Application Of Magnetic-Assistant Fenton Reagent For Treatment Of Surfactant Simulative Wastewater

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ABSTRACT

The treatment of surfactant simulative wastewater by magnetic-assistant Fenton reagent system has been studied under different magnetic-assistant reaction time and the optimum dosage of Fenton reagent. The results showed that the removed rate of CODcr was 15% under the existence of magnetic field better than without the existence of magnetic field.

INTRODUCTION

Environment was largely harmed by the surfactant. The foam was easily formed by the anion detergent in water. It debased the velocity and degree of reaeration. It made fish death or malformation. When its concentration was 10 mg·L⁻¹, the harvest of the rice decreased 50%. When its concentration was 45 mg·L⁻¹, all of rice was killed and nothing was harvested. Sodium dodecylbenzene sulfonate (DBS) which was hardly degraded by biochemical method was degradation, H₂O₂ was oxidant, FeSO₄·7H₂O was catalyst, magnetic field was the added field. The effect and efficiency which the DBS was degraded by magnetic-assistant Fenton reagent catalytically oxidation method was researched. The mechanism of magnetic field co-operative effect was theoretically discussed.

EXPERIMENTAL

Instruments and reagents

Magnetic force mixer (Shandong, China), quick director for CODcr (Beijing, China), 30% H₂O₂ (AR), FeSO₄·7H₂O (AR), KC-70C magnetizer (Shanghai, Chian), SXG-1B teslameter (Shanghai, Chian)
Simulative Wastewater

The simulative wastewater was confected by DBS and the distilled water. Its CODcr was 320 mg·L⁻¹ and concentration was 200 mg·L⁻¹.

<table>
<thead>
<tr>
<th>TABLE 1: The quality of raw wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg·L⁻¹)</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>200</td>
</tr>
</tbody>
</table>

Method

The experiment were performed in 250mL beakers according to the following steps: (1) take 100mL simulative DBS wastewater in a 250mL beaker on a stirred; (2) regulated the pH value of the aqua; (3) add definite dosage of FeSO₄·7H₂O and turn on the stirrer; (4) drip 30% H₂O₂ solution into the simulative DBS wastewater. After reaction had completed, regulated the pH value of the aqua to alkalescence, deposited some time, filtered the aqua and took the pure liquid to measure the CODcr.

The magnetic-assistant oxidation experiment was same to last. The discrimination was that the beaker of the kind of water was clipped in magnetic field in the magnetic-assistant oxidation experiment. The influence of the productivity and productive rate of hydroxyl radical was studied.

The influencing factors which affected the rate of CODcr removal were researched. These factor included the dosage catalyst and oxidant, pH value, reaction time, magnetic-assistant reaction time, intensity of magnetic field.

Method of analysis

The removed rate of CODcr could be calculated by the formula as following:

\[
\text{Removed rate of CODcr} = (1 - \frac{CODcr}{CODcr}) \times 100\%
\]

Note: CODcrₐ, CODcr respectively denoted chemical oxygen demand (K₂Cr₂O₇) of DBS simulative wastewater before and after treatment.

RESULT AND DISCUSSIONS

All kinds of influential factors of removal CODcr by common Fenton reagent

The main influential factors were dosage of H₂O₂, dosage of FeSO₄·7H₂O, pH and oxidation time.

1. Effect of the dosage of H₂O₂ on CODcr removal

100mL sample, the dosage of FeSO₄·7H₂O was 300mg, pH value was 3, oxidation time was 90 min, change the volume of H₂O₂.

From figure 1, it can be seen that removed rate of CODcr reached 86.9% when the volume of H₂O₂ was 0.5mL. On the contrary the removed rate of CODcr descended when the volume of H₂O₂ was 0.2 0.3 0.4 0.5 0.6 0.7 0.8

![Figure 1: Effect of H₂O₂ dosage on CODcr removal](image)

2. Effect of FeSO₄·7H₂O dosage on CODcr removal

100mL sample, the dosage of FeSO₄·7H₂O was 300mg, pH value was 3, oxidation time was 90 min, change the volume of H₂O₂.

From figure 2, it can be seen that removed rate of CODcr reached 86.9% when the volume of H₂O₂ was 0.5mL. On the contrary the removed rate of CODcr descended when the volume of H₂O₂ was
continuously increased. The reason was that when volume of H₂O₂ was low, increased volume of H₂O₂ made concentration of •OH which was generated by H₂O₂ increased. But when volume of H₂O₂ was high, superfluous H₂O₂ did not generate more •OH and Fe²⁺ was oxidized to Fe³⁺ in the beginning. It made the oxidation reaction was catalyzed by Fe³⁺ not Fe²⁺. On the one hand volume of H₂O₂ was consumed and generation of •OH was restrained, on the other hand CODcr of filtrate was increased because of reducibility of H₂O₂. According to these reasons, the optimum volume of H₂O₂ was 0.5mL.

2. Effect of the dosage of FeSO₄·7H₂O on CODcr removal

100mL sample, the volume of H₂O₂ was 0.5mL, pH value was 3, oxidation time was 90 min, change the dosage of FeSO₄·7H₂O.

It was essential to generate •OH which was catalyzed by Fe²⁺. Under no Fe²⁺ conditions, H₂O₂ hardly generated •OH. Reaction speed of Fe²⁺ + H₂O₂ → 2Fe³⁺ + •OH + OH⁻ was very slow when concentration of Fe²⁺ was very low. Therefore dosage of •OH was very small, reaction speed was very slow and degradation was restrained. When the dosage of Fe²⁺ was superfluous, it could deoxidize H₂O₂ and it was oxidized to Fe³⁺. On the one hand superfluous Fe²⁺ consumed H₂O₂, on the other hand it increased chromaticity of filtrate. From Fig.2, it can be seen that the removed rate of CODcr reached 87.2% when the dosage of FeSO₄·7H₂O was 300mg. On the contrary total removed rate of CODcr descended when the dosage of FeSO₄·7H₂O was continuously increased. The reason was that CODcr of filtrate was increased because of reducibility of Fe²⁺. According to these reasons, the optimum the dosage of FeSO₄·7H₂O was 300mg.

3. Effect of oxidation time on CODcr removal

100mL sample, the volume of H₂O₂ was 0.5mL, the dosage of FeSO₄·7H₂O was 300mg, pH value was 3, change oxidation time.

From figure 3, it can be seen that removed rate of CODcr reached 86.5% when oxidation time was 60 min. It also can be seen that removed rate of CODcr increased indistinctively when oxidation time was increased. According to practical application and economic aspects, the optimum oxidation time was 60 min.

4. Effect of pH on CODcr removal

100mL sample, the volume of H₂O₂ was 0.5mL, the dosage of FeSO₄·7H₂O was 300mg, oxidation time was 60 min, change pH value.

Under the acidic condition, Fe²⁺ catalyzed H₂O₂ produced •OH. But under the neutral or alkaline condition Fe²⁺ did not catalyze H₂O₂ produced •OH. According to classical Fenton reagent theory, the generation of •OH was restrained because of pH value being increased and Fe²⁺ exited in form of Fe(OH)₂ with pH value being continuously increased, Fe²⁺ lost its catalysis. When pH value under 3, reaction of Fe²⁺ + H₂O₂ → 2Fe³⁺ + •OH + OH⁻ was restrained when concentration of H⁺ was very high. Catalytic reaction was restrained because Fe(III) was not deoxidized to Fe(II) namely Fe²⁺ and Fe³⁺ of coordination balance system was directly destroyed by changing pH value. It weakened the oxidation of Fenton reagent. From figure 4, it can be seen that removed rate of CODcr reached the highest point when pH value was 3. But removed rate of CODcr obviously descended with pH value continuously being increased. The reason was that under pH value being 3 condition, composition of ferryl iron was created and it was the actually catalytic ingredient in the Fenton reagent reaction.

5. Effect of the added sequence of oxidant, cata-
TABLE 2: Effect of the addition order of pH, catalyst and oxidant on CODcr removal

<table>
<thead>
<tr>
<th>Added sequence</th>
<th>Firstly regulated pH value finally added the oxidant and catalyst</th>
<th>Firstly added the oxidant and catalyst finally regulated pH value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removed rate of CODcr (%)</td>
<td>94.6</td>
<td>87.1</td>
</tr>
</tbody>
</table>

TABLE 3: Effect of the addition order of catalyst and oxidant on CODcr removal

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</tr>
</thead>
<tbody>
<tr>
<td>Removed rate of CODcr (%)</td>
<td>94.6</td>
<td>94.2</td>
</tr>
</tbody>
</table>

**lyst and pH value on CODcr removal**

100mL sample, the volume of H₂O₂ was 0.5mL, the dosage of FeSO₄·7H₂O was 300mg, oxidation time was 60 min, pH value was 3, change the sequence of oxidant, catalyst and pH value.

From TABLE 2, it can be seen that removed rate of CODcr reached 94.6% when pH value was firstly regulated, the oxidant and catalyst was finally added. It was higher 7.5% than which the oxidant and catalyst was firstly added, pH value was finally regulated. The reason was that the hydrolysis of FeSO₄·7H₂O was restrained in the acidic condition. It can exerted its catalysis in maximum.

From TABLE 3, it can be seen that removed rate of CODcr reached the close value when pH value was firstly regulated, the oxidant and catalyst was finally added. It was higher 7.5% than which the oxidant and catalyst was firstly added, pH value was finally regulated. The result showed that the added sequence of oxidant and catalyst was not affected removed rate of CODcr if pH value was firstly regulated.

**Magnetic-assistant oxidation experiment**

1. **Effect of magnetic-assistant reaction time on CODcr removal**

100mL sample, the volume of H₂O₂ was 0.5mL, the dosage of FeSO₄·7H₂O was 300mg, pH value was 3, change the sequence of oxidant, catalyst and pH value.

From figure 5, it can be seen that removed rate of CODcr in intensity of magnetic field being 427.8mT was higher than that without magnetic field at different magnetic-assistant reaction time. But with the magnetic-assistant reaction time increasing, removed rate of CODcr in intensity of magnetic field being 427.8mT was close to which without magnetic field. The result showed that the productive rate of hydroxyl radical was improved, but the productivity of hydroxyl radical was not improved.

2. **Effect of intensity of magnetic field on CODcr removal**

100mL sample, the volume of H₂O₂ was 0.5mL, the dosage of FeSO₄·7H₂O was 300mg, pH value was 3, change the intensity of magnetic field.

From figure 6, it can be seen that removed rate of CODcr in intensity of magnetic field being 427.8mT was higher than that without magnetic field at different magnetic-assistant reaction time. But with the magnetic-assistant reaction time increasing, removed rate of CODcr in intensity of magnetic field being 427.8mT was close to which without magnetic field. The result showed that the productive rate of hydroxyl radical was improved, but the productivity of hydroxyl radical was not improved.
of CODcr increasing with the intensity of magnetic field increasing at different magnetic-assistant reaction time. But with the magnetic-assistant reaction time increasing, removed rate of CODcr in different intensity of magnetic field were close to each other. The result showed that the productive rate of hydroxyl radical from Fenton reagent increased when the intensity of magnetic field was augmented.

Mechanism

The hydroxyl radical was formed by the Fe$^{2+}$ and H$_2$O$_2$ quick reaction. It had strong oxidation ability. When Fe$^{3+}$ existed, Fe$^{3+}$ slowly reacted with H$_2$O$_2$ formed Fe$^{2+}$, then in succession Fe$^{2+}$ quickly reacted with H$_2$O$_2$ formed •OH. The newly formed •OH had strong oxidation ability which electrolyzed oxidizing was 2.8V. It was only lower than F$_2$ which electrolyzed oxidizing was 2.87V.

DBS was the ramifications of benzene. It with passive groups was difficultly oxidized by the normal oxidant. But •OH could quickly oxidize them. Its velocity of oxidation was quicker than only H$_2$O$_2$. The reason was that under the acidic condition Fenton reagent rapidly generated •OH. It had a stronger oxidation which could effectively decompose organic pollutions. The conjectural oxidation procedure was as follows: First, the passive groups of intermediates were substituted by •OH, it made aromatic rings active. Then the aromatic rings were decomposed and generated low fatty acid compounds. At last they were turned into CO$_2$ and H$_2$O.

A lot of study about UV-Fenton system was reported and it was applied in practice. The electrical Fenton which based on Fe/C micro-electrolysis technology was attached importance because of its broadly application range and low cost. But waste-water was not treated by magnetic-assistant advanced oxidation technology. For example magnetic-assistant Fenton reagent was not reported.

Hydroxyl radical was obviously affected by magnetic field. It was found by people long before. Forming hydroxyl radical reaction was the main reaction in Fenton oxidation reaction, so magnetic-assistant Fenton reagent method was speculated to improve the velocity of oxidation degradation of contaminations and didn’t consume excess electric resource. But UV or ultrasonic needed added electric resource, so magnetic-assistant Fenton reagent method was easily applied.

Under not sur-magnetic field condition, a magnetic field which being from the molecular interior (is called partial magnetic field) could provide the magnetic moment for the change of the spinning condition of the free radical. Under sur-magnetic field condition, the Larmor spinning velocity of the spinning vector of the free radical can be changed. The difference of the spinning velocity of two spinning vectors ($\Delta \omega$) can be expressed by the formula$^{[4]}$.

$$\Delta \omega = \left( \frac{\Delta g \mu_B H_0}{h} \right) \pm (a_1 - a_2) I$$

In the formula, $\Delta g = |g_1 - g_2|$, $g_1$, $g_2$ respectively notes the g value of two free radicals alone electron, g value is related with the system nature, $\mu_B$ is a Bohr's magneton, h is the Planck constant, H$_0$ is the intensity of sur-magnetic field, $a_1$, $a_2$ are ultra fine coupling constants of two free radicals, I is the nuclear spin quantum number. The transformation speed which the two spinning vectors of free radicals from S state to To state is decided by $\Delta \omega$ value. According to above formula, the above transformation speed can increase with $\Delta g$ or H$_0$ enhancing$^{[5]}$. Speaking of the DBS simulative wastewater, $\Delta g$ is a definite value in the microscopic structure, therefore the difference of the Larmor spinning velocity ($\Delta \omega$) is only decided by the intensity of macroscopic sur-magnetic field. According to $\Delta g$ mechanism, the bigger H$_0$ will be, the shorter transformation time from S state to To state will be, the quicker transformation speed from S state to To state will be, Namely the more little singlet state total will be, the smaller possibility of re-combination will be, the quicker the rate of chemical reaction will be. This is the degeneration process mechanism of magnetic Fenton reagent.

CONCLUSIONS

(1) The added magnetic field improved the productive rate of hydroxyl radical, but didn’t improve the productivity of hydroxyl radical from Fenton reagent.

(2) The productive rate of hydroxyl radical from
TABLE 4: Index of sample before and after treatment

<table>
<thead>
<tr>
<th>Index</th>
<th>CODcr (mg·L⁻¹)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original sample</td>
<td>320</td>
<td>5~6</td>
</tr>
<tr>
<td>Fenton reagent oxidation</td>
<td>18.6</td>
<td>7</td>
</tr>
<tr>
<td>Magnetic-assistant Fenton reagent oxidation</td>
<td>17.3</td>
<td>7</td>
</tr>
</tbody>
</table>

Fenton reagent increased with the intensity of magnetic field augmenting.

REFERENCES