

Rapid Degradation of *p*-Chlorophenol by the Activated Percarbonate

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Chlorophenols (CPs) are widely used in the industrial production of wood preservatives, herbicides, fungicides, and pesticides. Because of its widespread existence and low biodegradability, CPs have caused harm to the environment, ecology and human health. In this study, we report a dechlorination system for the rapid degradation of *p*-chlorophenol (*p*-CP), in which hydroxylamine hydrochloride (HAH) promotes the activation of sodium percarbonate (SPC) with ferrous ions (Fe^{2+}). The effect of the different parameters, including the pH, temperature, concentrations of percarbonate and inorganic anions (Cl^- , SO_4^{2-} , NO_3^-) on the degradation of *p*-CP was investigated. The results show that the degradation efficiency reached 99 % with a HAH: Fe^{2+} : SPC: *p*-CP molar ratio of 5:5:5:1 at 20 °C for 5 min. The free radicals quenching experiments were performed to identify active species. The results show that *p*-CP is mainly degraded by hydroxyl radicals ($\text{HO}\cdot$) in the dechlorination system. This dechlorination system showed excellent degradation performance for the chlorophenols, making it to be a potential oxidant for treatment of the contaminated water.

1. Introduction

Chlorophenols are widely used in pesticides, pharmaceuticals, dyes, plastics and other industries (Igbinosa et al., 2013). They are common pollutants in water with environmental stability, bioaccumulation and biological toxicity (Czaplicka, 2004). The degradation of CPs in nature is slow, and it is easy to bind tightly with humus in sediments and persists in the environment for a long time (Antizar-Ladislao and Galil, 2003). They have a serious impact on the stability and balance of ecosystems and human health. It is of great significance to develop efficient dechlorination systems for treatment of the contaminated water.

To date, some dechlorination systems have been reported on the degradation of chlorophenol. For example, the zero-valent iron/rectorite was used to catalyze the degradation of chlorophenol by H_2O_2 (Bao et al., 2019). The *p*-CP was degraded completely within 210 min. Jiang et al. (2020) prepared a porous carbon aerogel to activate persulfate (PS) for the removal of *p*-CP, achieving a degradation efficiency of 95.4 % within 120 min. Besides the oxidation systems, the reductive dechlorination has also received much interest with the use of zero-valent iron. In our previous studies, we adopted the natural polyphenol, tannic acid (Liu et al., 2018) or procyanidine (Liu et al., 2019), as a stabilizer to synthesize high activity palladized nanoscaled zero-valent iron (Pd/Fe) and scavenger of the generated Fe ions to keep the rapid dechlorination of *p*-CP. Generally, for these systems, it still takes more than 30 min to completely degrade chlorophenols. In this work, we attempt to develop a more efficient dechlorination system to achieve rapid degradation of chlorophenols.

Sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$, SPC) has recently been considered as an alternative oxidant in the treatment of contaminated water (Tang et al., 2019). For example, the sono-photo activation of percarbonate was developed for the degradation of organic dye and 93% of Acid Orange 7 was eliminated within 90 min (Eslami et al., 2020). Huang et al. (2020) found that the trichloroethylene (TCE) was completely removed with the SPC: Fe^{2+} :TCE molar ratio of 40:80:1 in the presence of surfactant sodium dodecyl sulfate. In this study, we report a dechlorination system for the rapid degradation of *p*-CP, in which hydroxylamine hydrochloride (HAH) promotes the activation of percarbonate with ferrous ions (Fe^{2+}). The degradation of *p*-CP by the activated SPC

in the different systems was tested and the effect of pH, temperature, concentrations of percarbonate and inorganic anions (Cl^- , SO_4^{2-} , NO_3^-) on the degradation of *p*-CP was also investigated. The free radicals quenching experiments were performed to identify free radical species in the reaction system.

2. Experimental

2.1 Materials

p-Chlorophenol (AR), sodium percarbonate (SPC, AR), and hydroxylamine hydrochloride (HAH, AR) were purchased from Shanghai Yien Chemical Technology Co., Ltd.; Isopropanol (AR), chloroform (AR), and sodium hydroxide (AR) were obtained from Aladdin Reagent Company (Shanghai, China); Methanol (AR), ferrous sulfate heptahydrate (AR), sodium chloride (AR), sodium sulfate (AR), sodium bicarbonate (AR), and sodium nitrate (AR) were purchased from Shanghai Macklin Biochemical Co., Ltd. Hydrochloric acid (36 %) was obtained from Real & Lead Chemical (Tianjin).

2.2 Degradation of *p*-chlorophenol

The stock solution of *p*-CP was prepared by dissolving *p*-CP in water to a final concentration of 1000 mg/L. In a typical experiment, the HAH, ferrous sulfate, SPC, *p*-CP solution were sequentially added to the anaerobic bottle, where the final concentrations of *p*-CP was 100 mg/L, the molar ratio of HAH: Fe^{2+} : SPC was 1:1:1, and the molar ratio of SPC: *p*-CP was in the range from 1:1 to 8:1. The resulting mixture was then placed on a magnetic stirrer at 150 rpm for 20 min. The reaction conditions, including pH, inorganic anions, and reaction temperature, were investigated in order to maximize the degradation efficiency.

2.3 Free radicals quenching experiment

In quenching experiments, the scavengers were added into the solution at the beginning of the dechlorination experiment. Scavengers used in this study were isopropanol (IPA, the molar ratio of IPA: *p*-CP was 50) and chloroform (CF, the molar ratio of CF: *p*-CP was 50). The hydroxide free radical ($\text{HO}\cdot$) and superoxide radical anion ($\text{O}_2^{\cdot-}$) were quenching by IPA and CF. Control experiment without any scavenger was the same as described in section 2.2.

2.4 Analytical method

1 mL of the liquid sample was taken at predetermined time points and then diluted to 5 mL. The diluted sample was detected by high-performance liquid chromatography (HPLC, 1200 series, Agilent Technologies, Santa Clara, CA, USA) analysis with UV detection at 280 nm after filtered with a syringe membrane filter (0.22 μm). The column used was an Eclipse XDB-C18 (4.6 x 150 mm, 5 μm , Agilent Technologies), and methanol/water (70: 30, v/v) was used as mobile phase at a flow rate of 0.6 mL/min in this study. Each sample was tested twice and the average value was reported. A pH meter (Aaone IP57) was used to measure the pH of reaction solution.

3. Results and discussion

3.1 Degradation of *p*-CP in the different systems

Figure 1a shows the time-course of the degradation of *p*-CP in the different systems including Fe^{2+} , SPC, Fe^{2+} /SPC, and HAH/ Fe^{2+} /SPC. After 20 min, less than 2 % of *p*-CP loss was observed in the blank and Fe^{2+} system, indicating that the volatilization of *p*-CP was negligible and the Fe^{2+} alone can't degrade *p*-CP. As shown in Figure 1b, in the SPC system, the degradation efficiency of *p*-CP was approximately 10 % at 20 min, while in the Fe^{2+} /SPC system, the value increased to 66 %. The results was agree with the research by Fu et al. (2015), who demonstrated that the benzene was removed by Fe^{2+} -catalyzed SPC. In the presence of HAH, the concentration of *p*-CP decreased quickly from 100 mg/L to 7.8 mg/L within 5 min, and the degradation efficiency was 92.2 % in HAH/ Fe^{2+} / SPC system (Figure 1). The results indicate that HAH promote the activation of percarbonate with Fe^{2+} , because HAH can convert Fe^{3+} (formed after SPC activation) to Fe^{2+} (Zou et al., 2013). The results show that a rapid degradation of *p*-CP occurred in the first 5 min and after that the concentration of *p*-CP is almost constant. This is due to the presence of a large amount of Fe^{2+} and SPC at the beginning of reaction. With the reaction proceeds, the insoluble iron hydroxide precipitation was formed due to the accumulation of Fe^{3+} ions (Bokare and Choi, 2014).

The effect of SPS dosage on the degradation of *p*-CP was investigated with the molar ratio of HAH: Fe^{2+} : SPC kept constant as 1:1:1. As shown in Figure 2, when the molar ratio of SPC: *p*-CP is 1:1, the degradation efficiency was only 56 %, which increased to 92 % and 99 % with increasing the molar ratio to 3:1 and 5:1. With the further increase in molar ratio to 8:1, there is no obvious increase in the degradation efficiency of *p*-CP. We set 3:1 as the optimum SPC dosage for the further experiments.

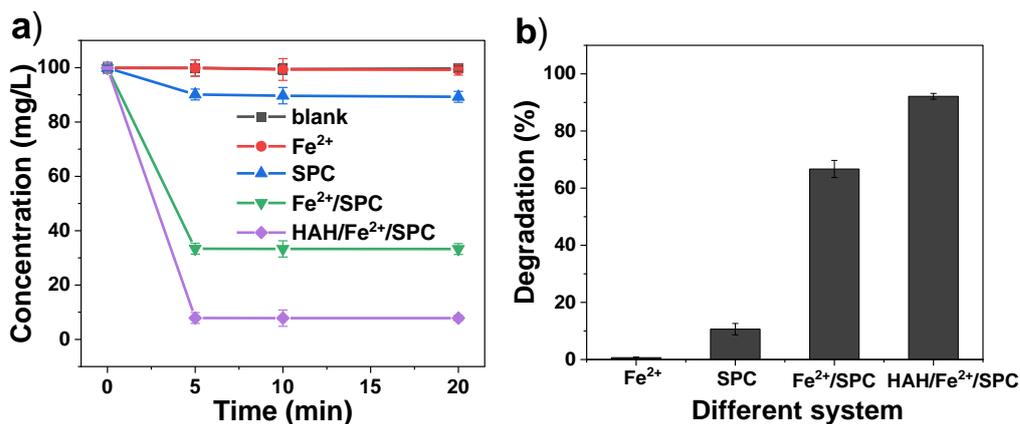


Figure 1: a) The time course of concentration of *p*-CP in the different system. b) Degradation efficiency of *p*-CP in the different system at 20 min (Conditions: initial *p*-CP concentration = 100 mg/L, the molar ratio of HAH: *p*-CP, Fe²⁺: *p*-CP and SPC: *p*-CP were 3:1, T=20 °C)

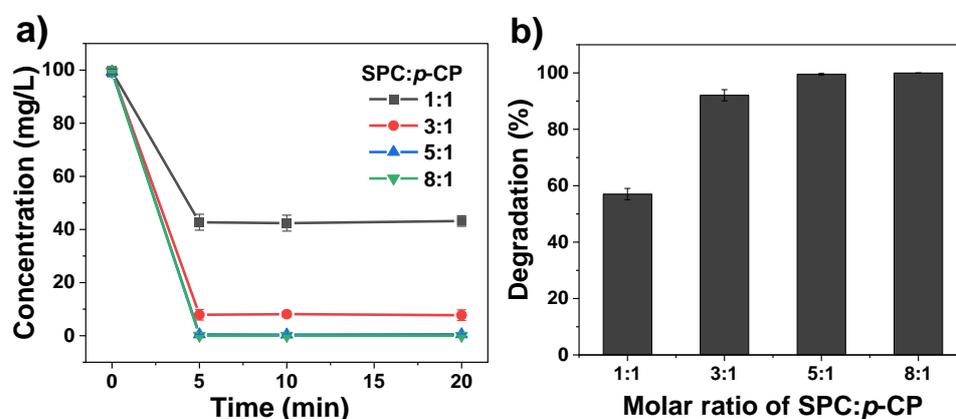


Figure 2: a) The time course of concentration of *p*-CP at various SPC: *p*-CP molar ratio. b) Degradation efficiency of *p*-CP at various SPC: *p*-CP molar ratio at 20 min. (Conditions: initial *p*-CP concentration = 100 mg/L, the HAH: Fe²⁺: SPC molar ratio was 1:1:1, T = 20 °C)

3.2 Effect of the different parameters on the degradation of *p*-CP

Naturally, groundwater contains various mineral ions, which may affect the process of pollutants degradation. In this study, Cl⁻, SO₄²⁻ and NO₃⁻ were selected to investigate the effect of mineral ions on the dechlorination. The molar ratio of the above ions to *p*-CP was set to 1, 10, or 100. As shown in Figure 3, in the presence of Cl⁻, SO₄²⁻ or NO₃⁻, there is no obvious change in the degradation of *p*-CP with increasing the concentrations of the ions, indicating that the HAH-assisted activation of SPC with Fe²⁺ is not significantly affected by these inorganic anions. In previous studies, Cl⁻ has an inhibitory effect on the hydroxyl radical-based advanced oxidation processes (Wang et al., 2019), such as the Co²⁺/peroxymonosulfate (Huang et al., 2017), and UV/persulfate system (Fang et al., 2017). It has also been reported that Cl⁻ has a dual effect, that is, inhibiting the reaction at low concentrations and speeding up the reaction at high concentrations (Wang et al., 2011). In this study, when the molar ratio of Cl⁻ to *p*-CP was 100: 1, the degradation of *p*-CP decreased slightly from 91.9 % to 87.6 %. However, the effect of Cl⁻ at higher concentrations on the degradation of *p*-CP requires further study.

The effect of initial pH on HAH/Fe²⁺/SPC system was further investigated under three different pH values of 3.0 (adjusted with H₂SO₄), 5.6 (unadjusted) and 7.0 (adjusted with NaOH). As shown in Figure 4, the degradation efficiency of *p*-CP was higher at pH 3.0, reaching 97.9 % after 20 min, in comparison with that at pH 5.6 and pH 7.0. This is due to the presence of more Fe²⁺ in the system under acidic conditions, which leads to the enhancement of SPC activation. The degradation efficiency of *p*-CP was 92.1 % without pH adjustment, and 82.7 % when the pH is adjusted to neutral. The results show that the HAH/Fe²⁺/SPC system was affected by pH and performed better under acidic conditions, which is consistent with the phenomenon in the classic Fenton reaction (Zhu et al., 2019). However, even under neutral conditions, the HAH/Fe²⁺/SPC system still had a high

oxidative ability. The results suggest that the HAH/Fe²⁺/SPC oxidation system can be widely used for the treatment of the contaminated water.

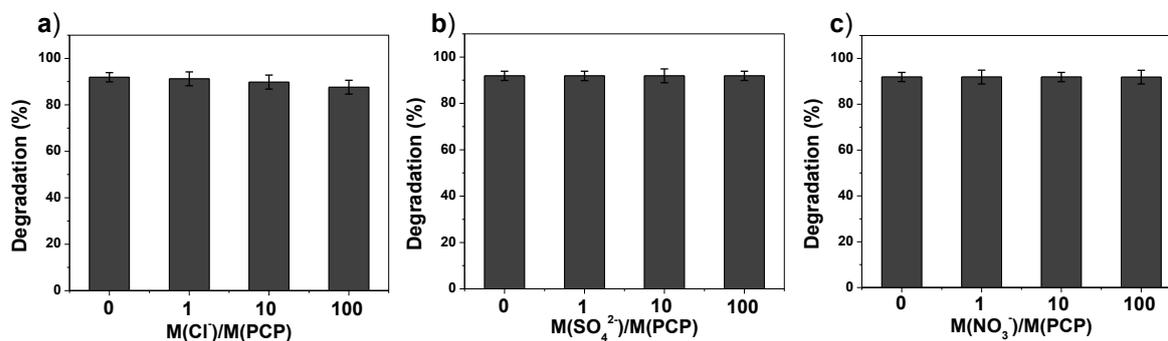


Figure 3: Effect of inorganic anions on degradation of *p*-CP in HAH/SPC/Fe²⁺ system: a)Cl⁻, b)SO₄²⁻, c)NO₃⁻ (Conditions: initial *p*-CP concentration = 100 mg/L, the HAH: Fe²⁺: SPC: *p*-CP molar ratio = 3:3:3:1, T = 20 °C, reaction time = 20 min)

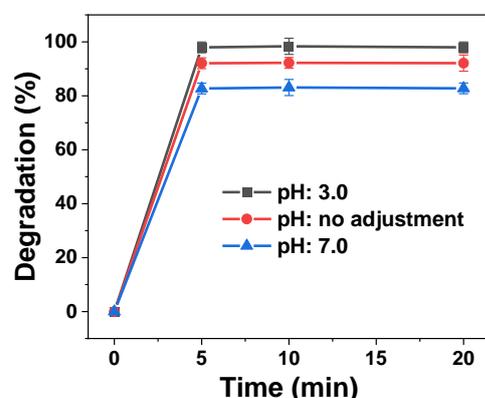


Figure 4: Effect of initial solution pH on *p*-CP degradation performance in HAH/Fe²⁺/SPC system (Conditions: initial *p*-CP concentration = 100 mg/L, the HAH:Fe²⁺:SPC: *p*-CP molar ratio = 3:3:3:1, T = 20 °C)

The effect of reaction temperature on the degradation of *p*-CP in the HAH/Fe²⁺/SPC system was investigated when the initial concentration of *p*-CP was 100 mg/L and the molar ratio of HAH: Fe²⁺: SPC: *p*-CP was 3:3:3:1. As shown in Figure 5, the degradation efficiency of *p*-CP is 92.1 % at 20 °C and 90.6 % at 35 °C. The degradation decreased slightly at 35 °C compared to 20 °C. This may be due to the enhanced decomposition of H₂O₂ to O₂ at a higher temperature. The results show that the temperature had no significant effect on the oxidation performance of HAH/Fe²⁺/SPC system within the temperature range (20 - 35 °C).

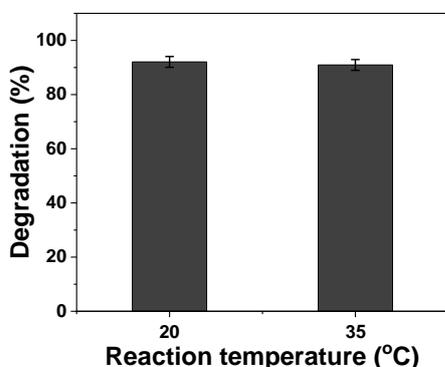


Figure 5: Effect of temperature on *p*-CP degradation performance in the HAH/Fe²⁺/SPC system (Conditions: initial *p*-CP concentration = 100 mg/L, the HAH: Fe²⁺: SPC: *p*-CP molar ratio = 3:3:3:1, reaction time = 20 min)

3.3 The mechanism of *p*-CP removal in HAH/SPC/Fe²⁺ system

A free radical scavenging experiment was performed to study the role of HO· and O₂⁻ in *p*-CP removal in the HAH/Fe²⁺/SPC system. Isopropanol (IPA) was used as a scavenger for HO· in the experiment because it has high reactivity with oxidants ($k_{\text{HO}\cdot} = 3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and low reactivity with the reductants ($k_e = 1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$). Chloroform (CF) was used as a scavenger for O₂⁻ because CF has low reactivity with HO· ($k_{\text{HO}\cdot} = 7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) and high reactivity with reductants ($k_e = 3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) (Teel and Watts, 2002). As shown in Figure 6a, the degradation of *p*-CP decreased from 92 % to 23 % in the presence of IPA, which indicates HO· was involved and mainly contributed to *p*-CP removal. Figure 6b shows that the degradation of *p*-CP decreased from 92 % to 88 % when CF was added, indicating that O₂⁻ also participates in the degradation of *p*-CP. The results are consistent with the findings in a previous study, in which the main active radicals in the Fe/SPC oxidation system are HO· and O₂⁻ (Fu et al., 2015).

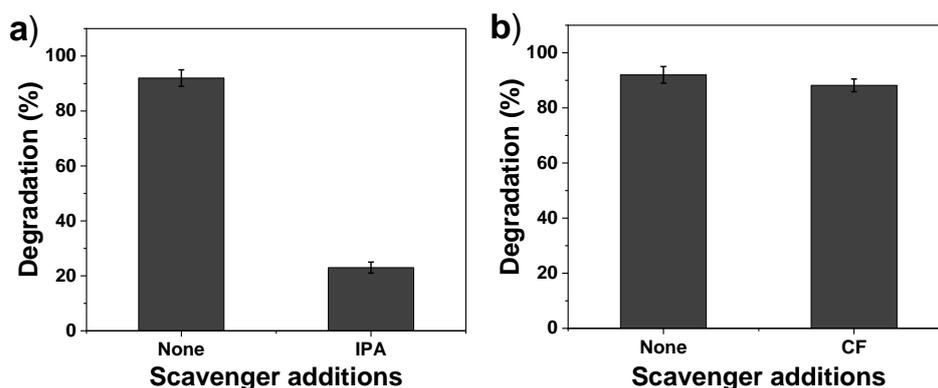


Figure 6: The effect of scavengers on the degradation of *p*-CP in the HAH/Fe²⁺/SPC system (initial *p*-CP concentration = 100 mg/L, the HAH: Fe²⁺: SPC: *p*-CP molar ratio = 3:3:3:1, molar ratios of IPA: *p*-CP and CF: *p*-CP were both 50:1, reaction time=20 min)

4. Conclusions

In summary, the rapid degradation of *p*-CP was successfully demonstrated in the HAH/Fe²⁺/SPC system. The results showed that the addition of HAH significantly enhanced the degradation of *p*-CP with an increase in degradation efficiency from 66 % to 92.6 %. With increasing the molar ratio of SPC to *p*-CP to 5:1, the degradation efficiency reached 99 % within 5 min. The HAH/Fe²⁺/SPC system performed better under acidic conditions and it was also suitable under neutral conditions. The oxidation performance of HAH/Fe²⁺/SPC system is not significantly affected by the addition of Cl⁻, SO₄²⁻ or NO₃⁻, as well as the reaction temperature. Free radical scavenging studies indicate that both HO· and O₂⁻ were evidenced to oxidize *p*-CP in HAH/Fe²⁺/SPC system, while HO· was primarily responsible for the degradation. The dechlorination system showed excellent performance for the degradation of *p*-CP. It is a potential oxidation system for treatment of the contaminated water.

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