Application of ferric-carbon inner electrolysis coupling Fenton process pretreatment of coal tar distillation wastewater with a focus on optimization by the response surface method

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\textbf{Abstract}

Coal resources are abundant in China. The coal deep processing industry produces a large amount of coal tar. In China, the coal tar distillation process is important for obtaining chemical products such as naphthalene, anthracene, and phenanthrene. However, the wastewater generated from the coal tar distillation process is a typical degradation-resistant effluent, and the conventional sewage treatment process is not sufficient to treat it well. Alternative technologies must be developed. In this study, coal tar distillation wastewater was degraded utilizing the ferric-carbon inner electrolysis (FCIE) process following the Fenton process. The single-factor method and response surface method (RSM) were used to obtain the optimal conditions of the FCIE and Fenton processes, respectively. Under the optimal conditions, the total organic carbon (TOC) removal rates of the real coal tar distillation wastewater can reach 24.3% for the FCIE process, 65.1% for the Fenton process, and 73.6% in total. An analysis of variance was implemented, and the Box–Behnken RSM cubic model was obtained. This model shows less than 5% error between the calculated results and the experimental results. The TOC removal rate by the Fenton process followed the pseudo-zero-order kinetic model. This study could provide technical support for coal tar distillation wastewater pretreatment.

\textbf{Keywords:} Fenton; Wastewater; Coal tar distillation; Pretreatment

\section{Introduction}

Coal tar is the key chemical material in China. Chemicals such as naphthalene, anthracene, and phenanthrene can be obtained by treating the coal tar with the distillation process \cite{1,2}. However, wastewater is also produced in the separation and purification unit of the coal tar treatment plant \cite{3,4}. Coal tar distillation wastewater is a typical refractory organic wastewater that has the characteristics of high organic matter concentration, complex composition, high toxicity, and mutagenic and carcinogenic features \cite{5,6}. It is challenging for engineers to treat coal tar distillation wastewater cheaply, effectively, and safely. Because traditional sewage treatment processes are not qualified for this type of refractory polluted water, an alternative treatment technology must be developed. The ferric-carbon inner electrolysis (FCIE) and Fenton combination process could be a feasible choice to
achieve this treatment task. FCIE is a typical high concentration wastewater pretreatment process that is mostly used in the treatment of industrial wastewater [7,8]. After the FCIE process, the chemical oxygen demand (COD) of wastewater can be reduced by approximately 50%. Moreover, biodegradability can be increased to different levels [9]. However, the coal tar distillation wastewater concentration is too high to meet the effluent standard after undergoing the solo FCIE process treatment [10]. The Fenton process can also be used to pretreatment industrial wastewater [11,12]. The Fenton process degrades organic pollutant reactions, as illustrated by the hydroxyl radical theory [13,14]. The FCIE-Fenton combination process is a feasible choice for coal tar distillation wastewater pretreatment. In this study, real coal tar distillation wastewater was selected as the research object. FCIE factors, such as Fe:AC mass ratio, pH, and [Fe] 0 concentration, were studied, and the optimal conditions of FCIE were obtained. Furthermore, the response surface method (RSM) is utilized to analyze and optimize the Fenton process. The results of this study could supplement technical support for the coal tar distillation wastewater pretreatment.

2. Materials and methods

2.1. Chemicals

Coal tar distillation wastewater selected for this study was from a chemical plant located in Northeast of China. The pH value and total organic carbon (TOC) content of this wastewater were in the range of 7.5–8.8 and 14,000–17,000 mg/L, respectively. Iron powder (analytical reagent grade, 99%) and active carbon (analytical reagent grade, 99%) were utilized in the FCIE process. H 2SO 4 (analytical reagent grade, 98%), and NaOH (analytical reagent grade, 99%) were utilized to adjust the pH value. FeSO 4·7H 2O (analytical reagent grade, 99%) and H 2O 2 (analytical reagent grade, 30%) were prepared to carry out the Fenton process. All chemicals were purchased from Sinopharm Chemical Reagent Co., China. All sample solutions were prepared with deionized water from an ion exchange system.

2.2. Degradation experiments

The FCIE process was studied in a 100 mL volume beaker. The coal tar distillation wastewater was adjusted to preset pH value, and then a certain amount of iron powder and active carbon was added, which followed a certain Fe:AC mass ratio. The reaction was maintained for 4 h with magnetic stirring (150 rpm). The samples were collected after treatment, and the TOC content was tested by a Vario TOC analyzer (Elementar Analysensysteme GmbH, Germany). The TOC removal rate, which was calculated following function (1), was a key factor to evaluate and optimize the FCIE process. The optimal FCIE conditions, such as Fe:AC, pH, and [Fe] 0, were obtained by the single factor studied method.

where \( \eta \) is the TOC removal rate (%) at reaction time \( t \), and \( t \) is the reaction time (min). \( C_0 \) is the initial TOC of wastewater (mg/L), and \( C_t \) is the TOC at reaction time \( t \) (mg/L).

After the FCIE treatment process, the coal tar distillation wastewater was filtered and then moved to another beaker. The pH value was adjusted, and the preset amount of FeSO 4·7H 2O was added. The preset amount of H 2O 2 was injected five times over 2 h. Then, after 1 h of sedimentation, the TOC content was tested. In the kinetics study, the samples were collected at the Fenton reaction time of 10, 20, 30, 60, 90, and 120 min. These study data are the arithmetic means of two solo test results under the same conditions.

2.3. RSM factors and level design

The RSM is an effective tool to evaluate the reaction factors and obtain the optimal conditions by limiting the experimental results [15]. The TOC removal law can also be indicated by the fitting calculation with the Box–Behnken RSM model. However, the Box–Behnken RSM requires suitable factors and levels, which could have a large influence on the reaction. According to previous studies [16,17], the initial pH value, initial FeSO 4 concentration ([FeSO 4] 0), and total H 2O 2 concentration ([H 2O 2]) were selected because these factors can determine the Fenton reaction efficiency. The factors and levels of this study are shown in Table 1. The pH levels do not reach alkaline conditions because most reports indicated that the Fenton process is efficient under acidic conditions. The experimental list and the setting conditions are shown in Table 2.

3. Results and discussion

3.1. FCIE process

To illustrate the optimal conditions of the FCIE process, single factor experiment studies were implemented. The Fe:AC mass ratio, initial pH value, and [Fe] 0 concentration were considered, and the results are shown in Fig. 1. The Fe:AC mass ratio was the first factor to be obtained under the condition of 20 g/L [Fe] 0, and pH of 2.0. The 1:1 mass ratio of Fe:AC has better performance on the TOC removal rate at 22.5%. When the Fe:AC mass ratio changed to 1:2 and 2:1, the TOC removal rate only achieved 19.7% and 20.3%, respectively. Therefore, the optimal Fe:AC mass ratio was considered to be 1:1, which was consistent with previous research [10]. Next, the influence of pH value was tested under the condition of 20 g/L [Fe] 0, and a 1:1 mass ratio of Fe:AC. TOC removal rates reached 22.5%, 14.5%,

<table>
<thead>
<tr>
<th>Factors</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A: ) pH</td>
<td>3.0 5.0 7.0</td>
</tr>
<tr>
<td>( B: ) [FeSO 4] 0 (g/L)</td>
<td>5.0 12.5 20.0</td>
</tr>
<tr>
<td>( C: ) [H 2O 2] (30%, mL/100 mL)</td>
<td>2.0 3.5 5.0</td>
</tr>
</tbody>
</table>
16.5%, 22.2%, 8.1%, and 7.7% when the initial pH value was adjusted to 2.0, 3.0, 4.0, 5.0, 7.0, and 9.0, respectively. The results indicated that the FCIE reaction was hampered under alkaline conditions, which has also been reported previously [10,18]. An optimal initial pH of 5.0 was selected after a comprehensive consideration of the TOC removal rate and concentration for pH adjustment. Under conditions of pH 5.0 and a 1:1 mass ratio of Fe:AC, the influence of [Fe] concentration was studied. The results indicated that an excess or a deficiency in [Fe] concentration both had a negative impact on TOC removal. The optimal [Fe] concentration was 40 g/L in this study, and the TOC removal rate reached 24.3%.

3.2. RSM results of the Fenton process

To investigate the interaction effects of the selected factors on the Fenton process, the Box–Behnken RSM was utilized in this study. The RSM experiment results are listed in Table 2. Based on these results, an analysis of variance (ANOVA) was carried out using Design-Expert software (V8.05b, Stat-Ease, Inc., USA), and the results are shown in Table 3. The cubic model was selected, and the ANOVA results were shown in Eq. (2). The fitted equation is shown in Eq. (2). The $R^2$ is 0.9960, and $R^2_{adj}$ is 0.9872. The standard deviation (S.D.) is 1.35. The mean is 51.16, and the coefficient of variation (C.V.) is 2.63%. The $F$-value of 113.17 and $p$-value (Prob > $F$) of <0.0001 imply that this cubic model is significant and valid. There is only a 0.01% chance that this cubic model exhibits deviation due to noise. The model is applicable to further discussion in this research.

$$\eta_{TOC} = 232.21167 - 91.08333 \cdot \text{pH} - 12.12833 \cdot [\text{FeSO}_4]_0 + 12.35667 \cdot [\text{H}_2\text{O}_2] + 6.28pH \times [\text{FeSO}_4]_0 - 4.63333pH \times [\text{H}_2\text{O}_2] + 0.24889 [\text{FeSO}_4]_0 \times [\text{H}_2\text{O}_2] + 9.07833pH^2 - 0.070578 [\text{FeSO}_4]_0^2 - 0.36444 [\text{H}_2\text{O}_2]^2 - 0.63833 pH^2 \times [\text{FeSO}_4]_0 + 0.51667 pH^2 \times [\text{H}_2\text{O}_2] \quad (2)$$

where the $\eta_{TOC}$ is the TOC removal rate, %; [FeSO$_4$]$_0$ is the initial FeSO$_4$ concentration, g/L; [H$_2$O$_2$] is the total H$_2$O$_2$ amount, 30% (mass concentration), mL/100 mL. The three-dimensional response surfaces of this cubic model are shown in Fig. 2. The total H$_2$O$_2$ amount is a key factor in the Fenton process. From Figs. 2a and b, it can be found that a high H$_2$O$_2$ amount leads to a more significant efficiency in TOC removal. Under the condition of 5.0 mL/100 mL [H$_2$O$_2$], the TOC removal rate can reach approximately 70%. However, when the [H$_2$O$_2$] amount was reduced to 2.0 mL/100 mL, only approximately 55% of TOC removal rate could be obtained. It can also be observed from Figs. 2a and b that the shapes of the response surfaces are similar. When [FeSO$_4$]$_0$ maintains low concentrations from 5.00 to 14 g/L, the TOC removal rate is sensitive to the initial pH value. The acidic and neutral conditions had better TOC removal performances. However, when [FeSO$_4$]$_0$ is maintained at a high level (higher than 14 g/L), the influence of the initial pH value on TOC removal decreases. The [FeSO$_4$]$_0$ is also an important factor, as indicated by the ANOVA results. The shapes of the response surface under different [FeSO$_4$]$_0$ conditions present dramatic changes, and the results can be found in Figs. 2c and d. When [FeSO$_4$]$_0$ is 12.5 g/L, the response surface has a concave shape. A pH of 5.0 is a bad choice because the TOC removal rates maintain low values regardless of the [H$_2$O$_2$] concentrations. However, when [FeSO$_4$]$_0$ is 20 g/L, the response surface changes to a convex shape. A pH of 5.0 becomes the optimal condition in this study.
initial pH is 7.0 and $[\text{H}_2\text{O}_2]$ is 5.0 mL/100 mL, Fig. 2e shows that the TOC removal rates are both higher than 60% under both conditions. The influence of $[\text{FeSO}_4]$ condition is not obvious. Similar results can also be obtained at pH 3.0 (Fig. 2a). However, when the initial pH is 5.0, the influence of $[\text{FeSO}_4]$ on the TOC removal rate is remarkable (Fig. 2f). This could be because the lower $[\text{FeSO}_4]$ condition can cause the Fenton reaction to undergo competition with flocculation that is occurring. Under acidic conditions, the Fenton reaction occurs predominately, and under neutral conditions, flocculation becomes important. Therefore, both acidic and neutral conditions are acceptable. However,
under the higher [FeSO\textsubscript{4}]\textsubscript{0} condition, the FeSO\textsubscript{4} concentration is high enough to support both reactions. Furthermore, the high state hydrated ion of Fe(IV) could be generated, and the degradation process is more complicated and efficient. The optimal conditions obtained by this cubic model were an initial pH value of 5.14, 20 g/L [FeSO\textsubscript{4}]\textsubscript{0}, and 5.0 mL/100 mL [H\textsubscript{2}O\textsubscript{2}]. The calculated TOC removal rate is 68.12%.

3.3. The degradation kinetics study

To evaluate the authenticity and reliability of the model, the degradation kinetics study was carried out under two selected conditions: initial pH of 5.0, 20 g/L [FeSO\textsubscript{4}]\textsubscript{0}, and 5.0 mL/100 mL [H\textsubscript{2}O\textsubscript{2}] and initial pH of 3.4, 20 g/L [FeSO\textsubscript{4}]\textsubscript{0}, and 5.0 mL/100 mL [H\textsubscript{2}O\textsubscript{2}]. The results are shown in Fig. 3. TOC removal rates increased steadily under both conditions. After 120 min of degradation, the TOC removal rate reached 65.1% and 61.6% for initial pH values of 5.0 and 3.4, respectively. Moreover, the calculated TOC removal rate values under these two conditions (68.1% for pH of 5.0, 64.8% for pH of 3.4) were also calculated and pointed out.

The calculation and experimental result errors were maintained within 5%. The kinetics study was implemented with the Origin Pro 8 software (v8.0724), and the pseudo-zero-order, first-order, and second-order results are shown in Table 4. The pseudo-zero-order kinetic model is more reliable.

Fig. 2. Estimated response surface of Fenton degradation coking wastewater: (a) actual factor [H\textsubscript{2}O\textsubscript{2}] = 5.0 mL/100 mL; (b) actual factor [H\textsubscript{2}O\textsubscript{2}] = 2.0 mL/100 mL; (c) actual factor [FeSO\textsubscript{4}] = 12.5 g/L; (d) actual factor [FeSO\textsubscript{4}] = 20.0 g/L; (e) actual factor pH = 7.0; (f) actual factor pH = 5.0, temperature: 20°C ± 2°C, reaction time: 120 min, magnetic stirring 150 r/min.
for the highest $R^2$ values of the model. The pseudo-zero-order law was selected to simulate the degradation process because the organic pollutant concentration is high enough to react directly with the hydroxyl radical or Fe(IV) without degradation being disturbed. Therefore, the TOC removal process was not affected by the TOC concentration.

### 4. Conclusion

The FCIE-Fenton combination process was utilized to pretreat coal tar distillation wastewater in this research. Optimal conditions of the FCIE and Fenton processes were obtained by the single factor influence method and RSM. Under optimal conditions of pH of 5.0, a 1:1 mass ratio of Fe:AC, and 40 g/L [Fe]$_0$, the TOC removal rate reached 24.3% under the FCIE process. The Fenton process was utilized to degrade the FCIE-treated coal tar distillation wastewater. The RSM and ANOVA results indicated that the cubic model can be used to predict the wastewater TOC removal rate. The initial FeSO$_4$ concentration is the key factor affecting the Fenton degradation process. The TOC removal rate can reach 65.1% under the optimal conditions of initial pH of 5.0, 20 g/L [FeSO$_4$]$_0$, and 5.0 mL/100 mL [H$_2$O$_2$]$_0$, and the TOC removal rate could reach 68.1% by model calculations. The model calculations and experimental results errors were within 5% under the two different conditions.

In this study, TOC removal followed the pseudo-zero-order kinetic model. The total TOC removal rate of coal tar distillation wastewater can reach 73.6%. The results of this study could be supplemented with technical support for coal tar distillation wastewater pretreatment.

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### References


