Removal of Toxic Organic Pollutants from Coke Plant Wastewater by UV-Fenton

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ABSTRACT: Coke plant wastewater containing lots of toxic organic pollutants should be treated before being discharged into the environment. It is challenging to treat toxic and refractory compounds using conventional methods. In this study, a UV-Fenton technology was investigated. When the initial COD, NH3-N concentration and SS of wastewater were 5080 mg/L, 329.9 mg/L, and 847.7 mg/L, results showed that the removal rate of COD, NH3-N and SS were 88.0%, 58.4% and 99.2% respectively under the optimal reaction conditions. Under the identified optimal condition, H2O2 concentration is 75 mmol/L, the concentration ratio of H2O2 and Fe2+ is 3:1, and original pH is 4 within 30 min. GC-MS analysis, revealed that organic substances such as indole and quinoline were degraded effectively.

INTRODUCTION

WASTEWATER from coke plants is often produced from coke refining, high-temperature carbonization, purification and by-product recovery processes. It is a kind of poisonous and harmful wastewater with a high concentration of refractory organic matter [1]. It has a complicated composition, mainly including phenol and phenol derivatives (about 60 %), benzene and its derivatives and quinolines as well as other polycyclic or heterocyclic organic compounds. Those compounds have an inhibitory effect on microorganism growth and are recalcitrant to degradation. Meanwhile, they could cause deactivation of human cell by tissue necrosis, and can post treats to crops, water and aquatic life. It is challenging to meet the requirements of emission standard of pollutants for coking chemical industry GB16171-2012 by conventional processes which has aroused people’s concern.

Wastewater treatment processes for coke plants can be divided into three levels [2]. The first processes mainly include solvent extraction steam cycle to remove oil or phenol from high phenol concentration waste water; Secondary treatment methods are mainly biochemical treatment; Tertiary treatment methods include flocculation, activated carbon adsorption, ozone oxidation, etc. Biological treatment is the most costly but effective method in treating coke plant wastewater. However, toxicity and inhibition effects of phenols compounds to microorganisms often limit the removal efficiency of organic pollutants [3]. Advanced Oxidation Process (AOPs) is a kind of new technology treating persistent organic pollutants, it can be used in the area of wastewater treatment and sludge minimization [4]. The reaction is essentially using highly reactive hydroxyl free radical (HO•) to oxidize refractory organic pollutants in wastewater and finally degrade them into non-toxic or low toxicity of small molecules. Such organic pollutants could be even degraded into carbon dioxide and water [5]. In traditional Fenton reaction processes, Fe2+ can be oxidized into Fe3+ by hydrogen peroxide and hydroxyl free radicals could be produced. Additionally, Fe3+ could be reduced into Fe2+, as shown in Equations (1) and (2).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^* + \text{OH}^- \quad (1)
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \quad (2)
\]

In the presence of catalyst on the surface, the certain wavelength ultraviolet light can catalytic oxidation of organic pollutants in wastewater and oxidative degradation of the organic matter [6]. Under the irradiation of ultraviolet light whose wavelength is less than 300 nm, H2O2 can produce hydroxyl radicals and convert Fe2+ to Fe3+ efficiently. At the same time, Fe3+ can also produce hydroxyl radicals with the irradiation of ultraviolet. The main reactions in Fenton with ultraviolet light irradiation are shown in Equations (3) and (4).
The generated hydroxyl radicals could oxidize organic pollutants (RH) in waste water and produce new radical (R•), which could be oxidized by Fe^{3+} to generate carbon dioxide and water [7].

In this study, UV-Fenton technology is used to dispose coke plant wastewater before biochemical treatment. The effects of various factors for the treatment processes are also discussed.

METHODS

The Raw Materials

Wastewater samples were obtained from coking plant of Chengde Iron & Steel Company, Hebei, China. Water quality parameters of wastewater samples and reagents used in the experiments are shown in Table 1 and Table 2.

Experimental Setup

The optical experimental setup was self-designed with low pressure mercury lamp which was put into a water proof tube made by quartz glass with good UV transmittance. The reactor is tubular which was made by organic glass with bottom aeration. Low pressure mercury lamp was immersed into water to cool down. The parameters are shown in Table 3 and Figure 1.

Because coke plant wastewater is of high turbidity and it is difficult for the light to penetrate through it, wastewater samples were diluted 10 times and poured into the reactor with a certain amount of Fenton reagents and reacted under the irradiation of ultraviolet light through air mixing for a certain time. The pH was then adjusted to form iron ion precipitation settling down. The main factors such as H_{2}O_{2} concentration, reagent ratio, reaction time, pH and ultraviolet light illumination were investigated in experiments.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>Ammonia Nitrogen (mg/L)</th>
<th>COD (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>6.8</td>
<td>847.7</td>
<td>3.29</td>
<td>5080</td>
</tr>
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</table>

Table 2. Reagents Used in the Experiments.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Molecular Formula</th>
<th>Molecular Weight</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen peroxide</td>
<td>H_{2}O_{2}</td>
<td>34.02</td>
<td>30</td>
</tr>
<tr>
<td>Ferrous sulfate</td>
<td>FeSO_{4}·H_{2}O</td>
<td>278.02</td>
<td>≥ 99.0</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H_{2}SO_{4}</td>
<td>98.08</td>
<td>95.0~98.0</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>40.00</td>
<td>≥ 96.0</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Effect of H_{2}O_{2} Concentration

The effect of initial H_{2}O_{2} concentration on the degradation of coke plant wastewater was studied under a constant ratio between H_{2}O_{2} and Fe^{2+}.

The initial concentration of H_{2}O_{2} is a very important parameter. As shown in Figure 2, removal rates of COD and ammonium nitrogen increased with increasing H_{2}O_{2} concentration from 10–75 mmol/L, but decreased when the H_{2}O_{2} concentration exceeded 75 mmol/L. The optimal removal rate for COD and NH_{3}-N is 78.7% and 58.4%, respectively. Hydroxyl radicals were generated from Fenton under ultraviolet light irradiation, which could be used to degrade organic molecules. A chain reaction could be triggered to consume organic molecules completely. Under a constant intensity of ultraviolet light, a higher dosage of Fenton produced more hydroxyl radicals, resulting in a higher removal rate of COD and ammonium nitrogen. The treatment effect, therefore, improved with increasing H_{2}O_{2} concentration. However, in the excess of Fenton,
hydroxyl radicals were consumed by H₂O₂ to form hydroperoxyl radical, resulting in lower oxidation capability of O₂ [8,9].

**Effect of Reagent Ratio**

The reagent ratio on the degradation of organic pollutants is also very important. As shown in Figure 3, when the ratio of H₂O₂ and Fe²⁺ concentration was 3:1, treatment effect was the best. Removal rate of COD and NH₃-N was 81.6% and 7.21%, respectively.

The main reaction of UV-Fenton is that Fe²⁺ initiates and promotes the decomposition of H₂O₂, forming hydroxyl free radicals to react with organic matters and degrade them into small inorganic species. The concentration of Fe²⁺ determines the conversion rate of H₂O₂ to hydroxyl free radicals. When the ratio of H₂O₂ and Fe²⁺ was lower, low concentration of ferrous ion could not induce the formation of enough hydroxyl free radicals. In addition, after the pH was adjusted, H₂O₂ could generate oxygen and influence the treatment effect. While the ratio of H₂O₂ and Fe²⁺ was lower, overmuch ferrous ion quickly catalyzed hydrogen peroxide and produced a large number of hydroxyl radicals reacting with each other. Excessive Fe²⁺ ions also consumed hydroxyl radicals, being unfavorable to degradation of organic pollutants in coke plant wastewater [10].

**Effect of pH**

Effect of pH on the degradation of organic pollutants was shown in Figure 4. The influence of pH of the solution on UV-Fenton system is complex. It affects the activity of both oxidant and substrate. H₂O₂ can capture proton from the solution to form H₂O₂⁻ which is unfavorable to be activated by Fe²⁺ at a low pH. Under such conditions, Fe(OH)²⁺ could be generated to react with H₂O₂ slowly to reduce the generation of •OH. When pH of solution was higher than 4, Fe²⁺ could form complex compound. Some Fe³⁺ ions generated by Fenton reactions were easily precipitated as Fe(OH)₃ [11]. Preventing it from reduction into Fe²⁺ could remarkably affect the formation of •OH. H₂O₂ was unstable in alkaline solutions and could be easily decomposed into oxygen and water. Thus, the most suitable pH condition in UV-Fenton system was 4 when Fe²⁺ mainly existed in the form of Fe(OH)₂. Under such conditions, Fe(OH)₂ could react much faster with H₂O₂ than Fe²⁺ [12]. COD removal rate was 85%. By adjusting the pH to 6 after the reaction, removal rate of COD could be increased to 88%. Because iron ions reacted with water molecules and hydroxyl ions, complex iron compounds and flocculation were formed and the suspended solid particles were settled down, resulting in clean water in the outlet.
Effect of Reaction Time

Experimental results indicated that the reaction was very fast in UV-Fenton process at first. However, it increased slowly after 5 min, as shown in Figure 5.

When the reaction time reached 30 min, removal rates of NH₃-N and COD were 31.9% and 79.7%, because the concentration of reagent and pollutants in wastewater was matching in the process of reaction. In addition, sufficient stirring and abundant \( \cdot \mathrm{OH} \) could lead to a strong degradation effect in a shorter time. However some intermediate products created in the processes were hard to be oxidized by \( \cdot \mathrm{OH} \). Hence, the removal rate of organic pollutants decreased gradually.

Effect of Ultraviolet Light Illumination

Results indicate that ultraviolet light affected the efficiency of pollutant degradation and improved the utilization rate of Fenton reagent, as shown in Figure 6. COD removal rate improved from 81.1–88.2% at dosage of reagents of 120 mmol/L.

The speed of reducing Fe³⁺ to Fe²⁺ was very slow, and limited the reaction rate. It limited the reduction of Fe³⁺ to Fe²⁺. Hence, Fe²⁺ concentration in the solution was getting lower and lower. On the contrary, Fe³⁺ gradually accumulated, and the amount of Fe²⁺ needed to be increased to make efficient reaction. Combining Fenton reagent with ultraviolet light can promote the decomposition of hydrogen peroxide and induce the
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Identification by GC-MS

The composition of coke plant wastewater before biochemical treatment was complex. The main organic matters contained phenol, benzene, pyrrole, naphthalene, imidazole, and carbazole. As shown in Table 4, main organic compounds were 3-methyl phenol (C\textsubscript{7}H\textsubscript{8}O), quinoline (C\textsubscript{9}H\textsubscript{7}N), phenol (C\textsubscript{6}H\textsubscript{6}O), indole (C\textsubscript{8}H\textsubscript{7}N), 2, 4-dimethyl phenol (C\textsubscript{8}H\textsubscript{10}O), 2-methyl phenol, butylated hydroxytoluene (C\textsubscript{15}H\textsubscript{24}O), as identified using GC-MS analysis.

After treated by UV-Fenton, most of the organic pollutants such as phenols, indoles and quinolines were removed, as shown in Table 5. Only a small amount of butylated hydroxytoluenes, phenols, and docosanes were identified. Phenols, indoles and quinolines could hardly be detected. A small amount of chain alkanes were generated and part of the benzene ring was broken to produce some new substances.

CONCLUSIONS

The composition of coke plant wastewater is complex. Biodegradation of refractory organics, such as phenol substance, quinoline (C\textsubscript{9}H\textsubscript{7}N), indole (C\textsubscript{8}H\textsubscript{7}N), and butylated hydroxytoluene (C\textsubscript{15}H\textsubscript{24}O) were detected. Using UV—Fenton method, when the initial concentration of COD and NH\textsubscript{3}-N was 5080 mg/L and 329.9 mg/L, the removal rate was 88.0% and 58.4% respectively under the optimal condition. Under the optimal condition, the H\textsubscript{2}O\textsubscript{2} concentration was 75 mmol/L; the ratio of H\textsubscript{2}O\textsubscript{2} and Fe\textsuperscript{2+} ratio was 3:1; pH was 4 and the reaction duration was 30 min. Based on GC-MS analysis, lots of organic substances such as indole and quinoline were degraded effectively. UV—Fenton, as one of effective methods, can be used in advanced treatment for coke plant wastewater.

ACKNOWLEDGEMENTS

This study was financially supported by National Natural Science Foundation (51174031).

REFERENCES

Table 4. The Constituents of Coke Plant Wastewater After Treatment by UV-Fenton.

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>Content (%)</th>
<th>Formula</th>
<th>Compound</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40.65</td>
<td>C₁₅H₂₄O</td>
<td>Butylated Hydroxytoluene</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>6.02</td>
<td>C₂₂H₄₆</td>
<td>Docosane</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5.05</td>
<td>C₁₅H₁₆O₂</td>
<td>Phenol, 4,4′-(1-methylethylidene)bis-</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3.79</td>
<td>C₂₄H₃₂O₉</td>
<td>5H-Cyclopropa[3,4]benz[1,2-e]azulen-5-one, 9,9a-bis(acetoxy)-1,1a,1b,2,4a,7a, 7b,8,9,9a-decahydro-2,4a,7b-trihydroxy-3-(hydroxymethyl)-1,1,6,8-tetramethyl-</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>3.49</td>
<td>C₂₈H₄₃NO₆</td>
<td>(5a)Pregnane-3,20α-diol, 14α,18α-[4-methyl-3-oxo-(1-oxa-4-azabutane-1,4-diyl)]-, diacetate</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>3.46</td>
<td>C₁₅H₁₉NO₈</td>
<td>1h-Pyrrole-3,4-diacetic acid, 2-acetoxyethyl-5-methoxy- carbonyl-, dimethyl ester</td>
<td>6</td>
</tr>
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