Oxidative degradation of phenol in aqueous solution by using heat, ZVI, AC, heat/ZVI, or heat/AC activated persulfate

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Degradation of phenol by heat-activated, ZVI-activated, AC-activated, heat/AC-activated, and heat/ZVI-activated persulfate have been investigated. As a result, the degradation of phenol fitted well with pseudo-first order kinetic model. For the solution with phenol concentration of 100 mg/L, degradation efficiency of nearly 100% and reaction rate constant of \(0.0506 \text{ min}^{-1}\) are realized by heat-activated persulfate when reaction temperature is 70°C, concentration of persulfate is 15 g/L, reaction time is 120 min under neutral pH. Besides, the highest degradation efficiency and reaction rate constant of phenol by ZVI-activated are respectively, 92.85% and 0.0198 \text{ min}^{-1}\) when concentration of ZVI is 5 g/L, concentration of persulfate was 15 g/L, and reaction time is 120 min under neutral pH. Furthermore, the highest degradation efficiency and reaction rate constant of phenol by AC-activated persulfate are 99.1% and 0.0373 \text{ min}^{-1}\), respectively with persulfate concentration of 5 g/L and AC concentration of 5 g/L under neutral pH in 120 min. Moreover, the heat/AC-activated and heat/ZVI-activated persulfate are showing obvious synergistic effect during degradation process of phenol, and the reaction rate constants of heat/AC-activated and heat/ZVI-activated persulfate are respectively, 0.0512 and 0.0561 \text{ min}^{-1}\). The radical scavenger experiments proved that both \(\text{SO}_4^*\) and \(\text{OH}^*\) are significant radicals in degradation of phenol by ZVI-activated and AC-activated persulfate, and \(\text{SO}_4^*\) are predominant radicals in degradation of phenol.

**Keywords:** Activated persulfate, Free radicals, Oxidative degradation, Phenol degradation, Reaction kinetics

Refractory phenolic pollutants are often present in industrial wastewater from industries such as coal, petrochemical, pharmaceutical, plastic processing, paint, papermaking and wood processing wastewater, etc.¹⁻³ Phenolic pollutants are so toxic and biorefractory that they are classed by the related official environmental protection agency as one kind of primary pollutant that abide by specific regulation. Therefore, phenolic pollutants should be treated before discharging into the environment. At present, the treatment method of phenolic pollutants include steam distillation, absorption, extraction, membrane separation, chemical oxidation, and advanced oxidation, etc.² Compared with the other treatment technologies of phenolic pollutants, advanced oxidation processes have unparalleled advantages, such as high degradation and mineralization efficiency, low reagent dosage, low energy consumption, and low secondary pollution.

The degradation of refractory organic pollutants by advanced oxidation process based on sulfate radicals (\(\text{SO}_4^*\)) has attracted much attention due to its economical, efficient, environmentally friendly, safe and stable advantages. Peroxydisulfate (PMS), or persulfate (PS) caused by the activators could generate highly active sulfate radicals and hydroxyl radical (\(\text{OH}^*\)) to oxidize and degrade refractory organic pollutants⁶. Up to now, degradation of phenolic pollutants by activated PMS/PS contains external energy, external catalyst, and synergistic activation. The external energy activation involves heat-activated, microwave irradiation-activated, light-activated, sono-activated, electro-activated, and plasma-activated PMS/PS, etc.⁷⁻¹² Besides, the external catalyst activation embraces transition metals-activated, and carbon materials-activated PMS/PS, etc.¹³⁻¹⁴ Among them, heat-activated, transition metals-activated, and carbon materials-activated PMS/PS are the most common degradation methods of phenolic pollutants. Recently, Bisphenol A (BPA) is oxidized and degraded by heat-activated persulfate at temperature of 40~70°C and initial pH of 3~11. The acidic and neutral pH values are more favourable for BPA degradation than basic pH values¹⁵. Furthermore, the degradation of chloroxynlenol in aqueous solution by thermally activated persulfate has been realized at neutral pH. The sulfate radicals and hydroxyl radicals work...
together in combination, and sulfate radicals play the predominant role during process of degradation of chloroxylenol. Besides, the mixture of nonylphenol and triclosan in aqueous solution by thermally activated persulfate has been effectively degraded. It is proved that a single-electron coupling reaction induced by OH$^\cdot$ as the degradation dominant route in the mixed system. Except for heat-activated PMS/PS, there are also some examples on transition metals-activated PMS/PS. For example, the synergistic degradation of phenol and reduction of chromium(VI) by FeS$\_2$/Fe$^0$(ZVI) activated persulfate have been successfully achieved with a pH range of 3.0–9.0 (Ref. 18). The degradation of phenol by FeCo$_3$O$_4$ activated PMS/PS are also carried out under near neutral and alkaline conditions. The results indicate that sulfate radical (SO$_4^\cdot$), hydroxyl radical (OH$^\cdot$) and singlet oxygen (O$_2^\cdot$) play significant roles in degradation of phenol in PMS system. At the same time, both non-radical and free radical mechanisms between PS and the FeCo$_3$O$_4$ catalyst surface play major roles in phenol degradation. Moreover, the degradation of phenol by biochar activated PS is reported. It indicates that SO$_4^\cdot$•, OH$^\cdot$ and O$_2^\cdot$ are responsible for degradation of phenol. O$_2^\cdot$ plays the dominant role, OH$^\cdot$ takes a secondary position and SO$_4^\cdot$ plays the least role. However, there are few attempts on degradation of phenol by heat-activated, Fe$^0$(ZVI)-activated, and activated carbon (AC)-activated PMS/PS. Therefore, the degradation processes of phenol by heat-activated, ZVI-activated, AC-activated, heat/AC-activated, and heat/ZVI-activated PS have been investigated in this paper. The reaction rate constants have been also calculated. Finally, free radicals in degradation process of phenol have been inferred through free radical scavenger experiments and the related literature.

**Experimental Section**

**Materials and instruments**

The details of materials in the paper are listed in Table 1. All the materials were purchased from Shanghai Macklin Biochemical Co., Ltd. and Sinopharm Chemical Reagent Co., Ltd. The details of the instruments were listed in Table 2.

**Experimental procedures**

100 mL phenol solution of concentration of 100 mg/L was injected into the reactor. Then, certain amount of sodium persulfate and catalysts were successively put in the reactor. The reaction temperature was set and the stirrer was turned on until the experiment completed. After degradation experiment, the solution was filtered by filter paper for several times and the clear filtrate was ready for determination of phenol concentration.

**Determination of phenol concentration**

The phenol concentration in aqueous solution is analyzed by a 4-aminoantipyrine (4-AAP) spectrophotometric method described in the previous literature.

**Pseudo-first order kinetic model**

The pseudo-first order kinetic model during degradation of phenol can be expressed as follows:

\[
\frac{d(C/C_0)}{dt} = -k_{obs}(C/C_0) 
\]

...(1)

Where $C_i$ and $C_0$ are concentration of phenol at time $t$ and initial concentration of phenol, respectively, $k_{obs}$ is reaction rate constant, $t$ is reaction time, $C$ is related constant. Eq. (2) can be obtained from Eq. (1).

\[
\ln(C/C_0) = -k_{obs}t + C 
\]

...(2)

$\ln(C/C_0)$ and $t$ are taken as vertical ordinate and horizontal ordinate, respectively, and a straight line is
plotted. $k_{obs}$ is equal to the absolute value of slope of the straight line.

**Degradation efficiency**

The degradation efficiency ($D$) of phenol is defined as follows:

$$D = \left( C_0 - C_t \right) / C_0 \times 100\% \quad \ldots \quad (3)$$

**Results and Discussion**

**Degradation of phenol by activated persulfate**

**Heat-activated persulfate**

The effects of reaction temperature and time on degradation of phenol by heat-activated persulfate are shown in Fig. 1 and Table 3. It was seen that dimensionless residual phenol concentration ($C_t / C_0$) decreased sharply with reaction time in the first 60 minutes, then decreased slowly and remained steady at 120 min. The dimensionless concentration of residual phenol decreased with reaction temperature ranging from 50 to 100℃. The dimensionless concentration of residual phenol decreased from 1 to almost 0 in 120 min at 70-100℃. It meant that the degradation efficiency of phenol could be close to 100% at 70-100℃ in 120 min under neutral pH. In view of degradation efficiency, heat-activated persulfate might be a good choice for degradation of phenol. However, the process of heat-activated persulfate consumed more energy. Hence, comprehensive consideration was needed when reaction temperature was chosen. The degradation process of phenol by heat-activated persulfate fitted well with pseudo-first order kinetic model. The reaction rate constant $k_{obs}$ increased rapidly from 0.0020 min$^{-1}$ (in 120 min) to 0.0506 (in 120 min) to 0.1213 min$^{-1}$ (in 60 min) at reaction temperature ranging from 50 to 70 to 100 ℃ under neutral pH. These results were similar with the findings of previous literature. The reason can be explained by Arrhenius equation as given below.

$$\ln(k_{obs}) = \ln A - \Delta E_f / (RT) \quad \ldots \quad (4)$$

![Fig. 1 — Degradation of phenol by heat activated persulfate (other conditions: $C_0=100$ mg/L, $C_{PS}=15$ g/L, near neutral pH)](image)

<table>
<thead>
<tr>
<th>Activation</th>
<th>$C_0$/mg·L$^{-1}$</th>
<th>$C_{Fe}$/g·L$^{-1}$</th>
<th>$C_{AC}$/g·L$^{-1}$</th>
<th>$C_{PS}$/g·L$^{-1}$</th>
<th>$T$/℃</th>
<th>pH</th>
<th>$t$/min</th>
<th>$D$/%</th>
<th>$k_{obs}$/min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat</td>
<td>100</td>
<td>—</td>
<td>15</td>
<td>50</td>
<td>70</td>
<td>—</td>
<td>120</td>
<td>19.17</td>
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</tr>
<tr>
<td>heat</td>
<td>100</td>
<td>—</td>
<td>15</td>
<td>70</td>
<td>100</td>
<td>100</td>
<td>0.1213</td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat</td>
<td>100</td>
<td>—</td>
<td>15</td>
<td>100</td>
<td>60</td>
<td>100</td>
<td>0.0011</td>
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<tr>
<td>Fe$^0$</td>
<td>100</td>
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<td>—</td>
<td>—</td>
<td>120</td>
<td>14.02</td>
<td>0.0011</td>
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</tr>
<tr>
<td>Fe$^0$</td>
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<td>1</td>
<td>3</td>
<td>—</td>
<td>120</td>
<td>23.12</td>
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<td></td>
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<tr>
<td>Fe$^0$</td>
<td>100</td>
<td>5</td>
<td>—</td>
<td>5</td>
<td>120</td>
<td>40.38</td>
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<tr>
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<td>15</td>
<td>—</td>
<td>120</td>
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<td>1</td>
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<tr>
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<td>—</td>
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<td>70</td>
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<td>0.0512</td>
<td></td>
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<tr>
<td>Heat/AC</td>
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<td>5</td>
<td>5</td>
<td>70</td>
<td>120</td>
<td>100</td>
<td>0.0561</td>
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</table>
In the above equation, \( A \) is the pre-exponential factor, \( E_a \) is the apparent activation energy (kJ mol\(^{-1}\)), \( R \) is universal gas constant (8.314 × 10\(^{-3}\) kJ·mol\(^{-1}\)·K\(^{-1}\)), \( T \) is reaction temperature (K). \( A \) and \( E_a \) are constants in the specific reaction system. Therefore, \( k_{obs} \) increases with reaction temperature. More \( \text{SO}_4\text{•} \) and \( \text{OH}• \) could be produced at higher reaction temperature leading to more phenol being degraded. Taking the degradation efficiency and energy saving into consideration, 70\(^\circ\)C is chosen as the optimal reaction temperature in degradation of phenol by heat-activated persulfate.

**Fe\(^0\)-activated persulfate**

The degradation of phenol by Fe\(^0\)-activated persulfate are shown in Fig. 2 and Table 3. As can be seen that concentration of Fe\(^0\) and persulfate play vital roles in degradation of phenol. Increasing concentration of Fe\(^0\) and persulfate facilitated degradation of phenol. The dimensionless concentration of residual phenol was 0.8598 and the degradation efficiency of phenol was 14.02% in 120 min when the concentration of Fe\(^0\) and persulfate were 1 g/L under neutral pH. Likewise, the dimensionless concentration of residual phenol decreased to 0.5962 and the degradation efficiency of phenol increased to 40.38% in 120 min when the concentration of Fe\(^0\) and persulfate were 5 g/L under neutral pH. Furthermore, the dimensionless concentration of residual phenol decreased to 0.0715 and the degradation efficiency of phenol was up to 92.85% in 120 min when concentration of Fe\(^0\) was 5 g/L, and concentration of persulfate was 15 g/L under neutral pH. It is due to the increased amount of Fe\(^0\) increasing the release of Fe\(^2+\) and then facilitating activation of persulfate to produce \( \text{SO}_4\text{•} \). The existence of Fe\(^2+\) can significantly affect the degradation efficiency of organic pollutants. A similar result was found in the literature\(^{23}\). Furthermore, more persulfate molecular could react with Fe\(^0\) and Fe\(^2+\) on surface of iron powder due to increasing of persulfate concentration and result in improvement of degradation of phenol. The reaction rate constant \( k_{obs} \) were 0.0011, 0.0019, 0.0044 and 0.0198 min\(^{-1}\), respectively, in 120 min when the concentration of Fe\(^0\) and persulfate were 1 g/L and 1 g/L, 1 g/L and 3 g/L, 5 g/L and 5 g/L or 5 g/L and 15 g/L under neutral pH. In order to gain high degradation efficiency of phenol, the recommended concentration of Fe\(^0\) and persulfate were respectively, 5 g/L and 15 g/L.

**AC-activated persulfate**

The degradation of phenol by AC activated persulfate are shown in Fig. 3 and Table 3. It could be seen that the increased concentration of persulfate hindered degradation of phenol with the same dosage of AC. The dimensionless concentration of residual phenol with addition of persulfate concentration of 3 g/L was higher than that with 1 g/L. Similarly, the degradation of residual phenol with addition of persulfate concentration of 15 g/L was also higher than that with 5 g/L. Although, increasing the concentration of persulfate could improve the degradation of phenol when there was lack of free radicals in solution. However, the existence of excessive free radicals could lead to quenching between free radicals and decrease the degradation of phenol when the dosage of persulfate was excessive. The increased persulfate and AC concentration simultaneously could improve the degradation of...
phenol. The dimensionless concentration of residual phenol with addition of persulfate concentration of 5 g/L and AC concentration of 5 g/L was lower than that with addition of persulfate concentration of 1 g/L and AC concentration of 1 g/L. The least dimensionless concentration of residual phenol reached 0.009 and the highest degradation efficiency of phenol was 99.1% with persulfate concentration of 5 g/L and AC concentration of 5 g/L in 120 min under neutral pH. It was explained that there were two degradation paths of phenol by AC-activated persulfate. One was free radical path and the other was non-radical path. The excessive AC offered non-radical path more active sites and facilitated degradation of phenol. On the contrary, the excessive persulfate caused quenching between free radicals and weakened degradation of phenol. Once the non-radical contribution to degradation of phenol exceeded free radical contribution to degradation of phenol, the degradation of phenol was improved by the increased persulfate and AC concentration simultaneously. The highest reaction rate constant $k_{obs}$ was 0.0373 min$^{-1}$ with persulfate concentration of 5 g/L and AC concentration of 5 g/L under neutral pH.

**Synergistic activation**

The degradation of phenol by heat/AC-activated and heat/Fe$^{0}$-activated persulfate are shown in Fig. 4 and Table 3. The dimensionless concentrations of residual phenol by heat/AC-activated and heat/Fe$^{0}$-activated persulfate were far lower than that by heat-activated persulfate in the first 60 min. The heat/AC-activated and heat/Fe$^{0}$-activated persulfate showed obvious synergistic effect during degradation process of phenol. However, all the final degradation efficiencies of phenol by heat, heat/AC-activated and heat/Fe$^{0}$-activated persulfate were close to 100% in 120 min. Besides, the degradation of phenol by heat/AC-activated and heat/Fe$^{0}$-activated persulfate
The degradation efficiency of phenol by AC activated persulfate with tert-butanol at the same concentration of scavengers decreased to 87.5% in 120 min. The results showed that the inhibited degree of phenol degradation efficiency with methanol was comparatively stronger than that with tert-butanol at the same concentration of scavengers. It meant that both SO₄•⁻ and OH• were significant radicals in degradation of phenol. SO₄•⁻ played more important role than OH• in degradation of phenol. The contribution of SO₄•⁻ could be calculated by the following equation:

\[ \text{Contribution of } SO_4^{2-} = \left( \frac{D_{\text{OH}}}{D_{\text{OH}^*}} \right) \times 100\% \]  \hspace{1cm} (5)

where \( D_{\text{OH}} \) was degradation efficiency of phenol with \( \cdot \text{OH} \) scavenger, \( D \) was degradation efficiency of phenol without scavenger. Therefore, the contribution of \( SO_4^{2-} \) and \( \cdot \text{OH} \) were 88.29% and 11.71%, respectively, in degradation of phenol by AC activated persulfate.

The degradation of phenol by \( Fe^0 \) activated persulfate with and without scavengers are shown in Fig. 6. The degradation efficiency of phenol by \( Fe^0 \) activated persulfate without scavengers was 92.85% in 120 min. The degradation efficiency of phenol by \( Fe^0 \) activated persulfate with methanol decreased to 14.79% in 120 min. The degradation efficiency of phenol by \( Fe^0 \) activated persulfate with tert-butanol decreased to 88.41% 120 min. It indicated that inhibited degree of phenol degradation efficiency with methanol was comparatively stronger than that with tert-butanol at the same concentration of scavengers. Hence, both \( SO_4^{2-} \) and \( \cdot \text{OH} \) were significant radicals in degradation of phenol, and \( SO_4^{2-} \) are predominant radicals in degradation of phenol by \( Fe^0 \) activated persulfate. The contribution of \( SO_4^{2-} \) and \( \cdot \text{OH} \) were 95.21% and 4.78% respectively.
Conclusion

The degradation of phenol by heat-activated, Fe$^0$-activated, AC-activated, heat/AC-activated, and heat/Fe$^0$-activated PS have been carried out. The degradation of phenol fitted well with pseudo-first order kinetic model. During degradation of phenol by heat-activated PS, reaction temperature played a significant role in degradation of phenol. The degradation efficiency and reaction rate constant of phenol were nearly 100% and 0.0506 min$^{-1}$ respectively, when reaction temperature was 70°C, concentration of persulfate was 15 g/L, reaction time was 120 min under neutral pH. During degradation of phenol by Fe$^0$-activated PS, increasing concentration of Fe$^0$ and persulfate facilitated degradation of phenol. The highest degradation efficiency and reaction rate constant of phenol were 92.85% and 0.0198 min$^{-1}$, respectively when concentration of Fe$^0$ was 5 g/L, concentration of persulfate was 15 g/L, and reaction time was 120 min under neutral pH. During degradation of phenol by AC-activated PS, the increased persulfate and AC concentration simultaneously could improve degradation of phenol. The highest degradation efficiency and reaction rate constant of phenol by AC-activated PS were 99.1% and 0.0373 min$^{-1}$, respectively, with persulfate concentration of 5 g/L and AC concentration of 5g/L in 120 min under neutral pH. The heat/AC-activated and heat/Fe$^0$-activated persulfate showed obvious synergistic effect during degradation process of phenol, respectively. The degradation efficiency of phenol by heat/AC-activated and heat/Fe$^0$-activated persulfate were close to 100% in 120 min while the reaction rate constants with heat/AC-activated and heat/Fe$^0$-activated persulfate were 0.0512 and 0.0561 min$^{-1}$ respectively. The radical scavenger experiments proved that both SO$_4$$^-$• and OH• were significant radicals in degradation of phenol by Fe$^0$-activated and AC-activated persulfate, and SO$_4$$^-$• are predominant radicals in degradation of phenol.

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