Optimisation of reactive dye removal by sequential electrocoagulation–flocculation method: comparing ANN and RSM prediction

M. Mohsen Nourouzi, T. G. Chuah and Thomas S. Y. Choong

ABSTRACT

The removal of Reactive Black 5 dye in an aqueous solution by electrocoagulation (EC) as well as addition of flocculant was investigated. The effect of operational parameters, i.e. current density, treatment time, solution conductivity and polymer dosage, was investigated. Two models, namely the artificial neural network (ANN) and the response surface method (RSM), were used to model the effect of independent variables on percentage of dye removal. The findings of this work showed that current density, treatment time and dosage of polymer had the most significant effect on percentage of dye removal (p < 0.001). In addition, interaction between time and current density, time and dosage of polymer, current density and dosage of polymer also significantly affected the percentage of dye removal (p = 0.034, 0.003 and 0.024, respectively). It was shown that both the ANN and RSM models were able to predict well the experimental results (R^2 > 0.8).

Key words | artificial neural network (ANN), electrocoagulation (EC), energy consumption, flocculation, optimisation, response surface method (RSM)

NOMENCLATURE

- C: Metal concentration (gL^{-1})
- I: Current (A)
- E: Energy consumption (kWhm^{-3})
- E_{A}^{0}: Standard anode potential
- E_{C}^{0}: Standard cathode potential
- F: Faraday's constant (96,486 Cmol^{-1})
- f: Function
- k: Number of numerical factors
- t: Time (min)
- M: Molecular weight (gmol^{-1})
- U: Voltage (V)
- W: Volume of the electrochemical cell (L)
- x_i: Variable
- y_i: Variable
- \bar{y}_i: Mean of y_i
- \hat{y}_i: Predicted value of y_i
- Z: Chemical equivalence
- \beta: Measure of the effects of variables

INTRODUCTION

In Malaysia, one of the main pollution sources of wastewater is generated from batik industry that comes from the dyeing processes. Remazol reactive dyes are commercially a very important class of textile dyes. Approximately 60–70% of manufactured dyes belong to azo compounds (Kim et al. 2008). Unadsorbed dyes, which enter the wastewater through processing, are significant and difficult to treat. Due to more stringent legislation, several studies have been performed to find an effective and economical way for treatment of dye-containing wastewater. Those studies can be categorised into physical, chemical and biological methods. Table 1 presents the advantages and disadvantages of these main treatment methods.

Electrocoagulation

The usage of electrocoagulation (EC) began before the 20th century when a plant was built in London in 1889 (Vik et al. 1984). Several studies have been initiated for
treatment of wastewaters using EC during past century. The EC has some advantages over the other methods, such as having simple equipment and operation, high efficiency, low settleable sludge, more separable flocs, low dissolved solids, ability to remove the smallest colloidal particles, non-necessity of chemicals, less maintenance and having potential to be used in rural area. On the other hand, EC has some disadvantages such as having dissolved sacrificial electrodes, expense of electricity and the need of high conductivity (Yousaf et al. 2001). The usage of EC has been increased along with minimising electrical power consumption and maximising effluent throughput rates. EC has been applied successfully in treating textile wastewater. EC is a complex process including multiple operating mechanisms that result in removing pollutants. There are a lot of hypotheses for key mechanisms and reactor configurations. Electrochemistry, coagulation and flotation are identified as the key foundation science for electrocoagulation (Mollah et al. 2001).

**Electrochemistry**

An electrocoagulation cell consists of an electrode which is in contact with wastewater. The coagulant is released from the anode with simultaneous formation of hydroxyl ions and hydrogen gas occurring at the cathode. Various electrode materials are used, such as aluminium, iron, stainless steel and platinum. The type of coagulant is associated with the used electrode material. Aluminium is the most used anode material. The pH, pollutant type and concentration, bubble size and position, floc stability and agglomerate size influence the operation of the EC cell. A current is passed through a metal electrode, oxidising the metal (Al) to its cation (Al$^{3+}$) (Equation (1)); thus EC introduces metal cations in situ, using sacrificial anodes. Oxygen development is also possible at the anode (Equation (2)).

$$\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- \\
E_A^0 &= -1.66 \text{ V} \quad (1)
\end{align*}$$

$$\begin{align*}
4\text{OH}^- & \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \\
E_A^0 &= -0.40 \text{ V} \quad (2)
\end{align*}$$

The reaction occurring at the cathode is dependent on pH. At neutral or alkaline pH, hydrogen is produced via Equation (3):

$$\begin{align*}
2\text{H}_2\text{O} + 2e^- & \rightarrow 2\text{OH}^- + \text{H}_2 \\
E_C^0 &= -0.83 \text{ V} \quad (3)
\end{align*}$$

While under acidic conditions hydrogen is produced via Equation (4):

$$\begin{align*}
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 \\
E_C^0 &= 0 \text{ V} \quad (4)
\end{align*}$$

Chemical dissolution of aluminium at both electrodes can be described by Equation (5) (Donini et al. 1994):

$$\begin{align*}
\text{Al} + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + 1.5\text{H}_2 \\
(5)
\end{align*}$$

Further hydrolysis of aluminium is presented by Equation (6).

$$\begin{align*}
\text{Al} + 4\text{H}_2\text{O} + e^- & \rightarrow \text{Al(OH)}_4^- + 2\text{H}_2 \\
(6)
\end{align*}$$

<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$–Fe(II) salts</td>
<td>Simplicity of application</td>
<td>Generation of sludge</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Not increase the volume of wastewater and sludge</td>
<td>Short half-life (usually 20 min) and high cost</td>
</tr>
<tr>
<td>Photochemical destruction</td>
<td>No sludge, low foul odour</td>
<td>Formation of by-products</td>
</tr>
<tr>
<td>Electrochemical destruction</td>
<td>Effective method for dye removal</td>
<td>High cost of electricity</td>
</tr>
<tr>
<td>Biological</td>
<td>Low cost and conventional</td>
<td>Limited to some kinds of dyes and long retention time</td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>Removes all dye types</td>
<td>Concentrated sludge</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Regeneration: no adsorbent loss</td>
<td>Not effective for all dyes</td>
</tr>
<tr>
<td>Fentons reagent</td>
<td>Effective decolorisation of both soluble and insoluble dyes</td>
<td>Sludge generation</td>
</tr>
<tr>
<td>Silica gel</td>
<td>Effective for basic dye removal</td>
<td>Side reactions prevent commercial application</td>
</tr>
</tbody>
</table>

Table 1 | Advantages and disadvantages of the current methods of dye removal from textile wastewater (Robinson et al. 2001; Ferreira-Leitao et al. 2007)
**Coagulation**

The cation hydrolyses in water, forming a hydroxide with the dominant species determined by the solution pH. Equations (7)–(10) illustrate the case of aluminium (Holt et al. 1999).

\[
\begin{align*}
\text{Al}^{3+} + \text{H}_2\text{O} &\rightarrow \text{Al(OH)}^{2+} + \text{H}^+ \\
\text{Al(OH)}^{2+} + \text{H}_2\text{O} &\rightarrow \text{Al(OH)}_2^+ + \text{H}^+ \\
\text{Al(OH)}_2^+ + \text{H}_2\text{O} &\rightarrow \text{Al(OH)}_3^+ + \text{H}^+ \\
\text{Al(OH)}_3^+ + \text{H}_2\text{O} &\rightarrow \text{Al(OH)}_4^+ + \text{H}^+ 
\end{align*}
\]

**Flocculation**

In principle, flocculant enhances the formation of larger flocs from fine colloidal particles. These larger flocs settle more rapidly and are easily removed by secondary operational processes such as filtration and thickening. Depending on the type of industrial unit operation, specific types of floc properties are desirable, e.g. in filtration, more porous and less dense flocs are required, whereas in the sedimentation process, dense flocs with minimum porosity are needed (Lu et al. 2005). The rate of flocculation increases with (Ives 1987):

1. increasing the collision radius of the particles. Flocculation improves as larger flocs are produced. On the other hand, the presence of pre-existing large particles will improve flocculation.
2. increasing the concentrations of particles present.
3. increasing the velocity gradient. However, the shear stress which flocs can endure limits the value of velocity gradient. Excessive gradients may cause floc break-up, particularly as the flocs grow in size. This occurrence can be overcome by decreasing the velocity gradient from an initially high value, when flocs are small, to lower values as the flocs grow.

**Energy consumption**

Application of EC method was evaluated by considering the energy consumption. Electrical energy consumption can be calculated by (Vorobiev et al. 2003):

\[
E = UI_{EC}
\]

where \( E \) is the energy consumption (kWh m\(^{-3}\)), voltage \( U \) (V), current \( I \) (A) and \( I_{EC} \) is the time of the EC.

**Artificial neural network (ANN)**

Artificial neural network (ANN) is a mathematical or computational model which simulates the biology of human brain. ANN predicts values of unmeasured target parameters using the correlation between measured parameters and the target parameters. A general ANN structure consists of an input layer, one hidden layer and an output layer. Each layer has its corresponding units (neurons or nodes) and weighted connections. The connections can be feed-forward or feedback. Each unit receives the sum of its weighted inputs and passes the result through a nonlinear activation function (transfer function). The activation function acts on the weighted sum of the unit’s inputs. One of the most commonly used transfer functions is the sigmoid (logistic) function. The outputs are fed through the network to optimise the weights between units. Optimum is achieved via minimising the error during training or learning phase. Training phase is the learning of mathematical relationship between inputs variables and corresponding outputs. The ANN changes the value of the weighted links to reduce the difference between the predicted and target (observed) values. This process is repeated across many training cycles (iteration or epoch) until specified level of accuracy is obtained. Figure 1 shows a feed-forward multilayer perceptron network (Rosenblatt 1958; Sun et al. 2003; Salari et al. 2005).

**Response surface method**

The response surface methodology (RSM) is a powerful experimental design tool and can be used to optimise and understand the performance of complex systems. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimising processes and can be used to evaluate the relative significance of several factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for a system or to determine a region that satisfies the operating specifications (Montgomery 1991).

![Figure 1](http://iwaponline.com/wst/article-pdf/63/5/984/445462/984.pdf)
A response surface is a curved surface that represents the relationship between the design variables \(x_i\) \((i = 1 \ldots n)\) and the response \(y\). This relationship can be presented by the following equation:

\[
y = f(x_1, \ldots, x_n) + \epsilon
\]

where \(\epsilon\) is the random error in \(y\).

There is no restriction in the form of function \(f\) that approximates the response surface. For simplicity, a polynomial to express the function \(f\) can be generally used. For example, if we use the second-order model with the following design variables, the model becomes:

\[
y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} x_i x_j + \epsilon
\]

where \(\beta_i\) and \(\beta_{ij}\) are the measures of the effects of variables \(x_i\) and \(x_i x_j\), respectively.

The unknown \(\beta\) are obtained by the technique of least squares which minimises the sum of squares of the residuals and estimated parameters.

The aim of this work is to optimise the removal of RB 5 from aqueous solution by investigating the influence of various parameters, i.e. treatment time, initial pH, current density, conductivity and dosage of polymer. ANN and RSM are used to create a reliable prediction of RB 5 removal.

### EXPERIMENTAL

The Reactive Black 5 (RB 5) was supplied by Texchem-Pack Bhd. The molecular sizes and structure of RB5 are shown in Table 2. To measure the dye concentration, samples were passed through filter paper and clarified solution was analysed using the UV/VIS double beam spectrophotometer (GENEYES 10 UV-USA), at maximum wavelength (\(\lambda_{\text{max}}\)) of 596 nm. The amount of dye retained by the filter paper was insignificant, and the data is estimated to be within 2% accuracy.

**Figure 2** Schematic diagram of an EC–Flocculation cell with DC power supply and Al electrodes.

**Table 2** Molecular structures and sizes of adsorbates RB 5 (Reactive Black 5)

<table>
<thead>
<tr>
<th>Type: Reactive dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure:</td>
</tr>
</tbody>
</table>

Max wavelength of adsorption (\(\lambda_{\text{max}}\)): 596 nm

**Electrocoagulation–flocculation experiment**

The schematic diagram of experimental set up is shown in Figure 2. The EC–Flocculation unit consisted of a 500 mL electrochemical cell followed by a 250 mL settling cell. The aluminium anode and cathode electrodes were of size of 50 mm \(\times\) 50 mm, and the distance between the electrodes was 2 cm. The current density was maintained constant by means of a precision DC power supply (HY 3003-2). The dye solution was prepared using RB 5 with initial concentration of 100 mgL\(^{-1}\). When the electrolysis was completed, the solution was discharged from the bottom of the EC cell into the settling cell from the top. Flocculant was added and mixed (at 50 rpm) for 15 min and final settling step lasted 1 h.

**Artificial neural network optimisation**

NeuralPower v2.5, a commercial artificial intelligence software, was used in the ANN studies. The input parameters used in training the best prediction model are listed in Table 3. Forty experiments were carried out and the range of variables studied is summarised in Table 4. The percentage of dye removal and the operating cost were chosen as the experimental response or output variable. The operating cost was based on economics data reported by Koby et al. (2006).

The maximum number of iterations was set to 1,000 (i.e. the default value). Furthermore, four individual data records (i.e. 10% of the training data) were taken out to check the performance of the network (Phaniraj & Lahiri 2003). The sigmoidal transfer function was used as a transfer function in all nodes of the hidden and output layers which is given by:

\[
f(x) = \frac{1}{1 + \exp(-x)}
\]

where \(f(x)\) is the hidden neuron output.
function. The correlation coefficient \( R^2 \) was used as the error function. The \( R^2 \) measures the performance of the network according to the following equation:

\[
R^2 = 1 - \frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}
\]  

(15)

where \( y_i \) is the experimental y values, \( \bar{y} \) is mean of \( y_i \), \( \hat{y}_i \) is predicted values and \( i \) is number of inputs.

The model with the highest \( R^2 \) was selected (\( R^2 = 0.9968 \)).

### Response surface method optimisation

The most popular class of second-order designs, the central composite design (CCD), was used for RSM in the experimental design and is presented in Table 4. The central composite design with three numerical factors at five levels and one categorical factor was applied using Design-Expert 6.0. Each independent variable was coded at five levels between \(-2\) and \(+2\) at the ranges determined by the preliminary experiments, where the independent variables were listed in Table 5. The total number of experiments with three numerical factors and one categorical factor was \( 40 \times 2 \), where \( k \) is the number of factors. Performance of the process was evaluated by analysing the responses, namely the percentage of dye removal and the operating cost.

### RESULTS AND DISCUSSION

Evaluation of experimental result with ANN and RSM

The experimental results were evaluated by Design-Expert 6.0 software using approximating functions of independent variables: time (\( A \)), current (\( B \)), conductivity (\( C \)) and dosage of flocculant (\( D \)). Equation (16) presents the approximating functions of percentage of dye removal obtained using Design-Expert software.

Percentage of dye removal \( = -50.8 + 6.5A + 0.71B \\
+ 2.9D - 0.16A^2 - 1.7E \\
- 0.03B^2 + 0.061D^2 \\
+ 3.7E - 0.03AB \\
- 0.0715AD - 2.6E \\
- 0.03BD \)  

(16)

The results of ANOVA derived from this quadratic model are listed in Tables 6 and 7. The Model F-value of 170.45 implies that the model is significant. There is only a 0.01% chance that a “Model F-Value” could occur due to noise. Values of “Prob > F” less than 0.05 indicate model terms are significant. In this case \( A, B, C, D, B^2, D^2, AB, AD, BD \) are significant model terms. The “Lack of Fit F-value” of 0.52 implies that the Lack of Fit is not significant relative to the pure error. There is a 82.89% chance that a “Lack of Fit F-value” could occur due to noise.

The plots of actual and predicted percentage of dye removal, together with test data, are presented in Figure 3. Actual values are the measured response data for a particular run, and the predicted values are evaluated from the models. It can be observed that the values of \( R^2 \) for both models are more than 0.9, which shows good fitness of the response models. Thus, both models are able to predict accurately the experimental results. The values of \( R^2 \) associated with the ANN model are slightly higher than those for the RSM model (0.9972 and 0.9764 vs. 0.9896 and 0.9446, respectively).

### Table 3 | The training parameters used with Neuralpower2.5

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>No. of hidden layers</td>
<td>1</td>
</tr>
<tr>
<td>No. of nodes in hidden layer</td>
<td>10</td>
</tr>
<tr>
<td>Learning Algorithm</td>
<td>QuickProp</td>
</tr>
<tr>
<td>Connection Type</td>
<td>Multilayer Normal feed Forward</td>
</tr>
<tr>
<td>Transfer Function</td>
<td>Sigmoid</td>
</tr>
<tr>
<td>Momentum factor</td>
<td>0.8</td>
</tr>
<tr>
<td>Learning rate</td>
<td>0.8</td>
</tr>
<tr>
<td>Maximum iterations</td>
<td>1,000</td>
</tr>
<tr>
<td>MS error</td>
<td>0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variables</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>5–20 (min)</td>
</tr>
<tr>
<td>current</td>
<td>30–240 (Am⁻²)</td>
</tr>
<tr>
<td>conductivity</td>
<td>1,000–5,000 (µS/cm⁻¹)</td>
</tr>
<tr>
<td>flocculant dosage</td>
<td>0–16 (mgL⁻¹)</td>
</tr>
</tbody>
</table>
Figures 4–6 show the percentage of dye removal as a function of two factors for the ANN and RSM models. These plots are used to understand the main and the interaction effects of different factors.

### Effect of current density

The 3D surface graphs were drawn to visualise the significant ($p < 0.05$) interaction effect of independent variables on percentage of dye removal. Figures 4 and 5 represent the 3D plots of current density versus treatment time and dosage of flocculant. As shown in Table 7, the percentage of dye removal was positively related to the main effect, current density. In general, three variables, i.e. current density, treatment time and dosage of polymer, have the most significant effect on the percentage of dye removal. The interaction effect between current density and treatment time, and dosage of polymer, presented the most significant effect on the percentage of dye removal ($p = 0.034$ and $0.024$, respectively).

It can be observed from Figures 4 and 5 that, as the current density increased from 30 to 240 A/m², the percentage of dye removal increased. Current density is one of the most important variables affecting the EC performance. The amount of current density determines the coagulant production rate and the size of the produced bubbles. The growth of flocs is affected by shear forces generated by a mixing source. In low current density, the shear forces due to the relatively few bubbles are low. As the current density increases, the density of bubbles flux increases and consequently higher shear forces damage and break the flocs apart and reduce the efficiency of pollutant removal. On the other hand, an increase in current density increases the coagulant concentration, which decreases the necessary contact time. Current density can also impact the path by which pollutant is removed, either by settling or flotation. In low current density, low bubble density leads to a low upward momentum flux and sedimentation is predominant (Chen 2004; Holt et al. 2005).

Bakshi & Fedkiw (1994) suggested that, to minimise the reduction of current efficiency due to metal ion depletion with time, current density should be decreased exponentially.
with time. The authors reported a 25% increase in the yield by applying continuous time-varying potential techniques in some electrochemical processes.

The rate of releasing metal ions into the solution from the anode follows Faraday's law, expressed as:

\[ C = \frac{ItECM}{ZFW} \]  

(17)

where \( C \) is the metal concentration in the CE cell, \( M \) the molecular weight of anode (aluminium), \( Z \) the chemical equivalence, \( F \) the Faraday's constant and \( W \) the volume of the electrolytic cell (Mollah et al. 2004a, b). The release of metal ions increased with current density, and was able to trap and precipitate more dye molecules (Holt et al. 2005). Moreover, an increase of current density increases the bubble generation rate with a decrease in bubble size. Consequently, a high dye removal efficiency is achieved via H₂ flotation (Chen 2004).

### Effect of electrolysis time

As reported in Table 7, treatment time and its interaction with current density and dosage of polymer have a significant effect on the percentage of dye removal (\( p < 0.05 \)). It can be observed that the interaction between treatment time and dosage of polymer has the most significant effect (\( p = 0.003 \)). The interaction effect between treatment time and two main effects, namely the current density and dosage of polymer, are shown in Figures 4 and 6. Electrolysis time affects the production of aluminium ions from aluminium electrode. The percentage of dye removal depends directly on the concentration of hydroxyl and aluminium ions produced by aluminium electrode. The same observations were reported by other workers (Daneshvar et al. 2006; Kobya et al. 2006).

It can be observed from the curvature of plots that the relationships between treatment time and other variables were nonlinear. The percentage of dye removal increased as the treatment time increased. Similar results regarding the effect of treatment time on percentage of dye removal were

<table>
<thead>
<tr>
<th>Variables</th>
<th>Main effects</th>
<th>Quadratic effects</th>
<th>Interaction effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_1 )</td>
<td>A 0.0001</td>
<td>B 0.0001</td>
<td>C 0.015</td>
</tr>
<tr>
<td></td>
<td>D 0.0079</td>
<td>( A^2 ) 0.071</td>
<td>( B^2 ) 0.0001</td>
</tr>
<tr>
<td></td>
<td>( C^2 ) 0.71</td>
<td>( D^2 ) 0.046</td>
<td>( AB ) 0.003</td>
</tr>
<tr>
<td></td>
<td>( AC ) 0.58</td>
<td>( AD ) 0.003</td>
<td>( BC ) 0.024</td>
</tr>
<tr>
<td></td>
<td>( BD ) 0.87</td>
<td>( CD )</td>
<td></td>
</tr>
</tbody>
</table>

\( p \)-value 0.0001 0.0001 0.015 0.0001 0.71 0.046 0.003 0.38 0.024 0.87

F-value 332.9 975.3 6.8 78.25 3.34 78.45 0.13 4.39 5.0 0.78 10.7 0.25 5.74 0.025
also reported by Kobya et al. (2006), and Gupta & Babu (2009).

**Effect of dosage of polymer**

Flocculant was added to the EC reactor to improve dye removal. Flocculant was added in sequential steps of 5, 10 and 15 min after electrolysis. The effect of dosage of polymer ($p = 0.0001$) and interaction effects with current density and treatment time are shown in Figures 4 and 5 ($p = 0.024$ and 0.003, respectively). It can be observed that addition of polymer was able to increase the percentage of dye removal. This improvement may be due to the ability of the flocculent to treat fine colloidal particles, creating larger flocs. Consequently, flocs settle rapidly and are easily removed by a settling tank (Lu et al. 2009). The dosage of polymer has a positive relationship with the percentage of dye removal. When the dosage was increased from 0 to 16 mgL$^{-1}$, the percentage of dye removal increased to an average of 25%. This suggested that an increase of polymer dosage enhanced the floc stability. The strength of floc is dependent on the attractive forces between component particles; thus stronger bridges between flocs can be created by a higher flocculant dosage (Records & Sutherland 2001).

**Effect of conductivity**

As shown in Table 7, the main effect conductivity has a significant effect on percentage of dye removal ($p = 0.015$). However, the interaction between conductivity and other main effects has no significant effect on the percentage of dye removal ($p > 0.05$). The main effect of conductivity was investigated between 1,000 and 5,000 µS/cm using NaCl as the supporting electrolyte. As can be observed from Figure 7, the percentage of dye removal increased slightly from 78.2 to 82.6% as the conductivity increased. Chen (2004) reported...
that the efficiency of dye removal increased with increase in NaCl concentration. The increase in efficiency was due to the reduction of the adverse effect of other anions such as HCO$_3^-$/CO$_3^{2-}$/SO$_4^{2-}$/CO$_3^{2-}$ as well as precipitation of Ca$^{2+}$ or Mg$^{2+}$ ions that formed an insulating layer on the surface of the electrodes. In solution containing less than 10 ppm of dissolved solid (as used in this work), the aforementioned effects were insignificant (Hartman et al. 1996). The effect of increase in dye removal efficiency with increase in conductivity was also reported by Mollah et al. (2004a, b) and Daneshvar et al. (2006). However, Kobya et al. (2006) reported a decrease of dye removal efficiency with an increase of conductivity. We are not able to further comment on the results reported by Kobya et al. (2006) as a different dye (Levafix Orange E3 GA) and a different concentration were used in their experiment.

The effect of conductivity on energy consumption was also calculated. The results are as listed in Table 8. The results showed that an increase in conductivity causes a decrease in energy consumption. Increasing conductivity from 1,000 to 5,000 $\mu$S/cm reduced the energy consumption from 13.5 to 3.3 kWh/m$^3$.

### Optimisation of operating cost

The total operating cost was calculated for one cubic metre of wastewater. The operating cost was calculated based on electricity, materials and labour. Economic data for operating cost are summarised in Table 9.

![Figure 8](image-url)  
**Figure 8** | The effect of treatment time, current density, conductivity and dosage of polymer on operating cost.

<table>
<thead>
<tr>
<th>Conductivity (µS/cm$^{-1}$)</th>
<th>Voltage (V)</th>
<th>Energy consumption (kWh/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000</td>
<td>30.1</td>
<td>13.5</td>
</tr>
<tr>
<td>2,000</td>
<td>15.6</td>
<td>7.0</td>
</tr>
<tr>
<td>3,000</td>
<td>10.3</td>
<td>4.6</td>
</tr>
<tr>
<td>4,000</td>
<td>8.1</td>
<td>3.6</td>
</tr>
<tr>
<td>5,000</td>
<td>7.3</td>
<td>3.3</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity ($$/kWh$^{-1}$)</td>
<td>0.06</td>
</tr>
<tr>
<td>Labour cost ($$/m$^3$)</td>
<td>0.06</td>
</tr>
<tr>
<td>Polymer ($$/kg)</td>
<td>7.0</td>
</tr>
<tr>
<td>Salt ($$/kg)</td>
<td>0.5</td>
</tr>
<tr>
<td>Al electrode ($$/kg$^{-1}$)</td>
<td>1.8</td>
</tr>
</tbody>
</table>

### Table 8 | Effect of conductivity on voltage and energy consumption

![Table 8](image-url)
2,000 μScm⁻¹ and after that the operating cost increased with further increase in conductivity. It can be due to the fact that the operating cost is influenced by the cost of electrolyte and the cost of energy. As mentioned before, energy consumption decreased when conductivity was increased.

The operating cost was minimised while the percentage of dye removal was at a maximum. The minimum point was obtained by using the approximating function of operating cost. The objective was to find the optimal operating condition. The results are presented in Table 10. It can be observed that the minimum operating cost of $1.74 was obtained when treatment time was 13.9 min, current density was 193.5 Am⁻², conductivity was 1,000.8 (mScm⁻¹/C₀)¹ and dosage of flocculant was 14.4 mgL⁻¹/C₀.

### Effect of pH

The effect of pH on electrocoagulation was studied by adjusting the pH of dye solutions with dilute H₂SO₄ or NaOH solution in the range 2.0 to 12.0. The study was conducted at the optimal operating condition with initial dye concentration of 100 mgL⁻¹.

Figure 9 represents the electrolyte pH after electrolysis versus initial pH. It can be observed that the value of final pH increased when the initial pH was acidic while the final pH remained almost constant when the initial pH was alkaline.

The importance of pH with regard to coagulation is well known. Figure 10 illustrates the effect of pH on electrocoagulation. The results showed that the percentage removal of dye decreased slowly when the initial pH was increased from 2 to 9 and then decreased rapidly for pH above 9. It can be attributed to optimal pH for the formation of Al(OH)₃. The main mechanism of coagulation after the addition of metal coagulant can be carried out via various mechanisms. When the initial pH is 2–3, the coagulation pathway is of double-layer compression and the dominant aluminium species are Al³⁺ and Al(OH)²⁺. For initial pH of 4–9, the sorption style mechanism occurs and the dominant aluminium species are polymeric species, such as Al₁₃O₄(OH)₂₄, which can take the form of Al(OH)₃. If the binding is by charge interaction, then the coagulation mechanism is charge neutralisation. For initial pH above 9, the dominant aluminium species is Al(OH)₄⁻ which is not able to decolorise (Holt et al. 2005; Mouedhen et al. 2008).

### CONCLUSION

The removal of Reactive Black 5 (RB 5) from aqueous solution by using sequential electrocoagulation was investigated. The results of this study showed that combination of electrocoagulation and flocculation methods could enhance dye removal and the optimum condition obtained when treatment time was 13.9 (min), current density was 193.5 (Am⁻²), conductivity was 1,000.8 (μScm⁻¹) and dosage of flocculant was 14.4 (mgL⁻¹).

In addition, comparing two models, artificial neural network (ANN) and response surface method (RSM), showed that both models were able to predict experimental results well, while accuracy of ANN model was slightly higher than that for the RSM model ($R^2 = 0.9764$ and 0.9446, respectively).

### REFERENCES


