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Study on Advanced Treatment Process for Drilling Wastewater by Fenton Oxidation

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Abstract—Two factors including the dosage rate of \( \text{H}_2\text{O}_2 \) and the interference of \( \text{Cl}^- \) concentration were analyzed to optimize the Fenton process. Results showed that when the dosage rate of \( \text{H}_2\text{O}_2 \) was at 1 mL/min the COD removal efficiency increased by 7% more than that of added instantly; \( \text{Cl}^- \) concentration had an inhibition effect on Fenton oxidation—when the \( \text{Cl}^- \) concentration was below 2500 mg/L the effect was negligible and the highest COD removal efficiency was up to 92%, which had reached the secondary standards (DB12-356-2008) of Tianjin. It was indicated that the process was an effective method in the advanced treatment of drilling wastewater.

Keywords—Fenton process; \( \cdot \text{OH} \); COD removal efficiency; \( \text{Cl}^- \) concentration

I. INTRODUCTION

Fenton oxidation is a common wastewater treatment process. Due to the advantages such as simple equipments, mild reaction conditions, easy operation and no secondary pollution and so on [1-3], Fenton oxidation process is widely used in pre-treatment of wastewater to improve its biodegradability [4] or in advanced treatment to improve its water quality [5], etc. Drilling wastewater was generated from the petroleum exploitation process on oil platform in Dagu bay of Tianjin. It contained complicated organic compounds, extremely high oil concentration and high salinity. Having been treated by “oil separation—flocculation pre-treatment—hydrolytic acidification—aerobic treatment” process, oil and COD load was significantly removed, but some water quality indexes of the effluent still couldn’t reach the discharge standards, so Fenton process was adopted in the experiment as an advanced treatment. Some water quality indexes of the wastewater were enumerated in Table I.

<table>
<thead>
<tr>
<th>Index</th>
<th>oil concentration [mg/L]</th>
<th>pH</th>
<th>chromaticity [times]</th>
<th>COD [mg/L]</th>
<th>( \text{Cl}^- ) [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>water quality</td>
<td>80</td>
<td>7.08–7.34</td>
<td>87–97</td>
<td>1646–1813</td>
<td>8367–10081</td>
</tr>
<tr>
<td>discharge standards</td>
<td>30</td>
<td>6-9</td>
<td>50</td>
<td>60</td>
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</table>

II. EXPERIMENTAL PART

A. materials

Drilling wastewater;

Reagents: 10%\( \text{FeSO}_4 \) solution; 30% \( \text{H}_2\text{O}_2 \) solution; 30% \( \text{H}_2\text{SO}_4 \) solution;

B. methods

Some wastewater (300 mL) was put in a 500 mL beaker stirred by magnetic stirrer; then a given amount of \( \text{FeSO}_4 \) was put in and regulated pH to acidity (its value was given in the following text); after that, some amount of \( \text{H}_2\text{O}_2 \) given in the text was injected into the solution; keep the mixture interchanging stir and regulated pH to neutral, finely some PAM was added in for getting the clean solution which was used to monitor COD and chromaticity.

III. RESULTS AND DISCUSSIONS

A. Conditions optimization in traditional Fenton process

Four factors include the ratio of \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \), the dosage of \( \text{H}_2\text{O}_2 \), the initial pH and the oxidation time were investigated to obtain the optimum operating conditions. COD of the wastewater in all of these experiments were monitored and the results were shown in Fig.1.
The effect of the four factors in the traditional Fenton process on the COD removal efficiency 

Fig.1 (a) showed that the process had the highest COD removal efficiency when the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was at 2:1. Beyond that, the removal efficiency was not high either the concentration of $\text{Fe}^{2+}$ was too high or low, for $\text{Fe}^{2+}$ was an essential catalyst for $\text{H}_2\text{O}_2$ generating $\cdot\text{OH}$. When the concentration of $\text{Fe}^{2+}$ was too low, the reaction given in Eq. (1) responded slowly and less $\cdot\text{OH}$ were produced,

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH}^-.$$  \hspace{1cm} (1)

so Fenton process had a poor oxidation effect; on the other hand, high $\text{Fe}^{2+}$ concentration caused swift decomposition of $\text{H}_2\text{O}_2$ and amount of $\cdot\text{OH}$ became $\text{O}_2$ before they oxidized organic compounds in the wastewater, which could be verified by the phenomenon that lots of bubbles emitted from the beaker. On the other hand, the chromaticity was greatly removed and almost had no relation with the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, so in the following optimum experiments COD removal was discussed only. And the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was kept at 2:1.

Fig.1 (b) indicated that the COD removal efficiency increased gradually with the increasing dosage of $\text{H}_2\text{O}_2$; while the dosage was up to 8.2mL/L, the COD removal efficiency reached 43%.

It could be indicated from Fig.1 (c) that the optimum initial pH was 3 or 4 and took 4 considering the economic factors. In addition, the COD removal efficiency declined as pH increased or decreased, for in acidic solution the oxidation ability of $\cdot\text{OH}$ was so fortissimo that it could easily oxidize many difficultly decomposed organic substances which could be described as the following:

$$\text{RH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{R}^-.$$  \hspace{1cm} (2)

$$\text{R}^- + \text{H}_2\text{O}_2 \rightarrow \text{ROH} + \cdot\text{OH}.$$  \hspace{1cm} (3)

$\cdot\text{OH}$ reacted rapidly with organic substances in the wastewater and the rate constant was about $10^8$-$10^{10}$mol·s$^{-1}$, on the other hand, the stability of $\cdot\text{OH}$ could be strengthened in fortissimo acidic environment and correspondingly its oxidation ability declined, as a result, the removal of COD declined too.

Fig.1 (d) reflected the effect of the oxidation time on COD removal. It showed that Fenton process had a quick rate within 2h and the COD removal efficiency kept increasing as times elapsed. When the oxidation time was over 3h, the efficiency no longer changed.

The COD removal efficiency under the optimum conditions was merely about 45%. So optimization experiments were carried out to optimize the Fenton process in two respects, the dosage rate of $\text{H}_2\text{O}_2$ and the interferences of $\text{Cl}^-$ in the solution respectively.

### B. Optimization of dosage rate of $\text{H}_2\text{O}_2$

The dosage rate of $\text{H}_2\text{O}_2$ strongly influenced Fenton process efficiency. Experiments were carried out with different dosage rate of $\text{H}_2\text{O}_2$ and the COD were monitored which was showed in Table II and Figure 2.

<table>
<thead>
<tr>
<th>dosage rate of $\text{H}_2\text{O}_2$[mL/min]</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<td>831</td>
<td>877</td>
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<tr>
<td>COD[mg/L]</td>
<td>43.0</td>
<td>51.7</td>
<td>51.4</td>
<td>50.5</td>
<td>48.8</td>
<td>46.3</td>
<td>44.0</td>
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<tr>
<td>COD removal efficiency[%]</td>
<td>43.0</td>
<td>51.7</td>
<td>51.4</td>
<td>50.5</td>
<td>48.8</td>
<td>46.3</td>
<td>44.0</td>
<td></td>
</tr>
</tbody>
</table>

TABLE II. OPTIMIZATION EXPERIMENTS ON OXIDATION TIME
Results showed that the COD removal efficiency declined as the dosage rate of \( \text{H}_2\text{O}_2 \) increased at the beginning. When \( \text{H}_2\text{O}_2 \) was added quickly in, most \( \cdot\text{OH} \) could generate \( \cdot\text{OH} \) in the catalysis of \( \text{Fe}^{3+} \), however, overquick dosage rate of \( \text{H}_2\text{O}_2 \) caused maldistribution of \( \text{H}_2\text{O}_2 \), which reacted with \( \cdot\text{OH} \) [6]:

\[
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O}. \quad (4)
\]

\[
\text{HO}_2^- + \cdot\text{OH} \rightarrow \text{O}_2 + \text{H}_2\text{O}. \quad (5)
\]

The reactions consumed some \( \text{H}_2\text{O}_2 \) and \( \cdot\text{OH} \), so the COD removal efficiency declined; when the dosage rate of \( \text{H}_2\text{O}_2 \) was between 0.5 and 1mL/min, most \( \text{H}_2\text{O}_2 \) reacted with \( \text{Fe}^{3+} \) and the COD removal efficiency was raised about 52%. When the dosage rate of \( \text{H}_2\text{O}_2 \) was controlled at 1 mL/min the COD removal efficiency could be increased by 7% more than that of injected instantly and the effluent COD load was about 815mg/L, which still hadn’t reached the discharging standard. The reason of the low efficiency might be repressed by the high Cl\(^-\) concentration in the wastewater. The Cl\(^-\) which could react easily with \( \cdot\text{OH} \), would inhibit Fenton process [7]. The process could be described in (6) and (7).

\[
\cdot\text{OH} + \text{Cl}^- \rightarrow \text{ClOH}^- + \text{H}_2\text{O}. \quad (6)
\]

\[
\text{ClOH}^- + \text{Fe}^{2+} \rightarrow \text{Cl}^- + \cdot\text{OH}^- + \text{Fe}^{3+}. \quad (7)
\]

Cl\(^-\) could contest for \( \cdot\text{OH} \) with organic compounds in the wastewater, as a result, some \( \cdot\text{OH} \) couldn’t oxidize organic compounds and the effect of Fenton process was restrained. On the other hand, Cl\(^-\) could react with \( \text{Fe}^{2+} \) and generate complex compounds:

\[
\text{Fe}^{3+} + \text{Cl}^- \rightarrow \text{FeCl}_2^2+, \quad \text{pK}_a = 10. \quad (8)
\]

\[
\text{FeCl}_2^2+ + \text{Cl}^- \rightarrow \text{FeCl}_3^+, \quad \text{pK}_a = 135. \quad (9)
\]

\[
\text{FeCl}_3^+ + \text{Cl}^- \rightarrow \text{FeCl}_3, \quad \text{pK}_a = 115. \quad (10)
\]

These complex compounds of \( \text{Fe}^{3+} \) could neither react with \( \text{H}_2\text{O}_2 \) nor be reduced to \( \text{Fe}^{2+} \), so they restrained the generation of \( \cdot\text{OH} \) and the effect of Fenton process [8]. In order to reduce the inhibiting effect of Fenton, the drilling wastewater was diluted by domestic sewage to reduce the Cl concentration.

### C. The influence of the Cl concentration

The wastewater was diluted multiple by the domestic sewage with other factors fixed as followed: \( \text{H}_2\text{O}_2/\text{COD}=2, \text{H}_2\text{O}_2/\text{Fe}^{3+}=2:1 \), the initial pH=4, the oxidation time =3h, then COD and chromaticity of the effluent were monitored and shown in TABLE III and Figure3.

Results in Fig.3 showed that when the wastewater was diluted by 1 times, the COD removal efficiency increased slowly, which indicated that the inhibition effect of Cl\(^-\) (the concentration was 5000mg/L) was still prominent; as the increasing of the dilution times, the inhibition effect of Cl\(^-\) got weaken and the COD removal efficiency increased correspondingly; when the dilution times was larger than 3, the COD removal efficiency increased significantly, it raised

<table>
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<th>serial number</th>
<th>1</th>
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<th>4</th>
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<th>6</th>
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<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
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<tr>
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<td>837</td>
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<td>419</td>
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<td>279</td>
<td>239</td>
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<td>chromatics before oxidation [times]</td>
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<td>46</td>
<td>31</td>
<td>23</td>
<td>18</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>dosage of ( \text{H}_2\text{O}_2 ) [mL/L]</td>
<td>8.2</td>
<td>4.1</td>
<td>2.7</td>
<td>2.0</td>
<td>1.6</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>dosage of ( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} ) [g/L]</td>
<td>13.69</td>
<td>6.85</td>
<td>4.56</td>
<td>3.42</td>
<td>2.74</td>
<td>2.28</td>
<td>1.96</td>
</tr>
<tr>
<td>COD[mg/L]</td>
<td>815</td>
<td>386</td>
<td>130</td>
<td>33</td>
<td>25</td>
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<td>14</td>
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<td>COD removal efficiency [%]</td>
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<td>53.9</td>
<td>76.7</td>
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<td>92.5</td>
<td>93.5</td>
<td>94.1</td>
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<tr>
<td>chromatics [times]</td>
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<td>5</td>
<td>4</td>
<td>2</td>
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<td>—</td>
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<tr>
<td>chromatics removal efficiency [%]</td>
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<td>85</td>
<td>83</td>
<td>83</td>
<td>89</td>
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</table>

![Figure 2](image_url) 
**Figure 2.** The effect of the dosage rate of \( \text{H}_2\text{O}_2 \) (a) and the dilution times on the removal efficiency of COD.

![Figure 3](image_url) 
**Figure 3.** The effect the dilution times on the removal efficiency of COD.
over 92% and the COD of the effluent was below 60mg/L; but kept diluting, the COD removal efficiency was stable. Experiment results showed that the optimum dilution times of the effluent was 3; the Cl⁻ concentration would be about 2500mg/L.

IV. CONCLUSIONS

1) In the traditional Fenton process, the optimum reaction conditions were ascertained: the ratio of H₂O₂/ Fe²⁺ was 2:1, the dosage of H₂O₂ was 8.2mL/L, the initial pH was 4, the oxidation was 3h and the COD removal efficiency was about 45%.
2) The dosage rate of H₂O₂ affected the Fenton process to a certain extent. When the rate was 1mL/min, the COD removal efficiency was about 52%, 7% higher than that of the traditional process.
3) The Cl⁻ concentration in the drilling wastewater affected the Fenton process strongly: when the concentration was more than 2500mg/L, the inhibition effect was prominent; when the concentration was below 2500mg/L, the effect was negligible. Under this condition the COD removal efficiency was over 92% and COD of the effluent could be below 60mg/L, which had reached the secondary standards (DB12-356-2008) of Tianjin. The Fenton process was proved to be an effective advanced process to treat the drilling wastewater.

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REFERENCES