

# The Co-Activation of Persulfate with Tannic Acid and Sodium Hydroxide for the Degradation of *p*-Chlorophenol

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Chlorinated compounds are widely used in the chemicals manufacturing industry. They have high toxicity and good stability, leading to the persistent pollution and damage of the ecological environment. In this study, *p*-chlorophenol (*p*-CP) was selected as the model, and a new dechlorination system was developed, that is, tannic acid (TA) and sodium hydroxide (NaOH) were used together to activate persulfate (PS). The effect of TA, NaOH, PS, and temperature on the degradation of chlorophenol was investigated. When 200 mg/L of TA, 0.4 M of NaOH and 100 mM of persulfate were used, the degradation efficiency of *p*-chlorophenol (50 mg/L) can reach 99 wt.%. There is no significant change in degradation efficiency when the reaction temperature is changed from 20 °C to 40 °C. The mechanism on the co-activation of persulfate with tannic acid and NaOH was proposed. The hydroxyl radicals and superoxide radicals play an important role in the degradation of *p*-CP. The dechlorination system showed excellent degradation performance for the chlorinated compounds, making it to be a potential oxidant for treatment of the contaminated groundwater.

## 1. Introduction

Persulfate (PS, e.g., peroxymonosulfate and peroxydisulfate) and the activated persulfate are currently the most commonly used in the remediation of contaminated soil and groundwater (Lee et al., 2016). Some activated radicals, such as hydroxyl radicals (HO•) and sulfate radicals anion (SO<sub>4</sub>•<sup>-</sup>) can be generated via the catalyzed decomposition of persulfate. These radicals have a high redox potential for electron transfer (Zhao et al., 2020), and are capable of rapidly oxidizing various organic compounds (Lee et al., 2016). Although PS is a very powerful oxidant, it reacts relatively slowly with the recalcitrant contaminants. The oxidation efficiency of the persulfate has to be increased by activation of persulfate, increasing the rate of persulfate decomposition and the formation of free radical. To date, various strategies, such as transition metals, heat, UV and NaOH, have been developed to be employed for PS activation. For example, Huang et al. (2019) presented a fast and effective method for the degradation of high molecular weight polyacrylamide (PAM) (M<sub>w</sub> = 3×10<sup>7</sup> Da) by a OH<sup>-</sup>/PS system. It is demonstrated that a high PAM degradation efficiency (nearly 90 wt.%) can be obtained within 20 min. Peng et al. (2015) found that alkali activated persulfate was effective in the degradation of hexachlorocyclohexanes (HCH), which rapidly dehydrochlorizes into trichlorobenzenes and are further degraded by persulfate under high pH conditions. Generally, the high loading of NaOH or high pH value is required for the alkali activated persulfate. Ahmad et al. (2010) also demonstrated that soil organic matter (SOM) containing numerous phenolic moieties can also activates persulfate. The phenols or their ionized form, phenoxides, function as activators of persulfate. However, these phenolic compounds on activating persulfate are limited as they are pollutants and the secondary pollution may be caused. The tannic acid (TA) as a natural polyphenol was used to activate persulfate.

In this study, the co-activation of persulfate with tannic acid and NaOH was developed for the degradation of *p*-chlorophenol (*p*-CP). The degradation of *p*-CP by the activated PS with different systems (PS/TA, PS/NaOH and PS/TA/NaOH) was tested. The effect of PS concentration (50 - 300 mM), NaOH concentration (0 - 0.5 M),

TA concentration (0 - 500 mg/L), and reaction temperature (20 - 40 °C) on the degradation of *p*-chlorophenol were investigated. A possible activation mechanism was proposed.

## 2. Experimental

### 2.1 Materials

*p*-Chlorophenol (99 wt.%), tannic acid (AR), sodium hydroxide (AR) were purchased from Aladdin Reagent Company (Shanghai, China). Sodium persulfate (AR) was purchased from Lianlong Bohua (Tianjin) Pharmaceutical Chemical Co., Ltd., Methanol (CH<sub>3</sub>OH, HPLC) was purchased from Tianjin Concord Technology Co., Ltd. *p*-benzoquinone (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>, 99 wt.%) was purchased from Shanghai Titan Technology Co., Ltd. Butanol (C<sub>4</sub>H<sub>10</sub>O, 95 wt.%) was purchased from Tianjin Yuanli Chemical Co., Ltd. All the chemicals were directly used in the experiments without further purification.

### 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 500 mg/L. The stock solution of PS (500 mM) and NaOH (5 M) were also prepared individually. In a typical experiment, 72 mL of water, 10 mL of PS solution, 10 mL of *p*-CP solution, 20 mg of TA and 8 mL of NaOH solution were sequentially added to the anaerobic bottle, where the final concentrations of *p*-CP, PS, NaOH, and TA, are 50 mg/L, 50 mM, 0.4 M, and 200 mg/L. The resulting mixture was then placed on a magnetic stirrer at 400 rpm for 150 min. The reaction conditions, including PS concentrations (50-300 mM), NaOH concentrations (0 - 0.5 M), TA concentrations (0 - 500 mg/L), and reaction temperature (20-40 °C), were investigated in order to maximize the degradation efficiency. Each experiment was repeated at least twice.

### 2.3 Analytical method

1 mL of the liquid sample was taken from the reaction solution and then added to the centrifuge tube containing the quencher to dilute 10 times. The diluted sample was transferred to the injection vial with a syringe membrane filter (0.22 μm) and further subjected to High-performance liquid chromatography (HPLC, 1200 series, Agilent Technologies, Santa Clara, CA, USA) analysis with UV detection at 280 nm. An Eclipse XDB-C18 column (4.6 x 150 mm, 5 μm, Agilent Technologies) was used for separation, and elution was performed with a mixture of methanol/water (70: 30, v/v) at a flow rate of 0.6 mL/min.

## 3. Results and discussion

### 3.1 Degradation of *p*-chlorophenol in different systems

Figure 1a shows the time-course of the degradation of *p*-CP in four different systems including PS, PS/TA, PS/NaOH, PS/TA/NaOH. Approximately 17 wt.% of *p*-CP loss was observed at 150 min in the PS and PS/TA system, indicating that TA alone can't improve the degradation of *p*-CP via the activation of PS. Approximate 50 wt.% of the *p*-CP was degraded in the PS/NaOH system, as summarized in Figure 1b, which is much higher than the values obtained with PS and PS/TA system. The results indicated that NaOH is effective on the activation of PS. When TA was introduced in the PS/NaOH system, the degradation efficiency increased to approximately 77 wt.% at 150 min, which is greatly enhanced compared to the PS, PS/TA, PS/NaOH systems. The result suggested that the synergistic action of TA and NaOH is crucial for the activation of PS to achieve an enhanced dechlorination performance.

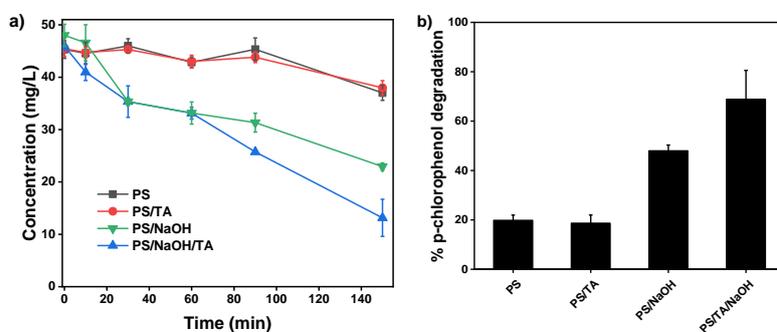


Figure 1: a) The time course of the degradation of *p*-CP by PS, PS/TA, PS/NaOH and PS/NaOH/TA. b) The comparison of the degradation efficiency of *p*-CP in different systems. Conditions: [*p*-CP] 50 mg/L, [PS] 50 mM, [NaOH] 0.4 M, [Tannic acid] 200 mg/L, 25 °C, 150 min

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

Figure 2a shows the time course of *p*-CP degradation when the PS concentration is 50 or 100 mM. The degradation of *p*-CP significantly increased with increasing concentration of PS from 50 to 100 mM. At 100 mM, the concentration of *p*-CP quickly decreased from 50 mg/L to approximately 10 mg/L within 60 min. With the reaction proceeded from 60 min to 150 min, the degradation rate was reduced. Figure 2b summarized the degradation efficiency under different PS concentrations. When the PS concentration was 50 mM, the degradation rate was 77 wt.%. The degradation efficiency of *p*-CP increased to 98.9 wt.% when the PS concentration increased to 100 mM, indicating the vital role of PS dosage on *p*-CP degradation. However, further increase of PS dosage to 300 mM, there is no change in degradation efficiency of *p*-CP. This result is consistent with the previous report, in which the removal of phenol increased significantly with PS increasing from 0.1 to 0.25 mM and further increase of PS dosage to 1 mM did not improve the phenol removal (Jiang et al., 2020). The self-quenching reaction of PS at high dosage might also contribute to the insignificant increase of phenol removal at PS concentration of 100 - 300 mM (Kang et al., 2018).

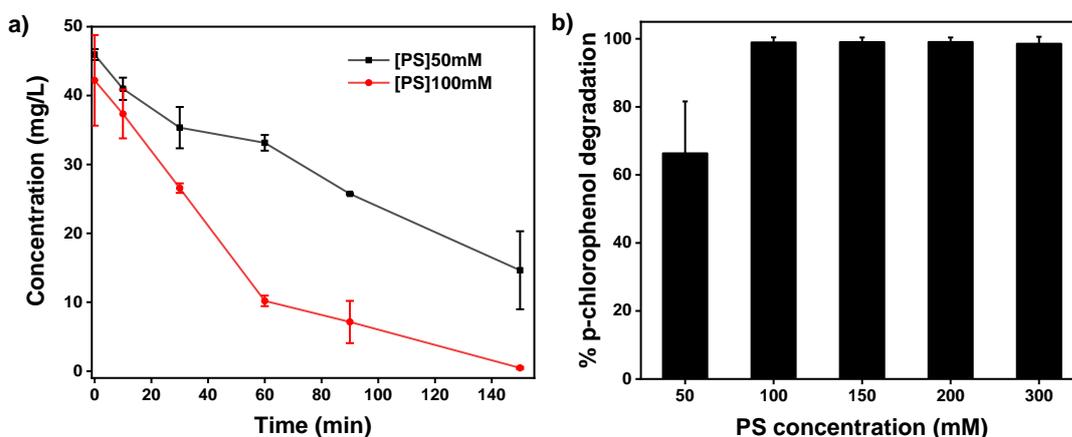


Figure 2: a) The time course of degradation of *p*-CP at different PS concentrations. b) Effect of PS concentrations on the degradation efficiency of *p*-CP at a reaction time of 150 min. Conditions: [*p*-CP] 50 mg/L, [NaOH] 0.4 M, [Tannic acid] 200 mg/L, 25 °C

In a previous study, Santos et al. (2018) found that alkali-activated persulfate can effectively degrade chlorobenzene, dichlorobenzene, trichlorobenzene and other chlorinated organics. It was important to evaluate the impact of alkali on persulfate activation in PS/TA/NaOH system. As shown in Figure 3a, the degradation efficiency of *p*-CP significantly increased with increasing concentration of NaOH. The degradation efficiency of *p*-CP increased from 17 wt.% to 98.6 wt.% when the concentration of NaOH increased from 0 to 0.2 M; There is no obvious increase in the degradation efficiency with the further increase in NaOH concentration to 0.5 M.

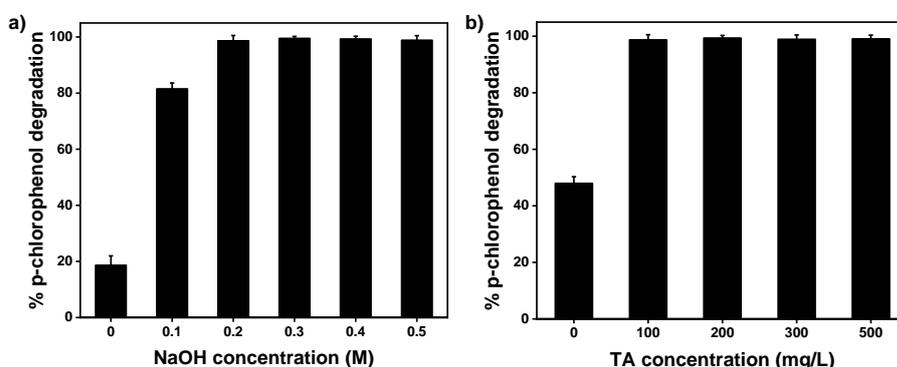


Figure 3: a) Effect of NaOH concentrations on the degradation of *p*-CP. Conditions: [*p*-CPI] 50 mg/L, [PS] 150 mM, [Tannic acid] 200 mg/L, 25 °C, 150 min. b) Effect of TA concentrations on the degradation of *p*-CP. Conditions: [*p*-CP] 50 mg/L, [PS] 150 mM, [NaOH] 0.2 M, 25 °C, 150 min.

The effect of TA dosage on the degradation of *p*-CP was investigated when the dosage of PS and NaOH was 150 mM and 0.2 M. As shown in Figure 3b, the degradation efficiency of *p*-CP increased from 50 wt.% to 98.1 wt.% when the TA concentration increased from 0 to 100 mg/L. However, there was no obvious change in the degradation when TA increased from 100 to 500 mg/L. In general, the cost of PS is higher than that of TA and NaOH. The mixture of 100 mM PS, 200 mg/L TA and 0.4 M NaOH was chosen for the degradation of *p*-CP. Recently, gallic acid (GA, is a natural polyphenol) was also used to improve the degradation of 2,2',4,4'-tetrabromodiphenyl ether (BDE47) in the Fe(III)/PMS system (Pan et al., 2020).

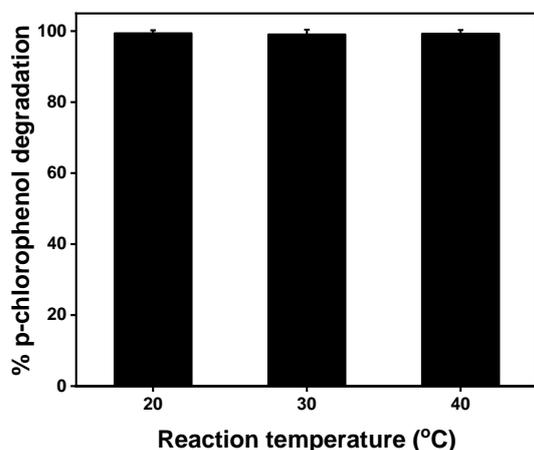


Figure 4: Effect of reaction temperature on the degradation of *p*-CP. Conditions: [*p*-CPI] 50 mg/L, [PS] 150 mM, [NaOH] 0.2 M, [Tannic acid] 100 mg/L, 150 min

The reaction temperature is also a key parameter for the practical use. It is necessary to evaluate the degradation of *p*-CP at different temperatures. Figure 4 shows the degradation efficiency of *p*-CP in the PS/TA/NaOH system in the temperature range from 20 to 40 °C. The degradation efficiency is nearly 100 wt.% under different temperature after 150 min of reaction, indicating that this system was not affected by the reaction temperature.

Table 1: Comparison of the degradation efficiency of *p*-CP in different systems.

Methods	Concentration of <i>p</i> -CP (mg/L)	Oxidant/reductant	pH	Time (min)	Degradation (wt.%)	Refs.
Oxidation	50	100 mM PS; 200 mg/L TA	13.6 (0.4 M NaOH)	150	100	This work
Oxidation	35	250 mM PS; 0.3 g/L CA	7	120	95.4	(Jiang et al., 2020)
Oxidation	33	7.4 mM PS; 0.6 g/L 3.2 wt.%Mg- CuO-Fe <sub>2</sub> O <sub>3</sub>	7	30	83.8	(Sun et al., 2020)
Oxidation	100	16 mM PS; 0.4 g/L Ag <sub>3</sub> PO <sub>4</sub> / Fe <sub>3</sub> O <sub>4</sub> /GO	3	120	96.1	(Jin et al., 2019)
Reduction	93	3.6 mol% PROC/Fe- 0.5 wt.% Pd/Fe;	9	60	97	(Liu et al., 2019)
Reduction	100	R <sub>Fe/<i>p</i>-CP</sub> =20:1 2.52 mol% TA/Fe- 0.5 wt.% Pd/Fe;	9	30	100	(Liu et al., 2018)
		R <sub>Fe/<i>p</i>-CP</sub> =20:1				

Some dechlorination systems had been developed in previous studies, as summarized in Table 1. For example, Jiang et al. (2020) prepared a porous carbon aerogel (CA) to activate persulfate (PS) for the removal of *p*-CP, achieving a degradation efficiency of 95.4 wt.% within 120 min by the addition of 250 mM PS and 0.3 g/L CA. Mg-CuO-Fe<sub>2</sub>O<sub>3</sub>/PS system was also developed to degrade *p*-CP with a degradation efficiency of more than 83.8 wt.% (Sun et al., 2020). About 96.1 wt.% of *p*-CP were degraded by Ag<sub>3</sub>PO<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub>/GO (graphene oxide)

photocatalytic oxidation (Jin et al., 2019). Beside the oxidation methods, the reductive dechlorination has received much interest recently with the use of zero-valent iron. For example, the natural polyphenol, TA (Liu et al., 2018) or procyanidine (PROC) (Liu et al., 2019), was adopted as 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. Compared with pristine Pd/Fe nanoparticles, the modified Pd/Fe had a dechlorination efficiency that was increased 20-fold (pH 9.0). In comparison with these dechlorination systems, the TA and NaOH co-activated PS has a superior or comparable degradation efficiency.

### 3.3 Mechanism of persulfate activation

In previous studies, Lin et al. (2019) pointed out that quercetin (QCR) is a natural polyphenol that can be decomposed and transformed into QCR radicals at pH 13, which can release electrons for PS activation upon stabilization to form benzoquinones.  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^\bullet$  were mainly detected in the QCR/PS system. Ahmad et al. (2013) showed that hydroperoxide anion is generated by the sodium hydroxide catalyzed hydrolysis of persulfate, which can reduce persulfate molecule to form sulfate radical ( $\text{SO}_4^{\bullet-}$ ) and superoxide radical anion ( $\text{O}_2^{\bullet-}$ ). The sulfate radical ( $\text{SO}_4^{\bullet-}$ ) can be further converted to hydroxyl radical ( $\text{HO}^\bullet$ ) under alkaline conditions (Liang et al., 2009). Based on the previous research reports, a possible reaction mechanism of TA and NaOH co-activated PS system was proposed. As shown in Figure 5, on one hand, TA mainly exists in ionized form in an alkaline environment. Then, the ionized form of TA reacts with persulfate anion ( $\text{S}_2\text{O}_8^{2-}$ ) to its oxidized form (quinone), the sulfate radical ( $\text{SO}_4^{\bullet-}$ ) is generated. On the other hand, in the presence of  $\text{OH}^-$  ions, the persulfate anion ( $\text{S}_2\text{O}_8^{2-}$ ) is converted to sulfate anion ( $\text{SO}_4^{2-}$ ) and hydroperoxide ( $\text{HO}_2^-$ ). Subsequently, the hydroperoxide reduces the persulfate to sulfate anion ( $\text{SO}_4^{2-}$ ) and sulfate radical ( $\text{SO}_4^{\bullet-}$ ), the hydroperoxide is oxidized to superoxide radical anion ( $\text{O}_2^{\bullet-}$ ). Finally, the sulfate radicals, generated from both TA and NaOH activated PS as mentioned before, were converted to sulfate anion ( $\text{SO}_4^{2-}$ ) and hydroxyl radical ( $\text{HO}^\bullet$ ) under alkaline conditions. It was speculated that both of hydroxyl radicals and superoxide radicals play an important role in the degradation of *p*-CP.

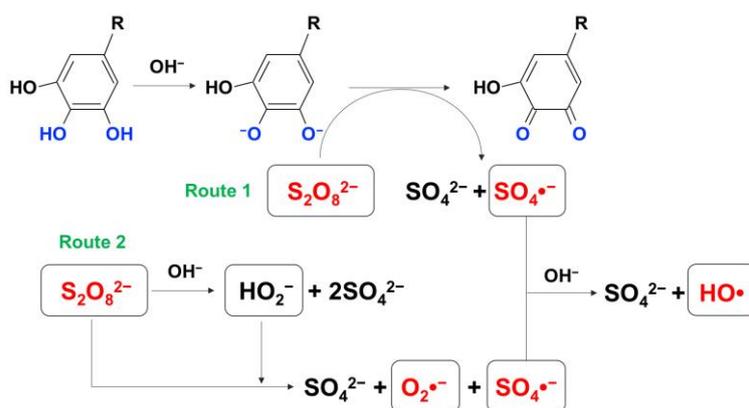


Figure 5: Schematic diagram of the mechanism of co-activation of PS with TA and NaOH

## 4. Conclusions

In summary, a new degradation system with the TA and NaOH co-activated persulfate was successfully developed. It is found that the degradation efficiency of *p*-CP increased with increasing of the concentration TA, NaOH, and PS. Under the optimal conditions, that is, 200 mg/L of tannic acid, 0.4 M of NaOH and 100 mM of persulfate, the degradation efficiency of *p*-CP (50 mg/L) can reach more than 99 wt.%. There is no significant change in degradation efficiency when the reaction temperature is changed from 20 °C to 40 °C. The mechanism on the co-activation of persulfate with tannic acid and NaOH was proposed. The ionized form of TA reacts with persulfate anion to produce sulfate radical ( $\text{SO}_4^{\bullet-}$ ), while the  $\text{HO}_2^-$  reacts with persulfate to generate superoxide radical anion ( $\text{O}_2^{\bullet-}$ ) and  $\text{SO}_4^{\bullet-}$  under alkaline conditions. The resulting  $\text{SO}_4^{\bullet-}$  was further converted to sulfate anion ( $\text{SO}_4^{2-}$ ) and hydroxyl radical ( $\text{HO}^\bullet$ ). Both of the hydroxyl radicals ( $\text{HO}^\bullet$ ) and superoxide radicals ( $\text{O}_2^{\bullet-}$ ) play an important role in the degradation of *p*-CP. In view of the easy availability and the low cost of TA, PS, and NaOH, it was believed that the PS/TA/NaOH system is a promising oxidant for the treatment of the chlorinated compounds, contaminated soil and groundwater.

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