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Base activation of peroxymonosulfate and its application in 2,4,6-trichlorophenol degradation

Mei-E Zhong[a,b,*], Daoxin Gong[b,*], Peng Yu[a], Chunxia Ding[a]

[a]*College of Science, Hunan Agricultural University, Changsha 410128, China, email: xiaomei9902@126.com (M. Zhong), yuzhiyipeng@163.com (P. Yu), dcxxcn@163.com (C. Ding)*
[b]*College of Resource and Environment, Hunan Agricultural University, Changsha 410128, China, Tel. +86 731 84617710, email: gdx0745@163.com (D. Gong)*

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ABSTRACT

This study evaluated the degradation of 2,4,6-TCP in NaOH/PMS system. The reaction kinetic of 2,4,6-TCP was related to the initial concentration of NaOH and PMS. When the concentration of NaOH varied from 8 to 40 mM, the highest degradation rate occurred at a NaOH concentration of 15 mM. High PMS dose increased the degradation rate of 2,4,6-TCP. Due to the competitive reaction of 2,4,6-TCP degradation and reactive species quenching, the initial 2,4,6-TCP concentration had little influence on its degradation. The degradation rate of 2,4,6-TCP exhibited a pseudo-first-order kinetics pattern at all the tested conditions. Furthermore, the reactive oxygen radicals in NaOH/PMS system were elucidated by radical scavenger. The results demonstrated that superoxide radical anion ($O_2^{\bullet-}$) was the predominant radical species responsible for 2,4,6-TCP degradation. In conclusion, NaOH activated PMS process is a promising option for the degradation of 2,4,6-TCP.

Keywords: Peroxymonosulfate; 2,4,6-TCP; Base activation; Influencing factor; Kinetics

1. Introduction

Sulfate radicals ($SO_4^{\bullet-}$) based advanced oxidation processes (AOPs) have recently attracted increased attention, due to their high efficiency and selectivity towards degradation of refractory organic pollutants. $SO_4^{\bullet-}$ can be produced via activation of persulfate (PS) and peroxymonosulfate (PMS) by heat [1–3], transition metals [4–6], base [7–9] and UV [10,11]. Among various activation methods, base activation is of particular interest, in which PS is usually utilized as a precursor of $SO_4^{\bullet-}$. The base activation of PS starts with an initial step of base induced hydrolysis of persulfate to form hydroperoxide (HO_2^-) and sulfate (SO_4^{2-}) ions (see Eqs. (1) and (2)) [7]. And then, the reduction of $S_2O_8^{2-}$ by HO_2^- generates $SO_4^{\bullet-}$ (E = 2.4 V) and superoxide radicals ($O_2^{\bullet-}$) in accordance with Eq. (3). Furthermore, under basic pH, the $SO_4^{\bullet-}$ can react with OH^- to produce HO· in accordance with Eq. (4) [10]. The results showed that multiple reactive species can be generated from base activated persulfate system. Different reactive species are suitable for degrading different organic contaminants. For example, chlorinated solvents with higher carbon oxidation states are prone to degradation via reduction (e.g., more reactive with reductant $O_2^{\bullet-}$); conversely, compounds with lower carbon oxidation states are inclined to degradation by oxidation (e.g. more reactive with HO· and $SO_4^{\bullet-}$)[9].

$$S_2O_8^{2-} + OH^- \rightarrow HSO_4^- + SO_5^{2-} \tag{1}$$

$$SO_5^{2-} + H_2O \rightarrow HO_2^- + SO_4^{2-} + H^+ \tag{2}$$

$$HO_2^- + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ + O_2^{\bullet-} \tag{3}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + HO\cdot \tag{4}$$

Recently, Furman et al. [7] proposed that peroxymonosulfate (SO_5^{2-}) is formed as a transient intermediate

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*Corresponding author.

during the base-catalyzed hydrolysis of persulfate, which rapidly decomposes to hydroperoxide (HO_2^-) and sulfate at basic pH [see Eqs. (1) and (2)]. Through these proposed base-activated persulfate reaction mechanisms, it can be concluded that if peroxymonosulfate (PMS) is utilized as a precursor of $SO_4^{\bullet-}$ in a base activation system, the formation of SO_5^{2-} according to Eq. (5) may enhance the generation of free radicals in accordance with Eqs. (2) and (3). Moreover, it was reported that base-activated persulfate technology has successfully destroyed highly chlorinated methanes in groundwater when base was used in excess [7]. However, the kinetic and mechanism on the degradation of highly chlorinated phenol derivatives, such as 2,4,6-trichlorophenol (2,4,6-TCP) was rarely studied in NaOH/PMS system.

$$HSO_5^- \rightarrow H^+ + SO_5^{2-} \quad pK_a = 9.4 \tag{5}$$

In this work, we attempted to assess the feasibility of employing base-activated PMS to degrade 2,4,6-TCP in aqueous solution. The motivation of this study is to explore a viable method to eliminate 2,4,6-TCP and related highly chlorinated phenol derivatives in waters. Kinetic studies were performed to gain insights into the influence factors including NaOH and PMS concentration on 2,4,6-TCP degradation .The quenching experiments were also conducted to confirm the main radicals in NaOH/PMS system.

2. Experimental sections

2.1. Materials

2,4,6-trichlorophenol (2,4,6-TCP, >98%) and potassium peroxymonosulfate (PMS, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 95%) were supplied by Aladdin Chemistry Co., Ltd. Sodium hydroxide were analytical grade and purchased from Beijing Chemical Reagents Company.

2.2. Experimental procedure

All reactions were performed in a series of 50 mL borosilicate vials at 25°C in a temperature controlled chamber. All experiments were initiated by mixing appropriate amounts of 2,4,6-TCP, NaOH, and PMS in this order. Approximately 1 mL of sample was periodically collected and quenched immediately with equivalent volume of 40 mM ascorbic acid before quickly analyzed by HPLC. All the experiments were conducted in duplicate, and the data were reported as the mean with error bars.

2.3. Analytical methods

2,4,6-TCP concentration was analyzed by Agilent 1260 high performance liquid chromatography system. Separate column used was a Waters symmetry C18 column (250 mm × 4.6 mm, 5 µm particle size). An eluent of water (containing 1% acetic acid) and methanol (20:80, v/v%) was used to separate 2,4,6-TCP at a flow rate of 0.8 mL/min. The concentration of 2,4,6-TCP was quantified at $\lambda = 290$ nm.

3. Results and discussion

3.1. PMS activation by NaOH

The activation efficiencies of PMS catalyzed by NaOH are presented in Fig. 1. It can be seen that the decomposition of 2,4,6-TCP was negligible in the presence of NaOH or PMS alone, suggesting that NaOH or PMS was under active toward 2,4,6-TCP. Unexpectedly, nearly 83% of the 0.2 mM 2,4,6-TCP was degraded by 10 mM PMS in 20 mM NaOH solution within 24 h. Hence it is evident that both NaOH and PMS are indispensable for the oxidative degradation of 2,4,6-TCP.

3.2. Effect of NaOH concentration on the degradation of 2,4,6-TCP

Fig. 2 illustrates the effect of NaOH dosage on 2,4,6-TCP degradation with fixed PMS concentration of 10 mM. When NaOH concentrations increased from 8 to 15 mM, the degradation efficiency of 2,4,6-TCP increased remarkably from 64% to 93%. However, when the NaOH concentration increased to 30 mM, the degradation of 2,4,6-TCP sharply decreased to 75%. This clearly confirms that NaOH directly participated in the 2,4,6-TCP degradation. Since NaOH itself cannot directly oxidize 2,4,6-TCP (see Fig. 1), it should act as an activator in this process. In this case, similar to transition metals [12], more NaOH generates more reactive species for faster degradation of 2,4,6-TCP, while excessive amount of NaOH might be rather undesirable.

3.3. Effect of PMS concentration on the degradation of 2,4,6-TCP

Fig. 3 presents the variation of rates of 2,4,6-TCP degradation as a function of PMS concentration in the NaOH/PMS system. The increase in concentration of PMS resulted in a significant degradation of 2,4,6-TCP. The degradation rate increased from 0.01614 to 1.12376 h^{-1} with the PMS concentration varied from 1 to 15 mM. The positive correlation of PMS dosage with degradation rate of 2,4,6-TCP implies

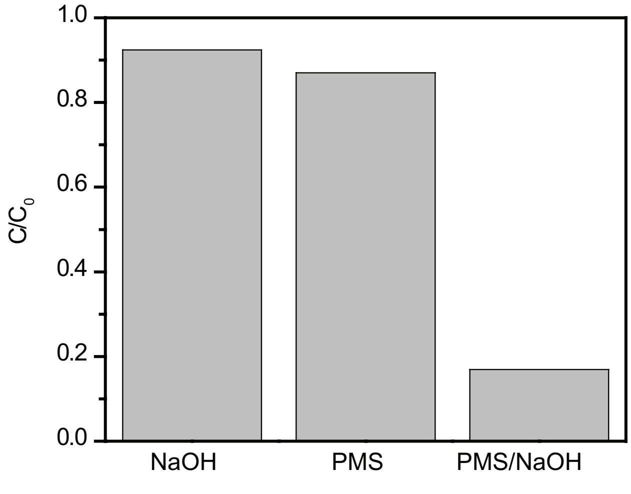

Fig. 1. 2,4,6-TCP degradation in NaOH/PMS system after 24 h condition: [NaOH] = 10 mM, [PMS] = 4 mM, [2,4,6-TCP] = 0.02 mM.

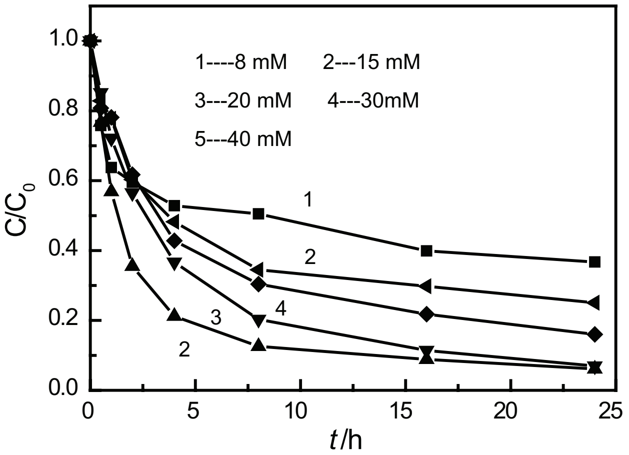

Fig. 2. Effect of NaOH concentration on the degradation of 2,4,6-TCP. Conditions: [2,4,6-TCP] = 0.2 mM, [PMS] = 10 mM.

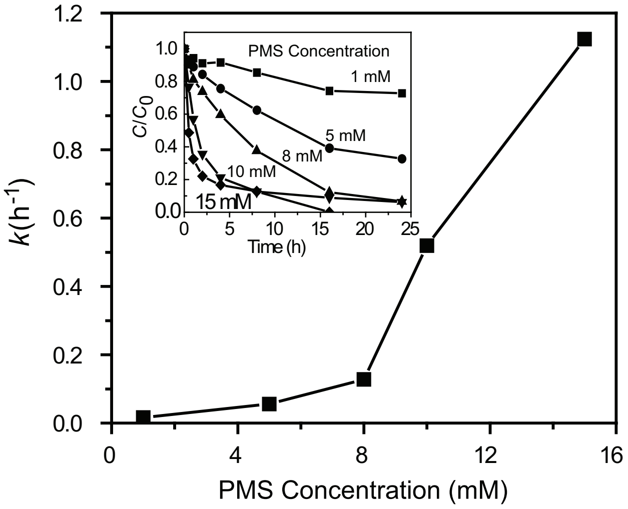

Fig. 3. Plots of pseudo first-order rate constants for 2,4,6-TCP degradation at various PMS concentration. Conditions: [2,4,6-TCP] = 0.2 mM, [NaOH] = 15 mM. Inset: effect of PMS dosages on 2,4,6-TCP degradation.

that PMS itself and/or its secondary decomposition species accounted for the attack of organic compounds. This dependence of degradation rate of organics on PMS dosage was consistent with the investigations of PMS activation by phosphate anion [13].

3.4. Effect of initial 2,4,6-TCP concentration on 2,4,6-TCP degradation

The effect of the initial 2,4,6-TCP concentration (0.05–0.4 mM) on 2,4,6-TCP degradation in NaOH/PMS system is shown in Fig. 4. At a fixed PMS dosage of 10 mM, the degradation kinetics at each concentration looks very similar, indicating the initial 2,4,6-TCP concentration had no significant effect on its degradation. While increasing the initial 2,4,6-TCP concentration, the degradation rate constant was slightly increased from 0.223 h^{-1} to 0.303 h^{-1} as shown in Table 1. This might be attributed to the competitive reaction of 2,4,6-TCP degradation and reactive species quenching. The similar phenomenon was observed by Chen et al [14]. They observed that the kinetic rate constant at 0.80 mM trichloroethylene (TCE) was 1.3 times higher than that at 0.11 mMTCE in pyrite Fenton system. The reason is that excess amount of HO· may be quenched by H_2O_2 at low TCE concentration, while HO· could be mostly used for degradation at high TCE concentration.

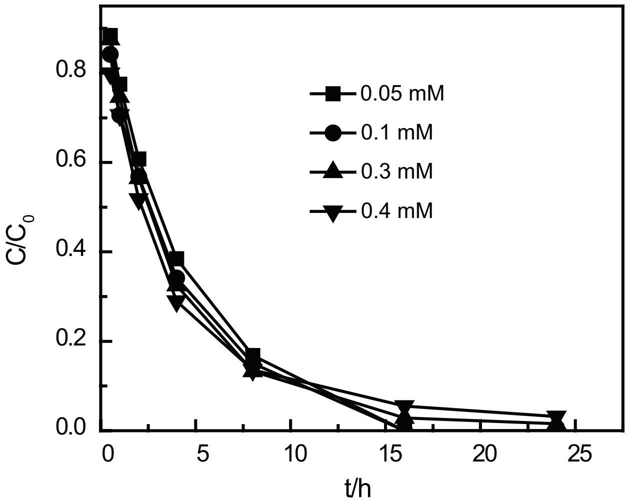

Fig. 4. Effect of initial 2,4,6-TCP concentration on the degradation of 2,4,6-TCP. Conditions: [PMS] = 10 mM, [NaOH] = 15 mM.

Table 1
Effects of initial 2,4,6-TCP concentrations on the pseudo-first-order rate constants

Initial 2,4,6-TCP concentrations (mM)	k_{obs}(h^{-1})	R^2
0.05	0.223	0.998
0.1	0.233	0.992
0.3	0.253	0.995
0.4	0.303	0.996

3.5. Predominant oxidizing species at NaOH/PMS system

In general, $SO_4^{\bullet-}$, HO· and $O_2^{\bullet-}$ are considered to be the dominant reactive species in base-activated persulfate system [7,9]. Based on the different reaction rates between radical species and specific alcohols (i.e. MeOH and TBA) in Table 2, a radical scavenging experiment was conducted for identifying the formation of $SO_4^{\bullet-}$ and HO· [15].

As depicted in Fig. 5, the addition of MeOH and TBA hardly affected the degradation of 2,4,6-TCP, which indicated that neither hydroxyl radical nor sulfate radical could be the reactive species involved in the Base/PMS system. The similar results were also reported by Wang and co-workers [16], in which the degradation of RhB was greatly suppressed when benzoquinone (0.1 mM) as the $O_2^{\bullet-}$ radical quencher was added to the Fe_3O_4/H_2O_2 system. Instead, the addition of 0.1 mM TBA has little affected.

Table 2
Second-order rate constants for selected chemical probes with hydroxyl radical and sulfate radical

Chemical probe	Reaction rate constant (M^{-1} s^{-1})	
	$SO_4^{\bullet-}$	$^{\bullet}OH$
Methanol, MeOH	3.2×10^6	9.7×10^8
tert-butyl alcohol, TBA	$(4–9.1) \times 10^5$	$(3.6–7.8) \times 10^8$

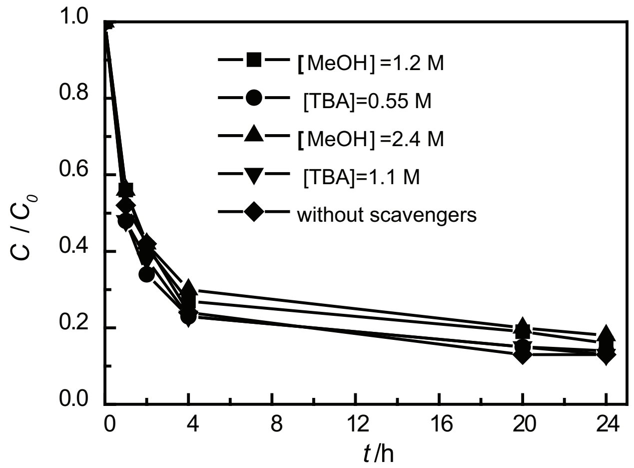

Fig. 5. Influence of radical scavengers (MeOH and TBA) on 2,4,6-TCP degradation in the NaOH/PMS system. Conditions: [2,4,6-TCP] = 0.2 mM, [PMS] = 10 mM, [NaOH] = 15 mM.

Therefore, they concluded that $O_2^{\bullet-}/HO_2\cdot$ radicals exhibited a much stronger effect than HO· radicals on the degradation of RhB. The results are also similar to those of Xiang et al. [17] who reported the degradation of MB in NaOH/PMS system. They observed the removal of MB was suppressed by about 50% with the addition of excess benzoquinone. These results means that $O_2^{\bullet-}$ radicals might be the predominant reactive species in the Base/PMS system.

To further identify the dominating radical species in NaOH/PMS system, ascorbic acid as an effectively quencher for reactive oxygen species (e.g. $O_2^{\bullet-}$ and HO·) was adopted in this study [18]. Fig. 6 illustrates the results of scavenging experiments with ascorbic acid. It can be seen that the removal rate of 2,4,6-TCP after 24 h reaction declined from 87.6% to 82.4% in the presence of 0.2 mM ascorbic acid. When ascorbic acid concentration was higher than 4 mM, 2,4,6-TCP degradation was substantially suppressed. The results presented in Fig. 5 and Fig. 6 suggest that most of the radical species would react with ascorbic acid, but not MeOH and TBA. Therefore, the major radicals responsible for the degradation of 2,4,6-TCP in NaOH/PMS system might be $O_2^{\bullet-}$ radicals. The results are consentient with those of Qi et al. [19] who investigated on the degradation of AO7 at base activated PMS system. Thus, the relevant radical mechanism can be proposed as shown in Eqs. (6–10)

$$HSO_5^- \rightarrow H^+ + SO_5^{2-} \tag{6}$$

$$SO_5^{2-} + H_2O \rightarrow H_2O_2 + SO_4^{2-} \tag{7}$$

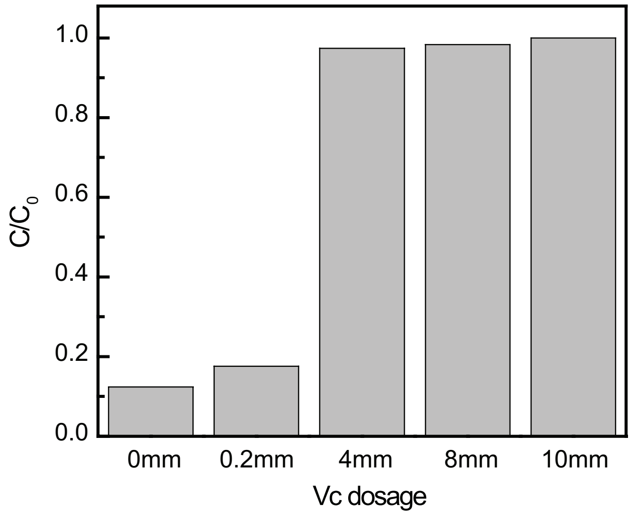

Fig. 6. Influence of radical scavengers (ascorbic acid) on 2,4,6-TCP degradation in the NaOH/PMS system. Conditions: [2,4,6-TCP] = 0.2 mM, [PMS] = 10 mM, [NaOH] = 15 mM.

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{8}$$

$$H_2O_2 \rightarrow 2HO\cdot \tag{9}$$

$$HO_2^- + HO\cdot \rightarrow O_2^{\bullet-} + H_2O \tag{10}$$

4. Conclusion

This study made an effort to explore a new method for the degradation of 2,4,6-TCP. As the results illustrated, 2,4,6-TCP can be effectively degraded by NaOH/PMS system. A proper amount of NaOH could enhance the reaction kinetics, and higher PMS dose might accelerate the degradation of 2,4,6-TCP. Due to the competitive reaction of 2,4,6-TCP degradation and reactive species quenching, the initial 2,4,6-TCP concentration had no obvious effect on its degradation. Radical scavenger tests showed that $O_2^{\bullet-}$ was the predominant reactive species responsible for 2,4,6-TCP degradation. The results strongly demonstrated that the NaOH/PMS system is a promising technique for the degradation of 2,4,6-TCP.

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