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Efficient metformin transformation in sulfite/UV process co-present with oxygen

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UV/sulfite process without oxygen has been extensively explored and used for the degradation of many micro-pollutants. In the present work, a UV/sulfite process in the presence of oxygen was applied to degrade a widely used pharmaceutical compound, metformin (MET). The results showed that the oxygen-involved UV/sulfite process could efficiently degrade MET. At an initial concentration of 2.5 mg/L, 86.0% of MET was removed from the contaminated water within 180 min irradiation at a sulfite dosage of 10 mM, solution pH of 9, and UV intensity of 4,092 $\mu\text{W}/\text{cm}^2$. In addition, sulfate radical ($\text{SO}_4^{\bullet-}$), hydroxide radical ($\bullet\text{OH}$), hydrogen atom ($\bullet\text{H}$), and hydrated electron (e_{aq}^-) were found to be the dominant active species contributing to MET removal in the studied process through scavenging experiments. The increase in UV intensity, sulfite dosage, solution pH, and reaction temperature enhanced MET degradation in the investigated process to a certain extent, whereas the introduction of bicarbonate and fulvic acid slightly suppressed MET degradation. Finally, the degradation products of MET were identified. The oxygen-involved UV/sulfite process exhibited a remarkable denitrification capacity (>80%) in MET. The findings of this study may offer a novel approach for treating emerging contaminants.

KEYWORDS

sulfite, UV, oxygen, metformin, AOPs

1 Introduction

Pharmaceutical and personal care products (PPCPs) comprise diverse organic substances, including antibiotics, analgesics, hormones for pharmaceuticals and cosmetics, antibacterial agent, preservatives for personal care products (Zhang et al., 2022). Metformin (MET), a common antidiabetic drug used for type II diabetes treatment, has been ranked among the most widely used PPCPs because more than 200 million people are suffering from diabetes worldwide (Yu et al., 2022). The widespread use of MET inevitably results in its emission into the environment through wastewater discharge as conventional wastewater treatment approaches (i.e., flocculation, activated carbon filtration, and bio-degradation) are ineffective for MET removal (Scheurer et al., 2009). Thus, the occurrence of MET in sewage, effluent in sewage treatment plants, and surface water is frequently reported (Ambrosio-Albuquerque et al., 2021). For example, a relatively high concentration of MET ranging from 70 to 325 $\mu\text{g}/\text{L}$ was found in the effluent of a Portuguese sewage treatment plant (Gaffney et al., 2017). The potential bio-toxicity of MET, such as causing estrogenic effects or acting as an endocrine disruptor, has been

reported in some literature (Niemuth and Klaper, 2015; Crago et al., 2016). Hence, MET has become an emerging pollutant in aquatic environments.

Several attempts have been made to alleviate MET contamination, including graphene oxide adsorption, photo-oxidation, and electro-oxidation (Zhu et al., 2017; Karimiana et al., 2020). Owing to the operational simplicity and cost-efficiency of light sources, photo-oxidation methods (i.e., UV/Fenton, UV/H₂O₂, and UV/TiO₂) have become the most favored treatment techniques for organic pollutants degradation (Zhou et al., 2017; George et al., 2022).

In recent decades, the UV/sulfite system has gained increasing attention as an often-mentioned advanced reduction process (ARP) because of the production of various reductive species, such as hydrated electron (e_{aq}^- , $E = -2.9$ V) and hydrogen atom ($\bullet H$, $E = -2.3$ V) (Vellanki et al., 2013; Ding et al., 2022). Several halogenated organic pollutants decomposition by the UV/sulfite system have already been investigated. For instance, Song et al. (2013) reported that perfluorooctanoic acid (PFOA), which is an extremely recalcitrant halogenated contaminant, can be completely decomposed in the UV/sulfite system after 1 h reaction, and a high defluorination efficiency of approximately 90% could be obtained by extending the reaction time to 24 h. Liu et al. (2015) achieved nearly 40% degradation efficiency of atenolol (20 μ M) even at a neutral solution pH. In the above-mentioned degradation process, e_{aq}^- was manifested the dominant reductive species contributing to the decomposition of the target pollutants, and oxygen was previously removed from the reaction system by purging nitrogen, because oxygen can react with e_{aq}^- and lead to superoxide radical ($O_2\bullet^-$) generation. Nevertheless, once oxygen is applied in the sulfite mediated UV photolysis system, another mild radical, namely sulfite radical ($SO_3\bullet^-$), is likely to be transformed into a highly reactive oxidant sulfate radical ($SO_4\bullet^-$) (Deister and Warneck, 1990), indicating that the oxygen-involved UV/sulfite system can be regarded as a prospective advanced oxidation process (AOP) (Huang et al., 2018; Li et al., 2020). Recently, (Chen et al. (2021) developed a synergetic-photoelectric sulfite mediated system where oxygen was continuously produced through water electrolysis. The combined effect of electrolysis and photolysis on sulfite brings about a large number of active species generation. The steady-state $SO_4\bullet^-$ concentration was determined as ranging from $.2 \times 10^{-12}$ to 1.1×10^{-12} M. Correspondingly, this reaction system had extraordinary oxidative capacity in removing micro-pollutants such as ibuprofen and bisphenol A. Although several researchers have explored treatment efficiency of the oxygen-involved UV/sulfite system towards some emerging contaminants (i.e., atrazine, bisphenol A, trichlorophenol) (Cao et al., 2021a), the systematic investigation on the degradation efficiency of the antidiabetic drug, namely MET, was still scanty. Furthermore, investigation of the oxygen-involved UV/sulfite system on target pollutant removal in the real water matrix was also scarce.

Herein, a UV/sulfite system with the co-presence of oxygen was built and utilized for MET degradation. The crucial species contributing to MET degradation were ascertained. The impact of several common factors such as pH value of testing solution, reaction temperature, sulfite dosage and co-present compounds on MET degradation was evaluated. In addition, MET degradation in a real water matrix was monitored. The degradation products of MET as well as the bio-toxicity change of the testing solution were also determined. Outcomes in the present work suggests a distinctive treatment technology for emerging contaminants.

2 Materials and methods

2.1 Materials

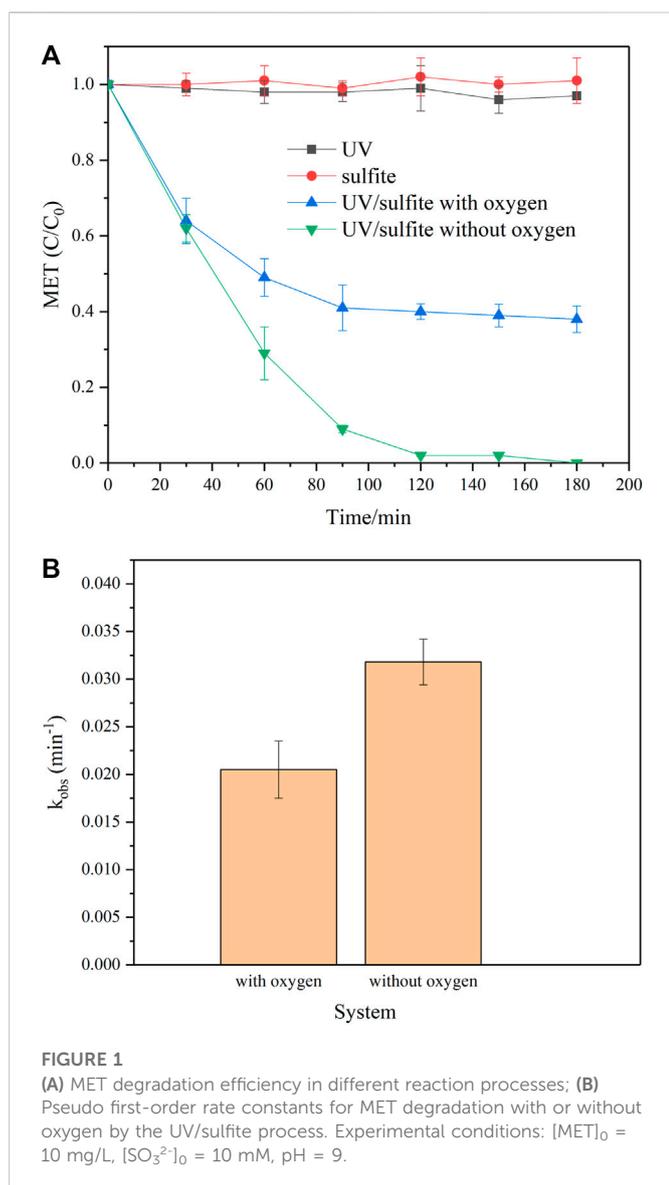
Metformin hydrochloride (MET, 97.0%, C₄N₅H₁₁•HCl), sodium sulfite (98.0%, Na₂SO₃), tertiary-butanol (TBA, $\geq 99.5\%$, C₄H₁₀O), methanol (MeOH, $>99.9\%$, CH₃OH), fulvic acid (85.0%, FA), potassium nitrate ($>99.0\%$, KNO₃), superoxide dismutase (SOD, $\geq 1,400$ units/mg dry weight), and sodium bicarbonate (99.7%, NaHCO₃) were purchased from Aladdin Co., LTD. (Shanghai, China) or Sigma-Aldrich Co., LTD. (Guangzhou, China). A Millipore purification system (Milli-Q IQ 7000, Darmstadt, Germany) was employed for the generation of ultrapure water and subsequent preparation for diverse reaction solution.

2.2 MET degradation experiments

MET degradation experiments were conducted in a 3-L cylindrical glass vessel (Supplementary Figure S1). A mixed solution containing MET and sulfite was filled into the vessel and magnetically stirred during the degradation process. In addition, the testing solution was purged with air or nitrogen gas (1 L/min) for 180 min. Apart from investigating the impact of solution pH on MET removal, the solution pH was maintained at approximately 9 with 10 mM phosphate buffer. A monochromatic low-pressure lamp ($\lambda = 254$ nm, 10 W, Dongguan, China) with a quartz sleeve enclosure was used as the irradiation source. The UV lamp was ignited and warmed for 30 min before commencing the irradiation experiments to obtain a stable output. MET batch degradation experiments were carried out at a constant temperature (25°C) through a thermostatic recirculation system (THD-1015, Ningbo, China). KNO₃ (5 mM), NaNO₂ (5 mM), MeOH (300 mM), TBA (300 mM), and SOD (3.3 mg/L) were introduced as scavengers to ascertain the contribution of different active species to MET degradation. Sulfite dosage was changed from 2.5 mM to 15 mM to study the impact of the sulfite dosage on MET removal. To reveal the impact of UV intensity on MET degradation efficiency, the UV lamp was wrapped with a few aluminum foil to change UV light emitted into the reaction solution (Li et al., 2014). The maximum UV intensity (100% I₀) entering into the reaction solution was measured to be 4,092 μ W/cm² using a UV irradiator (Linshang Co., LTD., Shenzhen, China). Additionally, effect of the coexisting constituents such as HCO₃⁻ and natural organic matter (NOM) on MET removal was monitored by adding diverse concentrations of HCO₃⁻ (0–2.0 mM) and FA (0–15 mg/L) to the reaction system. Additionally, two surface water samples from Dasha River in Nanshan District (Shenzhen, China) was obtained and used to evaluate MET degradation efficiency in a real water matrix. Water quality parameters of the surface water samples were listed in Supplementary Table S1. Samples were withdrawn at the preset intervals for immediate analysis. All experiments were performed in triplicate, and the mean values were presented.

2.3 Analysis procedures

MET concentration was analyzed by using a Waters high-performance liquid chromatography which was equipped with a



reversed C18 column (5 μm , 4.6×250 mm, Phenomenex, Torrance, United States) and a UV detector. The separation conditions were set as follows: A mixed solution which contained .1% acetic acid (80%) and MeOH (20%) was employed as mobile phase. The flow rate of mobile phase was determined as 1.0 mL/min. The wavelength of the UV detector for MET concentration measurement was 246 nm.

A pH meter (Mettler Toledo, Shanghai, China) was employed for solution pH determination. Inorganic degradation products of MET such as nitrite and ammonia nitrogen were detected through a colorimetric method. The detection of organic intermediates was performed in a ultra high-performance liquid chromatography (UPLC, Agilent 1290, CA, United States) coupled with time-of-flight mass spectrometry (AB SICEX Tripe TOF 4600, CA, United States). The mobile phase was a mixture of acetonitrile (10%) and .1% formic acid (90%) with a flow rate of .8 mL/min. The column temperature and injection volume of sample were set at 30°C and 10 μL , respectively. Bio-toxicity of the testing solution was determined by the luminescent bacteria toxicity test referring to the guideline from ISO standard (quality, 2007), and the relative

inhibition rate towards luminescent bacteria was used as an indicator to reflect bio-toxicity of the testing solution.

3 Results and discussion

3.1 MET degradation in direct UV and UV/sulfite systems

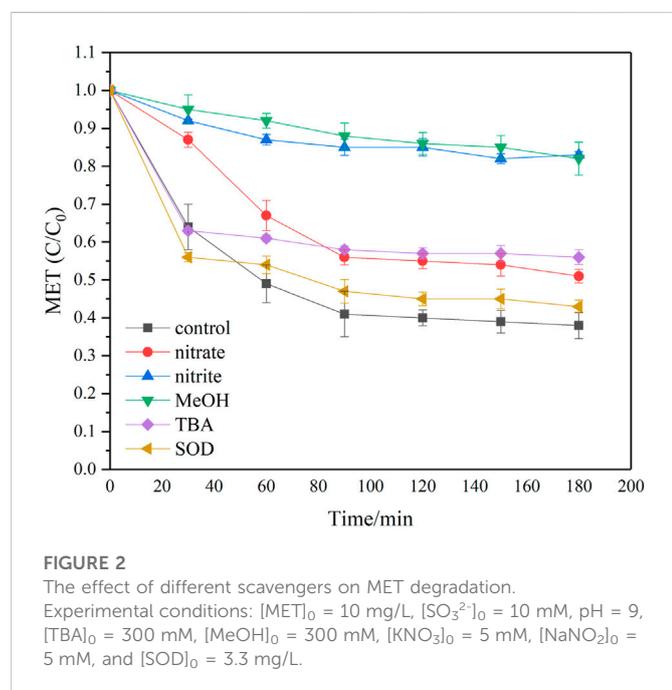
MET degradation in four different reaction systems was monitored, and the results were shown in Figure 1A, B. 62.0% MET removal was obtained after 180 min irradiation in the oxygen-involved UV/sulfite system at sulfite dosage of 10 mM, whereas negligible MET removal (<5%) was achieved in direct UV and sulfite systems, which was ascribed to the weak absorption of MET in the UV-C region and poor reduction capacity of sulfite (Maćerak et al., 2018; Karimiana et al., 2020). Although the oxygen-free UV/sulfite system behaved better MET treatment efficiency, it needed constant purging of nitrogen gas, which made it unpractical for real wastewater treatment. MET degradation kinetics in the two UV/sulfite system were found to fit the pseudo first-order model, and observed rate constants (k_{obs}) were .0205 min⁻¹ and .0318 min⁻¹, respectively. Comparison between this work and previous investigations concerning about MET removal by photolytic methods was conducted (Table 1), and k_{obs} of MET degradation in this work was a bit faster than that of previous studies. Additionally, energy consumption needed for MET removal to half of its initial concentration was calculated as .1 kJ/ μmol , which was at least 1–2 order of magnitude lower than that of other emerging contaminants (i.e., PFOA, ICMS) degraded by photolytic techniques (Vecitis et al., 2009; Gu et al., 2022). The obtained results suggested the studied oxygen-involved UV/sulfite process was promising for practical MET-containing wastewater treatment.

The extraordinary MET degradation performance in the UV/sulfite system was ascribed to the generation of reactive species. When sulfite undergoes UV photolysis, reactive species like e_{aq}^- , $\cdot\text{H}$, and $\text{SO}_3^{\cdot-}$ have been reported to be produced before (Milh et al., 2021). In addition, the studied system was continuously purged with air, thus oxygen was likely to react with $\text{SO}_3^{\cdot-}$ and lead to $\text{SO}_4^{\cdot-}$ generation (Eqs. 1–4). According to Yang et al. (2015), hydroxyl radical ($\cdot\text{OH}$) can be transformed from $\text{SO}_4^{\cdot-}$ in the testing solution. Hence, at least five kinds of reactive species, namely e_{aq}^- , $\cdot\text{H}$, $\text{SO}_3^{\cdot-}$, $\text{SO}_4^{\cdot-}$, and $\cdot\text{OH}$, were likely to exist in the studied system. Scavenging reactions were conducted to determine the primary active species that contributed to MET removal.

As shown in Figure 2, the introduction of both MeOH and TBA inhibited MET degradation. However, the inhibition effect of MeOH was more obvious, indicating that both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ contributed to MET degradation. Because MeOH reacted quickly with both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ at a comparable rate constant, whereas TBA merely efficiently quenched $\cdot\text{OH}$ (Supplementary Table S2). Moreover, nitrate and nitrite were employed in the reaction system to uncover the role of reductive species (i.e., e_{aq}^- , $\cdot\text{H}$) played in MET removal, and MET degradation was apparently suppressed in the presence of nitrate and nitrite, where nitrite exhibited a more obvious inhibition. When 5 mM of nitrate and nitrite were introduced into the reaction system individually, MET degradation ratio decreased by 13.0% and 44.7% after 180 min irradiation, respectively. It is well documented that both nitrate

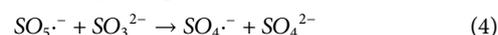
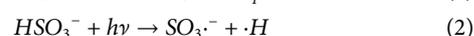
TABLE 1 Summary of previously reported literature for photolysis of MET.

Degradation methods	Reaction conditions	Removal ratio (%)	Time (min)	k_a (min^{-1})	Reference
UV/Fenton	$[\text{MET}]_0 = 1,027 \text{ ng/L}$	43	10	—	Cruz et al. (2012)
	$[\text{H}_2\text{O}_2]_0 = 50 \text{ mg/L}$				
	$[\text{Fe}^{2+}]_0 = 5 \text{ mg/L}$ pH near neutral				
	light source UV ₂₅₄				
UV/H ₂ O ₂	$[\text{MET}]_0 = 2 \text{ }\mu\text{M}$	≈45	60	.0152	Neamtu et al. (2014)
	$[\text{H}_2\text{O}_2]_0 = 300 \text{ }\mu\text{M}$ pH 6.5			$\tau_{1/2} = 45.6 \text{ min}$	
UV/TiO ₂	$[\text{MET}]_0 = 10 \text{ mg/L}$	31	30	—	Quintão et al. (2016)
	$[\text{TiO}_2]_0 = 120 \text{ mg/L}$ light source UV ₂₅₄				
UV/TiO ₂ /PDS	$[\text{MET}]_0 = 5 \text{ mg/L}$	91.6	210	.013	Nezar and Laoufi, (2018)
	$[\text{TiO}_2]_0 = 100 \text{ mg/L}$			$\tau_{1/2} = 53.3 \text{ min}$	
	$[\text{K}_2\text{S}_2\text{O}_8]_0 = 1,000 \text{ mg/L}$				
	pH free				
VUV/Fe ²⁺ /PMS	$[\text{MET}]_0 = 50 \text{ mg/L}$	89.7	30	—	Karimiana et al. (2020)
	$[\text{Fe}^{2+}]_0 = .05 \text{ mg/L}$				
	$[\text{PMS}]_0 = 50 \text{ mg/L}$ pH 6.3				
	light source VUV				
Oxygen-involved UV/sulfite system	$[\text{MET}]_0 = 10 \text{ mg/L}$	62.0	180	.0205	This work
	$[\text{SO}_3^{2-}]_0 = 10 \text{ mM}$ pH 9			$\tau_{1/2} = 33.8 \text{ min}$	
	light source UV ₂₅₄				



and nitrite can efficiently scavenge e_{aq}^- at $10^9 \text{ M}^{-1}\text{s}^{-1}$ level (Buxton et al., 1988). Nevertheless, nitrite reacts with $\cdot\text{H}$ approximately 500 times as fast as that for nitrate (Buxton et al., 1988), which led

to a similar e_{aq}^- concentration but a much lower $\cdot\text{H}$ concentration. The different $\cdot\text{H}$ and e_{aq}^- concentration was thus used to identify their impact on MET removal. Results in Figure 2 indicated both $\cdot\text{H}$ and e_{aq}^- participated in the MET degradation process. Considering another mild oxidant, $\text{SO}_3^{\cdot-}$ ($E_0 = .63 \text{ V}$, pH = 7) (Buxton et al., 1988), many studies have reported its negligible contribution to target pollutant decomposition in sulfite-based UV photolytic system (Li et al., 2012; Gu et al., 2016). Notably, the generated $\text{SO}_3^{\cdot-}$ can be transformed into highly oxidative $\text{SO}_4^{\cdot-}$ when co-present with oxygen, as demonstrated in the above discussion by alcohol inhibition experiments. Consequently, participation of $\text{SO}_3^{\cdot-}$ in MET degradation can be excluded. In the presence of oxygen, e_{aq}^- may be quickly quenched and resulted in $\text{O}_2^{\cdot-}$ generation (Deister and Warneck, 1990). Therefore, SOD was selected as the quencher and applied to the reaction solution to evaluate the contribution of $\text{O}_2^{\cdot-}$ to MET degradation. Negligible MET suppression (<5%) was observed when SOD was introduced into the UV/sulfite process, suggesting an insignificant role of $\text{O}_2^{\cdot-}$. In summary, it is highly probable that reactive species, including $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, $\cdot\text{H}$ and e_{aq}^- , mainly accounted for MET degradation in the oxygen-involved UV/sulfite system.



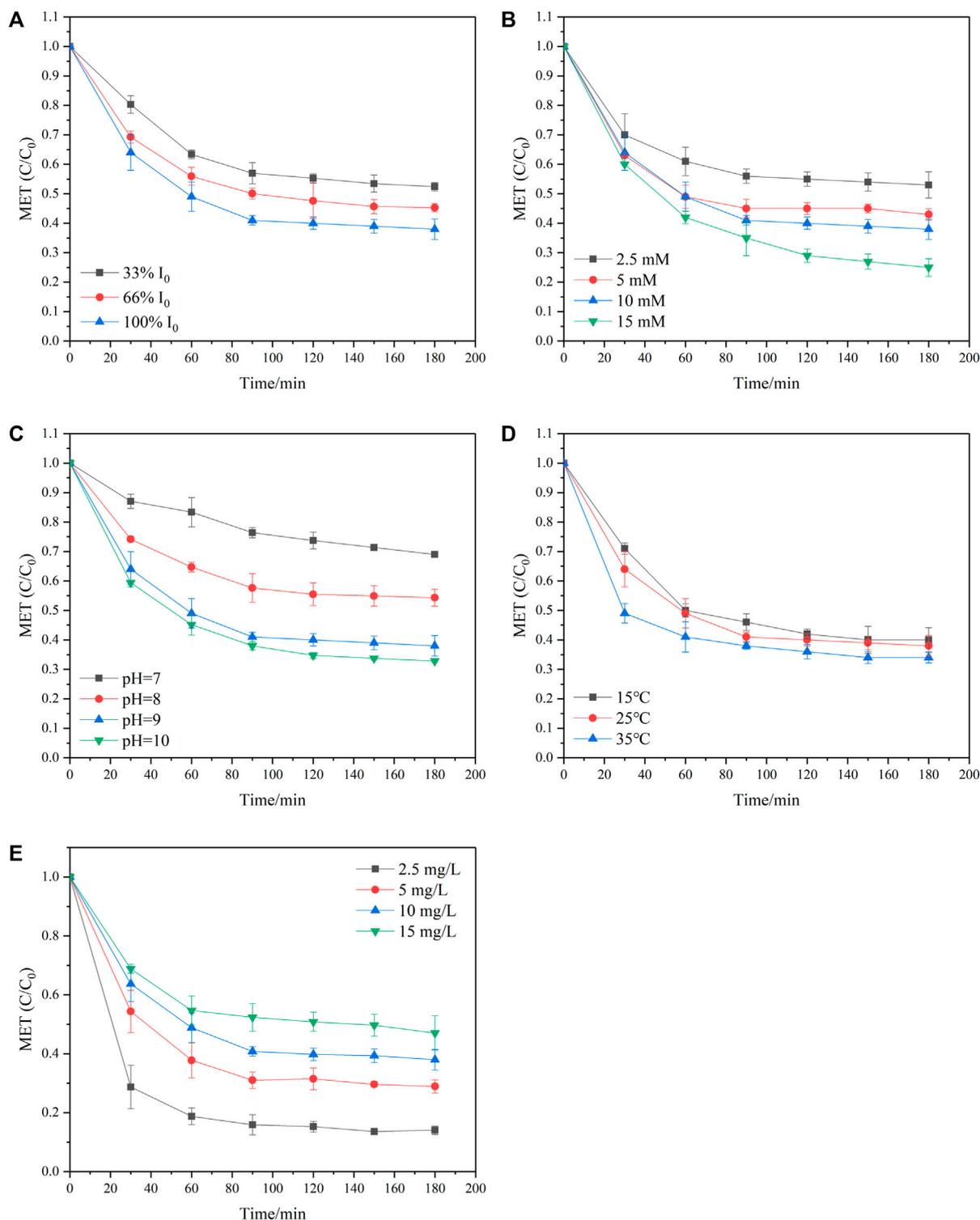


FIGURE 3

The effect of different water quality or operating parameters (A) UV intensity; (B) sulfite dosage; (C) solution pH; (D) reaction temperature; (E) initial MET concentration on MET degradation by the oxygen-involved UV/sulfite system. Experimental conditions: [MET]₀ = 10 mg/L, [SO₃²⁻]₀ = 10 mM, pH = 9, T = 25°C.

3.2 Influence of incident UV intensity

In the UV photolytic process, the incident UV intensity is a major factor determining the reaction rate between target pollutant and reactive species generated. Zhang et al. (2013) found methylene blue

removal rate in a UV/TiO₂/H₂O₂ system was positively proportional to the UV intensity. Similar results were reported by Liu et al. (2014) A higher UV intensity was found beneficial for enhancing dichloroethane removal in a UV/sulfite system, and the observed rate constant of dichloroethane removal showed a linear relationship

with UV intensity ($R^2 > .99$). MET degradation experiments at different UV intensity were carried out and results were presented in [Figure 3A](#). MET degradation ratio was obviously enhanced by increasing UV intensity. MET degradation efficiency altered from 47.6% to 62.0% after 180 min reaction when UV intensity varied from 33% I_0 to 100% I_0 . MET degradation in the UV/sulfite system followed pseudo first-order kinetics ($R^2 > .98$) ([Supplementary Table S2](#)). The observed rate constants of MET degradation at 100% I_0 was almost doubled when compared with that at 33% I_0 . When UV intensity entering the testing solution increased, the amount of generated radicals increased accordingly, which in consequence led to a faster MET removal. Referring to previous investigations, the generation rates of e_{aq}^- and $SO_3^{\cdot-}$ are proportional to UV intensity under alkaline pH conditions when sulfite undergoes UV photolysis ([Song et al., 2013](#)). e_{aq}^- and $SO_4^{\cdot-}$ which was produced through chain reactions between O_2 and $SO_3^{\cdot-}$, were manifested the governing active species accounting for MET degradation in [Section 3.1](#). Thus an increase in UV intensity would benefit MET transformation in the studied reaction system.

3.3 Influence of sulfite dosage

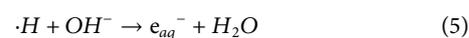
Different sulfite concentrations were introduced to monitor their influence on MET removal at an initial MET concentration of 10 mg/L, and the results were presented in [Figure 3B](#). MET degradation was apparently enhanced by increasing sulfite dosage. As depicted in [Figure 3B](#), increasing sulfite dosage from 2.5 mM to 15 mM led to a higher degradation ratio of MET, increasing from 46.9% to 75.5% after 180 min irradiation. The obvious promotion on MET removal at higher sulfite dosage further confirmed the negligible role of direct photolysis. If direct photolysis governs the MET degradation process, the augmentation of sulfite dosage may result in a decrease in UV intensity, which otherwise would be absorbed by MET, and thus causing a reduction in k_{obs} ([Liu et al., 2014](#)). As depicted in [Figure 3B](#) and [Supplementary Table S3](#), the optimal sulfite dosage was 10 mM, and further increasing the sulfite concentration slowed MET degradation rate. At a constant solution pH and UV intensity, the reactive species (i.e., e_{aq}^- and $SO_3^{\cdot-}$) production was positively correlated with sulfite dosage ([Yoon et al., 2014](#)), thereby causing the difference in MET degradation kinetics. When sulfite dosage was changed from 2.5 mM to 10 mM, a 1.1 fold increase in k_{obs} was observed ([Supplementary Table S3](#)). Nevertheless, a further increase in sulfite dosage to 15 mM led to a decline in k_{obs} to $.0175 \text{ min}^{-1}$. At higher sulfite dosages, the scavenging reactions between the generated reactive species (e.g., $\cdot H$, e_{aq}^-) and co-present constituents became vigorous, thus enormous reactive species were quenched, and their use in MET degradation was limited ([Fu et al., 2010](#); [Yazdanbakhsh et al., 2018](#)). Consequently, sulfite dosage exhibited less of enhancement effect on MET degradation, which was reflected by the reduction in k_{obs} .

3.4 Influence of solution pH

Apart from sulfite dosage, the solution pH also affected the degradation of target pollutants in the sulfite mediated photolysis process. [Figure 3C](#) presented the effect of solution pH on MET removal at a sulfite dosage of 10 mM. MET degradation was

substantially facilitated when the solution pH was changed from neutral to alkaline conditions. The optimal solution pH was at 9, further increasing the solution pH brought about slight enhancement both in degradation efficiency and rate of MET. Moreover, MET degradation kinetics in the investigated solution pH range was well depicted by the pseudo first-order model ([Supplementary Table S3](#)), which was in accordance with previous studies ([Li et al., 2012](#); [Liu et al., 2015](#)).

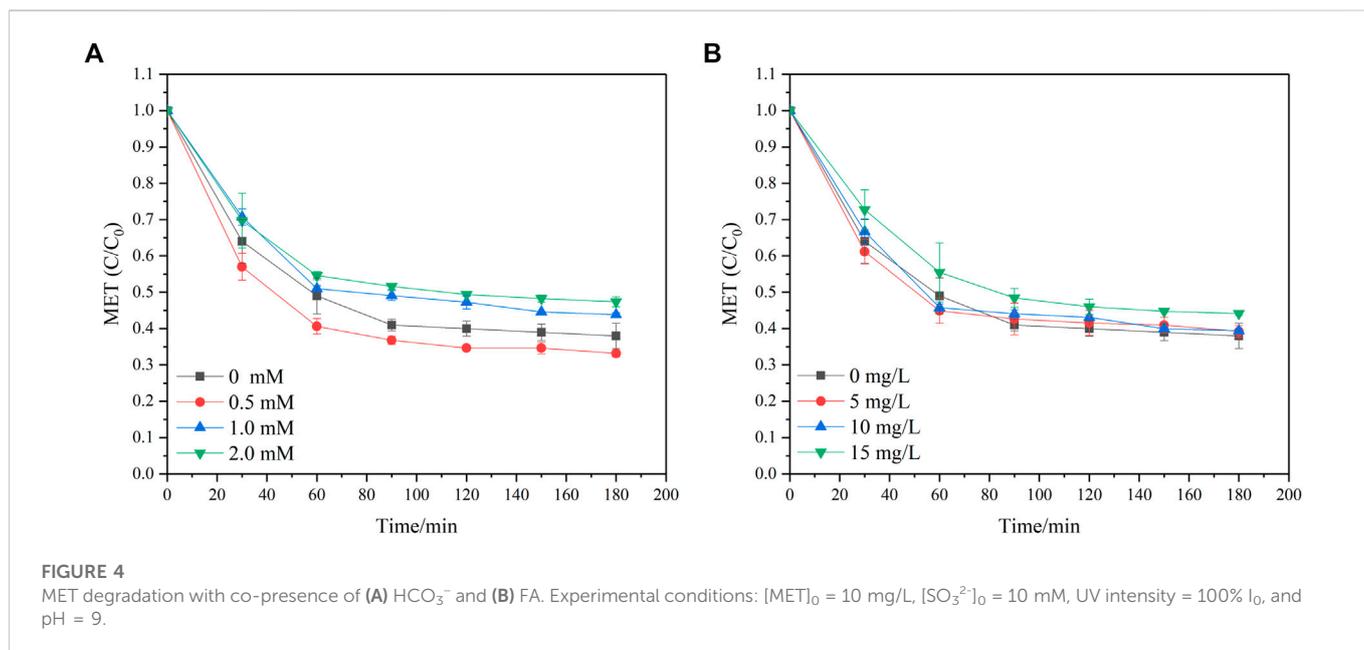
Two main reasons can be used to explain the impact of solution pH on MET removal in the UV/sulfite system. On one hand, sulfite distribution would change along with the alteration of solution pH. As shown in [Supplementary Table S4](#), the major form of sulfite at neutral pH condition is HSO_3^- , and its proportion gets declined with the increase of solution pH, which means the reactive species generated from HSO_3^- photolysis would accordingly decreased. On the contrary, the production of e_{aq}^- can be enhanced because of the increase of SO_3^{2-} proportion. Therefore, a dramatic promotion on MET degradation was obtained when solution pH was adjusted from pH seven to pH 9. SO_3^{2-} species accounts for more than 98% of sulfite species at pH 9, thus further increase of solution pH shows little effect on target pollutant degradation. On the other hand, solution pH also affected the transformation between $\cdot H$ and e_{aq}^- . The transformation from $\cdot H$ to e_{aq}^- was promoted at a higher pH condition (Eq. 5). Since e_{aq}^- was verified an important contributor for MET removal in the investigated system, the higher e_{aq}^- concentration would certainly lead to better MET treatment efficiency.



Moreover, the distribution of MET molecule was strongly dependent on the solution pH. As reported by ([Scheurer et al., 2009](#)), the principal existing form of MET was its neutral molecule when solution pH was above 12, whereas the protonation reaction occurred at two amino groups accompanied with a decrease in solution pH, which was nearly accomplished at pH 8. The change in the charged MET species may also impact its reaction with various oxidative or reductive species in the studied system, and then caused different MET degradation efficiency.

3.5 Influence of reaction temperature

Temperature is of great importance when determining the rates of chemical reactions. Hence the impact of reaction temperature on MET degradation was explored, and the results were shown in [Figure 3D](#). MET degradation was remarkably enhanced with the increase in reaction temperature. When we transformed [Figure 3D](#) to semilog plots, it was found that during the studied temperature range, MET degradation was well fitted with a pseudo first-order model ($R^2 > .97$) ([Supplementary Table S3](#)). Additionally, the MET degradation rate increased 1.1–1.8 folds when the reaction temperature was raised by increments of 10°C . Based on the Van't Hoff equation, the reaction rate of a common chemical process increases approximately 2–4 folds when the reaction temperature is increased by 10°C . Apparently, the impact of temperature on MET removal in the oxygen-involved UV/sulfite system was weakened, hinting the photo-chemical process played a key role during MET degradation. Moreover, the activation energy was calculated as 27.8 kJ/mol, which was comparable to that of a commonly used PPCPs, atenolol, treated by the sulfite-mediated UV irradiation process ([Liu et al., 2015](#)).



3.6 Influence of initial MET concentration

MET concentration was varied in different water matrix (Ambrosio-Albuquerque et al., 2021), thus it's necessary to evaluate the effect of initial MET concentration on MET degradation in the present system. As depicted in Figure 3E, approximately 86.0% MET was removed from the aqueous media at initial MET concentration of 2.5 mg/L, and the degradation ratio gradually decreased to 53.0% as the initial MET concentration increased to 15 mg/L. Under the circumstance of lower MET concentration, the produced reactive species in the oxygen-involved UV/sulfite system were such sufficient that most of MET could be degraded. As the initial MET concentration increased, the effective collision frequency between MET molecule and the reactive species was decreased. Additionally, more intermediates of MET would be generated when a higher initial MET concentration was employed in the investigated system, which also might compete for the reactive species with MET and accordingly slackened MET degradation (Shah et al., 2014).

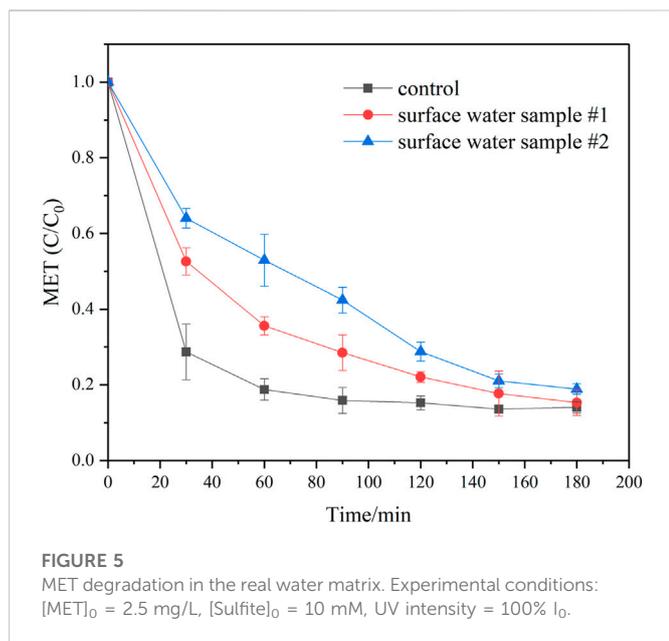
3.7 Influence of co-present compounds

In real aqueous environments, many compounds are co-present with MET, and their presence may impact MET degradation capacity in the UV/sulfite system. HCO_3^- and FA are ubiquitously present in natural water, thus they were selected as representative inorganic and organic substance, respectively, to investigate the water quality effect on MET degradation. The results are presented in Figure 4. In general, the introduction of HCO_3^- to the UV/sulfite system slightly suppressed MET removal, and the suppression effect of HCO_3^- was aggravated with an increase in HCO_3^- concentration. MET degradation ratio decreased from 62.0% to 52.6% when HCO_3^- dosage was increased by 2.0 mM after 180 min irradiation. The inhibitory effect of HCO_3^- on MET removal was ascribed to the following reasons. Firstly, it was reported that HCO_3^- can act as a quencher for $\cdot\text{OH}$ (Eq 6) (Buxton et al., 1988), thus the introduction of

HCO_3^- to the reaction solution may result in $\cdot\text{OH}$ consumption, which was attested to be responsible for MET degradation and further caused the reduction of MET degradation efficiency. Secondly, HCO_3^- could also react with another vigorous species, e_{aq}^- , in the studied system, thus a certain amount of e_{aq}^- may be consumed by HCO_3^- and consequently cause an inhibition effect on MET removal. Nevertheless, the rate constant between HCO_3^- and e_{aq}^- (or $\cdot\text{OH}$) was relatively slow ($k \approx 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988), which was at least 10 times smaller than that between perfluorooctanoic acid, a notorious persistent contaminant, and e_{aq}^- (Huang et al., 2007). Therefore, the co-presence of 2 mM HCO_3^- only led to a 10.2% decrease in MET removal in the UV/sulfite process during 180 min reaction.



Similarly, the introduction of FA resulted in a weak suppression on MET degradation. For instance, at the highest FA dosage of 15 mg/L, MET removal ratio was reduced by only 6.2%. These results differed slightly from those of other researches, which reported that the introduction of NOM to the sulfite-mediated UV photolysis process considerably reduced the target pollutant removal. Xiao et al. (2017) stated BrO_3^- removal ratio was evidently reduced in the sulfite-mediated UV photolysis process when humic acid was simultaneously added. They reported that the BrO_3^- removal ratio dramatically decreased from approximately 60.0%–44.8% and 17.0% at humic acid concentrations of 2 mg/L and 5 mg/L, respectively. The distinguishing behavior of the target pollutant removal in the investigated system was caused by the various water characteristics (i.e., DO and pH) and the different NOM used (Peldszus et al., 2004). The slight suppression of NOM in our study can be attributed to the following reasons. Firstly, NOM is rich in chromophores (Lyu et al., 2015), hence behaved competitively for UV light, which resulted in less UV light being absorbed by sulfite and the subsequent reduction of produced oxidative or reductive species. Moreover, several oxidative reactive species (i.e., $\cdot\text{OH}$, $^1\text{O}_2$, H_2O_2) were produced in the process of NOM photolysis, which may react quickly with reductive species such

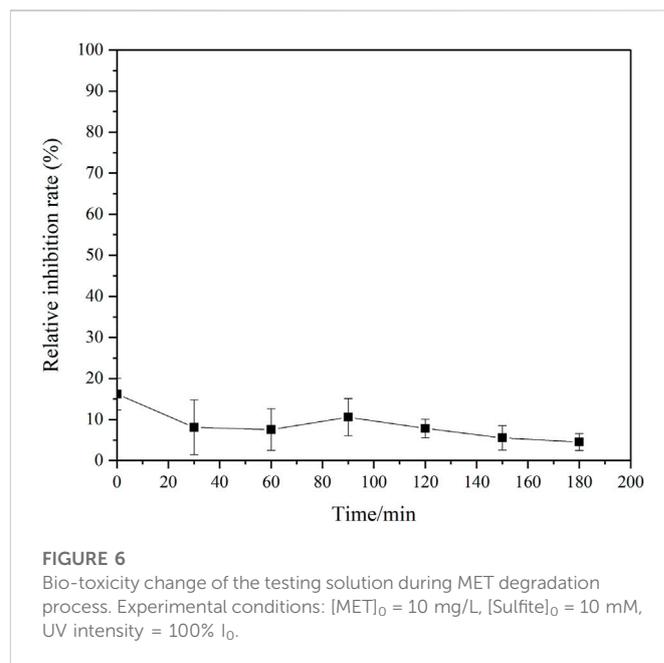


as e_{aq}^- (Lester et al., 2013) and reduce the proportion of e_{aq}^- used for MET degradation, thus causing an inhibition effect on MET removal. Nevertheless, some of the generated oxidative reactive species, such as $\cdot OH$, have been demonstrated to be beneficial for MET removal in the oxygen-involved UV/sulfite processes. Consequently, the impact of NOM on MET removal during the investigated process is complicated.

MET degradation experiments in a real water matrix were also performed, and the results were portrayed in Figure 5. In general, MET degradation was partly restrained in surface water samples when compared to the previous studied synthetic matrix. Several reasons may account for this phenomenon. Firstly, the solution pH of two surface water samples were less than 9 (Supplementary Table S1), which may result in less sulfite exist in the form of SO_3^{2-} and accordingly less e_{aq}^- generation. Secondly, NOM and inorganic ions were co-present in the surface water samples with certain extent (Supplementary Table S1). Their detrimental effect on target pollutants degradation in the UV/sulfite system has also been reported by other researchers (Cao et al., 2021b; Liu et al., 2022). Hence, MET degradation by the studied process in real water samples was impaired. Nevertheless, nearly 80% of MET was removed after 180 min irradiation, which suggested the studied oxygen-involved UV/sulfite process was prospective for MET-bearing wastewater treatment.

3.8 MET degradation products

In order to investigate the degradation pathway of MET in the oxygen-involved UV/sulfite system, the degradation products were detected. Nitrite and ammonium ions were the dominant inorganic degradation products (Supplementary Figure S2), among which ammonium accounted for the majority. The calculation of nitrogen balance indicated most of the nitrogen (>80%) in MET molecule was transformed into inorganic nitrogen species. Due to the relatively low concentration and small molecule weight, the organic intermediates of MET degradation were difficult to be determined. Therefore, MET degradation experiment at a higher initial MET concentration (1 g/L)



and longer reaction time (8 h) was conducted to better ascertain these organic intermediates, and the results were shown in Supplementary Table S5. Three organic N-containing products with lower molecule weight were detected with m/z at 125, 115, and 87, respectively. Referring to previous investigation (Badran et al., 2019; Carbuloni et al., 2020), their molecule structures were also given. The same degradation intermediates were also reported in another literature (Quintão et al., 2016), where MET degradation occurred in three oxidative reaction systems (i.e., sodium hypochlorite, ozonation, photocatalysis). A previous study by Trouillas et al. (2013) have explored the $\cdot OH$ induced oxidative degradation of MET, in which $\cdot OH$ was produced through water radiolysis reaction. There were totally four kinds of intermediates determined by using HPLC/MS, which included 4-amino-2-imino-1-methyl-1,2-dihydro-1,3,5-triazine (compound 2 in this study), methylbiguanide (compound 3 in this study), hydroperoxide of metformin and 2-amino-4-methylamino-1,3,5-triazine. $\cdot H$ abstraction, electron transfer and $\cdot OH$ addition were three main reaction pathways when MET was primarily attacked by $\cdot OH$. The bond dissociation enthalpies at C8 and C9 in MET molecule were very close, which hinted the two methyl functional groups were equal targets for $\cdot OH$ attacking, and further causing MET converted to methylbiguanide. In addition, the production of methylbiguanide was reported primarily occurred in the alkaline pH value, which was in good agreement with the reaction condition of our study (pH 9). Additionally, the bio-toxicity of the testing solution during the target pollutant degradation was monitored and presented in Figure 6. The bio-toxicity of the testing solution gradually declined along with MET degradation in general. Overall, the oxygen-involved UV/sulfite process exhibited a remarkable denitrification capacity in MET.

4 Conclusion

This work explored MET degradation in the oxygen-involved UV/sulfite process under different experimental parameters. A relatively higher degradation efficiency and k_{obs} were achieved in the

investigated process, where $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, e_{aq}^- and $\cdot\text{H}$ were manifested the major contributors to MET removal. Alkaline conditions ($\text{pH} \geq 9$) were favorable to the degradation of MET. The MET degradation efficiency was positively correlated with the incident UV intensity, sulfite dosage and reaction temperature, and negatively correlated with the initial MET concentration. The co-existed bicarbonate and FA slightly suppressed MET degradation. The oxygen-involved UV/sulfite system exhibited an extraordinary denitrification capacity in MET. Nitrite, ammonium ions and three kinds of N-containing organic compounds were detected as the dominant intermediates for MET degradation. This study offered a novel approach for treating emerging contaminants.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

YG Conceptualization, Methodology, Investigation, Software, writing—original draft preparation, Writing—review and editing, Validation, Funding acquisition. YZ Conceptualization, Methodology, Data curation. CJ Conceptualization, Writing—review and editing, Funding acquisition. ZD Conceptualization, Methodology, Investigation, Data curation, Writing—review and editing, Supervision, Funding acquisition, Visualization. XB Investigation, Validation, Data curation All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvs.2022.1071963/full#supplementary-material>

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