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Degradation of pCNB by Fenton like Process using 

$\alpha$-FeOOH

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Abstract

A heterogeneous Fenton-like process was studied using synthesised goethite ($\alpha$-FeOOH) and hydrogen peroxide ($H_2O_2$) to degrade $p$-chloronitrobenzene ($p$CNB) in water. The effect on the treatment efficiency of the initial pH, the dosage of hydrogen peroxide and goethite and the presence of humic acid and bicarbonate were quantified. At the optimal conditions (pH = 6.0, $H_2O_2$ = 6.6 mg/L, and goethite = 333 mg/L), over 80% of $p$CNB was removed within 30 min. Humic acid and bicarbonate were found to inhibit the $p$CNB degradation, probably because they compete with $p$CNB for the $\cdot OH$ produced. Intermediate oxidation products were identified, and a $p$CNB oxidation pathway is proposed. The findings demonstrate that $\alpha$-FeOOH combined with $H_2O_2$ has potential as an advanced oxidation process for water pollution control.

Key words: $\alpha$-FeOOH; $p$-chloronitrobenzene; oxidation; water treatment

1. Introduction

Toxic and refractory industrial wastewater severely challenges conventional wastewater treatment technologies. In the last decade, advanced oxidation processes
(AOPs) have become important technologies for water treatment [1, 2] and have been reported for the effective destruction of refractory pollution [2-4]. In AOPs, the principal oxidising species are highly active hydroxyl radicals (•OH), which have been proposed as an oxidant [5]. •OH has a high redox potential (up to 2.9 V), a short lifetime, and non-selective oxidation properties [6, 7]. The Fenton process is one AOP that has attracted much attention because only two common and low-cost chemical agents (ferrous salt and hydrogen peroxide) are required without any energy assistance [8–10].

The major reactions during the Fenton treatment of organic waste can be summarised as

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (1)
\]

\[
Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO' \quad (2)
\]

\[
\cdot OH + \text{organics} \rightarrow \text{intermediate products} \rightarrow \ldots \rightarrow CO_2 + H_2O \quad (3)
\]

During Fenton treatment, •OH is produced and Fe\(^{2+}\) is oxidised to Fe\(^{3+}\) through Eq. (1). Some of the soluble Fe\(^{3+}\) can be reduced to Fe\(^{2+}\) by H\(_2\)O\(_2\), as in Eq. (2). The •OH produced can degrade target organic compounds into less toxic intermediate oxidation by-products (e.g., formic, acetic, and oxalic acids) and can even mineralise them into benign water and CO\(_2\) [11–13]. Although the traditional Fenton process is simple and effective, its application is highly restricted in practice because of the following reasons. First, very acidic conditions (typically, pH 2 to 4) are required to optimise the treatment [14, 15]. Second, in the traditional Fenton process, much iron sludge is produced as the Fe\(^{3+}\) oxidation product, which must be properly disposed. Third, in
the traditional Fenton process, the total dissolved solids in the effluent may be substantially increased because much ferrous salt is added, in addition to acid and base for pH adjustment, leading to more iron hydroxide suspension during the Fenton treatment [16-21].

Among the AOP technologies, the Fenton-like reaction has been proven to be one of the most effective ways to degrade organic pollutants and is based on solid–liquid interface reactions and has more advantages than the homogeneous Fenton (H$_2$O$_2$+Fe$^{2+}$/Fe$^{3+}$) reaction with regard to reduced generation of ferric sludge and mild reaction conditions [22]. The heterogeneous Fenton-like reactions can eliminate pollutants efficiently in a wider pH range with much less iron loss than the homogeneous Fenton process. Until now, different heterogeneous catalysts for Fenton-like reactions have been studied, such as hematite, α-FeOOH, and β-FeOOH [23]. This study tested a proposed heterogeneous Fenton-like treatment system using H$_2$O$_2$ and goethite (α-FeOOH) as a catalyst that can be recycled to reduce the amount of iron sludge for disposal. Moreover, as an iron source, goethite does not increase the solids in solution. p-chloronitrobenzene (pCNB) was selected as a target contaminant to test the performance of this new Fenton-like treatment system because pCNB is a typical halogenated nitril aromatic hydrocarbon widely used in the production of pesticides, herbicides, dyes, lumber preservatives, pharmaceuticals, photographic film, antioxidants, gasoline additives, corrosion inhibitors and other industrial chemicals [24, 25]. pCNB is a major cause of methemoglobinaemia and anaemia and also exhibits genotoxicity and carcinogenic potential [26]. This paper focuses on the study
of the key factors governing $\alpha$-FeOOH/H$_2$O$_2$ oxidation of pCNB in water. The factors
tested were the initial solution pH, the H$_2$O$_2$ dose and the goethite dose, as well as
co-existing chemical species including humic acid and bicarbonate. The major
oxidation intermediates of pCNB were identified, and the oxidation pathways were
proposed.

2. Materials and methods

2.1. Chemical reagents

All of the chemicals used were analytical grade, except as noted. All solutions were
prepared using deionised water produced using a Millipore Milli-Q system ($\geq$ 18.0
MΩ cm). pCNB (99.5% purity) was purchased from Merck (Germany). Hydrogen
peroxide solution (30% v/v) and phosphoric acid were obtained from Merck
(Germany). The goethite ($\alpha$-FeOOH) catalyst was prepared with the method used by
Lin [27].

2.2. Experimental procedure

Bench-scale tests were conducted in duplicate at room temperature (25 ± 1 °C) in
a 1-L cylindrical glass reactor, as shown in Fig. 1.

[Fig. 1]

In a typical run, the treatment was initiated with the concentration of $\alpha$-FeOOH
particles of 333 mg/L and H$_2$O$_2$ was added to 300 mL of pCNB solution in the reactor.
If needed, the initial solution pH was adjusted with the buffer solution of 0.01 N
phosphoric acids and NaOH solution. Vigorous mixing with a mechanical stirrer
ensured complete dissolution, uniform distribution and full suspension of the
α-FeOOH catalyst particles.

At pre-determined times, 1-mL samples were collected and subsequently filtered through 0.45-µm Millipore membrane filters. In the tests studying α-FeOOH adsorption, H₂O₂ was not added, and the concentration of H₂O₂ was from 0 mg/L to 9.9 mg/L. The detection limit of H₂O₂ measurement was 0.2 mg/100 ml, and the calibration procedures have been described previously [28]. In the tests, to evaluate pCNB oxidation by hydrogen peroxide alone, α-FeOOH particles were not used.

2.3. Analysis

The specific surface area of the α-FeOOH particles was measured with the BET method using a Micromeritic 2020 M surface area and porosity analyser. Their crystalline structures were determined by X-ray diffraction analysis using Cu-\(K_{\alpha}\) radiation scanning from 10° to 90° 2\(\theta\) at a scan rate of 5° min\(^{-1}\) (D/max-RB, XRD, Rigaku, Japan). The wavelength of Cu-\(K_{\alpha}\) radiation is 0.15406 nm. The morphology and surface properties of the α-FeOOH particles were measured using a scanning electron microscope (SEM) (Hitachi S-4800) and Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer 2000 spectrometer), respectively. Their surface charge was determined with a Zen 2600 zeta potential analyser (Nanao-Z, Malvern, UK). H₂O₂ was fluorometrically quantified using the amplex red method [29, 30]. pCNB was measured using a liquid-liquid micro-extraction with hexane, followed by gas chromatography (Agilent 6890GC/ECD) at a detector temperature of 320 °C, an injector temperature of 250 °C, and in split/splitless mode.
The oxidation intermediate products were identified by gas chromatography coupled with mass spectrometry (GC/MS). The GC/MS analyses were performed using an Agilent 6890GC/5973MSD, and the column temperature was programmed as follows. The temperature was held at 35 °C for 2 min, increased to 150 °C at 1 °C min\(^{-1}\), then raised to 280 °C at 20 °C min\(^{-1}\), and finally to 300 °C, where it was held for 10 min. The dissolved organic carbon (DOC) was measured using a TOC-VCPN analyser (Shimadzu, Japan).

To obtain the adsorption isotherm curves and the removal kinetics of pCNB, we used six 250-ml brown glass bottles, and the same pCNB concentration of 5 mg/L was placed in each bottle. Next, different concentrations of \(\alpha\)-FeOOH (33 mg/L, 167 mg/L, 333 mg/L, 667 mg/L and 1000 mg/L) were placed in each bottle, and the bottles were fixed in an oscillating shaker. The temperature was controlled at 20 ± 2 °C. After 5 days, the sample solutions were centrifuged by a high-speed centrifuge at 8000 rpm for 5 min, and the concentration of pCNB in the water samples was measured using GC.

3. Results and Discussion

3.1. Characteristics of the \(\alpha\)-FeOOH catalyst

The structure and morphology of the goethite (\(\alpha\)-FeOOH) used in this study were determined by XRD (Fig. 2a) and SEM (Fig. 2b), respectively.

Fig. 2a shows that the main peak (110) is at 21.2° (2θ). The main peak intensities of
α-FeOOH are 100%. The XRD results also indicate that the prepared α-FeOOH has orthorhombic structure with a space group of Pbnm and $a = 4.608 \, \text{Å}$, $b = 9.956 \, \text{Å}$, and $c = 3.022 \, \text{Å}$. Fig. 2b shows that the goethite (α-FeOOH) catalyst synthesised had a uniform particle size distribution, but there was some agglomeration. The shape of the agglomerates resembled small snowflakes, and their size ranged from < 2 µm to 15 µm. The specific surface area of the catalyst was 116 m$^2$ g$^{-1}$. The pore volume and pore size were 0.276 cm$^3$ g$^{-1}$ and 2–400 nm (average 95 nm), respectively.

The FTIR spectrum of the goethite is shown in Fig. 2c.

The broad absorption peak between 1700 cm$^{-1}$ and 3650 cm$^{-1}$ reflects the stretching vibration of the surface hydroxyl group. The peaks at 638 cm$^{-1}$, 795 cm$^{-1}$ and 891 cm$^{-1}$ are the characteristic absorption peaks of Fe-O, Fe-OH-Fe and α-FeOOH, respectively. In addition, the sharpness and symmetry of those peaks confirms that the catalyst was well crystallised.

3.2. Removal of pCNB

The pCNB removal results using hydrogen peroxide only, α-FeOOH adsorption only, and the heterogeneous Fenton-like oxidation are shown in Fig. 3.

It is clear from the figure that at any specific reaction time, α-FeOOH/H$_2$O$_2$ combined could degrade more pCNB than H$_2$O$_2$ oxidation or α-FeOOH adsorption alone. For example, within 30 min, more than 80% of the pCNB was removed by the heterogeneous Fenton-like process (α-FeOOH/H$_2$O$_2$), while H$_2$O$_2$ oxidation alone
achieved only 10% removal and α-FeOOH adsorption alone achieved only 42%.

3.2.1. \( \text{H}_2\text{O}_2 \) decomposition

To better elucidate the action of \( \text{H}_2\text{O}_2 \) in the presence of α-FeOOH, \( \text{H}_2\text{O}_2 \) decomposition was monitored with and without α-FeOOH. The results are shown in Fig. 4.

Clearly, \( \text{H}_2\text{O}_2 \) decomposition was promoted in the presence of α-FeOOH. Equations 4–6 are the reactions associated with the enhanced \( \text{H}_2\text{O}_2 \) decomposition [31].

\[
\begin{align*}
\equiv \text{Fe}^{\text{III}} + \text{H}_2\text{O}_2 & \rightarrow \equiv \text{Fe}^{\text{III}} \text{H}_2\text{O}_2 \quad (4) \\
\equiv \text{Fe}^{\text{III}} \text{H}_2\text{O}_2 & \rightarrow \equiv \text{Fe}^{\text{II}} + \text{HO}_2 + \text{H}^+ \quad (5) \\
\text{H}_2\text{O}_2 + \equiv \text{Fe}^{\text{II}} & \rightarrow \text{OH}^- + \cdot\text{OH} + \equiv \text{Fe}^{\text{III}} \quad (6)
\end{align*}
\]

The catalytic activity of α-FeOOH might be attributed to its high surface area and mesoporous structure, which allowed \( \text{H}_2\text{O}_2 \) full access to the inner surfaces of the agglomerates, thus promoting \( \text{H}_2\text{O}_2 \) decomposition.

3.2.2. pCNB adsorption isotherms

The \( \text{N}_2 \) adsorption-desorption isotherm of the α-FeOOH is shown in Fig. 5a.

The figure shows that the adsorption is not reversible. Moreover, at \( p/p_0 = 0.6 \), the desorption hysteresis characteristic of a mesoporous structure began to appear. The mesoporous structure gives the catalyst its large specific surface area.
The adsorption kinetics of 5 mg L$^{-1}$ pCNB at various $\alpha$-FeOOH loadings are shown in Fig. 5b.

At any particular time, a higher catalyst concentration resulted in a higher pCNB removal rate. The classic adsorption isotherm model, Langmuir equations (Eq. 7), was evaluated to fit the experimental data (Table 1).

Langmuir equation:

$$\frac{q_e}{q_m} = \frac{KC_e}{1 + KC_e}$$  \hspace{1cm} (7)

In this equation, $q_e$ is the $\alpha$-FeOOH surface complex concentration at equilibrium in $\mu$g/mg, $q_m$ is the maximum adsorption capacity in $\mu$g/mg, $K$ is the Langmuir equilibrium constant (L/$\mu$g), and $C_e$ is the equilibrium concentration of adsorbate in solution in mg/L.

Table 1 shows that the Langmuir formulation provided a better fit to the experimental data ($R^2 = 0.983$). The adsorption equilibrium was achieved within 40 minutes, with 38.9% pCNB removal and an adsorption capacity of 5.8 mg/g. The reason for this behaviour is that the Langmuir equation is built based on the assumption that every adsorption site is equivalent and independent, while the ability of a molecule to bind is independent of whether neighbouring sites are occupied. Therefore, the Langmuir equation is also called the ideal localised monolayer model [32]. The results prove that the pCNB molecule was localised on the monolayer of the $\alpha$-FeOOH surface.
3.2.3 Removal kinetics of pCNB

The net rate of adsorption of pCNB on α-FeOOH can generally be expressed as

\[ r = k_{\text{ads}}[pCNB][\alpha\text{-FeOOH}] - k_{\text{des}}[\alpha\text{-FeOOH}+pCNB] \]  

Because the net rate of adsorption is zero at equilibrium and the amount of molecules on the monolayer of α-FeOOH was stable, the equilibrium relationship is

\[ K = \frac{[\alpha\text{-FeOOH}+pCNB]}{[\alpha\text{-FeOOH}][pCNB]} \]  

The removal of pCNB is ascribed to •OH-induced oxidation and to adsorption on the surface of the α-FeOOH catalyst. The degradation kinetics follow

\[ \frac{dC}{dt} = \frac{dC_0}{dt} + \frac{dC_2}{dt} = -KC[\text{FOOH}] - kC[•OH] \]  

Degradation by •OH follows pseudo-first-order kinetics with respect to the concentration of pCNB[33], as shown in Eq. 11.

\[ \frac{dC_2}{dt} = -kC \]  

Although the Langmuir-Hinshelwood (L-H) expression has been used to represent the kinetics of a photocatalytic system [34, 35], it has never been applied to a heterogeneous Fenton-like process. In this study, a modified L-H model (Eq. 12) was evaluated to represent the α-FeOOH/H₂O₂ process based on the success of such models in describing heterogeneous photocatalytic reaction kinetics [36, 37].

\[ \frac{dC}{dt} = -\frac{kKC}{1+KC} \]  

Here, C is the substrate concentration at any time t, k is the reaction rate constant, and K is again the Langmuir adsorption constant. As the treatment proceeded, intermediate products were formed, which potentially competed with the target...
compound for the active oxidising agents produced. When the particle concentration was sufficiently low (less than approximately 5 mg L\(^{-1}\) in this study) and there was no excess catalyst present, the degradation followed the first-order kinetics of Eq. 13.

\[
\ln \left( \frac{C}{C_0} \right) = -k_K t = -k_{app} t \tag{13}
\]

Where \(k_{app} = kK\).

[Fig. 6]

As Fig. 6 shows, the modified L-H model fit the experimental data well (\(R^2 = 0.97\)), with a reaction rate constant of 0.144 mg L\(^{-1}\) min\(^{-1}\). This finding validated the assumption that the degradation of \(p\)CNB was occurring on the surface of the \(\alpha\)-FeOOH.

3.2.4 Effect of the \(H_2O_2\) dose

Figure 7 shows the effect of \(H_2O_2\) dosage on \(\alpha\)-FeOOH/\(H_2O_2\) oxidation of \(p\)CNB.

[Fig. 7]

Generally speaking, more rapid \(p\)CNB degradation was achieved at higher \(H_2O_2\) doses because more \(^\cdot\)OH is available to attack the \(p\)CNB molecules. This rapid degradation was observed at \(H_2O_2\) doses from 1.3 mg/L to 6.6 mg/L. However, when the \(H_2O_2\) dose was further increased to 9.9 mg/L, the \(p\)CNB degradation slowed to a removal rate lower than that observed at 1.3 mg/L \(H_2O_2\), presumably because \(H_2O_2\) became a major sink for \(^\cdot\)OH at too high a \(H_2O_2\) concentration (Eq. 14).

\[
^\cdot OH + H_2O_2 \rightarrow HOO^* + H_2O \tag{14}
\]
3.2.5 Effect of the Initial pH

The effect of pH on pCNB removal is shown in Fig. 8.

[Fig. 8]

The figure shows the key role that pH plays in this Fenton-like oxidation process [38, 39]. In this study, the pCNB degradation generally decreased as the solution pH increased. One important reason is that iron oxide is more soluble at low pH and that more Fe(III) is released into the water. The Fe(III) can readily react with H$_2$O$_2$ in a Fenton-like process. In addition, a pH-dependence of the reduction potential of α-FeOOH/Fe$^{2+}$ might have an important influence on the pCNB degradation in the α-FeOOH/H$_2$O$_2$ process because the reduction requires protons (Eq. 15). The reduction potential $E_h$ in the reaction

$$FeOOH + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$$

(15)

can be expressed as

$$E_h = E_h^0 - 0.0592 \left[ \frac{[Fe^{2+}]}{[H^+]^3} \right]$$

(16)

where $E_h^0$ is the standard reduction potential for an FeOOH/Fe$^{2+}$ system, $[Fe^{2+}]$ is the molar concentration of Fe$^{2+}$, and $[H^+]$ is the molar concentration of H$^+$. For this system, $E_h = 1.07 - 0.18$ pH [27] and $E_{hr}$, relative redox potential, decreases linearly with the increasing pH.

3.2.6 Effects of humic acid and bicarbonate

Due to the low selectivity of hydroxyl radicals, the treatment efficiency is strongly affected by the presence of co-existing species. The effect of humic acid (HA)
(0–15 mg/L) on the removal of \( p\text{CNB} \) is shown in Fig. 9. [Fig. 9]

Figure 9 shows that the removal of \( p\text{CNB} \) decreases with increasing HA level. An initial 15 mg/L of HA reduced the removal of \( p\text{CNB} \) within 30 min by 40%.

The effect of the initial bicarbonate concentration on the removal of \( p\text{CNB} \) is similar, as Fig. 10 shows. [Fig. 10]

The inhibition of the \( p\text{CNB} \) removal was presumably due to the high reactivity of \( \cdot\text{OH} \) with bicarbonate (rate constant = \( 8.5 \times 10^6 \text{ M}^{-1} \text{s}^{-1} \)) \[40\]. Note, however, that the reduction in the \( p\text{CNB} \) removal decreased by only 2% when the initial bicarbonate concentration was increased from 100 to 200 mg/L, suggesting that the impact of the initial bicarbonate concentration is not very significant at \([\text{HCO}_3^-]\) > 100 mg/L.

3.2.7 \( p\text{CNB} \) degradation pathways

3.2.7.1 Mineralisation of \( p\text{CNB} \)

The removal of \( p\text{CNB} \) and the dissolved organic carbon (DOC) are shown together in Fig. 11. [Fig. 11]

The DOC decreased much more slowly than \( p\text{CNB} \), thus suggesting that only part of the \( p\text{CNB} \) was mineralised. Some degradation intermediate products were presumably formed during the degradation of \( p\text{CNBs} \).
3.2.7.2 Oxidation intermediates

The intermediate products of $p$CNB degradation identified by GC/MS are presented in Fig. 12 and Table 2.

The major oxidation by-products included phenols and fatty acids, such as phenol, 2-chlor-5-nitrophenol, 5-nitro-catechol, 5-nitro-1,2,3-trihydroxy phenol, parachlorophenol, malic acid, hlutaric acid, and oxalic acid. These compounds confirm that the oxidising agents produced could substitute six carbons of the benzene ring in $p$CNB to form various phenolic compounds. If the rings of the phenolic compounds were opened, fatty acids were formed. Therefore, the degradation pathway of Fig. 13 is proposed.

A $\pi$-complex is formed when $\cdot$OH attacks $p$CNB. As $\cdot$OH further links with a carbon atom of the $p$CNB benzene ring, a $\sigma$-complex forms, and the $sp^2$ hybrid orbital of the carbon atom becomes an $sp^3$ hybrid orbital. As the $\cdot$OH reacts with $p$CNB to generate a variety of phenolic compounds, the opportunities for substitution or addition at different functional groups on the benzene ring are roughly equal, allowing $\cdot$OH to substitute and produce phenols or to capture hydrogen atoms of the benzene ring to generate phenols whose rings are subsequently opened to generate low molecular weight fatty acids and $CO_2$. The oxidation products, in addition to $CO_3^{2-}$ and $HCO_3^-$, inhibit the mineralisation of the fatty acids, so the DOC in the solution decreases only
slowly, as shown in Fig. 11.

4. Conclusions

This study evaluated the performance of $\alpha$-FeOOH/H$_2$O$_2$ as a heterogenous Fenton-like system for the oxidation of $p$CNB in water. The results indicated that $\alpha$-FeOOH/H$_2$O$_2$ can degrade $p$CNB more effectively than either H$_2$O$_2$ oxidation or $\alpha$-FeOOH adsorption alone. The enhanced removal can be ascribed to the formation of ·OH that rapidly degrades the target compound. These encouraging data demonstrate that the $\alpha$-FeOOH/H$_2$O$_2$ system has potential as a treatment method for $p$CNB pollution.

5. Acknowledgements

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6. References


Table 1 Adsorption isotherms of pCNB on α-FeOOH

<table>
<thead>
<tr>
<th>Equation</th>
<th>$R^2$</th>
<th>Adsorption parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir model</td>
<td>$C_e/q_e=0.1044q_e+0.0899$</td>
<td>$0.983$</td>
</tr>
</tbody>
</table>

Table 2 Identified intermediates in pCNB degradation

<table>
<thead>
<tr>
<th>Retention Time (min)</th>
<th>Formula$^a$</th>
<th>$Q^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.81</td>
<td>HOCH$_2$COOH (glycolic acid)</td>
<td>64%</td>
</tr>
<tr>
<td>4.61</td>
<td>CH$_3$CH$_2$OHCOOH (hydracrylic acid)</td>
<td>83%</td>
</tr>
<tr>
<td>5.78</td>
<td>CH$_2$COCHOOH (pyruvic acid)</td>
<td>72%</td>
</tr>
<tr>
<td>6.50</td>
<td>HOCH$_2$CH$_2$CH$_2$COOH (hydroxy butanoic acid)</td>
<td>93%</td>
</tr>
<tr>
<td>7.91</td>
<td>(COOH)$_2$ (oxalic acid)</td>
<td>91%</td>
</tr>
<tr>
<td>8.20</td>
<td>C$_6$H$_5$OH (phenol)</td>
<td>95%</td>
</tr>
<tr>
<td>9.47</td>
<td>HOOCCH$_2$CHOOH (malonic acid)</td>
<td>90%</td>
</tr>
<tr>
<td>12.6</td>
<td>C$_6$H$_5$O$_2$ (p-benzoquinone)</td>
<td>90%</td>
</tr>
<tr>
<td>13.3</td>
<td>HOOC(CH$_2$)$_2$COOH (succinic acid)</td>
<td>75%</td>
</tr>
<tr>
<td>14.8</td>
<td>HOOCCH$_2$CHOCHOOH (malic acid)</td>
<td>59%</td>
</tr>
<tr>
<td>16.8</td>
<td>HOOCCH$_2$COCHOOH (mesoaxilic acid)</td>
<td>72%</td>
</tr>
<tr>
<td>23.1</td>
<td>HOOCCH(CHOH)COOH (tartronic acid)</td>
<td>86%</td>
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<tr>
<td>23.6</td>
<td>C$_6$H$_5$OCl (parachlorophenol)</td>
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<tr>
<td>27.3</td>
<td>HOOCCHCHCOOH (maleic aid)</td>
<td>74%</td>
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<tr>
<td>28.4</td>
<td>HOOC(CH$_2$)$_2$COO (hlutaric acid)</td>
<td>59%</td>
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<tr>
<td>33.5</td>
<td>HO$_2$C$_6$H$_4$OH (quinol)</td>
<td>90%</td>
</tr>
<tr>
<td>35.5</td>
<td>HOOCCHOHCOOH (hydroxymalonic acid)</td>
<td>65%</td>
</tr>
<tr>
<td>38.0</td>
<td>HOOC(CH$_2$)$_2$COOH 6 (trtaric acid)</td>
<td>72%</td>
</tr>
<tr>
<td>42.2</td>
<td>HOOC(CH$_2$)$_2$COOCOOH (glutaric acid)</td>
<td>42%</td>
</tr>
<tr>
<td>44.9</td>
<td>HOOC(CH$_2$)$_2$COOH (muconic acid)</td>
<td>65%</td>
</tr>
<tr>
<td>45.0</td>
<td>C$_6$H$_5$OHClNO$_2$ (2-chlor-5-nitrophenol)</td>
<td>91%</td>
</tr>
<tr>
<td>45.5</td>
<td>C$_6$H$_5$OHClNO$_2$ (5-chlor-2-nitrophenol)</td>
<td>99%</td>
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<tr>
<td>55.6</td>
<td>HOOC(CH$_2$)$_2$COOH (adipic acid)</td>
<td>64%</td>
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<tr>
<td>59.3</td>
<td>C$_6$H$_5$OHO$_2$NO (nitrophenol)</td>
<td>96%</td>
</tr>
<tr>
<td>64.0</td>
<td>C$_6$H$_5$(OH)$_2$NO$_2$ (5-nitro-resorcinol)</td>
<td>91%</td>
</tr>
<tr>
<td>64.3</td>
<td>C$_6$H$_5$(OH)$_2$NO$_2$ (5-nitro-catechol)</td>
<td>83%</td>
</tr>
<tr>
<td>97.3</td>
<td>C$_6$(OH)$_3$ trihydroxy semiquinone</td>
<td>85%</td>
</tr>
<tr>
<td>98.0</td>
<td>C$_6$H$_5$(OH)$_2$NO$_2$ (5-nitro-1,2,3-trihydroxy phenol)</td>
<td>97%</td>
</tr>
</tbody>
</table>

$^a$ The authentic structure was obtained by derivation with diazomethane.

$^b$ Q is the match quality when compared with the mass spectrum in the NIST database.
Fig. 1 Schematic diagram of the reactor used in this study

(1-sampling ports, 2-circulating water outlet, 3-circulating water inlet, 4-water inlet)
Fig. 2 XRD, SEM and FTIR results of the synthesized goethite (α-FeOOH) catalyst
Fig. 3

$p$CNB degradation by FeOOH/H$_2$O$_2$, H$_2$O$_2$ oxidation only, and FeOOH adsorption alone ([pCNB]$_0$ = 5 mg/L, [FeOOH]$_0$ = 333 mg/L, [H$_2$O$_2$]$_0$ = 6.6 mg/L)
Fig. 4

Fig. 4 H$_2$O$_2$ decomposition in the presence of the α-FeOOH sample and without α-FeOOH sample ([H$_2$O$_2$]$_0$ = 6.6 mg/L, pH 6.0 ± 0.1, [FeOOH]$_0$ = 333 mg/L)
Fig. 5 (a) N₂ adsorption-desorption isotherm of FeOOH; (b) pCNB adsorption with different dose of FeOOH ([pCNB]₀ = 5 mg/L, [H₂O₂]₀ = 6.6 mg/L, pH 6.0 ± 0.1)
Fig. 6 The fitting curves of kinetic model with experiment data
([pCNB]₀ = 5 mg/L, [FeOOH]₀ = 333 mg/L, [H₂O₂]₀ = 6.6 mg/L, pH 6.0±0.1)
Fig. 7 Effect of the $\text{H}_2\text{O}_2$ dose on the $p\text{CNB}$ degradation by FeOOH/$\text{H}_2\text{O}_2$

$([p\text{CNB}]_0 = 5 \text{ mg/L, [FeOOH]}_0 = 333 \text{ mg/L, pH 6.0 ± 0.1})$
Fig. 8 Effect of initial pH on the pCNB degradation by FeOOH/H$_2$O$_2$ ([pCNB]$_0$ = 5 mg/L, [FeOOH]$_0$ = 333 mg/L, [H$_2$O$_2$]$_0$ = 6.6 mg/L)
Fig. 9 Effect of humic acid on the pCNB degradation by FeOOH/H₂O₂

([pCNB]₀ = 5 mg/L, [FeOOH]₀ = 333 mg/L, [H₂O₂]₀ = 6.6 mg/L)
Fig. 10 Effect of bicarbonate on the \( pCNB \) degradation by FeOOH/H\(_2\)O\(_2\) 

\( [pCNB]_0 = 5 \text{ mg/L}, [H_2O_2]_0 = 6.6 \text{ mg/L}, [FeOOH] = 333 \text{ mg/L}, \text{ pH } 6.0 \pm 0.1 \)
Fig. 11 Degradation vs. mineralization of \( p\text{CNB} \) by FeOOH/H\(_2\)O\(_2\) 

\([p\text{CNB}]_0 = 5 \text{ mg/L}, [\text{H}_2\text{O}_2]_0 = 6.6 \text{ mg/L}, [\text{FeOOH}] = 333 \text{ mg/L, pH } 6.0 \pm 0.1\)
Fig. 12 GC/MS spectrum of intermediate products of pCNB degradation by FeOOH/H_2O_2 process
Fig. 13 The supposed pathway of the reactions between pCNB and ·OH
Graphical abstract:

[Diagram showing a reaction pathway involving a chlorinated compound and a Fenton-like reaction to produce mineralization and low molecular weight fatty acids and CO₂]
Highlights

- This work assessed the $p$-Chloronitrobenzene ($p$CNB) degradation by heterogeneous Fenton-like process in aqueous solution.
- The effect of different factors on the reaction was investigated.
- The intermediate products were identified and the kinetics and degradation pathway was proposed.