



Accelerated degradation of pesticide by permanganate oxidation: A comparison of organic and inorganic activations

Lei Xu^{a,b}, Huiyu Dong^{a,*}, Ke Xu^a, Jin Li^b, Zhimin Qiang^{a,*}

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100085, China

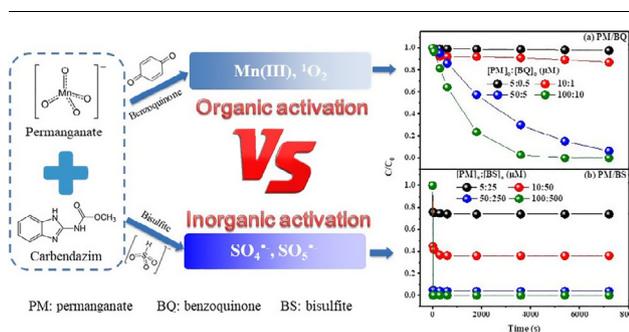
^b College of Environmental Science and Engineering, Qingdao University, Qingdao 266071, China



HIGHLIGHTS

- BS could activate PM more effectively than BQ.
- Both the PM/BQ and PM/BS systems showed strong dependences on DO.
- Mn(III) and $^1\text{O}_2$ mainly contributed to the accelerated degradation in the PM/BQ system.
- $\text{SO}_5^{\cdot-}$ and $\text{SO}_4^{\cdot-}$ mainly contributed to the accelerated degradation in the PM/BS system.

GRAPHICAL ABSTRACT



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ABSTRACT

Permanganate (PM) is a widely-used oxidant in water treatment. However, the oxidation rate of micro-pollutants by PM is highly variable, dependent on the electron density of certain moieties of micro-pollutants. Using a pesticide (carbendazim, CBZ) as a target micro-pollutant, this study compared the organic and inorganic activations of PM by benzoquinone (PM/BQ) and bisulfite (PM/BS), respectively. It was found that both the PM/BQ and PM/BS systems could accelerate the degradation of CBZ with different degradation rates. The PM/BS system completed the degradation of CBZ (96.6%) within 15 s, while the PM/BQ system took 2 h to achieve a 95.7% removal. The optimal molar ratios of $[\text{PM}]_0:[\text{BS}]_0$ and $[\text{PM}]_0:[\text{BQ}]_0$ were determined to be 1:5 and 1:0.1, respectively. Interestingly, both the degradation of CBZ in the PM/BQ and PM/BS systems were dependent on dissolved oxygen (DO) concentration. When DO was around 0.5 mg L^{-1} , the removals of CBZ by the PM/BQ and PM/BS systems were just 3.6% and 36.8%, respectively after 2 h, significantly lower than those under 9.1 mg L^{-1} DO (95.7% and 96.6%, respectively). Based on the quenching experiments, the enhanced degradation in the PM/BQ system was mainly ascribed to the formations of Mn(III) and $^1\text{O}_2$, while the formations of $\text{SO}_5^{\cdot-}$ and $\text{SO}_4^{\cdot-}$ mainly contributed to the accelerated degradation in the PM/BS system. The transformation products of CBZ in both the PM/BQ and PM/BS systems were identified and the degradation pathways including dehydrogenation, alkylation, carboxylation and hydroxylation were proposed. The inorganic activation of PM by BS exhibits a higher degradation rate and stability under different water matrices, indicating its potential engineering application in water treatment.

* Corresponding authors.

E-mail addresses: hydong@rcees.ac.cn (H. Dong), qiangz@rcees.ac.cn (Z. Qiang).

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1. Introduction

In recent years, the rapid development of agriculture worldwide has brought about many environmental problems and pesticide pollution is one of them [1]. In order to increase crop yields and eliminate pests and diseases, pesticides are prevalently used in agricultural production activities. The widespread use of pesticides in agricultural and non-agricultural applications has resulted in their residues being present in a variety of environments. Traces of these pesticide residues are often detected in surface water and groundwater [2], which has been diffusely reported worldwide. For example, carbendazim (CBZ), thiamethoxam (TEX) and metalaxyl (MLX) are three widely used pesticides and the concentrations detected in surface water ranged from 600 ng L⁻¹ to 6000 ng L⁻¹ in Spain [3], < 1.39 ng L⁻¹ to 1340 ng L⁻¹ in southern Ontario [4] and 20 ng L⁻¹ to 1330 ng L⁻¹ in southern Ontario [5], respectively. A large amount of pesticides remaining in surface water will seriously damage the aquatic environment and affect the ecological balance. It can affect aquatic plants, reduce dissolved oxygen (DO) in the water, and may cause physiological and behavioral changes in the fish population [6]. A decline in the number of different fish populations can be observed in the presence of excessive pesticide concentration [7]. For example, atrazine is toxic to certain fish species, which also indirectly affects the immune system of some amphibians [8,9]. Small concentrations of malathion have been shown to alter the abundance and composition of plankton and epiphytic populations, affecting the growth of frog ticks [10]. In addition, chlorpyrifos and endosulfan can cause serious damage to amphibians [11]. More seriously, pesticides are often detected in drinking water. For example, average residues of heptachlor from Ramgarh waters (tap water) was 0.231 mg L⁻¹, which exceeded the tolerance level (0.15 mg L⁻¹) [12]. The average concentrations of aldrin were 0.336 mg L⁻¹ and 0.136 mg L⁻¹ in Ramgarh waters and tube well water, respectively, which exceeded the tolerance level (0.1 mg L⁻¹) in the drinking water [12]. These pesticides detected in drinking water threaten human health via cancer, genetic malformations, neuro-developmental disorder and damage of the immune system [13–15]. Pesticide residues have been found in the blood of cancer patients compared to normal people and associated with leukemia, brain cancer, lymphoma, breast cancer, prostate cancer, ovarian cancer and testicular cancer [6]. The long-term presence of pesticides in the body affects reproductive capacity by altering the levels of male and female reproductive hormones, leading to stillbirth, birth defects, spontaneous abortion and infertility [6].

As conventional physio-chemical water treatment processes (e.g., coagulation, sedimentation and filtration) cannot efficiently remove pesticides, various oxidation processes including permanganate (PM), ozone, UV/H₂O₂ and adaptability have been exploited for the degradation of pesticides. PM is a widely-used mild oxidant in drinking water treatment to remove micro-pollutants. Compared to other oxidants, PM has the advantages of: (1) moderate price; (2) simple and safe transportation and storage; (3) no tendency to form halogenated or brominated by-products [16]. However, the oxidation rate of PM is variable [17] and greatly affected by pH. For example, the k_{obs} of sulfadiazine oxidized by PM is 0.498 min⁻¹ at pH 3.8, which is about 300 folds higher than that of pH 8.8 (0.00168 min⁻¹) [18]. In addition, previous studies have found that with the pH increased from 5 to 11, the second-order rate constants for the reactions of PM with 5,6,7,8-tetrahydro-2-naphthol and endocrine disrupting chemicals increased by more than 3 orders of magnitude [19]. Because of the slow degradation by PM under low pH, the degradation of target micro-pollutant under acidic circumstances is limited [20–23]. In order to improve the pH adaptation of PM and accelerate of removal of micro-pollutants by PM, continued efforts were conducted, including organic activation of PM by benzoquinone (BQ) [24] and inorganic activation of PM by bisulfite (BS) [25] via the formation of potent intermediates (See Table 1).

Quinones are widely present in water, soil, and atmospheric

environments [26–29], and are extremely powerful redox active substances. Previous studies have reported that quinones can participate in a variety of chemical and biochemical systems [30–32]. By forming ¹O₂, Mn(III) and other active substances, our previous study verified that BQ could accelerate the degradation of levofloxacin by PM (reactions 1–3), the degradation rate of levofloxacin is 0.443 min⁻¹, which is about 44.3 folds of PM alone [24]. Meanwhile, PM can be activated by BS to accelerate the degradation of pollutants. The PM/BS system has a powerful pH adaptability and an extremely fast oxidation rate as an emerging advanced oxidation system. The degradation rates of phenol, ciprofloxacin and methyl blue in the PM/BS system ($k_{\text{obs}} = 60\text{--}150\text{ s}^{-1}$) are 5–6 orders of magnitude faster than PM alone [25], aquo and hydroxo Mn(III) complexes were considered to be the main cause to accelerated degradation of micro-pollutants in the PM/BS system. And in situ formation pathways of aquo and hydroxo Mn(III) in the PM/BS system were proposed as reactions 4–6 [25,33].

Although the PM/BQ and PM/BS systems can accelerate the degradation of contaminants by PM, the differences of degradation rates, activation mechanism and transformation products are still not clear. In this work, CBZ, a grossly stable molecule under UV irradiation and the quantum yield was determined equal to 2.3×10^{-3} at pH 8.4 [34], was selected as the main target contaminant to compare the activation of PM by BQ and BS. CBZ has a detrimental effect on substrate-induced respiration, dehydrogenase and phosphatase activity [35]. When CBZ is orally administered to male mammals, there are reports of various adverse reactions, such as germ cell shedding [36,37], vas deferens atrophy [38], changes in hormone concentrations. The objective of this work was to compare the organic activation of PM by BQ with the inorganic activation of PM by BS. The accelerated degradation kinetics, activation mechanisms, the effect of water matrix and transformation products of CBZ were also investigated. It is expected to provide a better understanding and option for the accelerated oxidation of micro-pollutants by PM.

2. Materials and methods

2.1. Materials

All chemicals were commercially available and used as received: humic acid (HA) was purchased from Sigma-Aldrich. CBZ (97%), TEX (97%), MLX (95%) were purchased from Ark Pharm. Potassium permanganate (PM), sodium bisulfite (BS), sodium thiosulfate, ethanol (EtOH), sodium pyrophosphate (PP), 1-hexanol and *tert*-butanol (TBA) from Sinopharm Chemical Reagent Co. Ltd. China. BQ (99%) was purchased from Beijing InnoChem Co., Ltd. All other chemicals were at least analytical grade. All stock solutions were prepared in ultra-pure water (18.2 MΩ·cm) produced by an Advantage A10 Milli-Q system (Millipore). HA stock solutions were prepared following the previously described procedure [39]. PM stock solution was prepared by dissolving PM in deionized water and standardized spectrophotometrically at 525 nm ($\epsilon = 2500\text{ M}^{-1}\text{ cm}^{-1}$) [40].

2.2. Experimental procedures

2.2.1. Reaction steps

Degradation experiments were carried out in 50 mL glass conical flask and mechanically stirred under constant rate (250 r min⁻¹) at $25 \pm 2\text{ }^{\circ}\text{C}$. The reaction was initiated by rapidly adding PM to a solution containing micro-pollutants and BQ or BS while mixing with a magnetic stirrer in a glass bottles. UV–Vis spectra scanning experiments were carried out in 500 mL glass flask and mechanically stirred under constant rate (250 r min⁻¹) at $25 \pm 2\text{ }^{\circ}\text{C}$. PM (50 μM) and BQ (5 μM) were added to a PP solution (10 mM, pH 5.0). Samples were taken quickly at the set reaction time points and then scanned for UV–Vis spectra. The experimental procedure of UV–Vis spectra for the PM/BS (50 μM:250 μM) system was the same as above.

Table 1
Possible reactions in the PM/BQ and PM/BS systems.

No.	Reactions	Rate constants ($M^{-1} s^{-1}$)	Ref.
1	Mn(VII) + BQ → Mn(II) + oxidized BQ byproducts	–	[24]
2	Mn(II) + BQ + H ₂ O → Mn(III) + semiquinone radical + O ₂ → Mn(II) + BQ + ¹ O ₂ + O ₂ ^{·-}	–	[24]
3	Mn(VII) + 4Mn(II) + L → 5(Mn(III)-L) L:ligand, semiquinone radical	–	[24]
4	Mn(VII) + 2HSO ₃ ²⁻ → Mn(III) + 2OH ⁻ + 2SO ₄ ²⁻	–	[25]
5	Mn(VII) + 2SO ₃ ²⁻ + 2H ₂ O → Mn(III) + 4OH ⁻ + 2SO ₄ ²⁻	–	[25]
6	Mn(III) + micro-pollutants → Mn(II) + products	–	[25]
7	SO ₃ ^{·-} + O ₂ → SO ₅ ^{·-}	$k_7 = 1.5 \times 10^9$	[43]
8	SO ₅ ^{·-} + Mn(II) + H ⁺ → Mn(III) + HSO ₅ ⁻	$k_8 \approx 1.0 \times 10^8$	[46]
9	SO ₅ ^{·-} + HSO ₃ ⁻ → HSO ₄ ⁻ + SO ₄ ^{·-}	–	[44]
10	SO ₅ ^{·-} + HSO ₃ ⁻ → HSO ₅ ⁻ + SO ₃ ^{·-}	–	[44]
11	SO ₅ ^{·-} + SO ₃ ²⁻ → HSO ₄ ⁻ + SO ₄ ^{·-}	–	[44]
12	SO ₅ ^{·-} + SO ₃ ²⁻ → HSO ₅ ⁻ + SO ₃ ^{·-}	–	[44]
13	HSO ₅ ⁻ → SO ₄ ^{·-} + OH ⁻	–	[44]
14	SO ₄ ^{·-} + H ₂ O → SO ₄ ²⁻ + HO [·] + H ⁺	$k_{14} = 6.5 \times 10^7$	[45]
15	SO ₄ ^{·-} + OH ⁻ → SO ₄ ²⁻ + HO [·]	$k_{15} = 6.5 \times 10^7$	[45]
16	HO [·] + TBA → products	$k_{16} = 6 \times 10^8$	[43]
17	HO [·] + CBZ → products	$k_{17} = (2.2 \pm 0.3) \times 10^9$	[34]
18	NaN ₃ + ¹ O ₂ → products	$k_{18} = 1 \times 10^9$	[51]
19	FFA + ¹ O ₂ → products	$k_{19} = 1.2 \times 10^8$	[52]
20	HO [·] + EtOH → products	$k_{20} = 1.9 \times 10^9$	[43]
21	SO ₄ ^{·-} + EtOH → products	$k_{21} = 3.5 \times 10^7$	[45]
22	SO ₄ ^{·-} + 1-hexanol → products	$k_{22} = 1.6 \times 10^8$	[55]
23	HSO ₃ ⁻ ⇌ H ⁺ + SO ₃ ²⁻	$pK_a = 7.2$	[58]
24	MnO ₄ ⁻ + 8H ⁺ + 5e ⁻ → Mn ²⁺ + 4H ₂ O	–	[56]
25	SO ₃ ²⁻ - e ⁻ → SO ₃ ^{·-}	–	[57]

To investigate the effect of DO concentration (0.5–9.1 mg L⁻¹) on the reduction of CBZ in the PM/BQ and PM/BS systems, different flows of high purity nitrogen were pre-purged into the working solution for 30 min under magnetic stirring. The DO concentration of the working solution was monitored in real time by a DO meter to ensure that the DO remained near the desired concentration before the reaction started. The pH was adjusted using a solution of NaOH (0.1 M) and H₂SO₄ (0.1 M). At a predetermined interval, 1.0 mL of the sample was quickly transferred to a 1.5 mL centrifuge tube and immediately quenched by the addition of 100- μ L of Na₂S₂O₃ solution (5 mM). The quenched sample was then filtered through a 0.2- μ m polyethersulfone filter (ion chromatography acrodisc, PALL) and determined using a high performance liquid chromatography with diode array detector (HPLC-DAD). PP, TBA, EtOH, 1-hexanol, NaN₃ and furfuryl alcohol (FFA) were used to investigate the species and roles of formed intermediate during the activation of PM in the PM/BQ and PM/BS systems.

2.2.2. Transformation products

To identify the transformation products (TPs), two sets of 1 L working solution (pH₀ 7.5) containing 5 μ M CBZ were prepared and treated separately by the PM/BQ (50 μ M:5 μ M) and PM/BS (50 μ M/250 μ M) systems. The working solutions at the end of the reaction were filtered through a 0.22 μ m glass fiber membrane and subjected to solid phase extraction to enrich 1 mL of the sample to be tested. Finally, the analysis was carried out by ultra-performance liquid chromatography-tandem quadrupole time-of-flight mass spectrometry (UPLC-QTOF-MS/MS, AcQuity LC, Xevo G2 QTOF MS, Waters, USA).

2.3. Analytical methods

UV-vis absorbance in the range 200–800 nm was determined by a HACH DR 6000 UV-vis spectrophotometer. The concentration of CBZ were determined with an Agilent 1200 Series HPLC system equipped with an Atlantis C18 column (4.6 \times 250 mm, 5.0 μ m) at wavelengths of 282 nm. The mobile phase was a mixture of methanol/water/ammonia (99%) (60/39.9/0.1, v/v/v) at a flow rate of 1.0 mL min⁻¹. The injection volume was 100 μ L, and the column temperature was maintained at 25 °C. The DO concentration and pH were measured using a Cellox 325 DO electrode (WTW) and a pH meter (Mettler), respectively.

The transformation products of CBZ were identified with ultra-performance liquid chromatography-tandem quadrupole time-of-flight mass spectrometry. The mobile phases consisted of 0.2% formic acid in water (A) and acetonitrile (B) at a flow rate of 0.2 mL min⁻¹, and an Eclipse Plus C18 column (2.1 \times 150 mm, 3.5 μ m, Agilent, USA) was used. The gradient elution program (time in min, % mobile phase B) was set as follows: (0, 10), (20, 90), (25, 10). Under ESI⁺ mode, the MS system was operated in the following conditions: capillary voltage 3 kV, cone voltage 30 V, source temperature 100 °C, desolvation temperature 280 °C, desolvation gas flow rate 500 L h⁻¹, and MS/MS collision energy 15–35 eV.

3. Results and discussion

3.1. Comparison of degradation of CBZ by the PM/BQ and PM/BS systems

As shown in Fig. 1, the removal of CBZ by PM alone is limited. For the PM/BQ system, the removal of CBZ at 2 h increased from 1.4% to 95.7% when the molar ratio of [PM]₀: [BQ]₀ increased from 1:0 to 1:0.1. Previous studies showed that the formation of secondary oxidants (e.g., Mn(III), ¹O₂ and HO[·]) increased with the increase of BQ concentration [24], thereby accelerating the degradation of CBZ. However, when the molar ratio of [PM]₀: [BQ]₀ exceeded 1:0.1, the accelerated effect of CBZ degradation by the PM/BQ system exhibited a slowly continuous trend, probably due to BQ itself consuming a majority of formed intermediates [24].

Unlike the PM/BQ system, the degradation of CBZ by the PM/BS system was usually finished within several seconds (Fig. 1(b)), which was consistent with the previous results [41]. With the increase of molar ratio from 1:0 to 1:5, the removal of CBZ increased sharply (from 1.4% to 96.6% at 15 s). Interestingly, the degradation of CBZ was 95.4% at 1:10 which was less than 1:5. The reason might be that overdosed BS acted as a quencher for the key intermediates in the PM/BS system [41]. Note that when the molar ratio of [PM]₀: [BS]₀ exceeded the stoichiometric ratio of 1:2 (reaction 4), the removal of CBZ was still increased and the final result showed that the optimal molar ratio was 1:5, which far exceeded the stoichiometric ratio 1:2 [25]. Previous studies also found that the optimal molar ratio of [PM]₀: [BS]₀ was 1:5 [25,41]. With the identification of SO₃^{·-} formation in the PM/

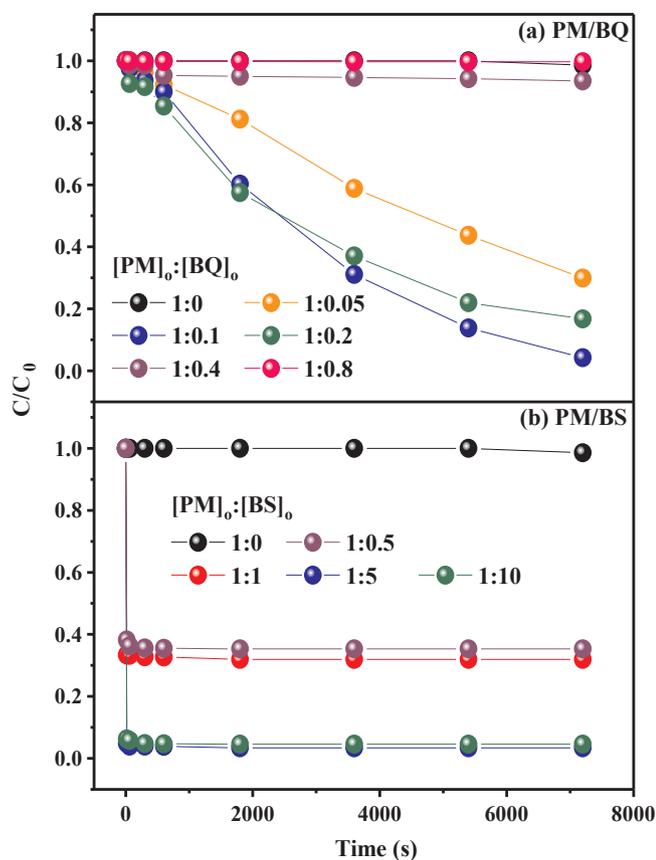


Fig. 1. Effect of $[PM]_0:[BQ]_0$ and $[PM]_0:[BS]_0$ on the removal of CBZ by the PM/BQ (a) and PM/BS (b) systems. Experiment conditions: $[CBZ]_0 = 5 \mu\text{M}$, $[PM]_0 = 50 \mu\text{M}$, $\text{pH}_0 = 7.5$ with ultra-pure water, $[BQ]_0 = 0\text{--}40 \mu\text{M}$ for (a), $[BS]_0 = 0\text{--}500 \mu\text{M}$ for (b), $T = 25^\circ\text{C}$.

BS system, Sun et al. speculated that O_2 reacted rapidly with $\text{SO}_3^{\cdot-}$ to generate $\text{SO}_5^{\cdot-}$ (reaction 7), which in turn led to an increase in the consumption of BS in the PM/BS system [25,42]. In addition, Gao et al. also observed similar stoichiometric ratio. They explained that in addition to being a producer and consumer of Mn(III), excessive BS may also be a complexing agent to stabilize Mn(III) [41]. However, in our study we find that Mn(III) is not a key intermediate for the degradation of CBZ in the PM/BS system, indicating the reaction stoichiometry reported in previous studies may be wrong. That's may be the main reason for why the optimal molar ratio far exceeded the stoichiometric ratio, which was further discussed in Section 3.2.

After determining the optimal reaction molar ratios of the PM/BQ and PM/BS systems, we investigated the effects of initial PM/BQ and PM/BS dosages on the degradation of CBZ (Fig. 2(a)). It should be specified that a trace amount of CBZ was degraded by the PM/BQ system when $[PM]_0:[BQ]_0 = 5 \mu\text{M}:0.5 \mu\text{M}$ and $10 \mu\text{M}:1 \mu\text{M}$, and the removals of CBZ were only 2.4% and 12.8% at 2 h, respectively. However, when the concentrations of the reactants increased to $50 \mu\text{M}:5 \mu\text{M}$, the decomposition of CBZ progressively improved with the increase of reaction time which reached 93.4% at 2 h. The removal of CBZ by the PM/BS system also exhibits an increasing trend with the increase of PM and BS dosages (Fig. 2(b)). Under the condition of $[PM]_0:[BS]_0 = 50 \mu\text{M}:250 \mu\text{M}$, the removal of CBZ by the PM/BS system reached 95.8% at 15 s. With the initial dosages increased to $100 \mu\text{M}:500 \mu\text{M}$, the removal of CBZ reached 100% at 15 s. All these results indicated that the inorganic activation of PM by BS was always superior to organic activation by BQ. The formed intermediates during the activation of PM contributed to the accelerated degradation of CBZ, which need a further identification to unveil its activation mechanism.

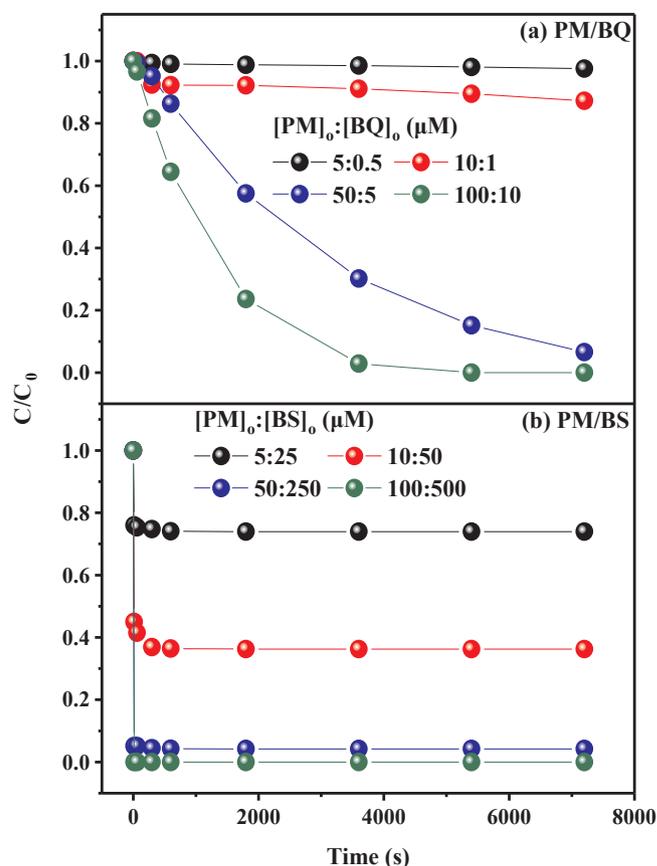


Fig. 2. Effect of different concentrations of PM, BQ and BS with fixed molar ratio on the removal of CBZ by the PM/BQ (a) and PM/BS (b) systems. Experiment conditions: $[CBZ]_0 = 5 \mu\text{M}$, $\text{pH}_0 = 7.5$ with ultra-pure water, $[PM]_0 = 5\text{--}100 \mu\text{M}$, $[BQ]_0 = 0.5\text{--}10 \mu\text{M}$ for (a); $[PM]_0 = 5\text{--}100 \mu\text{M}$, $[BS]_0 = 25\text{--}500 \mu\text{M}$ for (b), $T = 25^\circ\text{C}$.

3.2. Activation mechanisms of the PM/BQ and PM/BS systems

3.2.1. Role of DO

Previous studies showed that DO participated in the accelerated degradation of pollutants by PM [24,42]. Fig. 3 compares the removals of CBZ in the PM/BQ and PM/BS systems under different DO concentrations ($0.5\text{--}9.1 \text{ mg L}^{-1}$). The degradation of CBZ by the PM/BQ and PM/BS systems exhibited obvious DO-dependent trends. When DO was 0.5 mg L^{-1} , the degradation of CBZ in the PM/BQ and PM/BS systems at 2 h were only 3.6% and 36.8%, significantly lower than those of 95.7% and 96.6%, respectively ($[\text{DO}]_0 = 9.1 \text{ mg L}^{-1}$). Lower concentration of DO may inhibit the reaction of Mn(III) with the semiquinone radical for the PM/BQ system, thereby reducing the formation of active substances such as $^1\text{O}_2$, resulting in a lower removal of CBZ (reaction 2) [24]. In the PM/BS system, DO can oxidize $\text{SO}_3^{\cdot-}$ to form $\text{SO}_5^{\cdot-}$ (reaction 7) [43], which is important for the formation of powerful oxidizing substances such as $\text{SO}_4^{\cdot-}$, HO^\cdot and Mn(III) (reactions 8–15) [44–46]. In addition, $\text{SO}_3^{\cdot-}$ may accumulate and compete with the target pollutant for Mn(III) in the case of low DO in the PM/BS system, resulting in a decrease in removal of CBZ [42]. Xu et al. found that the low DO inhibited levofloxacin degradation in the PM/BQ system [24]. Sun et al. also observed that the degradation of phenol was dependent on DO concentration in the PM/BS system. When in an anaerobic environment, the PM/BS ($50 \mu\text{M}:250 \mu\text{M}$) system only degraded $< 3 \mu\text{M}$ phenol in 5 s, while $14.9\text{-}\mu\text{M}$ phenol was abated at 5 s when the DO concentration increased to 1 mg L^{-1} [42]. The DO-dependent degradation of CBZ indicated that DO participated in the accelerated degradation reactions in the PM/BQ and PM/BS systems.

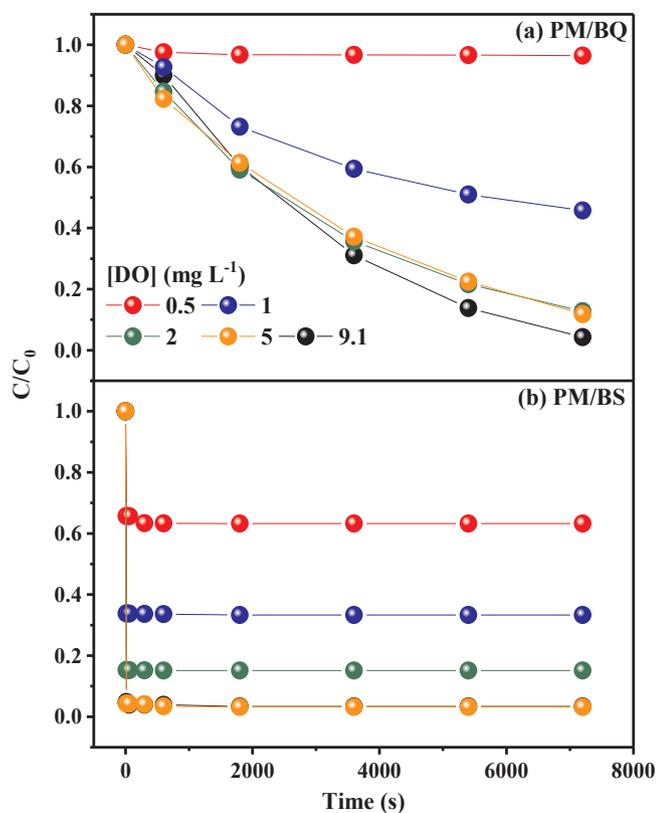


Fig. 3. Effect of [DO] on the degradation of CBZ by the PM/BQ (a) and PM/BS (b) systems. Experimental conditions: $[CBZ]_0 = 5 \mu\text{M}$, $\text{pH}_0 = 7.5$ with ultra-pure water, $[PM]_0 = 50 \mu\text{M}$, $[BQ]_0 = 5 \mu\text{M}$ for (a), $[BS]_0 = 250 \mu\text{M}$ for (b). $[DO] = 0\text{--}9.1 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$.

3.2.2. Identification of key intermediates in the PM/BQ and PM/BS systems

Based on the experimental results and analysis of the role of DO described above, the key intermediates in the PM/BQ and PM/BS systems were identified with different quenchers.

Xu et al. and Hu et al. found that Mn(III) was a key intermediate in both the PM/BQ and PM/BS systems, which contributed to the accelerated degradation of pollutants (reactions 2 and 6) [24,47]. PP is a specific ligand for Mn(III) and Mn(III)–PP usually has an absorption peak at 258 nm, which is often used to indicate the presence of Mn(III) [48]. Fig. 4 shows the transformation kinetics of Mn(VII) to Mn(III) in the PM/BQ and PM/BS systems. In the presence of overdosed PP, the concentration of Mn(VII) decreased and the concentration of Mn(III) continued to increase over time in the PM/BQ system, indicating that PM was continuously transformed to Mn(III). At 67.9 h, a 94.2% transformation ratio of Mn(VII) to Mn(III) was obtained (assuming a molar absorption coefficient at 258 nm = $6750 \text{ M}^{-1} \text{ cm}^{-1}$ [48]). While in the PM/BS system, the characteristic peak of Mn(VII) at 425 nm disappeared quickly and the Mn(III)–PP complex was formed after 15 s with a transformation ratio of 85%. Sun et al. also observed the quick formation of Mn(III) in the PM/BS system as soon as 10 ms [25]. The obvious difference between the transformation kinetics of Mn(VII) may contribute to the degradation differences of CBZ in the PM/BQ and PM/BS systems. The presence of CBZ in the PM/BQ system exhibited limited impact on the concentration changes of Mn(VII) and Mn(III) from Fig. S1(a), indicating that PP exhibited a high complexing ability of Mn(III), which cannot further produce $^1\text{O}_2$ and oxidize CBZ. This phenomenon is consistent with the limited removal of CBZ in the presence of PP (Fig. 5(a)). In the PM/BS system, the characteristic peak of Mn(VII) disappeared at 15 s (Fig. S1(b)). The formed Mn(III) in the PM/BS system in the presence of CBZ is a little lower than that in the absence of CBZ. It is speculated that CBZ may compete for intermediates against

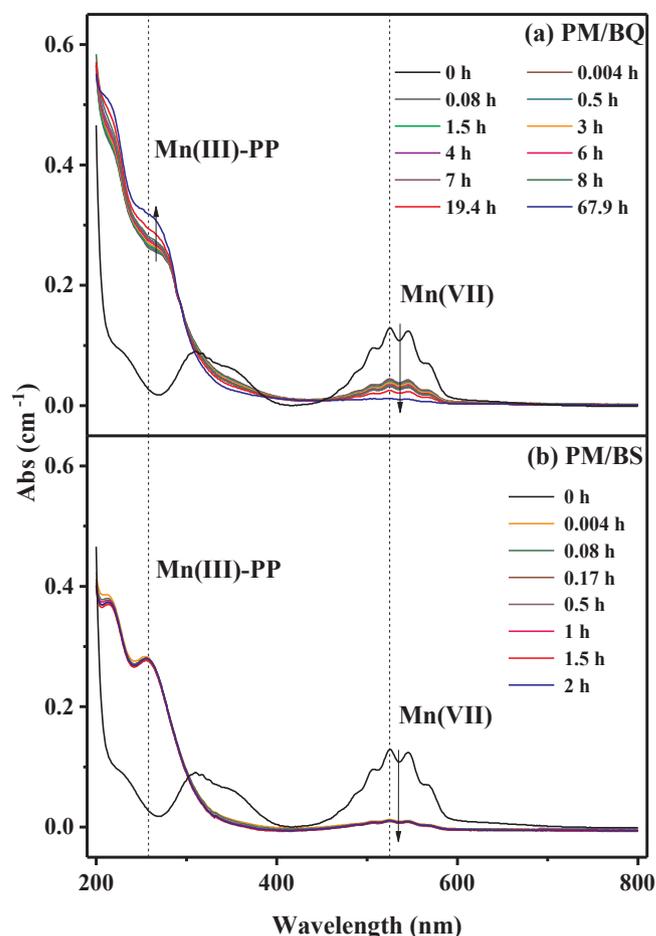


Fig. 4. UV-Vis spectra for the reaction solutions of the PM/BQ (a) and PM/BS (b) systems. Experimental conditions: $[PP]_0 = 10 \text{ mM}$, $\text{pH} = 5$, $[PM]_0 = 50 \mu\text{M}$, $[BQ]_0 = 5 \mu\text{M}$ for (a); $[BS]_0 = 250 \mu\text{M}$ for (b).

Mn(II) in the PM/BS system (reaction 8) [46], which lowered the formation of Mn(III). As shown in Fig. 5(a), the presence of PP inhibited the accelerated degradation of CBZ by the PM/BQ system even at a lowest 1 mM concentration. The effective quenching effect in the PM/BQ system indicated an important role of Mn(III) in the PM/BQ system. PP effectively complexed Mn(III) and inhibited the subsequent formation of $^1\text{O}_2$ (reactions 2 and 3) [24], which induced the decrease of removal for CBZ. On the contrast, the inhibitory effect of PP on the degradation of CBZ in the PM/BS system was limited (Fig. 5(b)). In the presence of different concentrations of PP (1–20 mM), the removal of CBZ ranged from 95% to 100% at 15 s, comparable to that in the absence of PP. To further investigate the role of Mn(III) in the PM/BS system, we prepared Mn(III)–PP complexes to degrade CBZ. As described in Fig. S2, the removal of CBZ is inapparent under different pH conditions. At 2 h, the removal of CBZ was less than 10%. Combined with PP complexation and Mn(III)–PP degradation experiments, it is speculated that Mn(III) may have a limited effect in the PM/BS system. The different degradations of CBZ in the presence of PP indicated that the accelerated degradation mechanisms and intermediates in the PM/BQ and PM/BS systems should be different, which needs a further investigation.

Previous study identified Mn(III), $^1\text{O}_2$ and HO^\cdot as the main active intermediates in the PM/BQ system [24]. TBA is adopted as a radical inhibitor based on reaction 16 ($k_{\text{HO}\cdot\text{-TBA}} = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [43]. The kinetic calculation [i.e., $(k_{\text{HO}\cdot\text{-CBZ}} \times [\text{CBZ}]) / (k_{\text{HO}\cdot\text{-TBA}} \times [\text{TBA}]) \approx (2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \times 5 \times 10^{-6} \text{ M}) / (6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \times 1 \times 10^{-3} \text{ M}) \approx 0.018$] (reactions 17 and 16) further implied that 1-mM TBA could completely quench HO^\cdot . However,

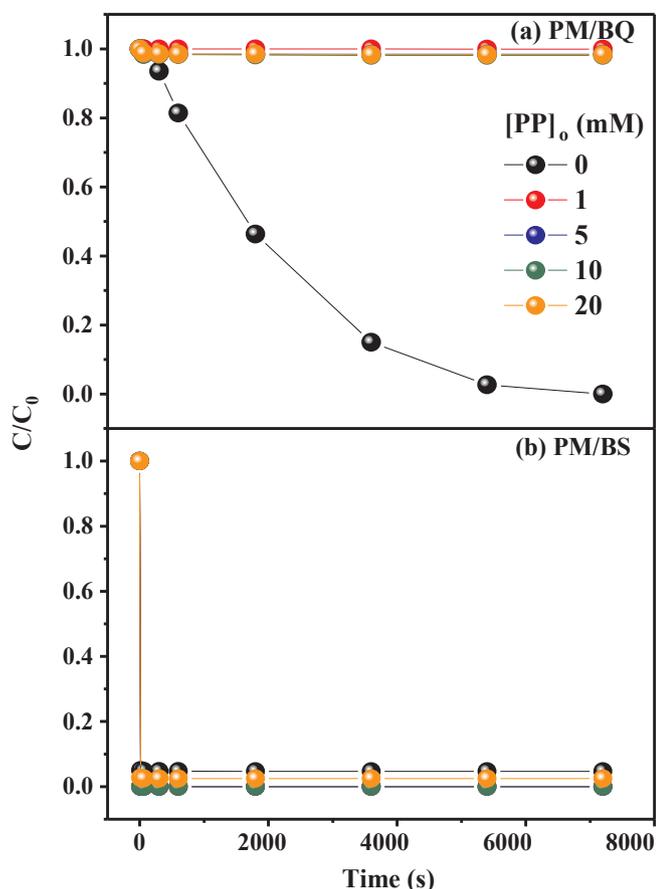


Fig. 5. Effect of $[PP]_0$ on the degradation of CBZ by the PM/BQ (a) and PM/BS (b) systems. Experimental conditions: $[CBZ]_0 = 5 \mu\text{M}$, $\text{pH}_0 = 5$, $[PM]_0 = 50 \mu\text{M}$, $[BQ]_0 = 5 \mu\text{M}$ for (a), $[BS]_0 = 250 \mu\text{M}$ for (b), $[PP]_0 = 0\text{--}20 \text{ mM}$, $T = 25^\circ\text{C}$.

the removal of CBZ remained above 84% with the increase of TBA concentration at 2 h (Fig. 6(a)), indicating that HO^\cdot is not a key intermediate in the PM/BQ system. Furman et al. found that $\text{O}_2^{\cdot-}$ underwent rapid disproportionation in water to produce HO^\cdot instead of directly degrading organic micro-pollutants [49]. In the PM/BQ system, BQ is a scavenger for $\text{O}_2^{\cdot-}$ with the reaction rate constant of $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [50], which may be the reason why HO^\cdot contributed less to the degradation of CBZ. The reaction rate constant of NaN_3 with $^1\text{O}_2$ is $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (reaction 18), which is usually adopted to probe the role of $^1\text{O}_2$ [51]. As shown in Fig. S3, when the concentration of NaN_3 is 1 mM, the degradation of CBZ by the PM/BQ system is significantly inhibited. The removal of CBZ remained around 3% at 2 h when the concentration of NaN_3 was 1–20 mM. $^1\text{O}_2$ quenching experiments with FFA (reaction rate constant with $^1\text{O}_2$ is $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) further verified the key role of $^1\text{O}_2$ in the PM/BQ system (Fig. S4) (reaction 19) [52]. Combined with PP complexation and quenching experiments, it is speculated that Mn(III) and $^1\text{O}_2$ mainly contribute to the accelerated degradation of CBZ in the PM/BQ system.

In the PM/BS system, the inhibited effect of overdosed TBA on the removal of CBZ is limited. When the TBA concentration was 20 mM, the removal of CBZ by the PM/BS system decreased to 83.9%, indicating that HO^\cdot may play a limited role in the PM/BS system (Fig. 6(b)). The transformation of $\text{SO}_4^{\cdot-}$ to HO^\cdot (reaction 14) could occur under acidic and alkaline circumstances, indicating the potential role of HO^\cdot on the degradation of CBZ. In our previous study, HO^\cdot was verified to be an important intermediate for the degradation of micro-pollutant in the activation of persulfate [53]. In addition, Shi et al. also found that HO^\cdot was a key intermediate in the degradation of ASA and NB by the Mn

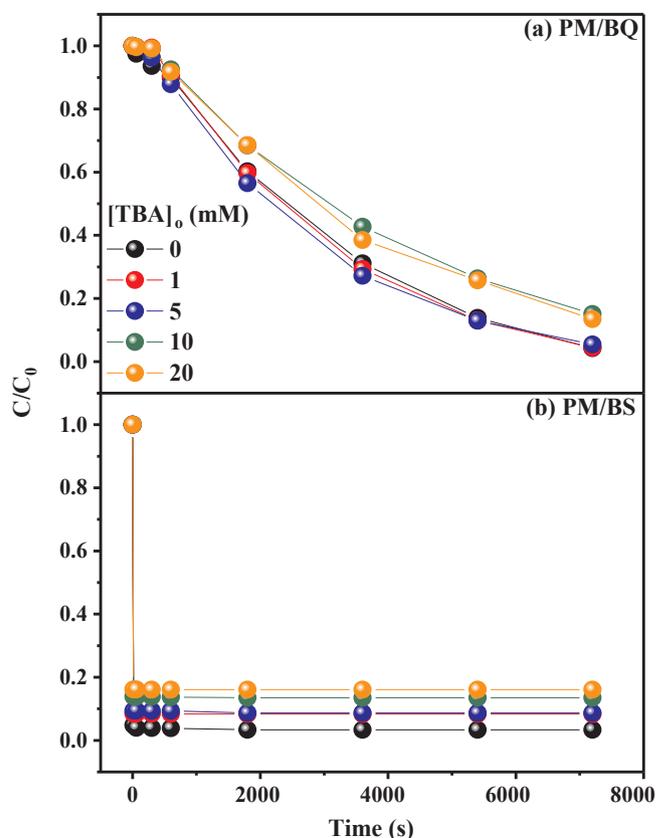


Fig. 6. Effect of $[TBA]_0$ on the degradation of CBZ by the PM/BQ (a) and PM/BS (b) systems. Experimental conditions: $[CBZ]_0 = 5 \mu\text{M}$, $\text{pH}_0 = 7.5$ with ultrapure water, $[PM]_0 = 50 \mu\text{M}$, $[BQ]_0 = 5 \mu\text{M}$ for (a), $[BS]_0 = 250 \mu\text{M}$ for (b), $[TBA]_0 = 0\text{--}20 \text{ mM}$, $T = 25^\circ\text{C}$.

(VII)–S(IV) system [59]. Therefore, we speculated that HO^\cdot may play a limited role in degradation of CBZ by the PM/BS system. EtOH can effectively suppress HO^\cdot and $\text{SO}_4^{\cdot-}$ with reaction rate constants of $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (reactions 20 and 21), respectively [43,45]. As illustrated in Fig. S5(b), the PM/BS system is obviously inhibited in the presence of EtOH. The removal of CBZ was only 19.5% at 15 s as the concentration of EtOH was 20 mM. However, the inhibitory effect of EtOH on the degradation of CBZ in the PM/BQ system was limited (Fig. S5(a)). The average removal of CBZ by the PM/BQ system was about 92.8% at 2 h. When the EtOH concentration was 20 mM, the removal of CBZ was still as high as 91.2%. This further indicated the limited effect of HO^\cdot in the PM/BQ system and shed light on the key role of $\text{SO}_4^{\cdot-}$ in the PM/BS system. Moreover, 1-hexanol has a stronger inhibitory effect on oxysulfur radicals than EtOH [54], and its reaction rate constant is about $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (reaction 22) [55]. It can be found in Fig. S6 that the presence of 1-hexanol effectively inhibited the removal of CBZ. When the concentration of 1-hexanol was 1 mM, the removal of CBZ in the PM/BS system was only 25% at 15 s. The degradation of CBZ by the PM/BS system was completely inhibited with 20-mM 1-hexanol. Based on all these quenching results, it is speculated that $\text{SO}_5^{\cdot-}$ and $\text{SO}_4^{\cdot-}$ are the key intermediates in the PM/BS system.

Accordingly, a simplified reaction pathway for accelerated degradation of CBZ by the PM/BQ system was proposed. The first step was the direct reaction of Mn(VII) with BQ to form Mn(II) and oxidized BQ byproducts (reaction 1). The second step was the reaction of Mn(II) with BQ to form Mn(III) and semiquinone radical. After that, Mn(III) reacts with the semiquinone radical in the presence of oxygen to form Mn(II), BQ, $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$ (reaction 2). The third step involved the reaction of Mn(VII) with Mn(II) to form Mn(III), after which Mn(III)

formed a complex with semiquinone radical (reaction 3). Mn(III) and $^1\text{O}_2$ produced by the above reaction underwent redox reactions with CBZ, thereby accelerating the degradation of CBZ. While in the PM/BS system, the first step was the direct reaction of Mn(VII) with BS. Mn(VII) accepts $5e^-$ forming Mn(II) from BS, and BS was rapidly oxidized to $\text{SO}_3^{\cdot-}$ (reactions 23–25) [56–58], which was in accordance with the optimal molar ratio of $[\text{PM}]_0:[\text{BS}]_0$ (i.e., 1:5) in Fig. 1. Then the formed $\text{SO}_3^{\cdot-}$ could be easily oxidized to $\text{SO}_5^{\cdot-}$ by DO (reaction 7) [43], which was a key reaction in the PM/BS system. Accordingly, it was speculated that the formation of Mn(III) in the PM/BS system was not reduced from Mn(VII) directly, but from the oxidation of Mn(II) by $\text{SO}_5^{\cdot-}$ (reaction 8) [46]. In the absence of DO, both the formations of $\text{SO}_5^{\cdot-}$ and Mn(III) were limited, which could explain the DO-dependent degradation of CBZ in the PM/BS system. Due to the powerful oxidizing ability of $\text{SO}_5^{\cdot-}$ and its conversion products ($\text{SO}_4^{\cdot-}$, HO^\cdot and HSO_5^-) (reactions 9–15) [44,45], all $\text{SO}_5^{\cdot-}$, $\text{SO}_4^{\cdot-}$, HO^\cdot and HSO_5^- might result in degradation of CBZ in the PM/BS system. Very recently, Shi et al. proposed that the key intermediate active substances in the Mn(VII)–S(IV) system were related to the structure of pollutants. In the process of degrading ASA and NB by the Mn(VII)–S(IV) system, the intermediate active substances that played a key role were $\text{SO}_4^{\cdot-}$ and HO^\cdot rather than Mn(III) [59]. This is basically consistent with the conclusions we have derived. Overall, DO participated in the formation of key intermediates in both the PM/BQ and PM/BS systems, which governed the accelerated degradation of CBZ.

3.3. Effect of water matrix on the degradation of CBZ

Water matrix has an important effect on the oxidation of micro-pollutants [60,61]. Fig. 7 exhibits the effects of pH_0 and NOM on the degradation of CBZ. The removal of CBZ under acidic circumstances was significantly better than that of alkaline circumstances for the PM/BQ system (Fig. 7(a)). With the increase of pH_0 from 5.5 to 8.5, the removal of CBZ at 2 h by the PM/BQ system decreased from 99.5% to 87.6%. Acidic circumstances could promote the formations of Mn(III)

and semiquinone radical during the reaction of Mn(II) with BQ [24], thus accelerating the degradation of CBZ by the PM/BQ system. Interestingly, the degradation of CBZ by the PM/BS system was almost unaffected by the pH_0 (Fig. 7(b)). In the pH_0 range 5.5–7.5, the removal of CBZ remained > 94.7% at 15 s. The removal of CBZ dropped to 62.5% at 15 s when the pH_0 increased to 8.5. Previous studies have speculated that low reactivity between BS and PM and Mn(III) disproportionation under alkaline conditions may be the reason of the reduction in target pollutant removal [25,58]. In addition, pH also affects the potential free radical chain reactions in the PM/BS system, such as reactions 9–15 and 23, which indirectly affect the formations of intermediate active substances such as $\text{SO}_4^{\cdot-}$, HO^\cdot , etc. These may be the cause of the slight decrease in CBZ removal at pH_0 8.5. NOM is widely present in natural waters and has an important influence on the abatement of micro-pollutants by oxidation. It was found that the degradation of CBZ in the PM/BQ system was gradually inhibited with the increase of HA concentration (Fig. 7(c)). When the concentration of HA was 5 mg L^{-1} , the degradation of CBZ was only 37.5% at 2 h, which might due to the excessive competition of the secondary oxidants between HA and CBZ [24]. On the contrary, the impact of HA on the degradation of CBZ by the PM/BS system was limited (Fig. 7(d)). The removal of CBZ by the PM/BS system even in the presence of 5 mg L^{-1} HA could reach > 75%, indicating that the PM/BS system has a better matrix adaptation. Previous study found that the consumptions of $\text{SO}_4^{\cdot-}$, HO^\cdot and S(IV) by HA in the Mn(VII)–S(IV) system should be the reason of the decrease in CBZ removal [59].

3.4. Transformation products of CBZ by the PM/BQ and PM/BS systems

UPLC–QTOF–MS/MS was used to identify the transformation products (TPs) in the PM/BQ and PM/BS systems and the degradation pathways of CBZ were tentatively proposed based on the TPs. There were 13 TPs identified in total, with TP204 and TP236 identified in both the PM/BQ and PM/BS systems. The specific molecular formula, chemical structure, observed and actual m/z of 13 TPs (Table S1) and

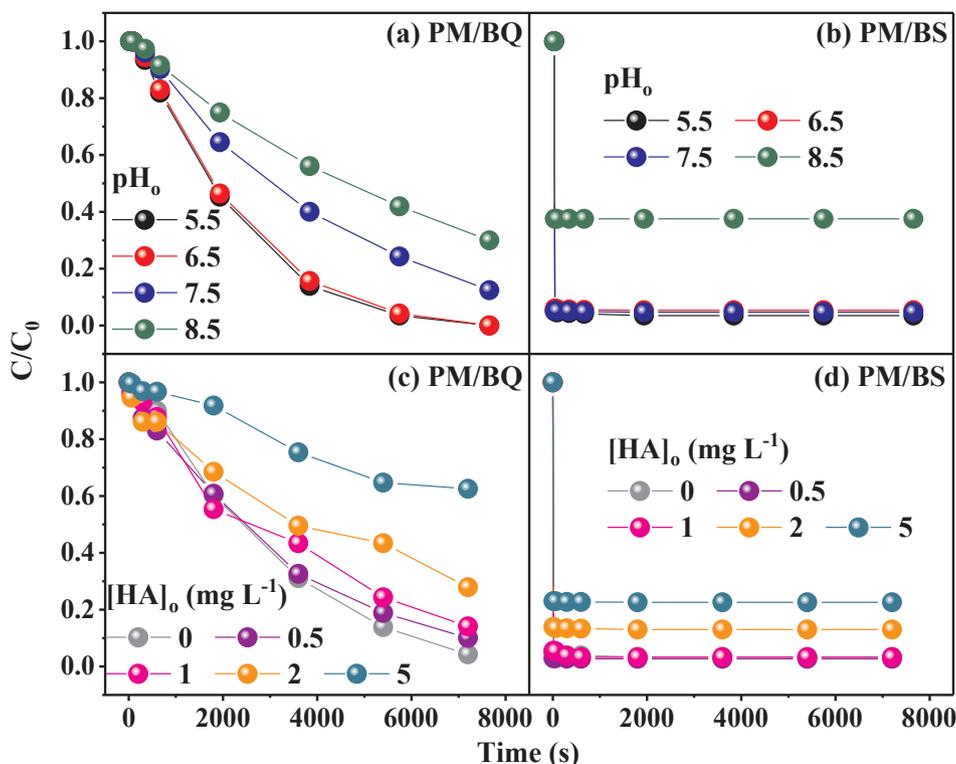


Fig. 7. Effects of pH_0 and $[\text{HA}]_0$ on the degradation of CBZ by the PM/BQ (a,c) and PM/BS (b,d) systems. Experimental conditions: $[\text{CBZ}]_0 = 5 \mu\text{M}$, $[\text{PM}]_0 = 50 \mu\text{M}$, $[\text{BQ}]_0 = 5 \mu\text{M}$ for (a), (c); $[\text{BS}]_0 = 250 \mu\text{M}$ for (b), (d). $\text{pH}_0 = 5.5\text{--}8.5$, $[\text{HA}]_0 = 0\text{--}5 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$.

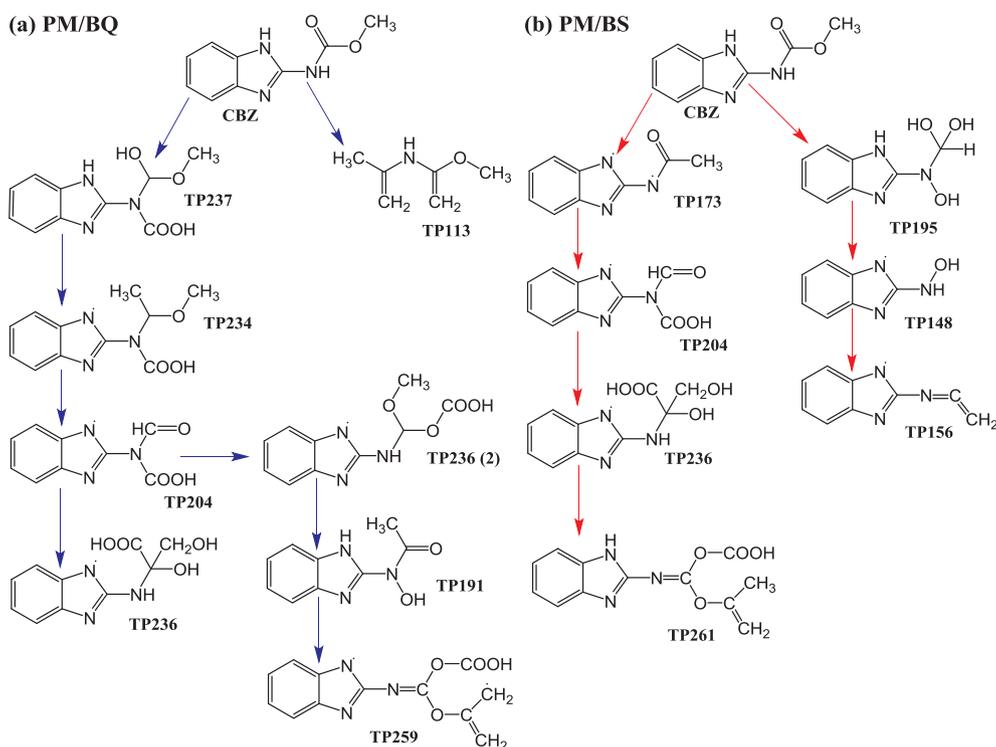


Fig. 8. Proposed CBZ degradation pathways by the PM/BQ (a) and PM/BS (b) systems.

MS spectra (Figs. S7 and S8) are available in SI.

Based on the identified eight TPs in the PM/BQ system (Fig. S9), three degradation pathways of CBZ were proposed in Fig. 8(a). CBZ was degraded mainly through hydroxylation, carboxylation, alkylation, dehydrogenation and dealkylation. The C=O double bond in CBZ was vulnerable to active intermediates (e.g., $^1\text{O}_2$, HO^\cdot) due to its high polarity, so the C=O double bond was broken. In addition, due to the electrophilic nature of Mn(III), the ring position is preferentially attacked by Mn(III) [47], thus causing a dehydrogenation reaction of N–H in TP237 to form TP234. It was reported that the main mechanism of degradation of 4-chlorophenol by Mn(III) or HO^\cdot was the substitution of hydroxyl groups [47]. The hydroxyl groups in TP237 and TP191 may be attacked by Mn(III) or HO^\cdot , yielding TP234 and TP259, respectively. Dumont et al. found that $^1\text{O}_2$ first attacked the –CH= group in guanine and then formed an endoperoxide group, which eventually was degraded to yield hydroxyl group [62]. Thus, the hydroxylation products in the PM/BQ system may be ascribed to the attack of $^1\text{O}_2$.

In contrast, the molecular weight of TPs by the PM/BS system was relatively smaller than those by the PM/BQ system, indicating a more complete degradation in the PM/BS system. The degradation of CBZ by the PM/BS system was classified into two pathways (Fig. 8(b)). CBZ mainly underwent dehydrogenation, hydroxylation, alkylation, carboxylation and dealkylation. Similar to the PM/BQ system, the position of the ring was susceptible to dehydrogenation by attack of the active substances (e.g., $\text{SO}_5^{\cdot-}$, $\text{SO}_4^{\cdot-}$, HO^\cdot), forming TP173 and TP148. The substitution of hydroxyl groups was also observed in the degradation of CBZ by the PM/BS system, such as TP195, TP148 and TP236, consistent with the previous study [47]. The hydroxylation reaction and dehydrogenation reaction would induce the formation of TP148 and TP156, which may be the main degradation pathway due to the relative high intensity of TP148.

3.5. Degradation of thiamethoxam and metalaxyl by the PM/BS system

Based on the above comparison, the PM/BS system showed a more effective and complete degradation of CBZ in terms of reaction rate and

adaptation. To verify the applicability of the PM/BS system, the removals of other two pesticides (i.e., TEX and MLX) were investigated. As shown in Fig. S10, both the removals of TEX and MLX in the PM/BS system at 15 s could reach as high as 100%. However, the removals of TEX and MLX by PM alone at 10 min were just 6.3% and 7.1%, respectively. Previous study has also reported that the PM/BS system could completely degrade phenol, ciprofloxacin and methylene blue in ultrashort time, 5–6 orders of magnitude higher than PM alone [25]. These results indicated that the PM/BS system also has a powerful degradation ability and applicability for other micro-pollutants. Fig. S11 shows the effect of three pesticides concentration on the removal of CBZ, TEX and MLX by the PM/BS system. With the increase of initial concentration of pesticides, all the removals of the target pesticides showed a declining trend. When the concentration was increased to 10 μM , the removals of TEX and MLX decreased to 89% and 96%, respectively, while the removal of CBZ decreased to 69%. When the concentration was further increased to 25 μM , the removals of TEX and MLX decreased to 65% and 78%, respectively, and the removal of CBZ decreased to 41%. Due to the formation of intermediate active substances during the degradation, increasing the concentration of pollutants also improves the consumption of these intermediate active substances. When the CBZ concentration was 5 μM , the degradation ability of the PM/BS (50 μM :250 μM) system reached the upper limit. While for TEX and MLX, the degradation capacity of the PM/BS (50 μM :250 μM) system reached the upper limit at a concentration of 10 μM . This indicated that the structure of CBZ was relatively stable and difficult to be degraded, which was also consistent with the description of Mazellier et al. [34]. According to the experimental results, it is speculated that in the PM/BS system, when the molar ratio of PM to pesticide is between 10:1 and 20:1, the removal of pesticides can reach about 90%, which may guide the practical application. In general, the PM/BS system can effectively degrade various pesticides.

4. Conclusions

This work compared the organic (PM/BQ system) and inorganic

(PM/BS system) activations of PM. Based on the above experimental results, the following conclusions can be obtained:

- 1) Both the organic and inorganic activations could accelerate the degradation of pesticides, while the PM/BS system outperformed the PM/BQ system in terms of degradation rate and adaptability under different water matrices.
- 2) Mn(III) and $^1\text{O}_2$ were the key intermediates in the PM/BQ system, while $\text{SO}_5^{\cdot-}$ and $\text{SO}_4^{\cdot-}$ mainly contributed to the accelerated degradation in the PM/BS system.
- 3) Both the PM/BQ and PM/BS systems showed a strong dependence on DO concentration. DO participated in the formation of key intermediates governing the accelerated degradation of pollutants.
- 4) The PM/BS system can oxidize organic micro-pollutants in an ultrashort contact time and exhibit good adaptability, which is expected to strengthen the degradation of micro-pollutants in drinking water treatment.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.03.157>.

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