



Involvements of chloride ion in decolorization of Acid Orange 7 by activated peroxydisulfate or peroxymonosulfate oxidation

Ping Wang^{1,2}, Shiyang Yang^{1,2,3,*}, Liang Shan^{1,2}, Rui Niu^{1,2}, Xueting Shao^{1,2}

1. Key Laboratory of Marine Environment and Ecology, Ministry of Education, Qingdao 266100, China

2. College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

3. Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong, China

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Abstract

The effects of chloride anion (Cl^-) (up to 1.0 mol/L) on the decolorization of a model compound, azo dye Acid Orange 7 (AO7), by sulfate radical ($\text{SO}_4^{\cdot-}$) based-peroxydisulfate (PS) or peroxymonosulfate (PMS) oxidation under various activated conditions (UV_{254 nm}/PS, Thermal (70°C)/PS, UV_{254 nm}/PMS, Co^{2+} /PMS) were investigated. Methanol and NH_4^+ were used as quenching reagents to determine the contributions of active chlorine species (dichloride radical ($\text{Cl}_2^{\cdot-}$) and hypochlorous acid (HClO)). The results indicated that the effects of Cl^- on the reaction mechanism were different under various activated conditions. For UV/PS and Thermal/PS, the inhibition tendency became more clear as the Cl^- concentration increased, probably due to the reaction between Cl^- and $\text{SO}_4^{\cdot-}$ and the generation of $\text{Cl}_2^{\cdot-}$ or HClO. For UV/PMS, Cl^- did not exhibit inhibition when the concentration was below 0.1 mol/L. As Cl^- concentration reached to 1.0 mol/L, the decolorization rate of AO7 was, however, accelerated, possibly because PMS directly reacts with Cl^- to form HClO. For Co^{2+} /PMS, Cl^- exhibited a significant inhibiting effect even at low concentration (≤ 0.01 mol/L). When Cl^- concentration exceeded 0.1 mol/L, the activation of PMS by Co^{2+} was almost completely inhibited. Under this condition, HClO maybe played a major role in decolorization of AO7. The results implicated that chloride ion is an important factor in $\text{SO}_4^{\cdot-}$ -based degradation of organic contamination in chloride-containing water.

Key words: chloride anion; activated peroxydisulfate oxidation; activated peroxymonosulfate oxidation; radicals; decolorization

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Introduction

Chloride (Cl^-), a common inorganic anion, is frequently present in water, wastewater or seawater. The effect of Cl^- on hydroxyl radical ($\cdot\text{OH}$)-based advanced oxidation processes (AOPs), such as Fenton, ozone, UV/ H_2O_2 , UV/Fenton and UV/ TiO_2 , has attracted widespread attention from researchers (Yang et al., 2005; Siedlecka and Stepnowski, 2006; Riga et al., 2007; Tizaoui et al., 2007). Generally, the degradation rate of organic contamination was retarded in the existence of Cl^- , in the matter of consuming $\cdot\text{OH}$.

Sulfate radical ($\text{SO}_4^{\cdot-}$)-based advanced oxidation processes (SR-AOPs), have come forth recently for the degradation of non-biodegradable compounds (Huang et al., 2002; Liang et al., 2003; Hori et al., 2005; Tsitonaki et al., 2008; Criquet and Leitner, 2009; Sun et al., 2009; Yang et al., 2009, 2010; Ling et al., 2010). Peroxydisulfate (PS) and peroxymonosulfate (PMS) are mostly used as oxidants in SR-AOPs. They could be activated to generate $\text{SO}_4^{\cdot-}$

with redox potential of 2.5–3.1 V vs. normal hydrogen electrode (NHE) (Neta et al., 1988) which can oxidize most of the organics in water. The widely studied SR-AOPs now mainly include UV/PS, Thermal/PS, UV/PMS and Co^{2+} /PMS.

However, compared with traditional $\cdot\text{OH}$ based-AOPs, the effect of Cl^- on SR-AOPs has only been discussed in only a few reports. An inhibition effect was found when the Cl^- concentration was greater than 0.2 mol/L in the degradation of TCE by Thermal/PS (Liang et al., 2006). Anipsitakis et al. (2006) studied the effect of Cl^- on the degradation of phenolic compounds by Co^{2+} /PMS and found that some chlorinated organic compounds were formed. Yet the radical mechanisms with the addition of Cl^- on SR-AOPs have not been involved in any in-depth study.

The involvement of Cl^- in photocatalytic process (Yang et al., 2005) and the degradation efficiencies of azo dye Acid Orange 7 (AO7) by the interaction of heat, UV and anions with PS, PMS (Yang et al., 2010) have been reported in our previous studies. The aims of this study were to investigate: (i) the effects of Cl^- on the decolorization

* Corresponding author. E-mail: shiningpup@hotmail.com

of AO7 by PS or PMS under various activated conditions (UV_{254 nm}/PS, Thermal (70°C)/PS, UV/PMS, Co²⁺/PMS); (ii) the role of active chlorine oxidizers (Cl₂^{••} or HClO), generated from the reaction of Cl⁻ with SO₄^{••} or ·OH. Methanol and NH₄⁺ were used as quenching reagents to study the contribution of active chlorine oxidizers on the activated PS and PMS oxidation of organic compounds. These results would be very useful for the treatment of organic compounds by SR-AOPs in water and wastewater containing Cl⁻.

1 General reaction mechanisms

Under UV/PS, Thermal/PS and Co²⁺/PMS conditions (Eqs. (1), (2), (3) as shown in Table 1), SO₄^{••} is the primary radical and plays a dominant role in the degradation of organic compounds, especially in acid aqueous medium. Under UV/PMS (Eq. (4)), PMS is activated to generate SO₄^{••} and ·OH. Both SO₄^{••} and ·OH may participate in the degradation of organic compounds. Cl⁻, a good radical scavenger, can also react with SO₄^{••} and ·OH to produce chloride radical (Cl[•]) (Eqs. (5)–(7)). Once Cl[•] is formed, it will react with Cl⁻ quickly and form equilibrium with dichloride radical (Cl₂^{••}) (Eq. (8)). The equilibrium constant associated with Eq. (8) is 1.4×10^5 L/mol, implying that Cl₂^{••}, not Cl[•], will be the predominant chlorine species. Alegre et al. (2000) also reported that the ratio of [Cl₂^{••}]/[Cl[•]] was greater than 10 at the Cl⁻ concentration over 10⁻⁴ mol/L. The bimolecular reaction between two Cl₂^{••} radicals produces Cl₂ (Eq. (9)). In the acidic aqueous medium, Cl₂ can combine with H₂O to generate hypochlorous acid (HClO) other than ClO⁻ (Eq. (11)). PMS, however, could directly react with Cl⁻ to produce HClO (Eq. (12)).

Therefore, under UV/PS, Thermal/PS and Co²⁺/PMS conditions, there may be mainly three strong oxidizers of SO₄^{••}, Cl₂^{••} and HClO in aqueous system. And under UV/PMS condition, there may be mainly SO₄^{••}, ·OH, Cl₂^{••} and HClO in aqueous system. Their standard oxidation-reduction potentials are 2.5–3.1 V vs. NHE (SO₄^{••}/SO₄²⁺) (Neta et al., 1988), 1.8–2.7 V vs. NHE (·OH/H₂O) (Buxton et al., 1988), 2.0 V vs. NHE (Cl₂^{••}/2Cl⁻) and 1.48 V vs. NHE (HClO/Cl⁻) (Wardman, 1989). All of these strong oxidizers may participate in the degradation of organic contamination.

2 Materials and methods

2.1 Materials

Sodium peroxydisulfate (Na₂S₂O₈, 99.0%), oxone (KHSO₄·K₂SO₄·KHSO₅, containing 42% KHSO₅), sodium chloride (NaCl, 99.8%), ammonium sulfate ((NH₄)₂SO₄, 99.8%), methanol (HPLC grade), sodium hypochlorite (NaClO, containing 8% effective chlorine) were purchased from Shanghai Chemical Reagent Company, China. The simulated water was prepared by AO7 and double distilled water. AO7 (4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid, 99.0%), which is

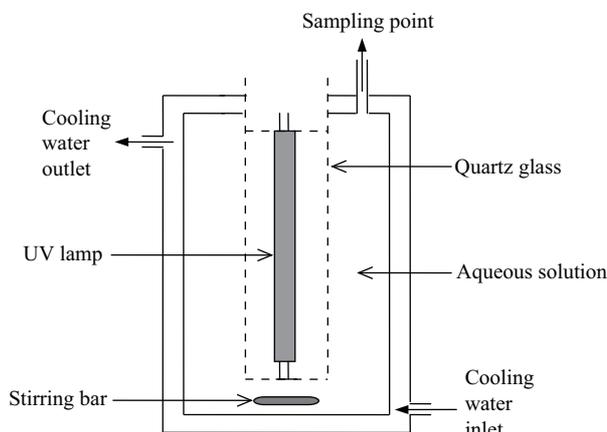


Fig. 1 Schematic diagram of reactor setup.

commonly used as a model compound for the study of the dye decolorization (Li et al., 2007; Aber et al., 2007; Zhao et al., 2010), was purchased from Shanghai Chemical Reagent Company, China and used without purification.

2.2 Reactor and procedure

The AO7 decolorization experiments were conducted in a jacketed reactor, and all comparisons were made using the same batch (Fig. 1). The total reactor working volume was 450 mL. In the UV/PS or UV/PMS experiment, a 6-W low pressure Hg UV lamp ($\lambda_{\max} = 254$ nm, product type ZSZ-6-A, Shanghai Anting Scientific Instrument Factory, China), was used as the UV light source. Its radiation intensity is $9 \mu\text{W}/\text{cm}^2$ provided by the manufacturer. In the Thermal/PS experiment, the temperature of AO7 solution was kept constant (70 ± 1)°C throughout the experiments by recirculation water. The initial concentration (C_0) of AO7 was fixed at 20 mg/L (0.057 mmol/L) and the initial oxidant (PS or PMS)/AO7 molar ratio was 10/1. The molar ratio of quenching reagent (methanol or NH₄⁺)/AO7 was 1000/1. To avoid the reactions of PMS with buffer anions, all experiments were performed without buffers. The pH was monitored by pH meter. The initial pH was determined before the oxidant was added. The final pH was determined after the reaction. The pH value ranged from 6.5 to 3.5 during the experiments.

The AO7 solution, NaCl and quenching reagent (methanol or (NH₄)₂SO₄) were added into the reactor before the experiment. As soon as the PS or PMS was added into the reactor, the experiment began. At given intervals, solutions (5.0 mL) were sampled. In the thermal experiments, samples were quickly cooled down to room temperature by ice-water.

2.3 Analysis method and data processing

The decolorization of AO7 was monitored by measuring the absorbance of samples at 484 nm (UNICO 2100 spectrophotometer, UNICO (Shanghai) Instruments Co., Ltd., China) as a function of reaction time.

Pseudo first-order kinetics are commonly used to describe oxidation by complex processes when oxidant concentration remains relatively constant, and only target contaminant changes with time (Liang et al., 2007). Every

Table 1 Possible chemistry reactions about activated PS or PMS

Item	Equation	k (L/(mol · sec))	Reference	
Activation of PS and PMS	(1) $S_2O_8^{2-} \xrightarrow{UV} SO_4^{\bullet-}$		Dogliotti and Hayon, 1967	
	(2) $S_2O_8^{2-} \xrightarrow{heat} SO_4^{\bullet-}$		Kolthoff and Miller, 1951	
	(3) $Co^{2+} + HSO_5^- \rightarrow Co^{3+} + SO_4^{\bullet-} + OH^-$		Anipsi takis and Dionysiou, 2003	
	(4) $HSO_5^- \xrightarrow{UV} \cdot OH + SO_4^{\bullet-}$		Hayon et al., 1972	
Role of active chlorine species	(5) $SO_4^{\bullet-} + Cl^- \xrightleftharpoons[k_{-5}]{k_5} SO_4^{2-} + Cl\cdot$	$k_5 = (3.2 \pm 0.2) \times 10^8$ $k_{-5} = (2.1 \pm 0.1) \times 10^8$	Yu et al., 2004	
	(6) $\cdot OH + Cl^- \xrightleftharpoons[k_{-6}]{k_6} ClOH\cdot$	$k_6 = (4.3 \pm 0.4) \times 10^9$ $k_{-6} = (6.1 \pm 0.8) \times 10^9$	Yu and Barker, 2003	
	(7) $ClOH\cdot + H^+ \xrightleftharpoons[k_{-7}]{k_7} Cl\cdot + H_2O$	$k_7 = (2.6 \pm 0.6) \times 10^{10}$ $k_{-7} = (3.6 \pm 0.6) \times 10^3$	Yu and Barker, 2003	
	(8) $Cl\cdot + Cl^- \xrightleftharpoons[k_{-8}]{k_8} Cl_2^{\bullet-}$	$k_8 = (7.8 \pm 0.8) \times 10^9$ $k_{-8} = (5.2 \pm 0.3) \times 10^4$	Yu et al., 2004	
	(9) $Cl_2^{\bullet-} + Cl_2^{\bullet-} \xrightarrow{k_9} Cl_2 + 2Cl^-$	$k_9 = (9 \pm 1) \times 10^6$	Yu et al., 2004	
	(10) $Cl_2^{\bullet-} + Cl\cdot \xrightarrow{k_{10}} Cl_2 + Cl^-$	$k_{10} = (2.1 \pm 0.05) \times 10^9$	Yu et al., 2004	
	(11) $Cl_2 + H_2O \rightarrow HOCl$		Lente et al., 2009	
	(12) $HSO_5^- + Cl^- \rightarrow SO_4^{2-} + HOCl$			
	Involvement of methanol and NH_4^+	(13) $SO_4^{\bullet-} + MA \xrightarrow{k_{13}} \text{Products}$	$k_{13} = (1.6 \pm 0.2) \times 10^7$	George et al., 2001
		(14) $Cl\cdot + MA \xrightarrow{k_{14}} \text{Products}$	$k_{14} = (3.2 \pm 0.1) \times 10^9$	Wicktor et al., 2003
		(15) $Cl_2^{\bullet-} + MA \xrightarrow{k_{15}} \text{Products}$	$k_{15} = (5.1 \pm 0.3) \times 10^4$	Jacobi et al., 1999
		(16) $HOCl + NH_4^+ \rightarrow NH_2Cl + H_2O$		Neta et al., 1978
(17) $SO_4^{\bullet-} + NH_4^+ \rightarrow HSO_4^- + NH_2^{\bullet} + H^+$			Neta et al., 1978	
Reaction in Co^{2+} /PMS system	(18) $Co^{2+} + H_2O \leftrightarrow CoOH^+ + H^+$		Yang et al., 2007	
	(19) $CoOH^+ + HSO_5^- \rightarrow CoO^+ + SO_4^{\bullet-} + H_2O$		Yang et al., 2007	
	(20) $CoO^+ + 2H^+ \leftrightarrow Co^{3+} + H_2O$		Yang et al., 2007	
	(21) $Co^{3+} + HSO_5^- \rightarrow Co^{2+} + SO_5^{\bullet-} + H^+$		Yang et al., 2007	

group of the experimental data, as shown in Table 2, was well fit pseudo first-order kinetics and all the R^2 were greater than 0.95. Every experiment was carried out three times and the variance of data was less than 3%. The data referred to in this article were the mean values.

3 Results and discussion

3.1 Radical identifying

The quenching experiments were conducted by using methanol and NH_4^+ to identify the roles of $Cl_2^{\bullet-}$ and $HOCl$.

Table 2 Pseudo first-order kinetics constants about activated PS or PMS

Activated method	Concentration of Cl^- (mol/L)	Without methanol or NH_4^+		With methanol		With NH_4^+	
		Rate constant (min^{-1})	R^2	Rate constant (min^{-1})	R^2	Rate constant (min^{-1})	R^2
UV/PS	0	0.1589	0.9926	0.0141	0.9962	0.1411	0.9867
	0.01	0.1530	0.9895	0.0182	0.9974	0.1394	0.9693
	0.1	0.1420	0.9965	0.0673	0.9843	0.1358	0.9838
	1.0	0.1342	0.9869	0.1242	0.9838	0.0948	0.9799
Thermal/PS	0	0.0285	0.9831	0.0001	0.9962	0.0272	0.9867
	0.01	0.0262	0.9856	0.0002	0.9974	0.0254	0.9753
	0.1	0.0248	0.9812	0.0009	0.9843	0.0237	0.9838
	1.0	0.0188	0.9548	0.0035	0.9838	0.0140	0.9763
UV/PMS	0	0.1670	0.9951	0.0259	0.9994	0.1686	0.9486
	0.01	0.1495	0.9849	0.0242	0.9984	0.1245	0.9996
	0.1	0.1558	0.9843	0.0634	0.9970	0.1288	0.9938
	1.0	0.3792	0.9886	0.3593	0.9519	0.1826	0.9524
Co^{2+} /PMS	0	0.1077	0.9820	0.0100	0.9878	0.0416	0.9976
	0.01	0.0311	0.9810	0.0117	0.9784	0.0051	0.9993
	0.1	0.0761	0.9749	0.0722	0.9685	0.0009	0.9916
	1.0	0.3023	0.9838	0.2912	0.9641	0.0024	0.9809

Molar ratio of quenching reagent (methanol or NH_4^+)/AO7 was 1000/1. PS: peroxydisulfate; PMS: peroxymonosulfate.

in the treatment of AO7 in water by activated PS and PMS oxidations.

Methanol is a quenching reagent of both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, which has been extensively used to identify the primary radical species in the degradation of organic compounds (Muller et al., 1996; Anipsitakis and Dionysiou, 2003; Liang et al., 2007). Methanol reacts with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ at high rates. If the decolorization of AO7 was immediately inhibited after the addition of methanol, it indicates that $\text{SO}_4^{\cdot-}$ and/or $\cdot\text{OH}$ play the dominant role in this degradation reaction. The reaction rate constant of $\text{SO}_4^{\cdot-}$ with methanol ($k = (1.6 \pm 0.2) \times 10^7 \text{ L}/(\text{mol}\cdot\text{sec})$) (Eq. (13)) is similar to that of $\text{SO}_4^{\cdot-}$ with Cl^- ($k = (3.2 \pm 0.2) \times 10^8 \text{ L}/(\text{mol}\cdot\text{sec})$) (Eq. (5)). Therefore, $\text{SO}_4^{\cdot-}$ could be both quenched by methanol and Cl^- . Moreover, Cl^- can be further oxidized to Cl^\cdot (Eq. (5)) which can also combine with Cl^- to produce $\text{Cl}_2^{\cdot-}$ (Eq. (8)). However, the reaction of $\text{Cl}_2^{\cdot-}$ with methanol is at extremely low rate ($k = (5.1 \pm 0.3) \times 10^4 \text{ L}/(\text{mol}\cdot\text{sec})$) (Eq. (15)). The degradation reaction of organic compounds will be fully inhibited in the absence of Cl^- in the aqueous solution, because $\text{SO}_4^{\cdot-}$ can

be totally quenched by methanol. While in the presence of both Cl^- and methanol, the degradation reaction of organic compounds will become faster, as the generated $\text{Cl}_2^{\cdot-}$ also can reduce organics. In order to clarify the above speculation, the effect of methanol with and without Cl^- on the decolorization of AO7 (20 mg/L) by UV/PS oxidation is shown in Fig. 2a. The concentration of Cl^- was 1.0 mol/L. It was found that the decolorization of AO7 was greatly inhibited by methanol and highly accelerated when Cl^- added. Therefore it indicates that the generated $\text{Cl}_2^{\cdot-}$ was a primary radical affecting the reaction rate.

NH_4^+ can be hardly oxidized by free radicals such as $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ (Neta et al., 1978), but it can react with HClO. The effect of NH_4^+ on the AO7 decolorization directly by HClO is shown in Fig. 2b. Since the solution pH was 6.5–4.6 during the experiments, HClO, other than ClO^- , was the main form. It was found that AO7 could be rapidly decolorized by HClO. However, once adding NH_4^+ into the reaction solution, the decolorization process was completely inhibited. Therefore, NH_4^+ is an excellent HClO quenching reagent and HClO is the premier factor

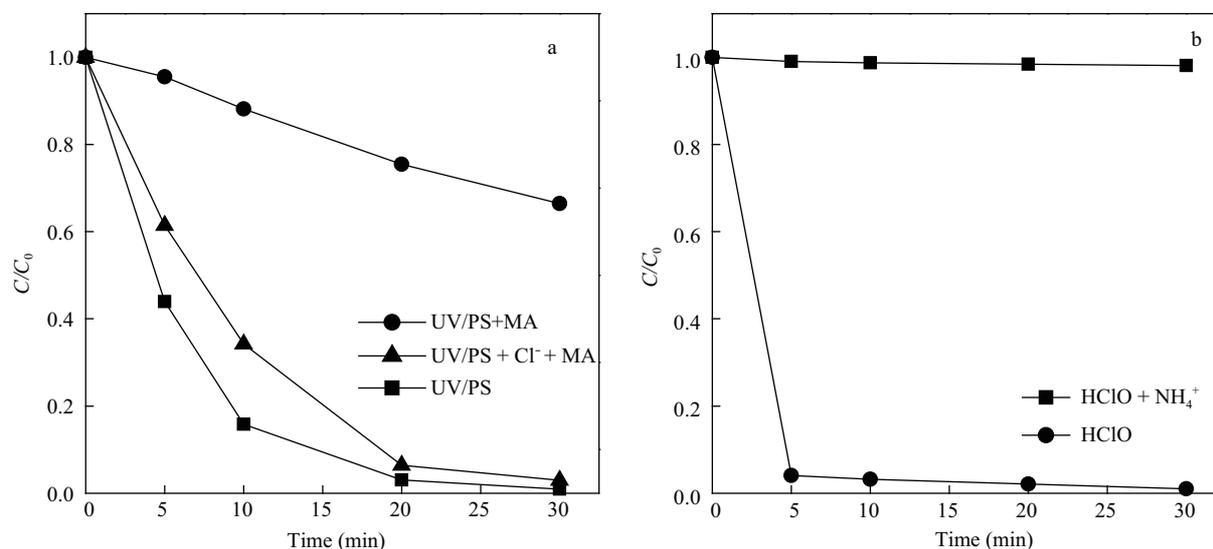


Fig. 2 Effect of methanol (MA) on the decolorization of AO7 by UV_{254 nm}/PS (a) and the effect of NH_4^+ on the decolorization of AO7 by HClO (b).

for AO7 decolorization.

3.2 Activated oxidation

The effect of Cl^- on the decolorization of AO7 and the quenching effect of methanol and NH_4^+ in UV/PS system are shown in Fig. 3a1, b1 and c1. And those in Thermal/PS system are presented in Fig. 3a2, b2 and c2.

3.2.1 UV/p peroxydisulfate system

As shown in Fig. 3a1, the effect of Cl^- concentration on the decolorization of AO7 ranging from 0.0 mol/L to 0.01 mol/L, exhibited no significant inhibition effect on the decolorization rate. However, when the concentration of Cl^- exceeded 0.1 mol/L, the decolorization was inhibited. The rate constants are presented in Table 2. When rising the concentrations to 0.1 mol/L and 1.0 mol/L, the rate constants decreased by 10.6% and 15.5%.

The quenching experiments were conducted to identify the oxidation species with the addition of methanol (Fig. 3b) and NH_4^+ (Fig. 3b2), respectively. From Fig. 3b1, the decolorization of AO7 by PS was restrained with the addition of methanol. In the absence of Cl^- , the rate constants decreased from 0.1589 to 0.0141 min^{-1} (Table 2), because $\text{SO}_4^{\cdot-}$ was quenched by methanol (Eq. (13)). When Cl^- was added, the decolorization of AO7 accelerated and the decolorization rate increased with increasing Cl^- concentration. The most possible reason is the competition mechanism of $\text{SO}_4^{\cdot-}$ between Cl^- and methanol. With the addition of Cl^- in the solution, $\text{SO}_4^{\cdot-}$ could react with Cl^- to form $\text{Cl}_2^{\cdot-}$ (Eqs. (5) and (8)). Then the $\text{Cl}_2^{\cdot-}$ may react with each other to generate Cl_2 . And also Cl_2 may react with H_2O to form HClO (Eqs. (9) and (11)). The $\text{Cl}_2^{\cdot-}$ or HClO could not be quenched by methanol. Therefore, $\text{Cl}_2^{\cdot-}$ or HClO plays a role in the AO7 decolorization by UV/PS.

The NH_4^+ quenching experiment was conducted to identify the role of HClO in the AO7 decolorization process. As shown in Fig. 3c, the decolorization of AO7 was not inhibited by NH_4^+ at Cl^- concentration below 0.1 mol/L, while it was obviously inhibited at the Cl^- concentration rising to 1.0 mol/L. The rate constants decreased from 0.1411 to 0.0948 min^{-1} (Table 2) when the Cl^- concentrations rose to 1.0 mol/L. As described in Section 3.1, if the decolorization of AO7 was restrained by addition of NH_4^+ , it is concluded HClO played an important role in decolorization. Therefore, the results showed that nearly no HClO generated for Cl^- concentration lower than 0.1 mol/L, while HClO was formed at the concentration rising to 1.0 mol/L.

3.2.2 Thermal/p peroxydisulfate system

The effect of Cl^- on the decolorization process in Thermal/PS system is present in Fig. 3a2. With the addition of different Cl^- concentration in the range from 0.0 to 0.1 mol/L, the decolorization rate exhibited no significant variation and the rate constants merely decreased from 0.0285 to 0.0248 min^{-1} (Table 2).

The quenching experiments with methanol are present in Fig. 3b2. At the Cl^- concentrations of 0.01 and 0.1 mol/L,

the decolorization process almost completely inhibited by methanol, which showed that $\text{SO}_4^{\cdot-}$ was the main oxidizing species in the decolorization of AO7 and that less $\text{Cl}_2^{\cdot-}$ and HClO were formed. When the Cl^- concentration reached to 1.0 mol/L, the decolorization rate of AO7 was accelerated, which showed that only at high concentration (1.0 mol/L), Cl^- could react with $\text{SO}_4^{\cdot-}$ to form $\text{Cl}_2^{\cdot-}$ and HClO . The inhibitory effect by methanol on decolorization under Thermal/PS was less than that under UV/PS. It was because less $\text{Cl}_2^{\cdot-}$ or HClO was formed under Thermal/PS. Liang et al. (2006) suggested that the reaction of Cl^- with $\text{SO}_4^{\cdot-}$ relates to the generation rate of $\text{SO}_4^{\cdot-}$. From Fig 3a and 3a2, it was concluded that the generation of $\text{SO}_4^{\cdot-}$ under Thermal/PS was slower than that under UV/PS.

The NH_4^+ quenching experiment is shown in Fig. 3c2. The decolorization of AO7 was not inhibited by NH_4^+ at Cl^- concentration below 0.1 mol/L. The rate constants only decreased from 0.0272 to 0.0237 min^{-1} (Table 2). When the Cl^- concentration rose to 1.0 mol/L, the rate constants decreased to 0.014 min^{-1} . It showed that the decolorization of AO7 was inhibited by NH_4^+ . The results indicated that HClO was formed under Thermal/PS condition, when the Cl^- concentration reach to 1.0 mol/L.

The effect of Cl^- on the decolorization of AO7 by UV/PS and Thermal/PS were similar. Cl^- reacted with $\text{SO}_4^{\cdot-}$ to generate $\text{Cl}_2^{\cdot-}$. When the Cl^- concentration rose to 1.0 mol/L, $\text{Cl}_2^{\cdot-}$ may react with each other to generate Cl_2 . And then Cl_2 reacted with H_2O to generate HClO . Due to the efficiency of $\text{Cl}_2^{\cdot-}$ and HClO lower than that of $\text{SO}_4^{\cdot-}$, the decolorization of AO7 by UV/PS and Thermal/PS was inhibited. The slightly difference was that the inhibition of Cl^- on decolorization of AO7 by Thermal/PS oxidation was weaker than that by UV/PS oxidation. It is due to the generation rate of $\text{SO}_4^{\cdot-}$ under Thermal/PS was lower than that under UV/PS oxidation.

3.3 Activated peroxymonosulfate oxidation

The effect of Cl^- on the decolorization of AO7 and the quenching effect of methanol and NH_4^+ in UV_{254 nm}/PMS system are shown in Fig. 4a1, b1, c1. And those in Co^{2+} /PMS system are presented in Fig. 4a2, b2 and c2.

3.3.1 UV/p peroxymonosulfate system

The effect of Cl^- at various concentrations on the decolorization of AO7 is shown in Fig. 4a1. At the concentration below 0.1 mol/L, Cl^- inhibited the decolorization of PMS as the concentration increased. The rate constants were 0.1670, 0.1495, and 0.1558 min^{-1} at the presence of 0.0, 0.01, and 0.1 mol/L Cl^- , respectively, as shown in Table 2. The decolorization rate was significantly promoted when the concentration of Cl^- was increased to 1.0 mol/L. The rate constant was increased to 0.3792 min^{-1} .

The quenching experiments with methanol are present in Fig. 4b1. The decolorization of AO7 by PMS became faster with the Cl^- concentration increased. The rate constants increased from 0.0242 to 0.0634 min^{-1} when the Cl^- concentration rose from 0.0 to 0.1 mol/L. This is because with the increase of Cl^- concentration more $\text{Cl}_2^{\cdot-}$ or HClO were formed, which could not be quenched by methanol.

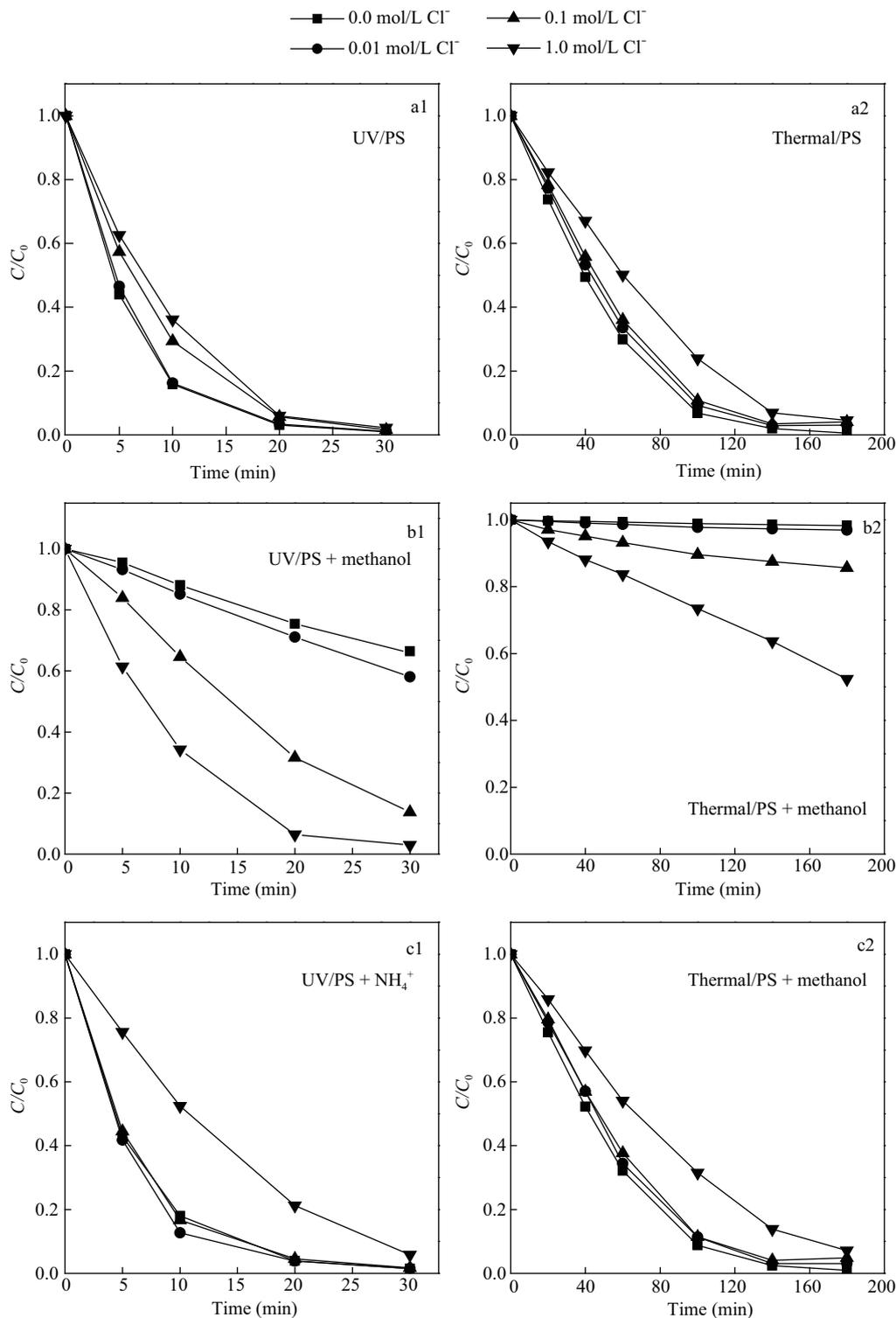


Fig. 3 Effect of Cl^- on the decolorization of AO7 under different conditions.

When the Cl^- concentration increased to 1.0 mol/L, the decolorization of AO7 was almost not inhibited by methanol. The result showed there was no $\text{SO}_4^{\cdot-}$ formed. HClO played a leading role on the decolorization of AO7.

The NH_4^+ quenching experiment showed that NH_4^+ had an inhibition function on AO7 decolorization (Fig. 4c1). As Cl^- concentration increasing, the inhibition of Cl^- on decolorization of AO7 increased. The rate constants decreased from 0.1686 to 0.0798 min^{-1} . It was evident that the HClO played an important role in the decolorization

process. Even at low Cl^- concentration (≤ 0.1 mol/L), HClO was also formed.

The effect of Cl^- on PMS oxidation was different from that of PS oxidation. Generally, two mechanisms were approached on the effect of Cl^- . One was the reaction of Cl^- with $\text{SO}_4^{\cdot-}$ generated from UV/PMS to form $\text{Cl}_2^{\cdot-}$ (Eqs. (5) and (8)). The other was the reaction of Cl^- with PMS to form HClO directly (Eq. (12)). As Cl^- concentration increasing, more HClO formed. Although the oxidation efficiency of HClO was also less efficient

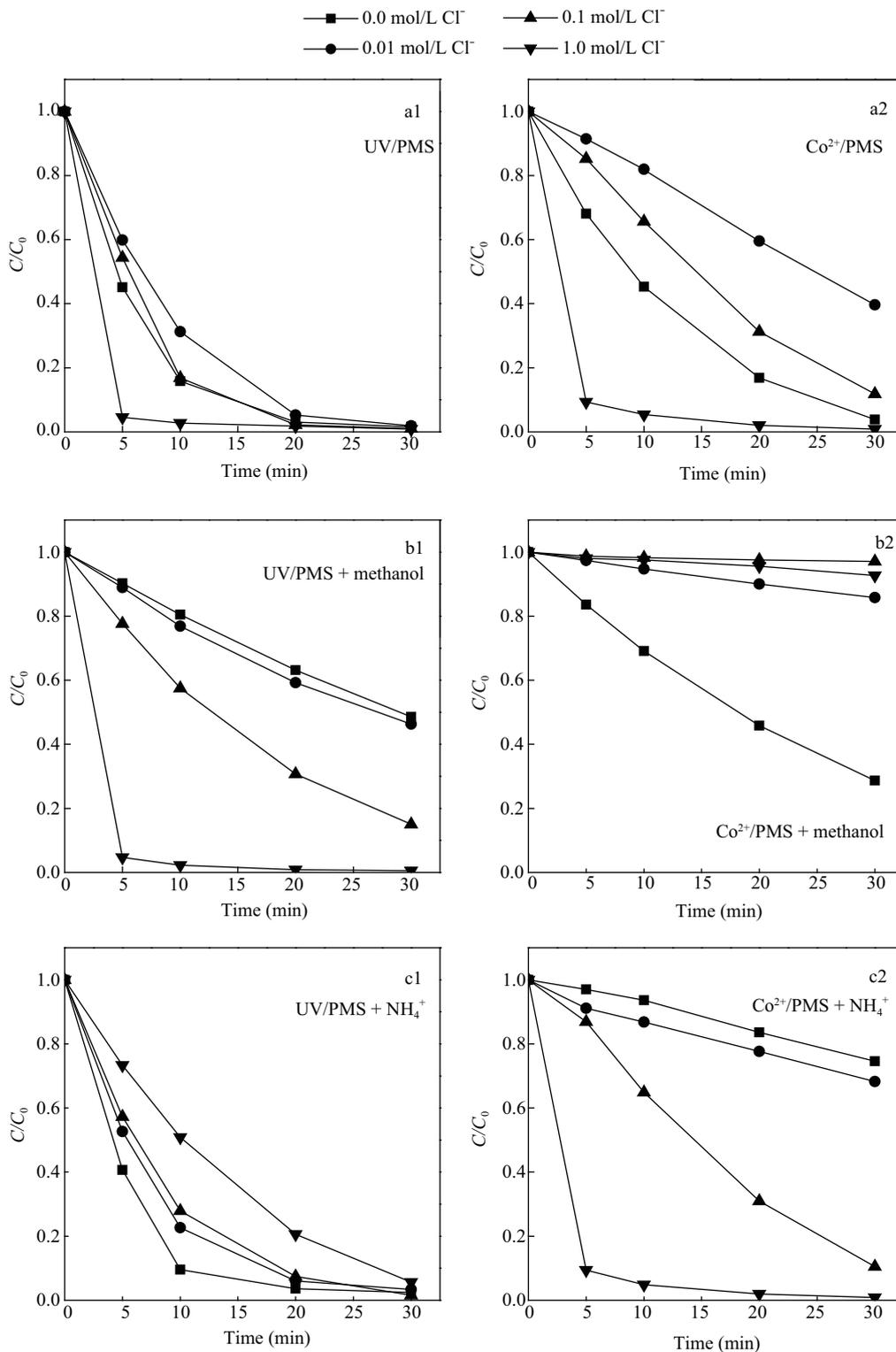


Fig. 4 Effect of Cl^- on the decolorization of AO7 under different conditions.

than that of $SO_4^{\cdot-}$, the reaction rate was faster than the generation rate of $SO_4^{\cdot-}$. At Cl^- concentration below 0.1 mol/L, the reaction of Cl^- with $SO_4^{\cdot-}$ played dominant roles which resulted in an inhibition in the decolorization process. At high concentration (1.0 mol/L), the reaction of Cl^- with PMS to form $HClO$ played a leading role.

3.3.2 Co²⁺/peroxymonosulfate system

The effect of Cl^- on the decolorization process in

Co²⁺/PMS system is shown in Fig. 4a2. The decolorization of AO7 with Co²⁺/PMS was significantly inhibited even at low Cl^- concentration (0.01 mol/L), which was different with the trends under UV/PS, Thermal/PS and UV/PMS. The decolorization rate constants decreased from 0.1077 to 0.0311 min⁻¹ (Table 2) as Cl^- concentration ranged from 0.0 to 0.01 mol/L. However, as the Cl^- concentration rose from 0.01 to 1.0 mol/L, the decolorization rates were accelerated and the rate constants rose from 0.0311 to

0.3023 min^{-1} . When the Cl^- concentration rose to 1.0 mol/L, the decolorization rate constant was even greater than that without Cl^- . Chan and Chu (2009) studied different cobalt counter anions (CoSO_4 , $\text{Co}(\text{NO}_3)_2$, CoCl_2 , $\text{Co}(\text{CH}_3\text{COO})_2$) and found that only CoCl_2 exhibited inhibitory effect. In that article, the concentration of Cl^- from CoCl_2 was 2.0×10^{-4} mol/L. It indicated that even at low concentration, the Cl^- can also restrain the decolorization process with Co^{2+} /PMS.

Previously some researchers have reported the effect of Cl^- in different AOPs. It has been found that the inhibition effects involving Cl^- resulted from the reaction Cl^- with $\text{SO}_4^{\cdot-}$ to generate less reactive radicals $\text{Cl}_2^{\cdot-}$. Liang et al. (2006) reported that when the concentration of Cl^- exceeded 0.2 mol/L, the TCE degradation was inhibited. In our experiments, the presence of Cl^- on the decolorization of AO7 by UV/PS, Thermal/PS and UV/PMS exhibited no significant inhibiting effect at Cl^- concentrations below 0.1 mol/L. It was concluded that at low concentration (0.1 mol/L), the inhibition effect involving Cl^- , resulting from the reaction Cl^- with $\text{SO}_4^{\cdot-}$ to generate less reactive radicals $\text{Cl}_2^{\cdot-}$, was negligible. This was inconsistent with the results in the Fig. 4a2. The reaction mechanism of Co^{2+} /PMS was listed in reactions (Eqs. (18)–(21)). In our Co^{2+} /PMS system, the molar ratio of Co^{2+} /PMS was low (1/100), so the circulation of Co^{2+} and Co^{3+} was important (Chen et al., 2007). It is speculated that the Cl^- can restrain the circulation of Co^{2+} and Co^{3+} and subsequently reduce the AO7 decolorization rate.

The quenching experiments with methanol and NH_4^+ in the Co^{2+} /PMS system are presented in Fig. 4b2 and c2. As can be seen in Fig. 4b2, with the addition of Cl^- , the decolorization rates were accelerated. Based on the comparison of the rate constants with and without methanol in Table 2, the methanol as quenching reagent exhibited no inhibition at Cl^- concentrations of 0.1 and 1.0 mol/L. It was concluded that there was nearly no $\text{SO}_4^{\cdot-}$ formed under activated PMS when the Cl^- exceeded 0.1 mol/L. The decolorization of AO7 may be attributed to HClO which was formed by the reaction PMS with Cl^- . The speculation was confirmed by the results in Fig. 4c2. The decolorization process was inhibited by NH_4^+ which was the quencher of HClO.

The AO7 decolorization process by Co^{2+} /PMS was inhibited by Cl^- at low concentration (0.01 mol/L). When the concentration exceeded 0.1 mol/L, the reaction of Co^{2+} /PMS to generate $\text{SO}_4^{\cdot-}$ was almost completely inhibited. The HClO, which was formed through the reaction of PMS with Cl^- , played an important role at high Cl^- concentration (above 0.1 mol/L).

4 Conclusions

This article studied the effect of Cl^- (0.0–1.0 mol/L) on the degradation of AO7 in water, by UV_{254 nm}/PS, Thermal (70°C)/PS, UV_{254 nm}/PMS and Co^{2+} /PMS, respectively. Under UV/PS and Thermal/PS conditions, Cl^- inhibited AO7 decolorization probably due to the generated $\text{Cl}_2^{\cdot-}$ and HClO with the reaction of Cl^- with $\text{SO}_4^{\cdot-}$. The

performance and mechanism of Cl^- in UV/PMS and Co^{2+} /PMS processes was different from that in UV/PS and Thermal/PS. PMS could combine with Cl^- to form HClO directly, which was fast and probably did not consume $\text{SO}_4^{\cdot-}$. Therefore, the effects of Cl^- maybe consist of two processes: (1) $\text{SO}_4^{\cdot-}$ reacts with Cl^- to form $\text{Cl}_2^{\cdot-}$; (2) PMS reacts with Cl^- to generate HClO. At low Cl^- concentration, the former played a dominant role in the decolorization process, while at high Cl^- concentration, the latter played a dominant role.

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