Parametric and energy consumption optimization of Basic Red 2 removal by electrocoagulation/egg shell adsorption coupling using response surface methodology in a batch system

Helder Pereira de Carvalho, Jiguo Huang, Meixia Zhao, Gang Liu, Xinyu Yang, Lili Dong and Xingjuan Liu

ABSTRACT

In this study, response surface methodology (RSM) model was applied for optimization of Basic Red 2 (BR2) removal using electrocoagulation/eggshell (ES) coupling process in a batch system. Central composite design was used to evaluate the effects and interactions of process parameters including current density, reaction time, initial pH and ES dosage on the BR2 removal efficiency and energy consumption. The analysis of variance revealed high $R^2$ values (>85%) indicating that the predictions of RSM models are adequately applicable for both responses. The optimum conditions when the dye removal efficiency of 93.18% and energy consumption of 0.840 kWh/kg were observed were 11.40 mAh/cm² current density, 5 min and 3 s reaction time, 6.5 initial pH and 10.91 g/L ES dosage.

Key words | adsorption, Basic Red 2, eggshell, electrocoagulation, optimization

INTRODUCTION

The increasing use of dyes in various industrial applications has resulted in the discharge of toxic dye effluents into the water streams causing serious environmental pollution (Kousha et al. 2012). These poisonous materials absorb the oxygen in the water (Mahmoodi & Arami 2009; Pirkaramia et al. 2013), and moreover are a dramatic source of esthetic pollution and perturbation in aquatic life (Parsa & Abbasi 2011; Daneshvar et al. 2011). Various studies have been reported in the literature (Can et al. 2005, 2006) on color removal techniques which can be classified into physical or physicochemical, chemical, biological and electrochemical. An increasing interest has been shown in combining process such as electrocoagulation (EC), electro-oxidation, adsorption, ozonation (De Oliveira et al. 2011) and reverse osmosis (Bhaskar Raju et al. 2008).

EC has been used for decades to treat different types of wastewater (Mollah et al. 2004). It is a process consisting of creating flocs of metallic hydroxides within the effluent to be cleaned, by electro dissolution of soluble anodes usually aluminum or iron (Ricordel & Djelal 2014). The advantages of EC include high removal efficiency, a compact treatment facility, relatively low cost, and the possibility of complete automation (Vasudevan & Lakshmi 2011). However, the formation of an impermeable oxide film on the cathode (Avsar et al. 2013), which results in higher energy consumption and lower efficiencies (Groterud & Smoczynski 1986; Mollah et al. 2001, 2004; Holt et al. 2005; Avsar et al. 2007), is considered as the main disadvantage of conventional EC (Avsar et al. 2007). One of the ways to enhance conventional EC systems besides the polarity changing of electrodes (Secula et al. 2013) has been suggested by Narayanan and Ganesan, who reported the use of granular active carbon which might be a more efficient and faster separation technique compared to conventional EC (Narayanan & Ganesan 2009). Similar studies have also been reported by Secula et al. (2012, 2013). On the other hand, coupling the EC technique with eggshell (ES) adsorption was not reported before and it deserves attention by the fact that ES is an effective and low-cost adsorbent.
and therefore ideal for application in developing countries. Furthermore, this method will economically reduce the removal time of dye effluents.

The main aim of the present work was to optimize Basic Red 2 (BR2) dye removal from aqueous solution by EC/ES adsorption coupling using response surface methodology (RSM). For this purpose, central composite design (CCD) was used to develop a mathematical correlation between responses (BR2 dye removal efficiency and energy consumption) and process variables (current density, retention time, initial pH and ES dosage). The optimal conditions for dye removal and energy consumption were also determined from the model obtained via experimental data.

**EXPERIMENTAL**

**Materials**

Discarded ESs were collected from dining hall of Jilin University. To prevent decomposition, ESs were first washed in tap water, then boiled in distilled water and dried at 105°C in a hot air oven for 2 h (Elkady et al. 2011). After that, the dried ESs were grinded by using a blender, and finally were sieved to a particle size of 60 meshes. The sieved materials were stored in a scaled bottle and used without further chemical or physical treatment.

BR2 was purchased from Shanghai Jinsui Biotechnology Co., Ltd (Shanghai, China) and was used without any purification. Its characteristics and chemical structure are presented in Table 1.

Solutions of BR2 (volume 1 L) were prepared before each experimental run by dissolving certain amounts of dye in ultrapurified water.

To adjust the solution conductivity, a weight of 1 g of NaCl (Beijing Shiji, Beijing Chemical Works, China) was dissolved in synthetic dye solutions (volume 1 L).

**Electrocoagulation experiments and energy consumption**

The EC reactor consisted of a parallel-plate EC cell provided with two facing electrodes and with six perforated tubes attached to its bottom to maintain a uniform gas flow and stirring into the cell. The experimental set-up used in this study is shown in Figure 1. The effective electrode area was 97 cm².

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**Table 1 | Characteristics and chemical structure of BR2**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour Index Number</td>
<td>50240</td>
</tr>
<tr>
<td>Synonyms</td>
<td>Safranin O; 3,7-Diamino-2,8-dimethyl-5-phenylphenazinium chloride; Safranin T</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₂₀H₁₉ClN₄</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>350.85</td>
</tr>
<tr>
<td>Chemical Abstracts Service Number</td>
<td>477-73-6</td>
</tr>
<tr>
<td>Molecular structure</td>
<td>Azine class</td>
</tr>
<tr>
<td>Solubility</td>
<td>Water + Alcohol</td>
</tr>
<tr>
<td>Dye content</td>
<td>95%</td>
</tr>
<tr>
<td>Chemical structure</td>
<td><img src="image" alt="Chemical structure of BR2" /></td>
</tr>
</tbody>
</table>

---

**Figure 1 | EC experimental set-up: 1 – anode (aluminum); 2 – cathode (stainless steel); 3 – reactor; 4 – aquarium air pumps with two outlets; 5 – perforated tubes; 6 – DC power supply.**
The anode and cathode were positioned vertically and fixed at a distance of 1 cm from each other. The electrodes were aluminum and stainless steel plate connected to a digital DC power supply (WYJ, 0–50 V; 0–5 A; DC Regulated Power Supply Double Way Output, TESTMART, Shanghai, China). The electrodes were polished with fine-grained emery paper, washed with 1 N H₂SO₄ and then with distilled water before each run. All the runs were performed at room temperature 20 ± 1 °C.

The experiments were carried out in batch mode. In each run, 1,000 cm³ of 50 mg/L dye solution was placed in the electrochemical cell and three aquarium air pumps with two outlets (SOBO SB-648, maximum output: 2 × 4 L/min, Zhejiang, China) were used to supply needed air to the bottom of the reactor through the perforated tubes. Then, a certain amount of ES was added to the solution. Thereafter, the initial pH of the solution (adjusted by H₂SO₄ and NaOH (Beijing Shijii, Beijing Chemical Works, China), and controlled using a PHS-3E pH meter (Shanghai INESA and Scientific Instrument Co., Ltd, China)) and current density were set to a desired value proposed with RSM according to Table 2.

At different electrolysis times proposed in Table 2, approximately 5 mL of sample was taken, allowed to settle, filtrated by means of Wattman 0.45 μm filters, and then analyzed.

The concentration of BR2 was determined at 520 nm using a UV/VIS Spectrophotometer (Shanghai Sunny Hengping Scientific Instrument Co., Ltd, China).

The color removal efficiency (Y (%)) was calculated from:

\[
Y = \frac{C_o - C_i}{C_o} \times 100
\]

where \(C_o\) is the concentration of dye before EC (mg/L), and \(C_i\) is the concentration of dye after \(t\) min of EC (mg/L).

The concentration of dye was determined using the initial calibration curve which was recorded after spectrophotometric measurement of the solution absorbance for dye standard concentration at the specific wavelength corresponding to the maximum absorption of dye.

Energy consumption (\(E_{\text{con}}\)) per kilogram of dye molecule was calculated using Equation (2).

\[
E_{\text{con}} = \frac{U \times I \times t_{\text{EC}}}{C_o}
\]

where \(E_{\text{con}}\) is specific electrical energy consumption per gram of dye (kWh/kg), \(C_o\) is initial dye concentration (kg), \(I\) is current (A), \(U\) is cell voltage (V), \(t_{\text{EC}}\) is electrolysis time (h).

Experimental design and data analysis

In this work, optimization of BR2 dye removal using CCD, 31 experiments consisting of 16 factorial points, eight axial points (\(a = 2\)) and seven replicates at the center point were designed. According to the obtained experimental data, levels of four main parameters investigated in this study are presented in Table 2. For statistical calculations, each independent parameter was coded in five levels (−2, −1, 0, 1 and 2) as \(x_i\) according to Equation (3):

\[
x_i = \frac{(X_i - X_0)}{\Delta X}
\]

where \(X_0\) is the value of \(X_i\) (selected parameters) at the center point and \(\Delta X\) represents the step change. BR2 removal efficiency and energy consumption were taken as the responses of the experiments (\(Y_i\)) according to Equation (4):

\[
Y_i = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} b_{ij} x_i x_j + \varepsilon
\]

where \(b_0, b_i, b_{ii}, b_{ij}\) are the constant coefficient, the regression coefficient for linear effects, the quadratic coefficient and the interaction coefficient, respectively; \(x_i, x_j\) are factors (independent variables) and \(\varepsilon\) is error.

The statistical and mathematical Minitab software version 17.1.0 was used for regression and graphical analysis of the experimental data obtained. The accuracy of the fitted models was justified through analysis of variance (ANOVA) and the coefficient of determination, \(R^2\).

RESULTS AND DISCUSSION

Development and analysis of the model

In order to study the combined effect of process variables, experiments were performed for different
combinations of the physical parameters. The experimental design matrix with observed and predicted results for BR2 removal efficiency and energy consumption are presented in Table 3.

Using the experimental results, the following empirical relationship between the BR2 removal efficiency ($Y_1$), energy consumption ($Y_2$) and independent parameters was established.

$$Y_1 = -198.5000 + 16.67000x_1 + 0.16600x_2 + 51.80000x_3 + 7.13000x_4 - 0.61660x_1^2 - 0.00108x_2^2 - 3.41600x_3^2 - 0.36000x_4^2 + 0.01670x_1x_2 - 0.70300x_1x_3 + 0.17350x_1x_4 - 0.02830x_2x_3 - 0.00540x_2x_4 - 0.20500x_3x_4$$

(5)
\[ Y_2 = 14.62000 - 1.01000x_1 - 0.25100x_2 - 2.37000x_3 \\
- 0.31300x_4 + 0.04010x_1^2 + 0.00098x_2^2 \\
+ 0.14850x_1^2 + 0.01191x_1x_2 + 0.03551x_1x_2 \\
+ 0.02260x_1x_3 - 0.00870x_1x_4 + 0.00560x_2x_3 \\
- 0.00161x_2x_4 + 0.02560x_3x_4 \] (6)

In principle, larger the magnitude of \( t \) (used to determine the significance of the regression coefficients of the parameters) and smaller the value of \( p \) (used as a tool to check the significance of each interaction between the parameters), the more significant is the corresponding coefficient term (Montgomery 1997). Estimated \( t \)- and \( p \)-values of the parameters for BR2 removal efficiency and energy consumption are presented in Table 4. It was observed that the coefficients for the current density \( (x_1) \) and initial pH of dye solution \( (x_3) \) (\( p \)-values of 0.000 and 0.011, respectively) except reaction time \( (x_2) \) and ES dosage \( (x_4) \) \( (p \geq 0.05) \) were significant to the response of BR2 removal efficiency. The same conclusion was found in all square terms \( (p = 0.000) \) except \( x_2^2 \) \( (p \geq 0.05) \), which were highly significant, whereas all interaction terms except \( x_1x_3 \) \( (p \)-value of 0.003) were not significant for this response. Also observed in Table 4 was a high significance of the coefficients for the current density and reaction time \( (p = 0.000) \) whereas initial pH of dye solution and ES dosage were not significant for energy consumption. Furthermore, all square and interaction terms except \( x_1^2 \) and \( x_1x_2 \) \( (p \)-values of 0.002 and 0.000, respectively) were not significant for this response.

The results of the ANOVA for BR2 removal efficiency and energy consumption presented in Table 5 justified the adequacy of the models. According to this table, in both developed models, the \( p \)-values of 0.000 \( (p \leq 0.05) \) for regression model equations imply that the fitted second-order polynomial models for the experimental results are suitable (at the confidence level of 95%). Moreover, the comparison of observed and predicted values of BR2 removal efficiency and energy consumption illustrated in Figure 2, which showed the \( R^2 \) and Adj-\( R^2 \) values of 94.83 and 90.31% for dye removal efficiency and 97.68 and 95.66% for energy consumption, confirmed the accuracy of the models.

<table>
<thead>
<tr>
<th>Term</th>
<th>Dye removal efficiency (%)</th>
<th>Energy consumption (kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( t )</td>
<td>( p )</td>
</tr>
<tr>
<td>Constant</td>
<td>51.37</td>
<td>0.000</td>
</tr>
<tr>
<td>( x_1 )</td>
<td>2.87</td>
<td>0.011</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>0.67</td>
<td>0.514</td>
</tr>
<tr>
<td>( x_3 )</td>
<td>-4.75</td>
<td>0.000</td>
</tr>
<tr>
<td>( x_4 )</td>
<td>1.78</td>
<td>0.094</td>
</tr>
<tr>
<td>( x_1^2 )</td>
<td>-10.71</td>
<td>0.000</td>
</tr>
<tr>
<td>( x_2^2 )</td>
<td>-0.18</td>
<td>0.857</td>
</tr>
<tr>
<td>( x_3^2 )</td>
<td>-8.35</td>
<td>0.000</td>
</tr>
<tr>
<td>( x_4^2 )</td>
<td>-9.77</td>
<td>0.000</td>
</tr>
<tr>
<td>( x_1x_2 )</td>
<td>0.68</td>
<td>0.506</td>
</tr>
<tr>
<td>( x_1x_3 )</td>
<td>-3.43</td>
<td>0.003</td>
</tr>
<tr>
<td>( x_1x_4 )</td>
<td>2.81</td>
<td>0.012</td>
</tr>
<tr>
<td>( x_2x_3 )</td>
<td>-0.43</td>
<td>0.672</td>
</tr>
<tr>
<td>( x_2x_4 )</td>
<td>-0.27</td>
<td>0.789</td>
</tr>
<tr>
<td>( x_3x_4 )</td>
<td>-1.25</td>
<td>0.230</td>
</tr>
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</table>

Table 5 | ANOVA for BR2 removal efficiency (%) and energy consumption (kWh/kg)

<table>
<thead>
<tr>
<th>Source</th>
<th>DF*</th>
<th>SS*</th>
<th>Adj-MS</th>
<th>f-value</th>
<th>p-value</th>
<th>SS*</th>
<th>Adj-MS</th>
<th>f-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>14</td>
<td>7,121.79</td>
<td>508.70</td>
<td>20.98</td>
<td>0.000</td>
<td>559.169</td>
<td>39.941</td>
<td>48.22</td>
<td>0.000</td>
</tr>
<tr>
<td>Residual error</td>
<td>16</td>
<td>388.01</td>
<td>24.25</td>
<td>-</td>
<td>-</td>
<td>13.253</td>
<td>0.828</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lack-of-fit</td>
<td>10</td>
<td>375.69</td>
<td>37.57</td>
<td>18.30</td>
<td>0.001</td>
<td>13.253</td>
<td>1.325</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure error</td>
<td>6</td>
<td>12.32</td>
<td>2.05</td>
<td>-</td>
<td>-</td>
<td>0.000</td>
<td>0.000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>30</td>
<td>7,509.81</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>572.423</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: BR2 removal efficiency – \( R^2 = 94.83 \%), adjusted \( R^2 = 90.31 \% \); energy consumption – \( R^2 = 97.68 \%), adjusted \( R^2 = 95.66 \%).

*Degree of freedom.

*Sum of squares.

*Adjusted mean square.
In addition to the regression coefficients, the adequacies of the models were evaluated by the residuals (differences between observed and predicted response values). Normal probability plots are a suitable graphical method for judging the normality of the residuals (Khataee et al. 2010). Normal probability and residual versus fitted values plots for BR2 removal efficiency and energy consumption are illustrated in Figure 3. As shown in Figure 3(a) and 3(c), the normality assumption for the models was relatively satisfied as the points in the plots form a fairly straight line. For a model
to be reliable, no series of increasing or decreasing points, patterns such as increasing residuals with increasing fits and a predominance of positive or negative residuals should be found in the plot of residuals versus fits (Taheri et al. 2013). Both plots in Figure 3 illustrate that the models are adequate to describe the BR2 removal and its relative energy consumption by RSM.

**Determination of importance of model terms**

In order to determine the important and effective terms of the developed models, the corresponding values of Student’s t distribution and related p-values (given in Table 4) were used. As is known, if the p-value is less than 0.05 (at the significance level of 95%), then the coefficient in the model is statistically significant. Therefore, in Equations (5) and (6), the coefficients with p-value greater than 0.05 were eliminated and the mentioned equations were rewritten to yield Equations (7) and (8) in conformity with the results presented in Table 4.

\[
Y_1 = -198.50000 + 51.80000x_3 - 0.61660x_1^2
- 3.41600x_3^2 - 0.36000x_4^2 - 0.70300x_1x_3
\]

(7)

\[
Y_2 = 14.62000 - 1.01000x_1 - 0.25100x_2 + 0.04010x_1^2
+ 0.03551x_1x_2
\]

(8)

**Response surface and counter plotting for evaluation of operational parameters**

For a greater perception of the parameters and their interactive effects on the BR2 removal, three-dimensional response surface and two-dimensional counter plots are

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**Figure 4** The response surface plots as a function of: (a) current density and reaction time; (b) initial pH and reaction time; (c) reaction time and ES dosage; (d) initial pH and current density; (e) ES dosage and current density; (f) ES dosage and initial pH. Hold values: current density = 11 mA/cm², reaction time = 27.5 min, initial pH = 6.5 and ES dosage = 10 g/L.
represented in Figures 4 and 5, respectively, for BR2 removal efficiency (%) and Figure 6 for energy consumption (kWh/kg). As shown in Figure 4(a), the increase of current density and reaction time improved BR2 removal efficiency which could be due to the increase in the amount of coagulants released from the anode (Amani-Ghadim et al. 2015), and the maximum dye removal was achieved at 11 mA/cm² and 27.5 min. However, higher values of current density above 11 mA/cm² led to decreasing dye removal efficiency. On the other hand, low removal efficiencies of dye were also found for ES dosage values above 10 g/L. It is be due to excessive amount of coagulant/adsorbent, which may provoke a not very effective procedure (Beltrán-Heredia & Martín 2008) and consequently lowering the dye removal efficiency. It is also observed from Figure 4(d) that the BR2 removal efficiency by EC/ES coupling process is highly dependent on initial pH. It is also shown (Figure 4(d)) that the coupling process showed higher dye removals at pH values close to neutral and the maximum removal was obtained when the initial pH of solutions was 6.5. It is because at neutral pH, Al (OH)₃ is stable and insoluble in the water and available for pollutant adsorption from water (Basiri Parsa et al. 2014). As illustrated in Figure 6, energy consumption increased by increasing current density and reaction time and, as is shown in Equation (8), the initial pH of dye solution and ES dosage are not as important as current density and reaction time in energy consumption. In other words, the current density and reaction time were the most important factors in energy consumption.

Optimization of the electrocoagulation/ES coupling process for Basic Red 2 removal

The main objective of the optimization in designing experiments using RSM is to determine the optimum values of parameters for BR2 removal with EC/ES coupling process from the models obtained. EC/ES coupling of BR2 was optimized for maximizing the Y₁ while minimizing the Y₂ simultaneously. Minitab 17 software was used to get the optimum values of the factors from the models developed by CCD to maximize the BR2 removal efficiency and minimize the energy consumption. The optimum values of the parameters, the predicted and observed and the response values for BR2 removal efficiency and energy consumption are given in Table 6.
The experiments with predicted values of the parameters were conducted to verify the optimized values of the parameters, and they were carried out in triplicate. The average values of the responses were found to be 93.18% for BR2 removal efficiency, and 0.840 kWh/kg of dye removed for energy consumption, which was in an acceptable concordance with the predicted values.

CONCLUSION

In this research, RSM was applied for parametric and energy consumption optimization of BR2 removal by electrocoagulation/ES coupling process in a batch system. A CCD was applied to give the experimental conditions for removing the dye. The effects of the parameters including current density, reaction time, initial pH and ES dosage were evaluated by the response surface and counter plots. The response surface models developed in this work for

![Figure 6](https://iwaponline.com/wst/article-pdf/73/11/2572/460516/wst073112572.pdf)

**Table 6.** The optimum values of parameters for the maximum BR2 removal efficiency and minimum energy consumption

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Optimum values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density</td>
<td>mA/cm²</td>
<td>11.40</td>
</tr>
<tr>
<td>Reaction time</td>
<td>min</td>
<td>5 min and 3 s</td>
</tr>
<tr>
<td>Initial pH</td>
<td>–</td>
<td>6.05</td>
</tr>
<tr>
<td>ES dosage</td>
<td>g/L</td>
<td>10.91</td>
</tr>
<tr>
<td>BR2 removal efficiency (predicted)</td>
<td>%</td>
<td>94.76</td>
</tr>
<tr>
<td>BR2 removal efficiency (observed)</td>
<td>%</td>
<td>93.18</td>
</tr>
<tr>
<td>Energy consumption (predicted)</td>
<td>kWh/kg</td>
<td>0.435</td>
</tr>
<tr>
<td>Energy consumption (observed)</td>
<td>kWh/kg</td>
<td>0.840</td>
</tr>
</tbody>
</table>
predicting BR2 removal efficiency and energy consumption were considered to be adequately applicable. ANOVA in both responses revealed high $R^2$ values of 94.85% for dye removal efficiency and 97.68% for energy consumption, ensuring a satisfactory adjustment of the second-order regression model with the experimental data. The optimum conditions when the maximum dye removal efficiency and energy consumption (93.18% and 0.840 kWh/kg of dye removed, respectively) were achieved were 11.40 mA/cm$^2$ current density, 5 min and 3 s reaction time, 6.5 initial pH and 10.91 g/L ES dosage.

According to the results of this work, the RSM model is an effective experimental design tool for parametric and energy consumption optimization of BR2 using EC/ES coupling process.

**AUTHOR DISCLOSURE STATEMENT**

No competing financial interests exist.

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