



On the kinetics of organic pollutant degradation with Co^{2+} /peroxymonosulfate process: When ammonium meets chloride



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HIGHLIGHTS

- Effects of ammonium and chloride ions on Co/PMS process were firstly reported.
- An inhibitory effect of ammonium on the rate of AO7 degradation was observed.
- It is recommended to monitor $\text{NH}_4^+/\text{Cl}^-$ in wastewater when Co/PMS is used.

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ABSTRACT

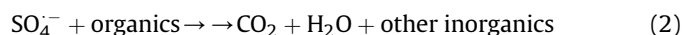
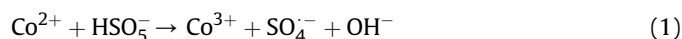
A large amount of chloride and ammonium ions were produced and released from industrial processes with non-biodegradable organic pollutants to affect efficiencies of advanced oxidation processes (AOPs). Here, the influences of chloride and ammonium ions on Co/peroxymonosulfate (Co/PMS) reaction system, a widely used AOPs to produce sulfate radicals, were investigated by examining the degradation efficiency of an azo dye (Acid Orange 7, AO7). The experimental results showed that a significant decrease in the degradation rate of AO7 was observed in the presence of NH_4^+ , while a dual effect of chloride on AO7 bleaching appeared. The presence of NH_4Cl was unfavorable for AO7 degradation at low concentration (<20 mM), whereas further addition of NH_4Cl (>20 mM) apparently accelerated AO7 discoloration rate. The apparent effects of the two co-existing inorganic ions were determined by roles of the dominating ions at varied molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$. The present study may have technical implications for the treatment of industrial wastewater containing diverse ions in practice.

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1. Introduction

Advanced oxidation processes (AOPs), based on reactive hydroxyl radical ($\cdot\text{OH}$), have gained significant importance in detoxification of contaminated wastewater, such as UV/TiO₂ and Fenton process (Yoon and Lee, 2005; Sun et al., 2009). Recently, sulfate radical ($\text{SO}_4^{\cdot-}$) has attracted an increasing attention on the environmental application, owing to its selectivity and high efficiency

(Anipsitakis and Dionysiou, 2003; Guan et al., 2011; Neta et al., 1988; Buxton et al., 1988). The activation of peroxymonosulfate (PMS) is one of the effective ways to produce $\text{SO}_4^{\cdot-}$ by transition metals and their oxides not only in the homogeneous systems (Nfodzo and Choi, 2011; Guo et al., 2013; Zhang et al., 2016) but also in the heterogeneous processes (Pang et al., 2016; Qi et al., 2013, 2014; Muhammad et al., 2012; Liu et al., 2014; Wang et al., 2015). Co^{2+} -catalyzed decomposition of PMS is considered to be most efficient to produce $\text{SO}_4^{\cdot-}$ (Eqs. (1) and (2)).



Nowadays, ammonium is one of the most commonly nitrogenous compounds in wastewater. Large amounts of ammonium

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were generated and released from industrial processes yearly, such as agriculture, oil refining and petrochemistry, chemical fertilizer production, metallurgy and wastewater treatment (Sutton et al., 2000; Fang et al., 1993; Van der Weerden and Jarvis, 1997; Vucebic, 1997; Salminen et al., 2001; Rostron et al., 2001). The previous investigations indicated that ammonium ion had a detrimental effect on the treatment performance of AOPs. The aqueous ammonium could convert into nitrate or/and nitrite in UV/peroxydisulfate (UV/PS) process (Lau et al., 2007; Salari et al., 2009; Roig et al., 1999). Hence, ammonium ion could be considered during AOPs treatment although its roles were often neglected in the past.

To date, most previous investigations paid attention to the effect of single ion on contaminant decomposition based on SO_4^- . Bennedsen and Muff (2012) found carbonates could enhance the p-nitrosodimethylaniline (RNO) bleaching rate during alkaline persulfate activation. Yang et al. (2010) reported the activation efficiencies of HCO_3^- , HPO_4^{2-} and Cl^- to PMS on AO7 degradation were enhanced with the increase of anion concentration. In our previous studies, Wang et al. (2011) observed a typical dual effect of chloride on AO7 bleaching in Co/PMS system. Similarly, Zhou et al. (2015) also reported the dual effect of chloride on the 4-chloro-2-nitrophenol (4C2NP) degradation process, whereas no measurable impact was found with low level of nitrate on Co/PMS process. To our best knowledge, there are usually various kinds of inorganic ions with different concentration in wastewater limiting the application of AOPs. However, few literature available were related to the combined effects of common inorganic ions on dye degradation.

Thus, the main objective of this work was to investigate the influence of NH_4^+ on Co/PMS process in the presence and absence of Cl^- on the bleaching of Acid Orange 7 (AO7). NH_4Cl , a combination with ammonium and chloride, was selected as the chemical for investigating the combined effects of inorganic ions on AO7 degradation process. The degradation kinetic analysis of this study reveals that the NH_4^+ combined with Cl^- in Co/PMS process exhibits dual effect on AO7 degradation process. Moreover, the critical molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$ was further analyzed for exploring the roles of each inorganic ion in AO7 decoloration process.

2. Experimental

2.1. Materials

Oxone® ($[2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4]$ salt, 95%) and Acid Orange 7 (AO7, pure) were purchased from Sigma-Aldrich. Cobalt(II) sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, >99%), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium chloride (NH_4Cl) were supplied by Sinopharm Chemical Reagent Co., Ltd, China. H_2SO_4 , NaOH, NaCl and Na_2SO_4 were of reagent grade and used without further purification. For the preparation of the sample solutions, all the chemicals were dissolved in Barnstead UltraPure water (18.3 M Ω cm) freshly before the experiment.

2.2. Experimental procedure

All reactions were prepared in 50 mL beakers containing the specific concentrations of target chemical compounds, 0.05 mM of AO7, 0.5 mM of PMS and 0.3 mM Co^{2+} at pH 7.0, respectively. The study adopted the time scan mode of a Hitachi U-2900 spectrophotometer to in situ monitor the AO7 bleaching at the maximum absorption ($\lambda = 485$ nm) of AO7 (Fernandez et al., 2003). The final data errors were less than 0.03% under the time scan mode, thus the error bars were not shown in the figure.

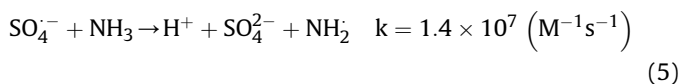
3. Results and discussion

3.1. Effect of NH_4^+ concentration

The AO7 degradation followed the pseudo-first-order kinetic model as shown in the following equation (Huang et al., 2002):

$$C = C_0 \exp(-kt) \quad (3)$$

where C_0 , C is AO7 concentration at time $t = 0$ and t , respectively, k is the degradation rate constant, t is the reaction time. As illustrated in Fig. 1, the kinetic rate constant (k) was 4.98×10^{-2} , 4.97×10^{-2} , 4.66×10^{-3} , 5.87×10^{-3} and $4.46 \times 10^{-3} \text{ s}^{-1}$ corresponding to 0, 5, 10, 20 and 30 mM NH_4^+ , respectively ($R^2 > 0.95$). This indicated that the addition of NH_4^+ had an adverse impact on the AO7 oxidation. Besides, with the NH_4^+ concentration increasing, the inhibitory effect of NH_4^+ became much obvious in Co/PMS system. It is known that NH_4^+ hydrolyzes into neutral amine which may react with SO_4^- forming NH_2 (Eqs. (4) and (5)), a relatively weak oxidant ($E^0(\text{NH}_2/\text{NH}_3) = 0.6 \text{ V}$) (Lou et al., 2003; Nakamura et al., 2014; Neta et al., 1988). Therefore, it is likely that NH_4^+ would compete SO_4^- with AO7, diminishing the AO7 degradation efficiency. Moreover, NH_3 is probably oxidized more effectively by PMS, resulting in less SO_4^- production (Nakamura et al., 2014).



For comparison, the AO7 oxidation process without adding Co^{2+} was also investigated. As shown in Fig. 1, the observed rate constant was $3.37 \times 10^{-5} \text{ s}^{-1}$ with 0 mM NH_4^+ when only PMS was present in solution. PMS is quite unstable under alkaline conditions ($\text{pH} \geq 7.0$) and could directly participate in the AO7 degradation process. Qi et al. (2016) also reported that pH was the dominant factor responsible for AO7 bleaching when the solution pH was less than 9. However, the oxidation process was terminated as soon as NH_4^+ was added. It can be owing to the quenching of SO_4^- generated from PMS activation and consumption of PMS directly by ammonium. Similarly, the addition of NH_4^+ has an inhibiting effect on AO7 degradation process in Co/PMS system (See Fig. S1).

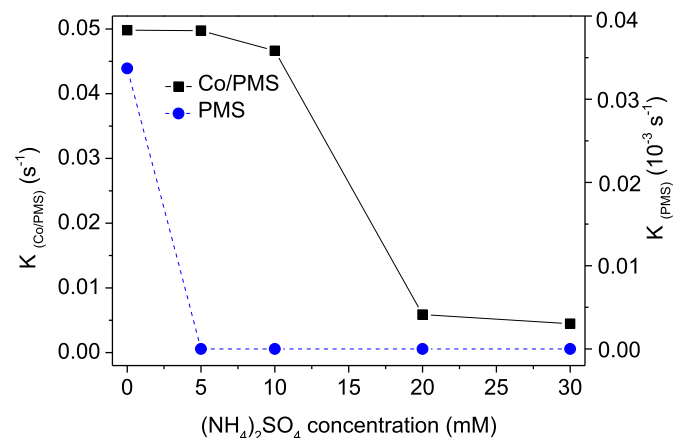


Fig. 1. Plots of the pseudo first-order rate constants for AO7 discoloration as a function of NH_4^+ concentration. Condition: $[\text{AO7}]_0 = 0.05 \text{ mM}$; $[\text{Co}^{2+}]_0 = 0.03 \text{ mM}$; $[\text{PMS}]_0 = 0.5 \text{ mM}$.

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