Degradation of phenol in water by Fe(II)-citrate activated persulfate oxidation

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Abstract. To enhance the degradation efficiency, complexing agent citric acid (CA) and trisodium citrate (TC) were introduced into the Fe(II)-persulfate (Fe²⁺/PS) oxidation system to degrade phenol. And the optimal operating conditions were determined. The results showed that Fe²⁺-citrate/PS system had higher degradation efficiency than the others. The optimal operating conditions to degrade phenol in water were: a PS concentration of 0.06 mol/L, a Fe²⁺ concentration of 0.02 mol/L and a TC concentration of 0.01 mol/L, while reaction temperature and the initial pH values had little influence on the phenol degradation.

1. Introduction

In recent years, the advanced oxidation processes (AOPs) utilizing sulfate radical were developed to eliminate refractory organic pollutants[1]. Persulfates (PS, S₂O₅²⁻) can generate sulfate radicals (SO₄⋅⁻) by various activators, such as UV, heat, transition metal ions, et.al[2-4]. SO₄⋅⁻ has a superior redox potential than most organic compounds, which makes it possible to degrade most organic pollutants. The methods of activating persulfate to produce sulfate radical by transition metals have been paid more and more attention by researchers because of their simple reaction system, mild reaction conditions and low energy consumption. Fe²⁺ is the most widely studied metal ion activating agent for activating persulfate because of its cheapness, obtainable and non-toxic. Some studies showed that, the Fe²⁺/S₂O₅²⁻ system ran well only under acidic conditions[5-8]. The rapidly formed SO₄⋅⁻ would be quenched by reacting with Fe³⁺, which resulted in low SO₄⋅⁻ utilization. Liang reported that, adding citric acid into the Fe²⁺/S₂O₅²⁻ system could significantly improve the degradation efficiency of the target pollutant trichloroethylene (TCE)[9]. Zhang et al. found that Diuron could be degraded efficiently by Fe²⁺-citrate/ S₂O₅²⁻ system[10]. The addition of complexing agent can form a complex with Fe(II), which makes Fe²⁺ release slowly into the solution and delays the formation rate of SO₄⋅⁻. Thus SO₄⋅⁻ could be prevented from being quenched by excessive Fe³⁺[2]. In addition, Fe³⁺ complexes can exist stably under neutral or alkaline conditions, which to a certain extent overcome the weakness that Fe³⁺ can only stabilize in acidic solution.

To the best of our knowledge, studies on phenol degradation by Fe²⁺-citrate/ S₂O₅²⁻ system are rarely reported. In the present study, Fe²⁺-citrate/ S₂O₅²⁻ system was employed to eliminate phenol in simulated phenol wastewater, and the influence of operational parameters on the phenol degradation efficiency was examined to determine the optimum conditions.
2. Materials and methods

2.1. Materials
Potassium persulfate, ferrous sulfate, trisodium citrate (TC), citric acid (CA), phenol were obtained from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Analysis methods

2.2.1. Determination of phenol. Phenol content in wastewater was determined by 4-aminoantipyrine method[11].

2.2.2. Phenol removal rate. The phenol removal rate η was calculated by equation (1) as follow:

\[ \eta = \frac{(C_0 - C_i)}{C_0} \times 100\% \]  

where \( C_0 \) is the initial phenol concentration in simulated wastewater, \( C_i \) is phenol concentration in the sample solution.

2.3. Phenol degradation experiment
0.1 g/L simulated phenol wastewater was obtained by transferring 10 mL of calibrated 1g/L phenol into 100 mL volumetric flask and then diluting with distilled water to 100 mL. The 100 mL 0.1 g/L simulated phenol wastewater was then transferred to 250 mL conical flask. A certain amount of TC or CA, ferrous sulfate and potassium persulfate (PS) were added to the conical flask successively while stirring. At different time points of the reaction, appropriate amount of reaction solution was transferred to 50 mL colorimetric tube. A certain amount of anhydrous ethanol was added to quench the radical, and then diluted with distilled water to 50 mL. The concentration of phenol in the sample was measured by 4-aminoantipyrine method.

3. Results and discussion

3.1. Standard curve of phenol concentration
According to 4-aminoantipyrine method, the standard curve of phenol concentration was drawn as figure 1.

![Figure 1. Standard curve of phenol concentration](image)

The linear fitting equation of the standard curve was equation (2):

\[ y = 0.2214x + 0.007 \]

\[ R^2 = 0.9997 \]

where \( y \) is absorbance, \( x \) is phenol concentration (mg/L).
3.2. Selection of the degradation system
The comparative results of phenol degradation by PS alone, Fe$^{2+}$/PS system, Fe$^{2+}$-CA/PS system and Fe$^{2+}$-citrate/PS system were displayed in figure 2. It was clearly observed that without activator, the removal rate of phenol was no more than 0.5%. The Fe$^{2+}$-CA/PS system has no more effectiveness than the Fe$^{2+}$/PS system, while the removal rate of phenol was obviously improved by the Fe$^{2+}$-citrate/PS system. The reason may be that the dissociation constant of citric acid was too small to provide enough concentration of citrate ions to form complexes with Fe$^{2+}$. TC could be completely dissociated in aqueous solution to form complexes with Fe$^{3+}$, which decreased the formation rate of SO$_4^{2-}$· and prevented SO$_4^{2-}$· from being quenched by excessive Fe$^{2+}$. So the Fe$^{2+}$-citrate/PS system was chosen as the degradation system. Figure 2 indicated that the removal rate reached a balance after 1h, so the rest experiments were all taken for 1h.

3.3. The effect of the initial PS concentration
While studying the effect of the initial PS concentration on phenol degradation, concentrations of 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.10 mol/L were adopted with the Fe$^{2+}$ concentration of 0.01 mol/L, a temperature of 25°C and an Fe$^{2+}$/TC mole ratio of 1:1. The experimental results were displayed in figure 3.

In figure 3, the removal rate of phenol fluctuated between 81% and 85% when the initial PS concentration was increased from 0.04 to 0.08 mol/L, after which the removal rate decreased to 78.5%. It suggested that higher PS concentration could not continuously improve the degradation efficiency due to the inhibition of SO$_4^{2-}$· by S$_2$O$_8^{2-}$ as reported[2]. Therefore, considering degradation efficiency and less use of oxidant, an optimized PS dose of 0.06 mol/L was selected.

3.4. The effect of initial Fe$^{2+}$ concentration
Fe$^{2+}$ was an important factor affecting the oxidizing ability of the system. The effect of the initial Fe$^{2+}$ concentration on phenol degradation was displayed in figure 4, and these experiments were conducted with initial PS concentration of 0.06 mol/L, initial TC concentration of 0.01 mol/L at a temperature of 25°C.

It can be clearly observed from figure 4 that there was a maximum phenol removal rate up to 92.35% when the initial Fe$^{2+}$ concentration was 0.02 mol/L. The phenol removal rate was decreased while the initial Fe$^{2+}$ concentration was increased. This result suggested that there was a critical value of the initial Fe$^{2+}$ concentration, after which Fe$^{2+}$ had a negative effect on PS degradation. Once the Fe$^{2+}$ concentration was increased above the critical value, the rapidly generated SO$_4^{2-}$· would prefer to react with Fe$^{2+}$, which decreased the phenol removal rate. Therefore, it is reasonable to believe that the proper initial Fe$^{2+}$ concentration was 0.02 mol/L.
3.5. Effect of the initial TC concentration

TC is an organic salt that can disassociate citrate ions when dissolved in water. Free citrate ions can form complexes with Fe$^{2+}$, which can slow down the Fe$^{2+}$ release. The effect of the initial TC concentration on phenol degradation was shown in figure 5. In these experiments, the PS and Fe$^{2+}$ concentration were 0.06 mol/L and 0.02 mol/L, separately, while the temperature was 25 °C.

Figure 4. The effect of the initial Fe$^{2+}$ concentration on phenol removal rate.

Figure 5. The effect of the initial TC concentration on phenol removal rate.

Figure 5 showed that when TC concentration was increased from 0.02 mol/L to 0.04 mol/L, phenol removal rate experienced a rapid decrease from 85.71% to 3.97%. This indicated that higher citrate concentration had a strong inhibitory effect on phenol degradation due to the degradation of excess citrate ions by SO$_4^{2-}$, which reduced the utilization of SO$_4^{2-}$. Hence, the dosage of TC was determined to be 0.01 mol/L.

3.6. Effect of temperature

The effect of temperature on phenol removal rate was evaluated under the conditions as a PS dose of 0.06 mol/L, a Fe$^{2+}$ dose of 0.02 mol/L and a TC dose of 0.01 mol/L. The effect of temperature on phenol removal was presented in figure 6. The figure showed that the phenol removal rate correlated weakly with the bulk temperature, as the phenol removal rate was 89.5% to 92.5% with little difference when the temperature changed from 15 °C to 45 °C. Considering saving energy, the temperature of reaction was chosen to be 25 °C.

3.7. Effect of initial pH

Five initial pH values were used to evaluate the effect of initial pH on phenol removal rate at a PS dose of 0.06 mol/L, a Fe$^{2+}$ dose of 0.02 mol/L and a TC dose of 0.01 mol/L. The phenol removal rate under different initial pH values was presented in figure 7. It could be found that the phenol removal rate was over 90% under bulk initial pH values. Hence, the Fe$^{2+}$-citrate/ S$_2$O$_8^{2-}$ system could be used under a wide range of pH values.
Figure 6. The effect of temperature on phenol removal rate.

Figure 7. The effect of the initial pH on phenol removal rate.

4. Conclusions
The present work showed that the Fe$^{2+}$-citrate/$\text{S}_2\text{O}_8^{2-}$ system was a highly efficient advanced oxidation system for degrading phenol and the removal rate was up to 93%. Optimum operating conditions were determined to be a PS concentration of 0.06 mol/L, a Fe$^{2+}$ concentration of 0.02 mol/L and a TC concentration of 0.01 mol/L. In addition, a relatively higher temperature of 35 ℃ and a relatively lower pH values could enhance the phenol removal rate.

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