and HO^\cdot , which were responsible for TC degradation. The changes in kinetic constants with the addition of quenchers are given in Figure 8(b). In the absence of quenchers, the kinetic constant for TC degradation was 0.02137 min^{-1} . When TBA was added, the kinetic constant dramatically decreased to 0.00515 min^{-1} . When MeOH was added, the kinetic constant further decreased, suggesting that the inhibition by MeOH was more intense. This also confirmed that two types of free radicals ($\text{SO}_4^{\cdot-}$ and HO^\cdot) were produced in the heat/PMS system. According to the degree of inhibition of TC degradation, the contribution of HO^\cdot (44.7% decline) to TC degradation is greater than that of $\text{SO}_4^{\cdot-}$ (20.3% decline).

According to previous studies (Xu *et al.* 2021; Gujar *et al.* 2023), the free radicals that play a major role in the US/PMS system are sulfate radicals and hydroxyl radicals. To consider the major radicals often found in this system, TBA and MeOH were used as quenchers to examine their inhibitory effects on TC degradation. It can be seen from Figure 9(a) that TBA and MeOH inhibited TC degradation, respectively. Since TBA can only inhibit HO^\cdot and MeOH can inhibit both $\text{SO}_4^{\cdot-}$ and HO^\cdot , the system generated at least these two radicals as judged from the curves. It was also found that MeOH did not completely inhibit TC degradation and that there was still some removal of TC, meaning that there were likely

Table 7 | Kinetic parameters at different US power values

Power	350 W	400 W	450 W	500 W	550 W
k	-0.00909	-0.01339	-0.01626	-0.01986	-0.02292
Intercept	-0.04338	-0.09638	-0.19694	-0.21970	-0.26390
R^2	0.97407	0.96261	0.90824	0.92037	0.91717

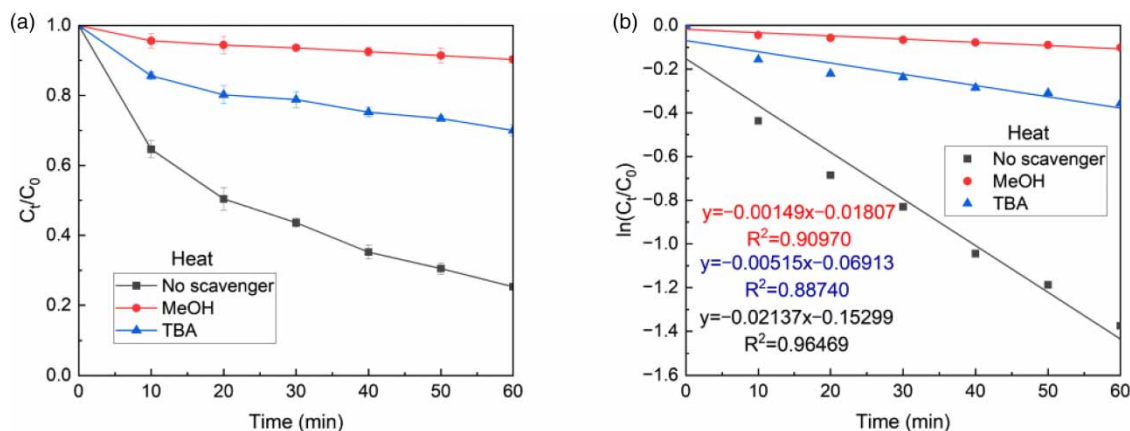


Figure 8 | (a) The effect of quenchers in the heat/PMS system and (b) kinetics of TC degradation in the heat/PMS system. Conditions: [TC] = 20 mg/L, [PMS] = 0.3 mM, $T = 60^\circ\text{C}$, pH = 6.4, [TBA] = [MeOH] = 300 mM.

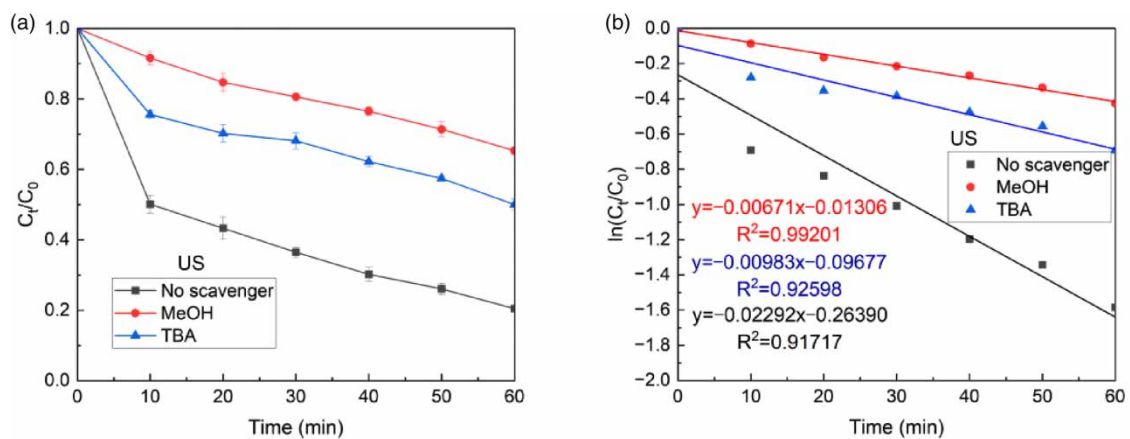


Figure 9 | (a) The effect of quenchers in the US/PMS system and (b) kinetics of TC degradation in the US/PMS system. Conditions: [TC] = 20 mg/L, [PMS] = 0.3 mM, $T = 20^\circ\text{C}$, pH = 6.4, US power = 550 W, [TBA] = [MeOH] = 300 mM.

other active species generated in the system. According to the finding of Yin *et al.* (2018), $^1\text{O}_2$ could appear in systems with US-activated PMS. Figure 9(b) testified that the degradation of TC under inhibited conditions still conformed to the pseudo-first-order kinetic equation.

It can be seen that both $\text{SO}_4^{\cdot-}$ and HO^\cdot were produced in heat/PMS/TC and US/PMS/TC systems in the presence of different types of energies (heat and US). This is due to the fact that both $\text{SO}_4^{\cdot-}$ and HO^\cdot systems activate PMS by splitting the peroxygen bond of PMS into $\text{SO}_4^{\cdot-}$ and HO^\cdot . However, a comparison of Figures 8 and 9 reveals that the production of HO^\cdot is more in the US/PMS system than in the heat/PMS system, perhaps due to the fact that US also breaks down water molecules into HO^\cdot (Equation (8)).

3.6. Comparison of the heat/PMS process and the US/PMS process

It is known from previous experiments that both US and heat can effectively activate PMS to degrade TC, and their performance is compared in Figure 10. As shown in Figure 10, under the same experimental conditions ([TC] = 20 mg/L, [PMS] = 0.3 mM, pH = 6.4), the removal of TC by US/PMS was slightly higher than that by heat/PMS. The advantage of US is the ability to activate PMS at room temperature. Nevertheless, the conventional heating method requires a certain volume of heating equipment. In addition, the PMS concentration, heating temperature, and ultrasonic power can be increased appropriately in order to achieve the complete removal of TC in a short period of time.

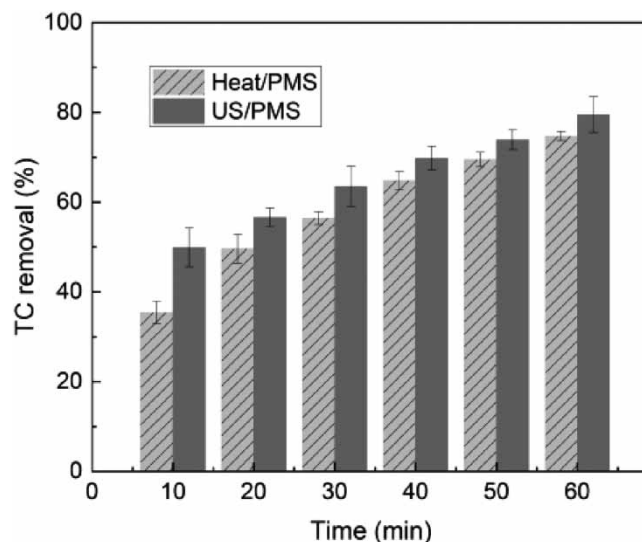


Figure 10 | Comparison of efficiencies of the two systems. Conditions: [TC] = 20 mg/L, [PMS] = 0.3 mM, pH = 6.4, $T = 60\text{ }^{\circ}\text{C}$ (for heat/PMS), $T = 20\text{ }^{\circ}\text{C}$ (for US/PMS), US power = 500 W.

4. CONCLUSIONS

In this study, heat and US were utilized to activate PMS to decompose antibiotic TC, and the following conclusions were reached.

- In both heat/PMS and US/PMS systems, PMS concentrations were positively correlated with TC removal, and the optimal PMS concentration was 3.0 mM.
- pH had little effect on the degradation of TC in the two systems, and a good removal rate was achieved at the original pH of 6.4.
- Temperature was very significant for the activation of PMS, and was able to break the O–O bond of PMS with an activation energy of $290.5\text{ kJ}\cdot\text{mol}^{-1}$ according to the thermodynamic equation.
- The power of the US is the source of energy for generating a large number of free radicals, and with 550 W of US power, the US/PMS system could remove nearly 80% of TC.
- The degradation of TC under various experimental conditions was in accordance with the pseudo-first-order kinetic equation. Under the same experimental conditions, US-activated PMS achieved better TC removal efficiencies than heat-activated PMS.
- In order to facilitate the practical application of energy-based AOPs, the following measures can be considered. In the heat/PMS process, industrial waste heat is used to heat the reactor to save energy; energy-based methods are used in combination with other methods, e.g. with heavy metal activation or as an adjunct to the photocatalytic methods; the US/PMS process is employed for treating small volumes of antibiotic-containing wastewater.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- Arvaniti, O. S., Ioannidi, A. A., Mantzavinos, D. & Frontistis, Z. 2022 Heat-activated persulfate for the degradation of micropollutants in water: A comprehensive review and future perspectives. *Journal of Environmental Management* **318**, 115568.
- Bose, S. & Kumar, M. 2022 Microwave-assisted persulfate/peroxymonosulfate process for environmental remediation. *Current Opinion in Chemical Engineering* **36**, 100826.
- Chao, Y., Yang, L., Ji, H., Zhu, W., Pang, J., Han, C. & Li, H. 2017 Graphene-analogue molybdenum disulfide for adsorptive removal of tetracycline from aqueous solution: Equilibrium, kinetic, and thermodynamic studies. *Environmental Progress & Sustainable Energy* **36**, 815–821.
- Chen, Y., Deng, P., Xie, P., Shang, R., Wang, Z. & Wang, S. 2017 Heat-activated persulfate oxidation of methyl- and ethyl-parabens: Effect, kinetics, and mechanism. *Chemosphere* **168**, 1628–1636.
- Chen, J., Fang, C., Xia, W., Huang, T. & Huang, C. H. 2018 Selective transformation of β -lactam antibiotics by peroxymonosulfate: Reaction kinetics and nonradical mechanism. *Environmental Science & Technology* **52**, 1461–1470.
- Fan, Y., Ji, Y., Kong, D., Lu, J. & Zhou, Q. 2015 Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process. *Journal of Hazardous Materials* **300**, 39–47.
- Gao, F., Li, Y. & Xiang, B. 2018 Degradation of bisphenol A through transition metals activating persulfate process. *Ecotoxicology and Environmental Safety* **158**, 239–247.
- Gao, Y., Cong, S., He, Y., Zou, D., Liu, Y., Yao, B. & Sun, W. 2020 Study on the mechanism of degradation of tetracycline hydrochloride by microwave-activated sodium persulfate. *Water Science and Technology* **82**, 1961–1970.
- Gheraout, D. & Elboughdiri, N. 2022 Antibiotics resistance in water mediums: Background, facts, and trends. *Applied Engineering* **4**, 1–6.
- Gujar, S. K., Divyapriya, G., Gogate, P. R. & Nidheesh, P. V. 2023 Environmental applications of ultrasound activated persulfate/peroxymonosulfate oxidation process in combination with other activating agents. *Critical Reviews in Environmental Science and Technology* **53**, 780–802.
- Hu, L., Wang, P., Shen, T., Wang, Q., Wang, X., Xu, P., Zheng, Q. & Zhang, G. 2020 The application of microwaves in sulfate radical-based advanced oxidation processes for environmental remediation: A review. *Science of The Total Environment* **722**, 137831.
- Kermani, M., Farzadkia, M., Morovati, M., Taghavi, M., Fallahizadeh, S., Khaksefidi, R. & Norzaee, S. 2020 Degradation of furfural in aqueous solution using activated persulfate and peroxymonosulfate by ultrasound irradiation. *Journal of Environmental Management* **266**, 110616.
- Kyzas, G. Z., Mengelizadeh, N., khodadadi Saloot, M., Mohebi, S. & Balarak, D. 2022 Sonochemical degradation of ciprofloxacin by hydrogen peroxide and persulfate activated by ultrasound and ferrous ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **642**, 128627.
- Li, T., Lu, S., Lin, W., Ren, H. & Zhou, R. 2022 Heat-activated persulfate oxidative degradation of ofloxacin: Kinetics, mechanisms, and toxicity assessment. *Chemical Engineering Journal* **433**, 133801.
- Liu, L., Lin, S., Zhang, W., Farooq, U., Shen, G. & Hu, S. 2018 Kinetic and mechanistic investigations of the degradation of sulfachloropyridazine in heat-activated persulfate oxidation process. *Chemical Engineering Journal* **346**, 515–524.
- Ma, J., Li, H., Chi, L., Chen, H. & Chen, C. 2017 Changes in activation energy and kinetics of heat-activated persulfate oxidation of phenol in response to changes in pH and temperature. *Chemosphere* **189**, 86–93.
- Malakootian, M. & Asadzadeh, S. N. 2020 Removal of tetracycline from aqueous solution by ultrasound and ultraviolet enhanced persulfate oxidation. *Desalination and Water Treatment* **197**, 191–199.
- Milh, H., Schoenaers, B., Stesmans, A., Cabooter, D. & Dewil, R. 2020 Degradation of sulfamethoxazole by heat-activated persulfate oxidation: Elucidation of the degradation mechanism and influence of process parameters. *Chemical Engineering Journal* **379**, 122234.
- Milh, H., Cabooter, D. & Dewil, R. 2021 Role of process parameters in the degradation of sulfamethoxazole by heat-activated peroxymonosulfate oxidation: Radical identification and elucidation of the degradation mechanism. *Chemical Engineering Journal* **422**, 130457.
- Norzaee, S., Taghavi, M., Djahed, B. & Mostafapour, F. K. 2018 Degradation of Penicillin G by heat activated persulfate in aqueous solution. *Journal of Environmental Management* **215**, 316–323.
- Oh, W. D., Dong, Z. & Lim, T. T. 2016 Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: Current development, challenges and prospects. *Applied Catalysis B: Environmental* **194**, 169–201.
- Qian, Y., Zhou, X., Zhang, Y., Sun, P., Zhang, W., Chen, J., Guo, X. & Zhang, X. 2015 Performance of α -methyl-naphthalene degradation by dual oxidant of persulfate/calcium peroxide: Implication for ISCO. *Chemical Engineering Journal* **279**, 538–546.
- Qi, C., Liu, X., Lin, C., Zhang, X., Ma, J., Tan, H. & Ye, W. 2014 Degradation of sulfamethoxazole by microwave-activated persulfate: Kinetics, mechanism and acute toxicity. *Chemical Engineering Journal* **249**, 6–14.
- Scaria, J. & Nidheesh, P. V. 2022 Comparison of hydroxyl-radical-based advanced oxidation processes with sulfate radical-based advanced oxidation processes. *Current Opinion in Chemical Engineering* **36**, 100830.
- Song, Q., Feng, Y., Liu, G. & Lv, W. 2019 Degradation of the flame retardant triphenyl phosphate by ferrous ion-activated hydrogen peroxide and persulfate: Kinetics, pathways, and mechanisms. *Chemical Engineering Journal* **361**, 929–936.
- Su, S., Guo, W., Yi, C., Leng, Y. & Ma, Z. 2012 Degradation of amoxicillin in aqueous solution using sulphate radicals under ultrasound irradiation. *Ultrasonics Sonochemistry* **19**, 469–474.

- Ulucan-Altuntas, K., Yazici Guvenc, S., Can-Güven, E., Ilhan, F. & Varank, G. 2022 Degradation of oxytetracycline in aqueous solution by heat-activated peroxydisulfate and peroxymonosulfate oxidation. *Environmental Science and Pollution Research* **29**, 9110–9123.
- Ushani, U., Lu, X., Wang, J., Zhang, Z., Dai, J., Tan, Y., Wang, S., Li, W., Niu, C., Cai, T., Wang, N. & Zhen, G. 2020 Sulfate radicals-based advanced oxidation technology in various environmental remediation: A state-of-the-art review. *Chemical Engineering Journal* **402**, 126232.
- Waldemer, R. H., Tratnyek, P. G., Johnson, R. L. & Nurmi, J. T. 2007 Oxidation of chlorinated ethenes by heat-activated persulfate: Kinetics and products. *Environmental Science & Technology* **41**, 1010–1015.
- Wang, J. & Wang, S. 2017 Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chemical Engineering Journal* **334**, 1502–1517.
- Xu, L., Wang, X., Sun, Y., Gong, H., Guo, M., Zhang, X., Meng, L. & Gan, L. 2020 Mechanistic study on the combination of ultrasound and peroxymonosulfate for the decomposition of endocrine disrupting compounds. *Ultrasonics Sonochemistry* **60**, 104749.
- Xu, L., Zhou, X., Wang, G., Zhou, L. & Sun, X. 2021 Catalytic degradation of acid red B in the system of ultrasound/peroxymonosulfate/ Fe_3O_4 . *Separation and Purification Technology* **276**, 119417.
- Yang, L., Xue, J., He, L., Wu, L., Ma, Y., Chen, H., Li, H., Peng, P. & Zhang, Z. 2019 Review on ultrasound assisted persulfate degradation of organic contaminants in wastewater: Influences, mechanisms and prospective. *Chemical Engineering Journal* **378**, 122146.
- Yin, R., Guo, W., Wang, H., Du, J., Zhou, X., Wu, Q., Zheng, H., Chang, J. & Ren, N. 2018 Enhanced peroxymonosulfate activation for sulfamethazine degradation by ultrasound irradiation: Performances and mechanisms. *Chemical Engineering Journal* **335**, 145–153.
- Yin, L., Wei, J., Qi, Y., Tu, Z., Qu, R., Yan, C., Wang, Z. & Zhu, F. 2022 Degradation of pentachlorophenol in peroxymonosulfate/heat system: Kinetics, mechanism, and theoretical calculations. *Chemical Engineering Journal* **434**, 134736.
- Zhang, B. T., Zhang, Y., Teng, Y. & Fan, M. 2015 Sulfate radical and its application in decontamination technologies. *Critical Reviews in Environmental Science and Technology* **45**, 1756–1800.
- Zhang, T., Yang, Y., Li, X., Yu, H., Wang, N., Li, H., Du, P., Jiang, Y., Fan, X. & Zhou, Z. 2020 Degradation of sulfamethazine by persulfate activated with nanosized zero-valent copper in combination with ultrasonic irradiation. *Separation and Purification Technology* **239**, 116537.
- Zhang, W., Yan, L., Wang, Q., Li, X., Guo, Y., Song, W. & Li, Y. 2021 Ball milling boosted the activation of peroxymonosulfate by biochar for tetracycline removal. *Journal of Environmental Chemical Engineering* **9**, 106870.

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