



# In situ chemical oxidation of tinidazole in aqueous media by heat-activated persulfate: kinetics, thermodynamic, and mineralization studies

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Received: 10 November 2023 / Accepted: 5 February 2024 / Published online: 14 March 2024  
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## Abstract

This study investigated the use of heat-activated persulfate (HAP) as a chemical oxidation technique for removing tinidazole (TNZ) antibiotic from aqueous solutions. The impact of various operating parameters, including TNZ initial concentration (20  $\mu\text{M}$ ), persulfate (PS) initial dose (0.2–2 mM), solution pH (3–11), solution temperature (20–60  $^{\circ}\text{C}$ ), and reaction time (10–120 min), was examined. The results indicated that sulfate radicals were the primary species responsible for TNZ degradation. Higher temperatures and PS concentrations improved the process, while higher pH values and TNZ initial concentrations slowed it down. Additionally, chloride and bicarbonate ions reduced reaction rates, with chloride ions having a more significant effect. Under optimal conditions (including  $[\text{TNZ}]_0 = 20 \mu\text{M}$ ,  $\text{pH} = 7$ ,  $[\text{PS}]_0 = 1 \text{ mM}$ , temperature = 60  $^{\circ}\text{C}$ , and reaction time = 120 min), the removal efficiency achieved was 91.15%, with a mineralization rate of 85.8%. These results suggest that the process is relatively safe. The degradation of TNZ was best described by the pseudo-first-order model compared to other models. Additionally, the process was found to be exothermic and spontaneous, with a negative Gibbs free energy change indicating that it is thermodynamically feasible. The study found HAP to be an effective and cost-efficient technique for removing TNZ antibiotic due to its ease of operation and the absence of the need for additional chemicals or waste handling. Based on these findings, HAP can be considered an advanced oxidation technique for treating antibiotic-contaminated water.

**Keywords** Tinidazole · Heat-activated persulfate · Chemical oxidation · Advanced oxidation

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## Introduction

In today's world, the use of drugs to maintain public health and improve the quality of life of humans is essential, so large amounts of drugs are produced daily worldwide and used to prevent diseases of humans and animals (Grenni et al. 2018; Almasi et al. 2016; Bazrafshan et al. 2021; Moghaddam et al. 2023; Dargahi et al. 2023; Shokoohi et al. 2018). Unfortunately, a large percentage of administered drugs (30–90%) is excreted unaltered or as active metabolites in urine and feces. This leads to their presence in wastewater, which is then directed to wastewater treatment plants (WWTPs) (Grenni et al. 2018; Shokoohi et al. 2020). However, adequate removal of these substances cannot be achieved due to the WWTPs' reliance on microbial activity for operation. As a result, the effluent from WWTPs is recognized as the major anthropogenic source for the discharge of antibiotic residues (McConnell et al. 2018). Indeed, the widespread occurrence of such contaminants poses a serious challenge due to their adverse effects on both human health and ecosystems (Foroughi et al. 2018).

Nitroimidazoles are a class of antibiotics widely used to treat infections caused by anaerobic bacteria and protozoa such as *Trichomonas vaginalis* and *Giardia lamblia*. They are also used as growth promoters and for feeding improvement in poultry (Rivera-Utrilla et al. 2010a). Tinidazole (TNZ), the most well-known member of this antibiotic family, has high water solubility, raised toxicity, and low biodegradability. As with other antibiotics, TNZ cannot be removed by conventional biologically-based WWTPs (Velo-Gala et al. 2017a). Due to the reasons mentioned earlier, there is a growing need for effective elimination of these challenging compounds.

Several techniques such as (electro) chemical-based techniques, oxidation by ozone, gamma irradiation, photolysis, and adsorption have been tried until now (Zarei et al. 2013; Rivera-Utrilla et al. 2010b; Sánchez-Polo et al. 2009; Velo-Gala et al. 2017b; Li et al. 2022). Among these methods, advanced oxidation processes (AOPs) are considered the most promising and popular alternative according to research published in the *Water Research* journal. These methods rely on the generation of reactive oxidation agents, including hydroxyl radical ( $\text{OH}^\bullet$ ) and sulfate ( $\text{SO}_4^{\bullet-}$ ) radicals, for the degradation of the compound (Foroughi et al. 2017). Among AOP-based processes, in situ chemical oxidation is considered an attractive option. Persulfate ion is one of the most effective oxidants utilized for remediation of organic pollutants. Its application has numerous advantages, including high oxidizing properties and water solubility, ease of storage and transportation, lower cost compared to other oxidants, safe generation of by-products, and proper persistence (Zarei et al. 2017).

In order to enhance the reaction rate of persulfate (PS) with reductants, it is preferable to decompose or stimulate it to sulfate radical ( $\text{SO}_4^{\bullet-}$ ) through an activation process. Common methods for achieving this include heat, transition metals, UV light, or base (Johnson et al. 2008; Ji et al. 2015a).  $\text{SO}_4^{\bullet-}$  ( $E_0 = 2.6$ ) has superior oxidation ability compared to PS and can effectively decompose contaminants, even under neutral pH conditions. In addition, it can selectively oxidize target molecules with carbon–carbon double bonds and benzene rings more effectively than PS (Qi et al. 2018). Among various activation strategies, heat activation is particularly promising when integrated with in situ chemical oxidation (ISCO) (Zarei et al. 2017). In addition to producing  $\text{SO}_4^{\bullet-}$ , heat can increase reaction rates, locally raise site temperature, and reduce cleanup time, which is especially important for large-scale applications. Moreover, thermally activated processes have fewer controversial issues related to chemical synthesis, handling, and waste generation than metal-catalyzed processes (Zhang et al. 2018; Qiu et al. 2022; Xu et al. 2023; Zou et al. 2022; Faria et al. 2019).

The objective of this study was to investigate the effect of heat-activated persulfate (HAP) on tinidazole (TNZ), a model antiprotozoal and antibiotic drug. TNZ was selected due to its appropriate characteristics, including low reactivity to ozone, high affinity for  $\text{OH}^\bullet$ , and a low adsorption rate on activated carbon, as well as its chemically complex structure. Furthermore, there are few reports on the capability of different treatment options for removing nitroimidazoles, which have recently been detected in environmental matrices such as aqueous media (9). The investigation focused on the impact of influential parameters such as TNZ initial concentration (20  $\mu\text{M}$ ), pH (3–11), PS initial dose (0.2–2), temperature (20–60  $^\circ\text{C}$ ), and reaction time (10–120 min) on the process kinetics, isotherms, and thermodynamics. The mineralization of the process was also determined.

In summary, the study offers a holistic approach, combining the unique challenges posed by nitroimidazoles, the integration of heat activation with ISCO, and a thorough exploration of influential parameters, contributing valuable insights to the field of wastewater remediation.

## Materials and methods

### Chemicals and instruments

All the chemicals used in this study were of analytical pure grade. TNZ (purity > 99%, Merck, Germany) was acquired from Merck.  $\text{Na}_2\text{S}_2\text{O}_8$  (99%, Merck, Germany) was used as the persulfate agent. The samples' pH was adjusted by adding either 0.1 N HCl or NaOH solution and measured with a pH meter (model WTW, Germany). Ethanol and tert-butyl alcohol were added to the system as radical scavengers.

Sodium chloride (NaCl, purity  $\geq 99.9\%$ ) and sodium carbonate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) or sodium bicarbonate ( $\text{NaHCO}_3$ , purity  $\geq 99.9\%$ ) were used to investigate the effect of chloride and alkalinity, respectively. All solutions were prepared using deionized water. TNZ concentrations were determined using a DR 5000 spectrophotometer at the predetermined maximum wavelength ( $\lambda$ ) of 310 nm, and total organic carbon (TOC) was detected using a TOC analyzer ANATOC™ SERIES II according to Standard Methods for the Examination of Water and Wastewater (Faria et al. 2019).

## Experiments

The effect of HAP on TNZ removal was investigated by varying the parameters of TNZ initial concentration (20  $\mu\text{M}$ ), pH (3–11), PS initial dose (0.2–2 mM), temperature (20–60 °C), and time (10–120 min). The degradation experiments were conducted in batch mode using a one-factor-at-a-time approach. For each experimental run, 200 mL of a known concentration of TNZ solution was prepared in a 250-mL Erlenmeyer flask, adjusted to the desired pH, and contacted with an ambient amount of persulfate. The flasks were agitated in a temperature-controlled shaker incubator at a constant stirring rate of 100 rpm. After the reaction, approximately 4 mL of the solution was extracted, immediately quenched with 1 mL of ethanol to prevent further possible oxidation reactions, and analyzed for TNZ. The removal efficiency was calculated using the following equation:

$$R_{\text{TNZ}} = \left( \frac{\text{TNZ}_i - \text{TNZ}_f}{\text{TNZ}_i} \right) \times 100 \quad (1)$$

where  $R_{\text{TNZ}}$  is the TNZ removal efficiency (%), and  $\text{TNZ}_i$  and  $\text{TNZ}_f$  indicate the concentrations of TNZ (mg/L) at the initial and final time points, respectively.

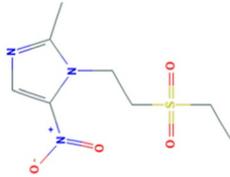
To identify the radical species formed during the process, ethanol and tert-butyl alcohol were employed as radical scavengers in molar ratios of 125/1 (either TBA/PS or EtOH/PS 700/1) before and after addition of persulfate. The TNZ and PS working solutions were freshly prepared. All experiments were performed in triplicate, and mean values were reported (Table 1).

## Results and discussion

### Effect of temperature

Figure 1 shows the efficiency of HAP on TNZ removal at different temperatures. As shown, increasing the temperature from 20 to 60 °C significantly enhanced TNZ degradation from 6.8% to 81.5% within 120 min. Moreover, the

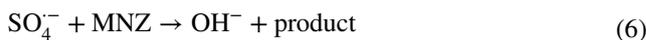
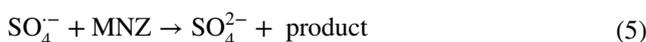
**Table 1** Physicochemical properties of TNZ

Characteristic	TNZ antibiotic
Structure	
Molecular formula	$\text{C}_8\text{H}_{13}\text{N}_3\text{O}_4\text{S}$
MW (g/mol)	247.269
Solubility (mol/L)	0.008
$\text{p}K_a$	2.3
Melting point (°C)	127–128

TNZ degradation process was best described by a pseudo-first-order kinetic model with  $R^2 = 0.95$ . The rate constants obtained using Eq. (2) are summarized in Table 2.

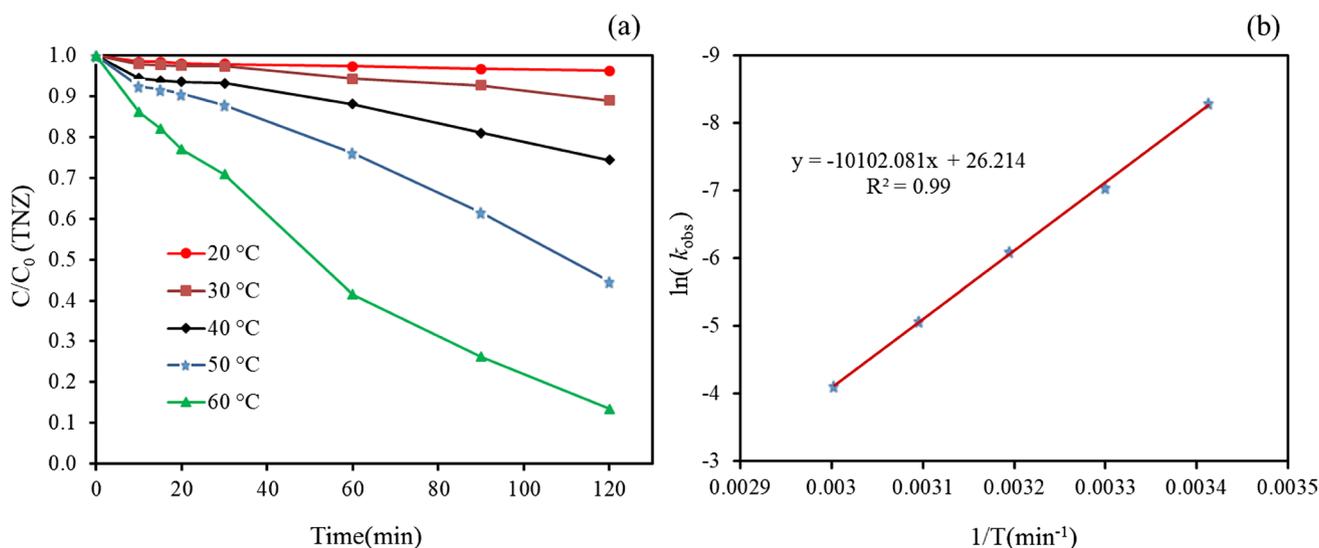
$$-\frac{d}{dt} = k_{\text{obs}} \quad (2)$$

where  $k_{\text{obs}}$  refers pseudo-first-order degradation rate constant ( $\text{min}^{-1}$ ) and  $d$  refers to TNZ concentrations (mM) at time  $t$ . As shown in Table 2,  $k_{\text{obs}}$  increased from  $0.3 \times 10^{-3} \text{ min}^{-1}$  to  $7.1 \times 10^{-3} \text{ min}^{-1}$  once temperature raised to 60 °C from 20 °C. This can be contributed to the increasing of thermal energy and enhancement of PS degradation rate, which in turn leads to increase of  $\text{SO}_4^{\bullet-}$  formation (Eq. 1) and other oxidants (Eqs. 3–6) for reaction with the target compound (Qi et al. 2018). These findings suggest that HAP may be an effective method for removing TNZ from certain environments or substances, and that higher temperatures can increase its efficiency.



In addition, to better explain the thermal dependency, the reaction rate constant ( $k_{\text{obs}}$ ) was calculated using Eqs. 7 and 8:

$$\ln k_{\text{obs}} = \ln A - \frac{E_a}{RT} \quad (7)$$



**Fig. 1** Effect of temperature on the oxidation of TNZ at different time intervals (a) and plot of  $\ln k_{\text{obs}}$  against  $T^{-1}$  for adopted from the Arrhenius equation (b) conditions:  $[\text{TNZ}]_0 = 20 \mu\text{M}$ ,  $\text{pH} = 7$ ,  $[\text{S}_2\text{O}_8]_0 = 0.8 \text{ mM}$

**Table 2** Pseudo-first-order rate constants for TNZ oxidation at different temperatures in HAP process (experimental conditions:  $[\text{TNZ}]_0 = 20 \mu\text{M}$ ,  $\text{pH} = 7$ ,  $[\text{S}_2\text{O}_8]_0 = 0.8 \text{ mM}$ )

Temperature (°C)	$K_{\text{obs}}$ ( $10^{-3} \text{ min}^{-1}$ )	$T_{1/2}$ (h)	$R^2$
20	0.25	46.45	0.8431
60	0.87	13.26	0.9769
40	2.23	5.18	0.9744
50	6.25	1.85	0.9641
60	16.38	0.705	0.9912

$$E_a = -\text{slope} \times R \quad (8)$$

where  $A$  and  $E_a$  represent the pre-exponential parameter and the apparent activation energy, respectively;  $R$  refers to the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  represents absolute temperature. By fitting the experimental data to Eq. 8, the value of  $E_a$  was found to be  $84 \text{ kJ/mol}$  (Fig. 1b), which falls within the normal range of  $60\text{--}250 \text{ kJ/mol}$  (Zhang et al. 2018). Moreover, the data of  $\ln k_i$  against  $1/T$  fit well with the Arrhenius equation ( $R^2 = 0.99$ ).

### The predominant radical(s) involved

To determine the primary type of reactive radical species responsible for TNZ degradation, we utilized two scavengers, EtOH and TBA, at a concentration of  $0.08 \text{ mM}$ . EtOH is well established as an effective quenching agent for both  $\text{SO}_4^{\cdot -}$  and  $\text{OH}^{\cdot}$  radicals, with its reaction rate toward the hydroxyl radical being 50 times greater than

that of sulfate radical. Conversely, TBA is known to be a suitable scavenger for  $\text{OH}^{\cdot}$  due to its reaction rate, which is 1000 times higher when compared to sulfate radicals (Eqs. 9–12) (Wang et al. 2018a). The rate constants of these scavengers reacting with the radicals were determined as follows:

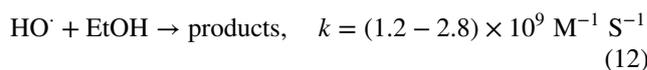
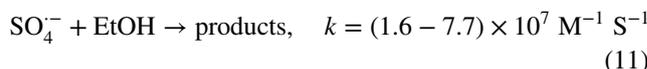
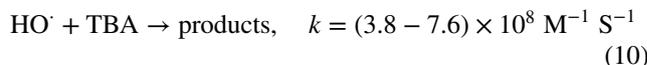
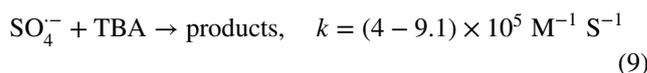
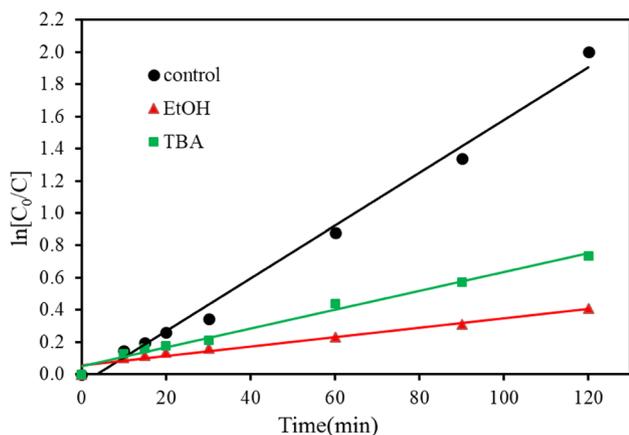


Figure 2 shows that the TNZ oxidation process was inhibited in the presence of both radical scavengers, mainly EtOH, as the corresponding values of the rate constants for the pseudo-first model in the presence of EtOH and TBA decreased by 82.94% and 65.88%, respectively. The results showed that both hydroxyl radicals ( $\text{OH}^{\cdot}$ ) and sulfate radicals ( $\text{SO}_4^{\cdot -}$ ) existed in the solution and contributed to the degradation of TNZ simultaneously. Despite the addition of radical scavengers, there is still some  $\text{SO}_4^{\cdot -}$  which can react with TNZ, as shown in Eqs. 9–12 and Fig. 2. Therefore, it seems that sulfate radicals are the predominant oxidants in TNZ decomposition, which is consistent with previous reports by Chen et al. (2018), Norzaee et al. (2018), and Ji et al. (2015b) on the oxidation of organic matter with HAP.



**Fig. 2** Effect of radical scavenger on different pseudo-first-order rate constants for TNZ oxidation by HAP process (experimental conditions:  $[TNZ]_0=20 \mu M$ ,  $pH=7$ ,  $[S_2O_8]_0=0.8 \text{ mM}$ ,  $[\text{radical scavenger}]_0=100 \text{ mM}$ )

**Effect of initial concentration of PS**

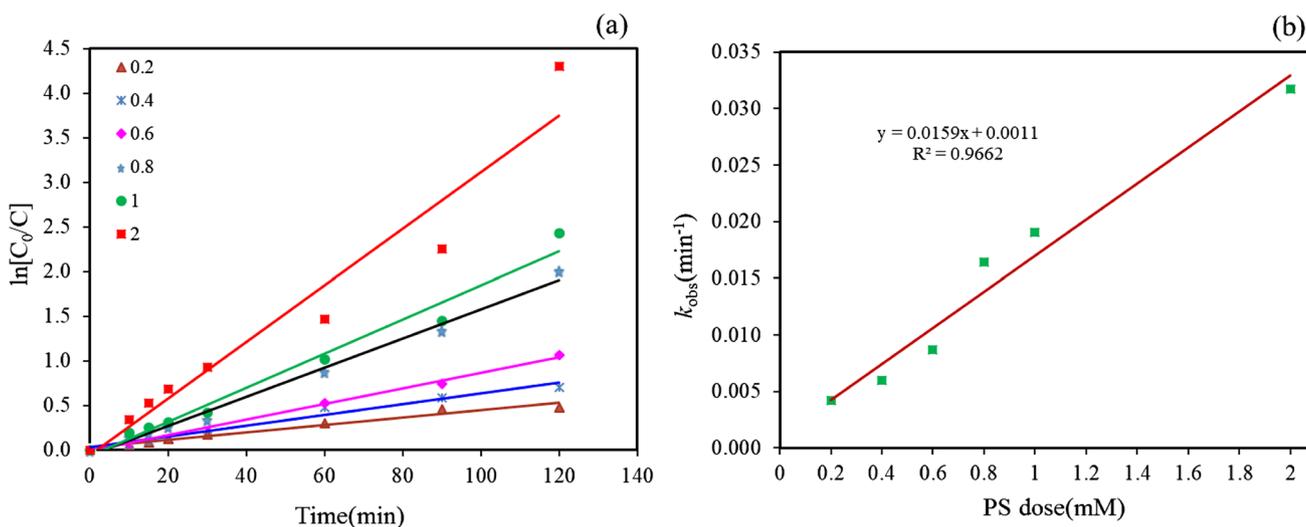
To optimize the PS initial dose, it was introduced at different concentrations from 0.2 to 2 mM at  $pH=7$ ,  $Temp=60 \text{ }^\circ C$ , and  $[TNZ]_0=20 \mu M$ . The results illustrated in Fig. 3 clearly showed that the TNZ removal efficiency significantly increased with increasing PS initial dose. The elimination efficiency of TNZ increased to more than 98% from 40% during 120 min at initial PS doses of 2 mM and 0.2 mM, respectively, mainly due to the improvement of sulfate radical production. The linear relationship between persulfate concentration and  $k_{obs}$  (Fig. 3) confirms that the reaction between the generated radicals ( $OH^\bullet$  and  $SO_4^{\bullet-}$ ) with the target antibiotic is predominant in comparison with other

possible side reactions. The higher level of oxidant generation at higher doses of persulfate is in close agreement with reports by Ji et al. (2015b) and Chen et al. (2017).

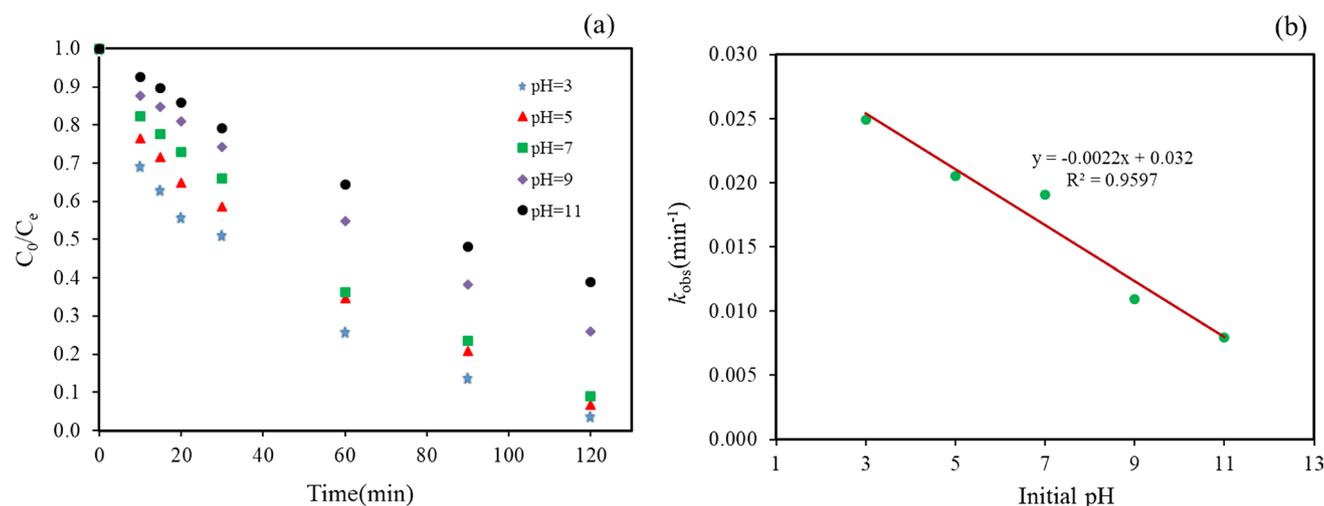
**Effect of initial pH**

It is well known that the production of active free radicals is the original mechanism in AOP-based processes. Solution pH has a detrimental effect on both the type and concentration of radicals contributing to the degradation of the target pollutant (Wang et al. 2018b; Liu et al. 2018; Mohammadi et al. 2017; Bazrafshan et al. 2012a, 2012b; Nguyen et al. 2006). The effect of initial pH values (3–11) on the process, along with their corresponding rate constants for TNZ decomposition, is illustrated in Fig. 4. As shown, there is a high correlation between process performance and pH. Additionally, at all pH values, TNZ degradation followed a pseudo-first-order reaction. Furthermore, TNZ decomposition accelerated as the solution pH increased, and  $k_{obs}$  decreased from 0.025 to 0.0079 with an increase in pH from 3 to 11.

This phenomenon can be attributed to the following reasons: (i) Due to its higher redox potential, persulfate can be catalyzed to form  $SO_4^{\bullet-}$  at acidic conditions, resulting in an enhancement of TNZ oxidation, as the highest efficiency was achieved at  $pH=3$ . (ii) With increasing pH up to 7, both  $OH^\bullet$  and  $SO_4^{\bullet-}$  contribute to the oxidation, while at higher pH values, the contribution of  $OH^\bullet$  would be increased. Since the ORP of  $OH^\bullet$  and its presence in an aqueous solution is lower than that of  $SO_4^{\bullet-}$ , a reduced efficiency would be expected at such pH values, as observed in this study. Therefore, the lowest efficiency and  $k_{obs}$  were achieved at  $pH=11$  as well. (iii)

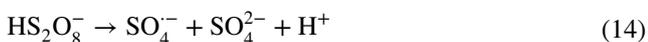


**Fig. 3** Effect of initial PS dose on the oxidation of TNZ at different reaction times (a) and  $k_{obs}$  against initial persulfate dose (b) (experimental conditions:  $[TNZ]_0=20 \mu M$ ,  $pH=7$ ,  $temp=60 \text{ }^\circ C$ )



**Fig. 4** Effect of initial pH on the oxidation of TNZ at different times (a) and pseudo-first-order rate constants ( $k_{obs}$ ) against pH, (b) conditions:  $[\text{TNZ}]_0 = 20 \mu\text{M}$ ,  $[\text{S}_2\text{O}_8]_0 = 1 \text{mM}$ ,  $\text{temp} = 60 \text{ }^\circ\text{C}$

Additionally, at alkaline conditions, hydroxide ions can act as  $\text{SO}_4^{\cdot-}$  scavengers and transform them into hydroxyl radicals (Eq. 4). While the latter is an unselective radical, it may also contribute to reactions 15 and 16 and decrease TNZ degradation rate (Norzaee et al. 2018; Chen et al. 2017). Therefore, it can be concluded that the relationship between  $k_{obs}$  and efficiency with pH is mainly due to pH governing the type and concentrations of produced radicals.

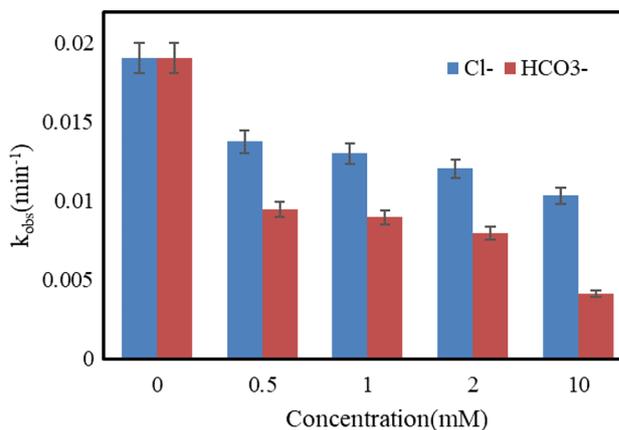


### Effect of coexisting ions

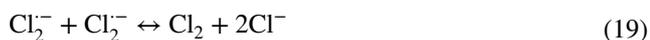
Natural waters contain various ions that may compete with the targeted species for adsorption sites or react with active oxidants in adsorption and AOP-based processes, respectively. Since this is an important issue, especially from a real-scale application perspective, such effects should be investigated (Nguyen et al. 2006). Therefore, the interference of competitive ions, such as chloride and bicarbonate, at different concentrations (0–10 mM), on TNZ degradation by HAP was assessed.

### The effect of chloride ion

The existence of chloride ions can generally decrease the efficiency of AOP processes in which sulfate and hydroxide radicals are the main oxidation agents (Liu et al. 2018). In the present study, it was also observed that TNZ removal using HAP followed the pseudo-first-order model well (with  $R^2$  for all cases  $> 0.97$ ), and  $k_{obs}$  decreased with an increase in Cl concentration (Fig. 5). This can be due to the reaction of  $\text{OH}^{\cdot}$  and  $\text{SO}_4^{\cdot-}$  with chloride radicals, which leads to the generation of different chloride oxidation species, as listed in Eqs. 17–21 (Ji et al. 2015a; Chen et al. 2017; Wang et al. 2018b), all of which have a lower ORP than the two original oxidants (i.e.,  $\text{OH}^{\cdot}$  and  $\text{SO}_4^{\cdot-}$ ).



**Fig. 5** Effects of chloride and bicarbonate concentration on the pseudo-first-order rate constants ( $k_{obs}$ ), Conditions:  $[\text{TNZ}]_0 = 20 \mu\text{M}$ ,  $\text{pH} = 7$ ,  $[\text{S}_2\text{O}_8]_0 = 1 \text{mM}$ ,  $\text{temp} = 60 \text{ }^\circ\text{C}$

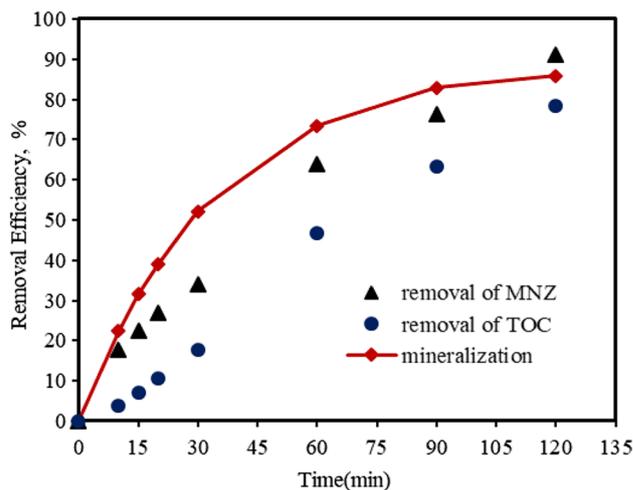


### The effect of bicarbonate

Bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) are two of the most important indicators of alkalinity in water solutions that can easily convert to each other, while their chemical equilibrium strongly depends on pH (Ji et al. 2015a; Chen et al. 2017). Several studies have shown that  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions can act as radical scavengers and reduce the performance of  $\text{OH}^{\cdot}$  and  $\text{SO}_4^{\cdot-}$ . The final product of such reactions is carbonate radicals, which react with organic carbon 2–3 times slower than their parents. Therefore, it is expected that an increase in  $\text{HCO}_3^-$  concentration would result in a decrease in AOP process efficiency. Figure 5 shows that at  $\text{HCO}_3^-$  concentrations between zero and 10 mM, the reaction rate constant decreased from 0.019 to 0.004, respectively. Additionally, it is clear from Fig. 5 that the inhibition effect is more pronounced at higher concentrations of  $\text{HCO}_3^-$ , which may be due to the greater pH decrease induced by the higher concentration, which, in turn, decreases the oxidation efficiency as discussed before.

### Mineralization

Achieving high removal efficiency cannot be interpreted as complete elimination of the target pollutant, and it may decompose into other organic by-products. Hence, the extent of mineralization in a process can determine how effectively the process removes the pollutant, without any concern for the production of by-products, whose dangers are sometimes equal to or even greater than those of the virgin pollutant. TOC concentrations, along with mineralization measurements, are presented in Fig. 6. As shown, during the 120 min reaction, approximately 91.15%, 85.8%, and 78.25% TNZ removal, mineralization, and TOC removal, respectively, can be achieved. Lynn et al. reported that after 120 min of contact time, 95% of the antibiotic ciprofloxacin was mineralized by UV-activated persulfate process (Lin and Wu 2014). Additionally, in the study by Norzaee et al., more than



**Fig. 6** TNZ and TOC removal and mineralization percentage during HAP process, conditions:  $[\text{TNZ}]_0 = 20 \mu\text{M}$ ,  $\text{pH} = 7$ ,  $[\text{S}_2\text{O}_8]_0 = 1 \text{mM}$ ,  $\text{temp} = 60^\circ\text{C}$

68% of ciprofloxacin was transformed into its mineral form within 75 min (Norzaee et al. 2018).

### Comparison with the other studies

Table 3 summarizes the literature reports on the removal of antibiotics by the HAP process. To make performance comparable, the listed studies have been normalized by the main effective operational parameters. As shown in Table 3, the results of the present study are in close agreement with those reported by similar studies. From a performance point of view, the findings are very close to the results reported by other studies. (Ji et al. 2015a; Arvaniti et al. 2022a, 2022b; Seid-mohammadi et al. 2020; Hasani et al. 2023). This study also highlights various aspects in comparison with other reported works. For example, TNZ abatement has been observed at a more natural pH (i.e., at pH 7) than in other studies where high efficiency only occurred at acidic or basic pH values (Chen et al. 2018, 2017; Norzaee et al. 2018; Ji et al. 2015b). Furthermore, TOC and COD abatement, as the main parameters for comparing degradation processes, are not reported in most of the listed studies. Therefore, more studies still need to be explored to overcome technical and practical barriers in scaling up the process for big- and real-scale applications.

### Conclusion

A clean and novel method based on thermally activated persulfate was successfully applied to remove TNZ from aqueous solutions. The main findings of this work can be categorized as follows:

**Table 3** Comparisons of the results for antibiotics removal using HAP

antibiotic	Operation conditions	Optimum conditions	Results	References
sulfamethoxazole	SMX = 30 $\mu$ M temp = 30–60 $^{\circ}$ C pH = 4–10.1 PS = 2 mM Time = 0–480 min	pH = 7 Temp = 50 $^{\circ}$ C Time = 600 PS = 2 mM	SMX degradation followed pseudo-first-order reaction kinetics R ~ 80%	Ji et al. (2015a)
Penicillin	PCN G = 0.02 mM Time = 0–75 Temp = 40–80 $^{\circ}$ C pH = 3–11 PS = 0.05–0.5 mM	Penicillin G = 0.02 mM Time = 75 Temp = 40 $^{\circ}$ K pH = 5 PS = 0.5 mM	PNE G removal = 98% - TOC removal = 68.7% - COD removal = 77.5%	Johnson et al. (2008)
Sulfamethazine	SMZ = 30 $\mu$ M pH = 3–11 PS = 0.25–4 mM Time = 0–360 min Temp = 40–60 $^{\circ}$ C	pH = 9 PS = 2 mM Time = 120 min Temp = 50 $^{\circ}$ C	Removal SMZ = 86%	Faria et al. (2019)
Cephalexin	CPN = 0.1 mM pH = 7 PS = 1.1 mM Time = 0–240 min Temp = 50–65 $^{\circ}$ C	Time = 120 min Temp = 65 $^{\circ}$ C	Removal CPN = 100%	Wang et al. (2018a)
Sulfachloropyridazine	SCP = 3.51 $\mu$ M pH = 3–10 PS = 0–280 $\mu$ M Time = 0–300 min Temp = 30–50 $^{\circ}$ C	Temp = 45 $^{\circ}$ C PS = 140 $\mu$ M pH = 3	Removal SCP = 100%	Qiu et al. (2022)
Tetracycline	TCN = 30 $\mu$ M pH = 7 PS = 2 mM Time = 0–240 min Temp = 40–70 $^{\circ}$ C	Temp = 70 $^{\circ}$ C Time = 30 min pH = 9	Removal TCN = 100%	Chen et al. (2018)
Trimethoprim	TMP = 30 $\mu$ M pH = 3–11 PS = 2 mM Time = 0–480 min Temp = 50–65 $^{\circ}$ C	Temp = 55 $^{\circ}$ C pH = 3	Removal = 100%	Norzaee et al. (2018)
Tinidazole	TZN = 20 $\mu$ M pH = 3–11 PS = 0.2–2 mM Time = 10–120 min Temp = 20–60 $^{\circ}$ C	pH = 7 [PS] <sub>0</sub> = 1 mM temp = 60 $^{\circ}$ C Time = 120 min	TZN removal = 91.15% TOC = 78.25%	This study

- Persulfate initial concentration can significantly increase TNZ removal efficiency mainly due to enhanced radical generation.
- Sulfate radicals were found to be the main oxidation agent in the degradation of TNZ using the HAP process.
- The process was also highly dependent on pH and temperature, with efficiency increasing at low pH values and high temperatures.
- An 85% TOC abatement at the optimum conditions, where TNZ removal was found to be 91.15%, indicates efficient mineralization of the antibiotic.

Overall, the results showed that the HAP process can be considered a promising method for addressing the

challenges related to high levels of recently detected TNZ in environmental matrices. However, more investigation is needed to evaluate the process at low TNZ concentrations as observed in real matrices. The effect of other interferences such as natural organic matter and coexisting anions and cations should also be considered.

**Acknowledgements** This project was financially supported by Torbat Heydariyeh University of Medical Sciences under grant number A-10-1350-4. Also, the project is in accordance with the ethical principles and the national norms and standards for conducting Medical Research in Iran (IR.THUMS.REC.1398.010).

**Author contributions** All authors had equal contributions in writing, review, and final approval of the paper.

**Funding** The current study was financially supported by Torbat Heydariyeh University of Medical Sciences.

**Data availability** The dataset and analyzed during the current study are available from the corresponding authors on realistic demand.

## Declarations

**Conflict of interest** The authors declare that there is no conflict of interest regarding the publication of this work.

**Ethical approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

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