Decoloration of waste PET alcoholysis liquid by an electrochemical method

Yanyan Li, Mengjuan Li, Jing Lu, Xiaoqiang Li and Mingqiao Ge

ABSTRACT

Disperse Red 60 simulated polyester alcoholysis liquid decoloration by electro-Fenton with Fe₃O₄ catalyst was studied. The influences of the main operating parameters such as catalyst dosage (0.3–0.9 g/L), current density (60–120 mA/cm²) and pH (1–7) were optimized by response surface methodology (RSM) based on Box–Behnken surface statistical design (BBD). In optimal conditions, the initial concentration of 25 mg/L disperse red polyester alcoholysis liquid was catalyzed by 0.6 g/L Fe₃O₄, and the decoloration efficiency was 97.18% with the current density of 90 mA/cm² and initial pH of 4.6. There was a relative error of 1.18% with the predicted model when the predictive value was 98.25% under the same conditions. In addition, ultraviolet-visible absorption spectra (UV-Vis), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were used to study the degradation mechanism during decoloration. The intermediates were identified and the proposed degradation pathways were investigated by liquid chromatography-mass spectrometry (LC-MS) analysis.

Key words | alcoholysis liquid, decoloration, Disperse Red 60, electrochemical

INTRODUCTION

With the rapid development of the world’s polyester industry, the comprehensive recycling of waste polyester is increasingly causing government-level concern. The efficient method of recycling waste polyester is alcoholysis, i.e. the chemical degradation by ethylene glycol (EG) (Li et al. 2014). In the process of alcoholysis, the molar ratio of EG to PET in practical production is higher than the theoretical value, which leads to excessive consumption of EG in the recovery process (Zahedi et al. 2012). High concentrations of alcohols in the liquid after degradation make the chemical oxygen demand (COD) value higher and the treatment more difficult than in regular wastewater. As a result, recycling is a better treatment for the alcoholysis liquid, compared with discharging it. After recycling, the alcohols in the liquid can be used to degrade the waste polyester again or turned into wetting agent, antifreeze or other chemical raw materials. However, the presence of dyes in polyester fabrics is highly visible and undesirable, and has a negative impact on the yield or color of products in further production after recycling. Thus, it is important to remove color from the alcoholysis liquid.

Methods used to remove color from dye-containing wastewater in the last few years have been based on physical, chemical and biological treatments. Recent research has demonstrated that among the advanced oxidation processes (AOPs) considered, Fenton has become the favored process because of its high performance, inexpensive cost, and mild running conditions. However, the large amount of acid required, the high cost of H₂O₂, and the huge amount of ferrous iron sludge produced are the main obstacles for its large-scale applications in wastewater treatment (Do et al. 2017). To avoid the drawbacks encountered during the Fenton process, the electro-Fenton (EF) process has been developed. In addition, the EF process can continuously produce H₂O₂ in situ from the two-electron reduction of O₂ (Equation (1)). It is considered a clean treatment by minimizing the use of reagent and avoiding parasitic reactions without any production of sludge (Moussset et al. 2016).

The dye structures are attacked and oxidized to less toxic compounds, and even turned into non-toxic chemicals such as CO₂ and H₂O (Equation (2)) by the active hydroxyl radicals produced in the EF process (Le et al. 2016). Among the various catalysts used in the EF process, magnetic iron oxides have attracted a great deal of attention due to their
remarkable properties such as strong recycling performance, large surface area, non-toxicity, biocompatibility, and stability (Yang et al. 2015). As a widely used iron oxide, Fe₃O₄ has shown high catalytic activity in the EF process. Fe²⁺ can be reversibly oxidized and reduced back through electron transfer between Fe²⁺ and Fe³⁺ with minimal Fe²⁺ leaching, as shown in Equation (3). The main reactions of the EF process catalyzed by Fe₃O₄ are presented in Equations (4) and (5).

\[ O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \]  \hspace{1cm} (1)

\[ \cdot OH + RH \rightarrow R \cdot + H_2 \]  \hspace{1cm} (2)

\[ Fe^{3+} + e^- \rightarrow Fe^{2+} \]  \hspace{1cm} (3)

\[ Fe^{3+} + H_2O_2 \rightarrow HO_2 \cdot + H^+ + Fe^{2+} \]  \hspace{1cm} (4)

\[ Fe^{2+} + H_2O_2 \rightarrow \cdot OH + OH^- + Fe^{3+} \]  \hspace{1cm} (5)

Anthraquinone dyes and azo dyes are the main kinds of dispersed dye, which are widely used in dyeing and printing PET textiles. There are many reports focusing on the decoloration of azo dyes by EF (Thiam et al. 2015). Nevertheless, to our knowledge, studies based on EF treatment of anthraquinone dyes have been reported. Compared with azo dyes, anthraquinone dyes are harder to degrade in alcohols as they have a more stable structure. Therefore, identifying the degradation mechanism of anthraquinone dyes in the alcoholysis liquid from the EF is crucial for the recycling of PET alcoholysis liquid. In this paper, Disperse Red 60 (DR 60) was chosen to investigate the degradation of biologically treated coking wastewater (Zhu et al. 2013). Zhu et al. used BBD to optimize Fenton and EF oxidation of biologically treated wastewater (Zhu et al. 2011). BBD is a graphical and statistical technique for improving and optimizing experiments.

In this study, DR 60 simulated polyester alcoholysis liquid was decolorized by the EF process, using magnetic Fe₃O₄ as the catalyst. The main operating parameters: catalyst dosage, current density, and pH were optimized by response surface methodology (RSM) based on BBD. Meanwhile, the changes after decoloration were examined using ultraviolet-visible absorption spectra (UV-Vis), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). Furthermore, liquid chromatography-mass spectrometry (LC-MS) was used to identify the intermediates and suggest the pathways of DR 60 degradation.

**MATERIALS AND METHODS**

**Materials**

DR 60 was purchased from Aladdin Inc. (Shanghai, China). The waste PET fibers for degradation were washed in water and acetone successively, then dried at 70°C for several hours until the weight of the fibers remained constant. Acetone and methanol used in the analysis were high-performance liquid chromatography grade. EG, zinc acetate dehydrate, conc. hydrochloric acid and sodium hydroxide, all of CP grade, were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Fe₃O₄ and NaBF₄ were also supplied by Sinopharm Chemical Reagent Co., Ltd. All solutions were prepared with ultrapure water obtained from an ultrapure water system (Milli-Q Gradient, USA).

**Glycolysis of PET**

Waste PET fibers were chemically depolymerized into bis-(2-hydroxyethyl) terephthalate (BHET) using EG. A 500 mL four-necked round-bottom glass flask equipped with a thermometer, a reflux condenser, a nitrogen catheter, and a magnetic stirrer was charged with 200 g EG, 100 g PET, and 0.2 g zinc acetate dehydrate (Li et al. 2014). As a simulation of real PET fabrics, 1 g DR 60 was added together with PET colorless fibers in the process. The alcohol degradation was processed at 196°C in a nitrogen atmosphere for 3 hours. The degradation products were purified by repeated crystallization to remove BHET and other impurities in the liquid.

**Electrochemical oxidation**

The Fe₃O₄ particles were dispersed in the alcoholysis liquid in an electrolytic cell with two parallel platinum electrodes (10 × 10 × 0.1 mm). In the EF treatment of water solutions, the cathode is usually based on carbon. We used platinum,
with its higher electro-catalytic activity, to replace carbon because it provides a higher current density in liquid with a large amount of EG. The distance between the two electrodes was 1.5 cm. Direct current was provided by a DC-regulated power supply (MCH-305D-II, Shen Zhen Mei Li Instrument Co., Ltd, China), so that the voltage and current could be accurately regulated and measured. Air was injected into the electrolytic cell at a flow rate 0.5 L/min to keep the solution well mixed during the experiments. In the electrochemical oxidation process, samples were taken every 30 min. Each group of data was measured three times to reduce error.

Response surface methodology

In this study, the three-level, three-factor Box–Behnken experimental design (a total of 17 experiments) was used to investigate parameters affecting the removal efficiency of DR 60 dye in alcoholysis liquid by electrochemical oxidation. The factor levels used in this study were 0.3, 0.6, and 0.9 g/L for catalyst dosage (A); 60, 90, and 120 mA/cm² for current density (B); 1, 4, and 7 for the pH (C). The samples were taken before and after 3 hours of the decoloration process. The decoloration efficiency of each sample was tested by UV-Vis analysis three times.

Analysis

The decoloration efficiency was estimated from its absorbance characteristics in the UV–Vis range (350-650 nm), using a UV–Vis spectrophotometer (UV-2600, Shimadzu Co., Ltd, Japan). Measurements were carried out in triplicate. Samples were collected and filtered using 0.45 μm membrane filters before the measurement. The decoloration efficiency could therefore be defined as follows:

\[
\text{Decoloration efficiency (\%)} = \frac{(A_0 - A_t)}{A_0} \times 100\% \quad (6)
\]

in which \(A_0\) and \(A_t\) are the initial absorbance of the alcoholysis liquid and the absorbance at a certain time respectively.

Freeze-dried samples were obtained by keeping the liquid at −20°C for 4 hours, followed by drying in a freeze-dryer at −50°C for 24 hours.

The infrared spectra of liquid were recorded on a FTIR spectrometer (NICOLET IS10, Thermo Fisher Scientific Co., Ltd, USA) with KBr discs. The FTIR spectrum of each sample ranged from 4,000 cm⁻¹ to 600 cm⁻¹, with a resolution of 4.0 cm⁻¹.

TGA curves of freeze-dried samples were obtained using a Q500 TG analyzer (TA Instruments, New Castle, USA), by heating from room temperature to 600°C at a rate of 10°C/min in a nitrogen atmosphere.

The degradation and decoloration intermediates were performed by an LC-MS (Waters Maldi Synapt Q-TOF MS, USA) equipped with BEH C18 column (2.1 × 150 mm, 1.7 μm) at 45°C. The mobile phase was composed of acetonitrile and 0.1% formic acid, at a flow rate of 0.3 mL/min, and the samples were filtered through a 0.45 mm filter membrane with an injection volume of 5 μL.

RESULTS AND DISCUSSION

Maximum absorption

As shown in Figure S1 (available with the online version of this paper), the absorbance of EG and its polymer in the liquid were monitored at a wavelength of 320 nm. Meanwhile, the characteristic peak of DR 60 was observed at 519 nm and 550 nm (El-sayed et al. 2022), all of these coincided with peaks in the alcoholysis liquid. The relationship between the absorbance value and the dye concentration at 550 nm is shown in Equation (7):

\[
\text{Abs}_t = 0.0276C + 0.0038 \quad (7)
\]

in which \(\text{Abs}_t\) and \(C\) are the absorbance and the actual concentration of alcoholysis liquid at a certain time respectively.

Box–Behnken analysis

Mathematical model development

Catalyst dosage, current density, and initial pH were the three main factors that affected the decoloration efficiency of DR 60 in the EF process. In the process of BBD analysis, A, B, and C were used to denote the three factors, respectively. The experimental scheme is shown in Table 1.

The statistical significance of the BBD model was assessed by analysis of variance (ANOVA). The empirical relationship between the response (Y1) and independent variables is reflected in a quadratic regression (Equation (8)):

\[
\begin{align*}
\text{Color removal efficiency (\%)} & = 97.96 + 0.68A + 1.44B + 0.75C - 0.45AB \\
& - 0.79AC + 0.04BC - 1.76A^2 - 2.28B^2 - 5.00C^2 \quad (8)
\end{align*}
\]
As shown in Table 2, the F-value of the model was 95.95, and value of [Prob > F] was less than 0.0001, which indicated that the model was significant (Li et al. 2014). The adequacy of the mathematical model was also evaluated by diagnostic plots such as predicted versus actual (Figure S2, available with the online version of this paper). The data points on this plot lay close to the diagonal line, which indicated adequate agreement between the experimental data and the predicted data (Fu et al. 2009). The multiple correlation coefficients ($R^2 = 0.9841$) indicated that most of the data variation can be described by this model. The predicted multiple correlation coefficient (pred. $R^2 = 0.8381$) was in reasonable agreement with the adjusted multiple correlation coefficient (adj. $R^2 = 0.9635$), implying the significance of the regression too. In summary, the fitted regression equation could describe the relationship between the decoloration efficiency and the three factors appropriately.

Depending on the results of ANOVA in Table 2, values of model terms [Prob > F] < 0.0500 designated that factors were significant (Tak et al. 2015). And the significant model terms for the response (color removal efficiency %) were A, B, C, AC, A², B², and C². The remaining terms AB and BC had less significance for the response, and therefore could be ignored to improve the model. The effective order of three factors was B (current density) > C(pH) > A (catalyst dosage).

**Effect of catalyst dosage**

The effect of catalyst dosage on DR 60 decoloration is shown in Figure 1(a) and 1(c). From the results,

### Table 1 | Box-Behnken design experiments and experimental results

<table>
<thead>
<tr>
<th>Run</th>
<th>A (catalyst dosage)</th>
<th>B (current density)</th>
<th>C (pH)</th>
<th>Actual/%</th>
<th>Predicted/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>90</td>
<td>1</td>
<td>87.18</td>
<td>87.15</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>90</td>
<td>7</td>
<td>92.04</td>
<td>92.06</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>90</td>
<td>4</td>
<td>97.09</td>
<td>97.61</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>90</td>
<td>4</td>
<td>98.44</td>
<td>97.61</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>90</td>
<td>7</td>
<td>91.32</td>
<td>91.85</td>
</tr>
<tr>
<td>6</td>
<td>0.9</td>
<td>60</td>
<td>4</td>
<td>94</td>
<td>93.43</td>
</tr>
<tr>
<td>7</td>
<td>0.6</td>
<td>120</td>
<td>1</td>
<td>86.26</td>
<td>86.22</td>
</tr>
<tr>
<td>8</td>
<td>0.3</td>
<td>90</td>
<td>1</td>
<td>84.1</td>
<td>83.57</td>
</tr>
<tr>
<td>9</td>
<td>0.6</td>
<td>60</td>
<td>1</td>
<td>82.85</td>
<td>83.44</td>
</tr>
<tr>
<td>10</td>
<td>0.9</td>
<td>120</td>
<td>4</td>
<td>95.34</td>
<td>95.4</td>
</tr>
<tr>
<td>11</td>
<td>0.6</td>
<td>120</td>
<td>7</td>
<td>93.5</td>
<td>92.91</td>
</tr>
<tr>
<td>12</td>
<td>0.3</td>
<td>120</td>
<td>4</td>
<td>94.05</td>
<td>94.62</td>
</tr>
<tr>
<td>13</td>
<td>0.6</td>
<td>90</td>
<td>4</td>
<td>97.85</td>
<td>97.61</td>
</tr>
<tr>
<td>14</td>
<td>0.6</td>
<td>90</td>
<td>4</td>
<td>97.46</td>
<td>97.61</td>
</tr>
<tr>
<td>15</td>
<td>0.3</td>
<td>60</td>
<td>4</td>
<td>90.91</td>
<td>90.85</td>
</tr>
<tr>
<td>16</td>
<td>0.6</td>
<td>90</td>
<td>4</td>
<td>97.23</td>
<td>97.61</td>
</tr>
<tr>
<td>17</td>
<td>0.6</td>
<td>60</td>
<td>7</td>
<td>89.9</td>
<td>89.94</td>
</tr>
</tbody>
</table>

As shown in Table 2, the F-value of the model was 95.95, and value of [Prob > F] was less than 0.0001, which indicated that the model was significant (Li et al. 2011). The adequacy of the mathematical model was also evaluated by diagnostic plots such as predicted versus actual (Figure S2, available with the online version of this paper). The data points on this plot lay close to the diagonal line, which indicated adequate agreement between the experimental data and the predicted data (Fu et al. 2009). The multiple correlation coefficients ($R^2 = 0.9841$) indicated that most of the data variation can be described by this model. The predicted multiple correlation coefficient (pred. $R^2 = 0.8381$) was in reasonable agreement with the adjusted multiple correlation coefficient (adj. $R^2 = 0.9635$), implying the significance of the regression too. In summary, the fitted regression equation could describe the relationship between the decoloration efficiency and the three factors appropriately.

### Table 2 | Analysis of variance table [partial sum of squares – type III]

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean square</th>
<th>F value</th>
<th>p-value (Prob &gt; F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>384.04</td>
<td>9</td>
<td>42.67</td>
<td>95.95</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>A – catalyst dosage</td>
<td>3.54</td>
<td>1</td>
<td>3.54</td>
<td>7.96</td>
<td>0.0257</td>
</tr>
<tr>
<td>B – current density</td>
<td>15.82</td>
<td>1</td>
<td>15.82</td>
<td>35.58</td>
<td>0.0006</td>
</tr>
<tr>
<td>C – pH</td>
<td>5.32</td>
<td>1</td>
<td>5.32</td>
<td>11.97</td>
<td>0.0106</td>
</tr>
<tr>
<td>AB</td>
<td>0.80</td>
<td>1</td>
<td>0.80</td>
<td>1.81</td>
<td>0.2206</td>
</tr>
<tr>
<td>AC</td>
<td>3.60</td>
<td>1</td>
<td>3.60</td>
<td>8.10</td>
<td>0.0248</td>
</tr>
<tr>
<td>BC</td>
<td>0.0092</td>
<td>1</td>
<td>0.0092</td>
<td>0.021</td>
<td>0.8898</td>
</tr>
<tr>
<td>A²</td>
<td>12.97</td>
<td>1</td>
<td>12.97</td>
<td>29.17</td>
<td>0.0010</td>
</tr>
<tr>
<td>B²</td>
<td>21.98</td>
<td>1</td>
<td>21.98</td>
<td>49.43</td>
<td>0.0002</td>
</tr>
<tr>
<td>C²</td>
<td>218.39</td>
<td>1</td>
<td>218.39</td>
<td>491.08</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>3.11</td>
<td>7</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of fit</td>
<td>1.93</td>
<td>3</td>
<td>0.64</td>
<td>2.17</td>
<td>0.2338</td>
</tr>
<tr>
<td>Pure error</td>
<td>1.18</td>
<td>4</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected total sum of squares</td>
<td>387.15</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$R^2 = 0.984$, $R_{adj}^2 = 0.964$. 

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Li et al. 2014, Y. Li et al. | Electrochemical decoloration of waste PET alcoholysis liquid | Water Science & Technology | 77.10 | 2018

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Decoloration efficiency improved with catalyst dosage increasing from 0.3 g/L to 0.6 g/L in 3 hours. The higher Fe₃O₄ concentration provided active sites on the catalyst surface, which accelerated the decomposition of H₂O₂ and enhanced leaching of iron (Jiang et al. 2016). However, when the catalyst dosage was further increased from 0.6 g/L to 0.9 g/L, the decoloration efficiency showed no obvious increase. This was because that excess catalyst dosage could reduce the accessible surface for reaction, which was not conducive to the decoloration process.

**Effect of current density**

The effect of current density on DR 60 decoloration is presented in Figure 1(a) and 1(e). From the results, it was found that the increase of current density from 60 to
90 mA/cm² significantly improved decolorization efficiency. Higher current density increased the concentration of \( \text{H}_2\text{O}_2 \), thus increasing the number of \( \cdot \text{OH} \) in the electrolyte, which was conducive to the degradation of DR 60 in the alcoholysis liquid. Furthermore, higher regeneration rate of \( \text{Fe}^{2+} \) could be obtained at the cathode, which accelerated the process of decoloration (Wang et al. 2008). However, there was no significant improvement in decolorization efficiency with further increase in current density from 90 to 120 mA/cm². This could be explained by side reactions, such as the decomposition of \( \text{H}_2\text{O}_2 \) at the anode, or polarization of the electrode (Jiang & Zhang 2007).

**Effect of pH**

The pH value was varied from 1 to 7 to examine its effect on the decolorization efficiency of the alcoholysis liquid catalyzed by \( \text{Fe}_3\text{O}_4 \). The results are shown in Figure 1(c) and 1(e). From the figures, it can be seen that the percentage of color removal increased with increasing pH up to 4.5. This could be explained by the fact that the high acidity enhanced free radical formation, therefore \( \text{DR 60} \) in the liquid could be decomposed (Rosales et al. 2009). The decrease of decolorization efficiency with higher pH could be attributed to the self-decomposition of \( \text{H}_2\text{O}_2 \) decreasing its concentration and the dissolution of iron at high pH.

The interactions between the three factors

The interaction between catalyst dosage (A) and current density (B) is shown in Figure 1(a) and 1(b). It is obvious that the increasing catalyst dosage (A) had a positive effect on color removal when the current density (B) was more than 80 mA/cm². Moreover, the color removal efficiency tended to decline with further increases in catalyst dosage (A) and current density (B). As expected, the increase of catalyst dosage (A) from 0.3 to 0.6 g/L and the current density (B) from 60 mA/cm² to 90 mA/cm² resulted in an increase in color removal from 92% to 98%.

In the contour map in Figure 1(d), the curve is close to elliptic, which shows the significant interaction between catalyst dosage (A) and pH (C). From the above results, the effect of pH (C) was greater than catalyst dosage (A). It was obvious that the increasing catalyst dosage (A) had no obvious contribution to color removal when the pH (C) was higher than 6, so pH exerted a pronounced effect on the catalytic performance of \( \text{Fe}_3\text{O}_4 \). In the process of decoloration, intermediates of dye structure became negatively charged ions by losing luminous units and hydrogen ions. The catalyst \( \text{Fe}_3\text{O}_4 \) had a point of zero charge (pHzPC) of 6.1 (Badruddoza et al. 2013), so the surface of the catalyst was positively charged at pH < pHzPC, neutral at pHzPC, and negative at pH > pHzPC. The electrostatic interaction or repulsion between dye anions and \( \text{Fe}_3\text{O}_4 \) at lower or higher pH may be the predominant reason for the change in catalytic performance. As a result, increasing the catalyst dosage (A) from 0.3 g/L to 0.6 g/L and the pH (C) from 1 to 4.5 resulted in a dramatic increase in color removal from 85% to 98%, but this positive effect abated at higher pH.

The interaction between current density (B) and pH (C) is shown in Figure 1(e) and 1(f). When the current density (B) increased from 60 mA/cm² to 108 mA/cm², the color removal efficiency increased gradually with a pH value between 4 and 6, but there was no obvious improvement of decolorization efficiency in other pH values. As a result, the increase of current density (B) from 60 mA/cm² to 90 mA/cm² and pH (C) from 1 to 4.5 considerably increased color removal efficiency from 85% to 98%.

**Optimization**

In the paper, three operating parameters, i.e. catalyst dosage, current density, and pH, were selected to be optimized, because they all determined the formation rate of hydroxyl radicals, as well as the final component of impurities in the treated liquid. Taking total cost, energy consumption and real conditions into account, we selected the three parameters and set the range of each parameter as: A: catalyst dosage (0.3–0.9 g/L), B: current density (60–120 mA/cm²) and C: pH (1–7). For the purpose of the highest efficiency, decolorization efficiency (Y1) was maximized. Optimal operating conditions to obtain the maximum removal of color were determined as follows: catalyst dosage of 0.64 g/L, current density of 99.07 mA/cm², and pH of 4.6. Under these conditions, the decolorization efficiency was predicted to be 98.25%. Combined with actual conditions, the optimal result was adjusted to 0.6 g/L \( \text{Fe}_3\text{O}_4 \), 90 mA/cm² current density, and initial pH of 4.6 for further research. Followed by additional experiments under the chosen conditions carried out three times, a mean value of color removal was 97.18% after three times, a mean value of color removal was 97.18% in actual operation. The good correlation between color removal rate in verification experiments and the predicted value indicated the reliability of BBD. The model could be effectively used to optimize the parameters in the decoloration of alcoholysis liquid.

The cost of \( \text{Fe}_3\text{O}_4 \) was 5.8 euros for treating each cubic meter of dye, including the alcoholysis liquid. It was essential to evaluate the reusability of \( \text{Fe}_3\text{O}_4 \) and the energy
consumption in decoloration due to economic demand for sustainability. The effect of recycling times of Fe₃O₄ on electrochemical performance was repeated five times under the optimum conditions. As shown in Figure S3 (available with the online version of this paper), the catalytic activity of Fe₃O₄ remained constant and no obvious deactivation was observed after being used five times. The decoloration efficiency of the alcoholysis liquid was still over 91%. From the results above, the magnetic catalyst Fe₃O₄ had good reusability in the electrochemical process. The cost of Fe₃O₄ could be saved by reuse.

Considering the energy-related experimental conditions for the maximum decoloration efficiency, the required electrical energy consumption (EEC) per cubic metre of the treated alcoholysis liquid was calculated by Equation (9) (Ahmadi et al. 2016):

\[
EEC \left( \frac{kWh}{m^3} \right) = \frac{I \cdot t \cdot V}{V_t} \times 10^{-3}
\]

(9)

where EEC is electrical energy consumption (kWh/m³), I is the applied current (A), t is time (h), V is voltage (v) and Vₜ is the volume of electrolyte (m³). As a result, under the optimized conditions with the current of 90 mA, the voltage of 10 V and the volume of 60 mL, 45 kWh/m³ electrical energy was required to remove the color of the alcoholysis liquid by 97.18% in 3 hours.

UV-Vis analysis

The UV–Vis absorption spectra changes of the alcoholysis liquid during decoloration process are depicted in Figure S4 (available with the online version of this paper).

It can be seen that the characteristic absorbance peaks of DR 60 dramatically decreased with the reaction time, indicating a rapid decomposition process of the luminous units in DR 60 molecules (El-sayed et al. 2012). After 3 hours of decoloration by the EF process, 97% of visible color was removed. The conjugate structure in DR 60 was destroyed to other products with no absorption under UV conditions at the wavelength of 300 nm to 600 nm.

FTIR analysis

The products before and after decoloration were examined after drying in a freeze-dryer at −50°C for 24 hours. The FTIR results are shown in Figure S5 (available with the online version of this paper).

According to the infrared spectrum, some absorption peaks disappeared after decoloration, but some new absorption peaks formed at the same time. The absorption peaks at 1,617 cm⁻¹, 1,150 cm⁻¹, and 1,410 cm⁻¹ were benzene ring vibrations (Shen et al. 2017). The stretching vibration bands at 2,879 cm⁻¹ and 2,963 cm⁻¹ were related to the symmetric and asymmetric C-H bonds, respectively, which became weak after decoloration (Bansode et al. 2017). In the curves, the C=O vibration (1,690 cm⁻¹), the C-O vibration (1,035 cm⁻¹) and the (CH₂)ₙ vibration (728 cm⁻¹) were observed, but all of them decreased after the reaction (Khataee et al. 2016). The characteristic peaks above suggested that 3 hours of electrochemical treatment failed to totally degrade the anthraquinone structure of DR 60 in alcoholysis liquid. Combined with the changes of UV-vis curves, some fragments of dye disappeared, but the new by-product with similar functional group constantly appeared during the process of decoloration. Other analyses were necessary to study the products after decoloration.

**Figure 2** | Changes of thermogravimetric curves of DR 60 in the decoloration process and pure DR 60.
The liquids before and after decoloration were freeze-dried and examined by TGA. The TGA curves are shown in Figure 2(a).

After degradation in the alcoholysis liquid, the weight loss of dyes occurred at 200°C and 400°C respectively. The decomposition temperature of DR 60 was 371°C in Figure 2(b), but it was not in the curve before the electrochemical...

**Figure 3**  | (a–d) Changes of total ions chromatogram and mass spectrometry of DR 60 in the degradation process. (e–g) Changes of total ions chromatogram and mass spectrometry of DR 60 in the decoloration process. (h) The UV absorption of DR 60 before and after the decoloration process at the wavelength of 550 nm.

**TGA**

The liquids before and after decoloration were freeze-dried and examined by TGA. The TGA curves are shown in Figure 2(a).
process, so it was predicted that the DR 60 structure was decomposed before decoloration.

After decoloration, the temperature for weight loss was not as clear as the previous one. The weight loss of components in temperature intervals of 200–300°C, 380–450°C, and 450–600°C had decreased. Meanwhile, the increased component at 100°C indicated that DR 60 had been decomposed again into simpler products.

**LC-MS analysis**

In order to understand the degradation pathway of DR 60 in the process of alcoholysis degradation, LC-MS analysis was carried out. The total ions chromatogram is shown in Figure 3(a), combined with mass spectrum at different retention time Figure 3(b)–3(d).

It was observed that the pattern of mass spectrometry showed a peak at 8.60 min, m/z of 330.2, confirming the existence of DR 60 (C_{20}H_{13}NO_{4}) molecule [M-H]. However, the peak disappeared and converted into fragments at 7.78 min, 5.28 min, and 4.92 min. At 7.78 min and 5.28 min, the strongest line observed at m/z of 254, which was Product 1 (C_{14}H_{9}NO_{4}), attributed to the removal of the benzene ring from DR 60 structure [M-C_{6}H_{6} + H]. Another line at 7.78 min with m/z 299 was considered to be Product 2 (C_{20}H_{12}O_{3}), attributed to the removal of hydroxy and amidogen from the DR 60 structure [M-NH_{2}OH + H]. The strongest line at 4.92 min in Figure 3(g) indicated the existence of m/z 207, which was the molecule of anthraquinone (Product 3: C_{14}H_{8}O_{2}), produced by further decomposition of DR 60.

The liquids before and after decoloration were examined by LC-MS analysis. The results were shown in Figure 3(e)–3(h).

Compared with the total ions chromatogram before decoloration in Figure 3(e), the one after decoloration depicted the decrease in intensity of the peak at 7.78 min, corresponding to the removal and decomposition of Product 1 (C_{14}H_{9}NO_{4}) and Product 2 (C_{20}H_{12}O_{3}). Furthermore, as shown in Figure 3(h), the structure under the UV light of 550 nm appeared at 7.78 min and disappeared after the decoloration process, which was related to the decomposition of luminous units and coincided with UV-vis absorption results.

Before decoloration, the strongest line of Figure 3(g) observed at 4.92 min had the m/z of 207 (Product 3: C_{14}H_{8}O_{2}), followed by the m/z of 165 (Product 4: C_{8}H_{6}O_{4}), results from the degradation of Product 3 (Le et al. 2016). After decoloration, the line of 207 and 165 decreased and converted to line 122, Product 5 (C_{7}H_{6}O_{2}), which appeared from the removal of carboxyl in Product 4. Meanwhile, the increasing peak at 4.25 min shown in Figure 3(f) was observed with m/z of 121 (Product 5: C_{7}H_{6}O_{2}) and 77 (Product 6: C_{6}H_{6}), corresponding to decomposition of the above products to create benzene ring.

Based on the data above, the predicted degradation pathway of DR 60 was described in Figure 4. The possible degradation mechanism mainly involved two processes.
In the process of alcoholysis degradation, DR 60 was partly decomposed at a high temperature of 196°C, the removal of hydroxy and amidogen generated the new Product 1, and the removal of benzene ring generated the new Product 2. After further degradation, Products 1 and 2 were decomposed to the anthraquinone structure (Product 3).

In the process of decoloration, Product 2 was totally decomposed. A large amount of Product 1 had turned into the anthraquinone structure (Product 3) for further degradation. After 3 hours of decoloration, the decomposition of Product 3 created Product 4. At the same time the removal of carboxyl from Product 4 created Product 5 and increased Product 6 (Nidheesh & Gandhimathi 2012; Khataee et al. 2016; Le et al. 2016).

**CONCLUSIONS**

The EF process was developed to investigate the decoloration efficiency of DR 60 simulated alcoholysis liquid. The main operating parameters during the process had been optimized by RSM based on BBD. After optimization, conditions were adjusted to 0.6 g/L Fe₃O₄, 90 mA/cm² current density and initial pH of 4.6, with a maximum decoloration efficiency of 97.18%.

UV-Vis, FTIR, and TGA analyses showed that the possible degradation mechanisms mainly involved two processes. In the process of alcoholysis degradation, DR 60 was partly decomposed by the removal of the benzene ring, amidogen and hydroxy. In the process of decoloration, the structure of DR 60 and its products were turned into small fragments like phthalic acid and benzene rings.

According to this study, based on RSM analyses and degradation mechanisms, it is reasonable to regard the EF process as a promising technology for the decoloration of anthraquinone dyes in alcoholysis liquid.

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**REFERENCES**


Li, M., Huang, Y., Yu, T., Chen, S., Ju, A. & Ge, M. 2014 Chemical recycling of waste poly(ethylene terephthalate) fibers into azo disperse dyestuffs. RSC Advances 4(87), 46476–46480.


Yang, X., Chen, W., Huang, J., Zhou, Y., Zhu, Y. & Li, C. 2015 Rapid degradation of methylene blue in a novel heterogeneous Fe₃O₄@rGO@TiO₂-catalyzed photo-Fenton system. Scientific Reports 5, 10632.


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