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

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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.

Keywords: chloride ion; ammonium ion; Co/PMS system; wastewater treatment

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/ TiO_2 and Fenton process (Yoon et al., 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 et al., 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 et al., 2011; Guo et al., 2013; Zhang et al., 2016) but also in the heterogeneous processes (Pang et al., 2016; Qi et al., 2014; Qi et al., 2013; 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 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 et al., 1997; Vucebic et al., 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 $\text{SO}_4^{\cdot-}$. Bennedsen et al. (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 literatures 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® ($[\text{2KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4]$ 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 $\text{M}\Omega \text{ cm}$) 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 ($\lambda=485 \text{ nm}$) 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 $\text{SO}_4^{\cdot -}$ forming $\text{NH}_2^{\cdot}$ (Eqs. 4 and 5), a relatively weak oxidant ($E^0(\text{NH}_2^{\cdot}/\text{NH}_3) = 0.6 \text{ V}$) (Lou et al., 2003; Nakamura et al., 2014; Neta et al., 1988). Therefore, it is likely that NH_4^+ would compete $\text{SO}_4^{\cdot -}$ with AO7, diminishing the AO7 degradation efficiency. Moreover, NH_3 is probably oxidized more effectively by PMS, resulting in less $\text{SO}_4^{\cdot -}$ 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 $\text{SO}_4^{\cdot-}$ 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).

3.2. Effect of Cl^- concentration

The influence of Cl^- concentration on AO7 decoloration is illustrated in Fig. 2. Interestingly, a dual effect was found in Co/PMS process. Cl^- ion ($<5 \text{ mM}$) showed an obvious deceleration for AO7 bleaching, while an accelerating effect of Cl^- ($>5 \text{ mM}$) on AO7 degradation was observed in the experiments. The inhibitory effect of Cl^- on AO7 degradation could be attributed to both scavenging effect of Cl^- on $\text{SO}_4^{\cdot-}$ and the much lower reactivity of chlorine radicals formed (Wang et al., 2011; Yuan et al., 2011).

Interestingly, a portion of AO7 bleaching in the presence of PMS alone occurred, although the reaction rate constant was 1000 times lower than that in Co/PMS system

(Fig. 2 and Fig. S2). Besides, the AO7 degradation rates enhanced rapidly with the Cl^- concentration increasing. Fig. 2 indicates that AO7 decoloration was a Co-independent process when adding a great amount of chloride. According to our previous studies, PMS could directly oxidize Cl^- through two-electron transfer (Eqs. 6 and 7) and produce active chloride species (HClO/Cl_2) for dye degradation (Wang et al., 2011; Yuan et al., 2011). Delcomyn et al. (2006) also reported oxone-chlorine is likely to form active chloride species. Nevertheless, the rates of active chlorine formation are extremely low ($1.35 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) when PMS is added without Co activation (Narender et al., 2002; Fortnum et al., 1960). Therefore, it is of significant importance to consider the impact of Cl^- in AO7 decoloration process in this work.

3.3. Effect of NH_4Cl concentration

To further explore the combined effect of NH_4^+ and Cl^- on AO7 oxidation process, NH_4Cl was used under the same experimental conditions. The dual effect of NH_4Cl with various concentration on AO7 degradation was found in Co/PMS system (Fig. 3): inhibitory impact within the range of 0-20 mM, whereas promoting effect when $[\text{NH}_4\text{Cl}] > 20 \text{ mM}$ (See Fig. S3). In comparison, the decoloration data of AO7 with increasing concentration of NaCl from 0 to 100 mM in Co/PMS system is also shown in Fig. 3. In these two processes, the dual effect of AO7 in decolorization is probably due to the different kinds of dominating active species at different reaction

stages. Anipsitakis et al. (2008) observed that $\text{SO}_4^{\cdot-}$ would not oxidize NH_4^+ directly when Cl^- was present in the solution according to reaction 8. An overall inhibitory impact of AO7 was observed at lower NH_4Cl concentration ($< 20 \text{ mM}$) in Co/PMS process, where both Cl^- and NH_4^+ would act as sulfate radical scavengers (Eqs. 5 and 9) and produce presumed less oxidizing efficient $\text{Cl}^\cdot$ and $\text{NH}_2^\cdot$. Note that the consumption of $\text{SO}_4^{\cdot-}$ by Cl^- and formation of less reactive chloride radicals also lead to an adverse effect of NaCl on Co/PMS performance. However, the formation of HOCl and Cl_2 (Eqs. 6 and 7) is the main reason for the promoting impact in AO7 decoloration when Cl^- is in excess.

Notably, the AO7 degradation rate increased in the presence of PMS alone with the initial NH_4Cl concentration varying from 0 to 100 mM. However, the kinetic constant for AO7 degradation as a function of NH_4Cl was inferior to NaCl obviously. This phenomenon can be explained by the fact that the amine hydrolyzed by NH_4^+ (Eqs. 4) could consume HClO (Eqs. 11-13) generated by excess chloride ion (Eqs. 10), which could result in the declining degradation of AO7.

It should be noted that the influence of NH_4^+ , Cl^- and NH_4Cl concentrations on rates of rhodamine B (RhB) degradation in Co/PMS system followed the similar tendency as AO7 did (Fig. S4). Moreover, as shown in Fig. S5, the TOC removal efficiency of Co/PMS system in the presence of chloride and ammonium was minimal, indicating their strong inhibitory effects on AO7 mineralization.

3.4. Effect of the molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$

The dual effect of NH_4Cl on AO7 degradation is observed in Fig. 3. Hence, it is expected that there is a critical molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$ at which a significant change of overall effects of $\text{NH}_4^+ + \text{Cl}^-$ (inhibitory to enhanced) with $(\text{NH}_4)_2\text{SO}_4$ and NaCl as sources of NH_4^+ and Cl^- in Co/PMS system, respectively. A series of experiments with different molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$ were carried out to gain the critical point (Fig. 4). Fig. 4a indicates that the maximum degradation rate was observed at 2:1 molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$ with a 78% removal efficiency of AO7 in 15 min. It did reflect the dual impact of NH_4^+ and Cl^- with different molar ratio on AO7 degradation: promoting impact within the range of 1:5 to 2:1, whereas inhibitory impact when $[\text{NH}_4^+]/[\text{Cl}^-] > 2:1$ (See Fig. S6). It is likely that ionic strength is one of the major influencing factor for the promotion impact with $[\text{NH}_4^+]/[\text{Cl}^-]$ ratio below 2:1. An empirical relationship between the rate constant k and the ionic strength is shown in the following equation:

$$\log k = b I + c \quad (14)$$

where k is the degradation rate constant, b and c are experimentally determined coefficients (Adam et al., 1999). Increases in rate constant k with increasing I could be ascribed to a positive primary salt effect (Church et al., 1995). Similarly, the ionic strength of the reaction medium was further adjusted by Na_2SO_4 , whose concentrations remained the same as $(\text{NH}_4)_2\text{SO}_4$. As shown in Fig. 4(a), the rate constant of $[\text{NH}_4^+]/[\text{Cl}^-]$ on AO7 degradation was lower than $[\text{Na}^+]/[\text{Cl}^-]$. Hence, the effects of cations on AO7 decoloration rate could be with an increasing order of $\text{NH}_4^+ < \text{Na}^+$, which was similar to the previous studies (Lou et al., 2003). However, NH_4^+ was the major species responsible for AO7 degradation with the molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$ above 2:1 when ammonium ion was sufficient in the solution. Therefore, the rate constant k is seen to decrease obviously within the molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$ varying from 2:1 to 10:1.

For comparison, experiments with the constant ammonium concentration (10 mM) were further investigated (Fig. 4b). It is noteworthy that the degradation rate of AO7 was rapidly improved with the molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$ increasing. It implies that Cl^- was dominant for accelerating the AO7 bleaching with the initial NH_4^+ concentration unchanged in the reaction.

Furthermore, the pseudo first-order rate constants for AO7 bleaching with 5 mM NH_4^+ were obtained (Fig. S7), which also showed a promoting effect of $[\text{NH}_4^+]/[\text{Cl}^-]$ on AO7 degradation process. Therefore, the molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$ was of great importance in controlling the rates of AO7 oxidation process.

3.5. Effect of pH

The pH value is a critical factor affecting the yields of free radicals in $\text{SO}_4^{\cdot-}$ -based oxidation system (Lu et al., 2009; Gao et al., 2012). The effect of pH on AO7 degradation were examined at different pH varying from 2.0 to 7.0. As shown in Fig. 5, the degradation rate of AO7 was enhanced with the increasing pH in Co/PMS system. The maximum degradation rate was 0.039, 0.027 and 0.003 s^{-1} at neutral pH for 10 mM NH_4^+ , Cl^- and NH_4Cl , respectively. The higher pH favors the Co^{2+} hydrolysis to form CoOH^+ (Eq. 15), which is the dominant species to decompose PMS (Eq. 16). Therefore, the yield of $\text{SO}_4^{\cdot-}$ was raised by the increasing pH of the solution, leading to a higher degradation efficiency at a higher pH (Xu et al., 2013).

4. Conclusions

The influences of ammonium, chloride and their co-existing ions on the degradation of AO7 by using cobalt-mediated activation of PMS were successfully investigated. An inhibitory effect of ammonium on the rate of AO7 degradation was shown in Co/PMS system. However, no significant degradation of AO7 in the presence of PMS alone occurred with ammonium in the solution. Moreover, there was a dual effect for chloride in bleaching AO7 under the experimental condition. It is also demonstrated

that AO7 degradation was a Co-independent process when adding a great amount of chloride. Notably, a dual effect was observed when ammonium co-existed with chloride in the solution. SO_4^{2-} would preferentially react with Cl^- rapidly and then react with ammonium until chloride is almost consumed over time. Besides, ionic strength is an influencing factor for the reaction medium. Increasing pH (from 2.0 to 7.0) was favorable for improving AO7 degradation rate even in the presence of ammonium and chlorine. This work may have significant technical implications for evaluating oxidation kinetics of oxidation of organic contaminants in the high salinity wastewater containing ammonium.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version.

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Fig.1 Plots of the pseudo first-order rate constants for AO7 discoloration as a function of NH_4^+ concentration.

Condition: $[\text{AO7}]_0 = 0.05 \text{ mM}$; $[\text{Co}^{2+}]_0 = 0.03 \text{ mM}$; $[\text{PMS}]_0 = 0.5 \text{ mM}$.

Fig.2 Plots of the pseudo first-order rate constants for AO7 discoloration as a function of Cl^- concentration.

Condition: $[\text{AO7}]_0 = 0.05 \text{ mM}$; $[\text{Co}^{2+}]_0 = 0.03 \text{ mM}$; $[\text{PMS}]_0 = 0.5 \text{ mM}$.

Fig.3 Plots of the pseudo first-order rate constants for AO7 discoloration as a function of NH₄Cl or NaCl concentration.

Condition: [AO7]₀=0.05 mM; [Co²⁺]₀=0.03 mM; [PMS]₀=0.5 mM.

Fig.4 Plots of the pseudo first-order rate constants for AO7 discoloration as a function of the molar ratio of $[\text{NH}_4^+]/[\text{Cl}^-]$. (a) $[\text{Cl}^-]_0 = 10$ mM; (b) $[\text{NH}_4^+]_0 = 10$ mM.

Condition: $[\text{AO7}]_0 = 0.05$ mM; $[\text{Co}^{2+}]_0 = 0.03$ mM; $[\text{PMS}]_0 = 0.5$ mM.

Fig.5 Effect of initial solution pH on AO7 decoloration rate constants (k). (a)

$[\text{NH}_4^+]_0 = 10 \text{ mM}$; (b) $[\text{Cl}^-]_0 = 10 \text{ mM}$; (c) $[\text{NH}_4\text{Cl}]_0 = 10 \text{ mM}$.

Condition: $[\text{AO7}]_0 = 0.05 \text{ mM}$; $[\text{Co}^{2+}]_0 = 0.03 \text{ mM}$; $[\text{PMS}]_0 = 0.5 \text{ mM}$.