The application of iron mesh double layer as anode for the electrochemical treatment of Reactive Black 5 dye

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ABSTRACT

In this work a novel anode configuration consisting of an iron mesh double layer is proposed for the electrochemical treatment of wastewater. The removal of Reactive Black 5 dye (RB5) from synthetic contaminated water was used as a model system. At a constant anode surface area, identical process operating parameters and batch process mode, the iron mesh double layer electrode showed better performance compared to the conventional single layer iron mesh. The double layer electrode was characterized by RB5 and chemical oxygen demand (COD) removal efficiency of 98.2% and 97.7%, respectively, kinetic rate constant of 0.0385/min, diffusion coefficient of $4.9 \times 10^{-5}$ cm$^2$/sec and electrical energy consumption of 20.53 kWh/kg dye removed. In the continuous flow system, the optimum conditions suggested by Response Surface Methodology (RSM) are: initial solution pH of 6.29, current density of 1.6 mA/cm$^2$, electrolyte dose of 0.15 g/L and flow rate of 11.47 mL/min which resulted in an RB5 removal efficiency of 81.62%.

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Introduction

Wastewater discharge from dye manufacturing and textile industries has become a global concern and is one of the major causes of environmental pollution. According to the Malaysian Department of Environment (DOE), approximately 160,000 tons of textile industrial wastewater were discharged within the years 2011 to 2012 and the amount continues to increase annually (DOE, 2012). Thus, the treatment of textile wastewater to a permissible concentration is essential before discharge to the aquatic environment.

Reactive dyes have complex chemical structures, which consist of organic ring, vinyl sulfonic groups and chloride atoms (Klemola et al., 2007). These dyes are widely used in the textile industry as their vivid colors and reactive groups easily attach to the textile fibers (Hassan et al., 2009). However, the relatively low fixation of reactive dyes on cellulose fibers during the dyeing process, resulted in the high amount of dyes released into dyebath effluent. Excessive amounts of reactive dyes discharged into receiving waters are dangerous and may pose a serious threat to the aquatic ecosystem. Moreover, these dyes are mutagenic and carcinogenic, and thus may cause a severe damage to liver, digestive and central nervous system of human beings (El-Zawahry et al., 2016).

Reactive dyes in dyeing wastewater are known as recalcitrant compounds as they have high alkalinity, high concentration of organic compounds and strong color compared with other dyes (Barka et al., 2010).

Many methods have been developed and investigated for the removal of dyes from effluents such as membrane...
filtration, adsorption, photocatalytic oxidation and biological treatment (Mook et al., 2016; Zeng et al., 2014; Szlachta and Wójtowicz, 2013; Rivera et al., 2011). The chemical coagulation is a conventional (and one of the most popular) technique used for the treatment of textile dyeing wastewaters. However, the costs of required coagulants (aluminum(III) or iron(III) salts) and generation of the considerable amount of sludge cause that in some cases, the employment of chemical coagulation for decolorizing wastewater is not economically justified.

An alternative method to the chemical coagulation is electrocoagulation, which based on the electrochemical technique. During the electrocoagulation process, the coagulant is produced in situ by electrolytic oxidation of sacrificial anode (Merzouk et al., 2011). Thus, the advantage of application of the electrochemical treatment, apart from the high efficiency of the process and its versatility, includes low cost and minimal sludge generation (Mook et al., 2012). The potential of electrocoagulation in dye removal from wastewater has already been proven by other researchers (Nandi and Patel, 2013; Zodi et al., 2013). The process is characterized by low sludge production, easy floc separation, low level of total dissolved solids (TDS) and no secondary pollution caused by external added coagulant (Mollah et al., 2001).

However, the sacrificial electrode used in the process needs to be monitored and replaced frequently as it participates in the anodic oxidation. Moreover, the electrocoagulation requires the energy input, thus the operating costs related with the price of electric current may limit its application. Hence, the optimum of electric current needs to be investigated as it is one of the important parameters that affect the lifetime of the electrodes and operating cost.

The configuration of the electrode used in the process is a crucial feature to increase anodic oxidation and hence, induce higher dye elimination. Several studies have been conducted for dye removal that used different anode shapes such as a plane (Mohan et al., 2007; Nandi and Patel, 2013; Pajoontan et al., 2012; Steter et al., 2014; Thiam et al., 2015) and mesh (del Río et al., 2012; Mendoza-Martinez et al., 2012). A mesh type electrode produces a higher discharge current than a plane (Mohan et al., 2007; Nandi and Patel, 2013; Pajoontan et al., 2012; del Río et al., 2012; Méndez-Martínez et al., 2012). A mesh type electrode produces a higher discharge current than a plane (Mohan et al., 2007; Nandi and Patel, 2013; Pajoontan et al., 2012; del Río et al., 2012; Méndez-Martínez et al., 2012).

RB5 dye is a diazoacidic reactive dye, which consists of two sulfonates and two sulfato-ethylsulfon groups. It is typically used in textile industries for dyeing of cotton, woolen and nylon fabrics (Elwakeel et al., 2016). In this study, RB5 has been utilized as a model dye because of its recalcitrant nature and the fact that it contributes to 50% of the total world demand for reactive dyes (Schumacher, 2012). The first part of this work is to investigate the performance of new anode configuration (iron mesh double layer electrode) on RB5 removal, by comparing it to the conventional single layer design. The configuration with superior removal efficiency was subsequently used in comparing performance of the system mode and RSM studies.

1. Mechanism of electrocoagulation

Electrocoagulation (EC) is an electrochemical process using iron or aluminum as the anode in which Fe$^{2+}$ or Al$^{3+}$ ions are released into the solution through anodic dissolution and their hydroxides then react with pollutants (Korbahti et al., 2011). Iron has been proven by several researchers to be a more effective electrode material than aluminum (Akanksha et al., 2013; Chafi et al., 2011). EC has been successfully applied for the removal of different types of dye from textile industry wastewater (Khandegar and Saroha, 2013).

Iron hydroxides can be produced through two mechanisms (Eqs. (1)-(8)) and they remove the pollutant molecules via surface complexation or electrostatic attraction. In surface complexation, the pollutant acts as ligand to bind with hydrous iron through precipitation and adsorption mechanisms (Eqs. (9)-(12)) (Korbahti et al., 2011).

**Mechanism I:**

Anode : $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)} + 2\text{e}^-$  \hspace{1cm} (1)

Chemical : $\text{Fe}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Fe(OH)}_{2(s)}$  \hspace{1cm} (2)

Cathode : $2\text{H}_2\text{O}_{(l)} + 2\text{e}^- \rightarrow \text{H}_2_{(g)} + 2\text{OH}^-_{(aq)}$  \hspace{1cm} (3)

Overall reaction : $\text{Fe}_{(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{Fe(OH)}_{2(s)} + \text{H}_2_{(g)}$  \hspace{1cm} (4)

**Mechanism II:**

Anode : $4\text{Fe}_{(s)} \rightarrow 4\text{Fe}^{2+}_{(aq)} + 8\text{e}^-$  \hspace{1cm} (5)

Chemical : $4\text{Fe}^{2+}_{(aq)} + 10\text{H}_2\text{O}_{(l)} + 4\text{OH}^-_{(aq)} \rightarrow 4\text{Fe(OH)}_{3(s)} + 8\text{H}^+_2(aq)$  \hspace{1cm} (6)

Cathode : $8\text{H}^+_{(aq)} + 8\text{e}^- \rightarrow 4\text{H}_2_{(g)}$  \hspace{1cm} (7)

Overall reaction : $4\text{Fe}_{(s)} + 10\text{H}_2\text{O}_{(l)} + 4\text{OH}^-_{(aq)} \rightarrow 4\text{Fe(OH)}_{3(s)} + 4\text{H}_2_{(g)}$  \hspace{1cm} (8)

Precipitation : dye + monomeric Fe $\rightarrow$ [dye.monomeric Fe]  \hspace{1cm} (9)

dye + polymeric Fe $\rightarrow$ [dye.polymeric Fe]  \hspace{1cm} (10)

Adsorption : dye + Fe(OH)$_n$ $\rightarrow$ [particle]  \hspace{1cm} (11)

[dye.polymeric Fe] + Fe(OH)$_n$ $\rightarrow$ [particle].  \hspace{1cm} (12)
2. Methodology

2.1. Materials and analytical methods

Iron mesh (woven mesh, hole size 0.5 cm × 0.6 cm) and round iron plate (diameter 9 cm) were supplied by KY Scientific, Malaysia. Each electrode was immersed in 0.01 mol/L H2SO4 for 24 hr and then rinsed with distilled water. Prior to use, the electrodes were polished by fine grade sandpaper to remove impurities and then rinsed with distilled water.

Stock solutions of RB5 solution were freshly prepared and the pH was adjusted by either 0.1 mol/L of sulfuric acid or sodium hydroxide solution. All the chemicals used in this study were of analytical grade and supplied by Sigma Aldrich, Malaysia.

Chemical oxygen demand (COD) was analyzed by the standard method (HACH DRB 200). The concentration of RB5 was determined by Lambda 35 UV–Vis spectrophotometer (PerkinElmer, USA) at a wavelength of 595 nm. Prior to analysis, all the samples were filtered through a 0.22 μm filter membrane to eliminate the suspended solids that may affect the analysis process. The RB5 removal efficiency, electrical energy consumption (EEC, kWh/kg dye removed) and operating cost (US$/m3) are defined in Eqs. (13)–(15) (El-Ashtoukhy et al., 2012; Ghosh et al., 2011).

\[
\text{RB5 removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (13)
\]

\[
\text{EEC} = \frac{UI}{V(C_0 - C_t)} \quad (14)
\]

Operating cost = \( a \times C_{\text{energy}} + b \times C_{\text{electrode}} \quad (15) \)

where, \( C_0 \) and \( C_t \) denote the concentration of RB5 at time \( t = 0 \) and \( t \), respectively, \( U \) (V) represents the voltage, \( I \) (A) is the current, \( t \) (hr) is the process time, \( V \) (L) is the volume of dye solution, \( a \) (0.06 US$/kWh) is the Malaysian electricity price in the year 2015, \( b \) (2.73 US$/kg iron mesh) is the Malaysia retail iron mesh price in year 2015; \( C_{\text{energy}} \) (kWh/m3) is the electrical energy consumption and \( C_{\text{electrode}} \) (kg/m3) is the iron electrode consumption.

2.2. Anode comparison experiments

The comparison anode configuration experiments were conducted in batch mode with the RB5 concentration of 40 mg/L and NaCl of 0.2 g/L in a 1000 mL beaker. Prepared solution (initial pH of 6.32) was stirred with a digital overhead stirrer (70 r/min). The diameter of iron mesh single layer anode is 3.02 cm, while the double layer configuration had a diameter of 1.3 cm and layer distance of 0.2 cm (Fig. 1). The anode and cathode (iron round plate with diameter 9 cm) were connected to a DC power supply with current density of 5.02 mA/cm2.

The relative kinetic rate constant was calculated using first-order model (Eq. (16)).

\[
C_t = C_0 e^{-kt} \quad (16)
\]

where \( C_0 \) (mg/L) and \( C_t \) (mg/L) are the amount of RB5 at time \( t = 0 \) and \( t \) (min), respectively; \( k_t \) (min) is the rate constant of first-order kinetic model.

The chronoamperometry technique was used to investigate the electrochemical diffusivity of RB5 toward the iron mesh single layer and double layer electrodes. The experiments were performed by an EC-lab potentiostat with EC-lab10.40 software. The blank and dye solution were 0.2 g/L NaCl and 40 mg/L RB5 mixed with 0.2 g/L NaCl, respectively. The following Cottrell equation was used to estimate the diffusivity for both anodes (Bard and Faulkner, 1980).

\[
I = \frac{nFAD^{0.5}C_0}{\pi^{0.5}D^{0.5}} \quad (17)
\]

where, \( n \) is number of electrons; \( A \) (cm2) is the surface area of electrode; \( D \) (cm²/sec) is the diffusion coefficient; \( C_0 \) (mol/cm³) is the initial concentration of RB5 and \( t \) (sec) is the time.

Sludge volume index (SVI, mL/g) was determined by using a 1000 mL Imhoff cone. The settled sludge volume (V, mL/L) at the bottom of the cone for 30 min was measured. The SVI was calculated according to Eq. (18). The total suspended solids (TSS) were determined by the standard technique (Amaral and Ferreira, 2005).

\[
SVI = \frac{V \times 1000}{TSS} \times 100\% \quad (18)
\]

where, TSS (mg/L) is the total suspended solids.

The hydrolyzed RB5 solution was prepared at a concentration of 40 mg/L and NaCl of 0.2 g/L. The pH solution was adjusted to 11 by 0.1 mol/L NaOH in order to stimulate the alkaline condition for reactive dye attached to the fibers during the dyeing process. The dye solution was heated to 60°C for 1 hr (Ojstršek et al., 2008; Zotou et al., 2002). Then, the solution was cooled down to the room temperature and the pH was adjusted to 6, because this is the minimum pH required for coagulant generation. The double layer configuration was used as the anode and applied with a current density of 5.02 mA/cm².

2.3. Batch and continuous process

The batch system was conducted in a Plexiglas cylinder with 9.5 cm inner diameter. The anode surface was 29.87 cm² and fixed at the bottom of the reactor. The round iron plate (cathode) was fixed in the reactor using four stainless steel rods. The inter-electrode spacing was kept at 1 cm. The stainless steel rods on top and beneath the reactor were connected to a programmable DC power supply (IPS-3202, RS Components, England) as illustrated in Fig. 1.

The setup of continuous flow system was the same as in the case of batch system, however it included a peristaltic pump to feed in the RB5 solution continuously. The batch and continuous flow process were operated in 60 min.

2.4. Interaction and optimization parameters

The Design Expert Software (trial version 9) was utilized for the statistical design of experiments and data analysis. In this work, Central Composite Design (CCD) and RSM were used to optimize the four process variables, namely pH, current density, electrolyte dose and flow rate. The coded values of these factors were set at five levels (−1, −0.5, 0, 0.5, 1) and are shown in Table 1. The total number of experiments designed by CCD was 27 runs, including three repeated experimental
runs at the central point to eliminate errors and curvature. The response function of RB5 removal efficiency was predicted and expressed following a quadratic equation as given by Eq. (19) (García-Gómez et al., 2014).

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j \]  

(19)

where, \( Y \) is the predicted response; \( X_i \) to \( X_j \) are coded variables; \( \beta_0 \) is the constant coefficient; \( \beta_i \) is the linear term coefficients; \( \beta_{ij} \) is the quadratic coefficients; and \( k \) is the number of variables studied in the experiment.

Analysis of variance (ANOVA) was used for statistical analysis and diagnostic checking to evaluate model adequacy. The quality of the model was checked by \( R^2 \) and its statistical significance was analyzed by the F-test. The significant model terms were examined by P-value (probability of error) at a 95% confidence level.

3. Results and discussion

3.1. Comparison of anode configurations

Fig. 2 shows the effect of the anode configuration on the effectiveness of RB5 removal. As can be seen, the electrocoagulation performance of the iron mesh double layer electrode was more efficient than for the single layer electrode. It was clearly observed that the trend of the RB5 removal rate on both electrodes during first 10 min of process time was comparable. After 10 min, the removal rate of RB5 over the double layer increased compared to the single layer electrode which might be attributed to the faster passivation of the single layer electrode. Passivation leads to the formation of a passive film on the electrode surface that prevents continuous iron dissolution and reduces mass transfer \( \text{Fe}^{2+} \) to electrolyte. This has the effect of decreasing the electrode efficiency for pollutant
removal (Aber et al., 2009; Arroya et al., 2009; Heidmann and Calmolo, 2008). Hence, electrode passivity has a great influence in the electrocoagulation process (Yang et al., 2015). In addition, as seen in Table 2, the COD removal efficiency for the single and double layer electrodes was 59.6 and 97.7, respectively. This confirmed that the double layer electrode demonstrated better performance in treating dye solution.

The electrocoagulation results of RB5 were subjected to kinetic analysis by the first-order model (Fig. 3). The concentration of RB5 reduced progressively for the single and double layer electrodes. The calculated first-order rate constant for the double layer and single layer electrodes was 0.0203 and 0.0385/min, respectively, which confirms that RB5 removal by electrocoagulation occurs more readily on the iron mesh double layer electrode than on the single layer electrode.

According to the mechanism of electrochemical reactions, the diffusion of ions from bulk solution to the electrode surface is a key step for the direct and indirect electro-degradation processes (Chu et al., 2010). In this study, the diffusion mechanism refers to the dye compound and hydroxide ions migrate to the anode surface film layer. The chronoamperometry technique and the Cottrell equation were used to estimate the diffusion coefficients of RB5 compound toward the single and double layer electrodes. The diffusion coefficients were $3.1 \times 10^{-5}$ and $4.9 \times 10^{-5}$ cm²/sec on the single layer and double layer electrodes. The values of current in both electrodes were higher in the RB5 solution than in blank solution due to the oxidation of RB5.

Table 2 – Performance summary for the single and double layer electrodes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Single layer electrode</th>
<th>Double layer electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>RB5 removal (%)</td>
<td>79.9</td>
<td>98.2</td>
</tr>
<tr>
<td>COD removal (%)</td>
<td>59.6</td>
<td>97.7</td>
</tr>
<tr>
<td>Kinetic rate constant (min)</td>
<td>0.0203</td>
<td>0.0385</td>
</tr>
<tr>
<td>Diffusivity (cm²/sec)</td>
<td>$3.1 \times 10^{-5}$</td>
<td>$4.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>SVI (mL/g)</td>
<td>126.0</td>
<td>132.0</td>
</tr>
<tr>
<td>EEC (kWh/kg dye removed)</td>
<td>22.88</td>
<td>20.53</td>
</tr>
<tr>
<td>Operating cost (US$/m³)</td>
<td>0.676</td>
<td>0.664</td>
</tr>
</tbody>
</table>

**Table 3 gives a comparison of RB5 removal efficiencies and EEC using iron as anode material. The achieved results in this study are comparable with other research.**
The double layer electrode produced a higher RB5 and COD removal efficiency than the single layer and it was therefore applied in subsequent experiments.

### 3.2. Comparison of batch and continuous processes

It is well known that most of the industrial wastewater treatment was classified into batch and continuous process. In the batch treatment system, a volume of wastewater is collected, treated and discharged after certain time. While in the continuous flow system, wastewater is continuously feed in and treated solution is continuously discharged (Batch, 2015). In the case of comparing the removal efficiency in the batch and continuous flow system, the electrode materials, current density, amount of metal ions produced per treated volume are identical. In addition, the flow rate for the continuous flow system is calculated based on the Eq. (21) (Ardhan et al., 2015).

\[
\frac{jAt}{V} \text{ batch} = \frac{jA}{Q} \text{ continuous}
\]  

where, \(j\) (A/m²) is the current density; \(A\) (m²) is the total electrode area; \(t\) (min) is the electrocoagulation time; \(V\) (m³) is the volume of the solution and \(Q\) (m³/min) is the flow rate.

Fig. 4 compares the performances of the batch and continuous flow process in removing RB5 at various supporting electrolyte doses. It was found that RB5 removal in the batch system was higher than those in continuous reactor. For the batch system, the volume of solution fixed and RB5 concentration decrease along the process time. While in the case of continuous flow system, the RB5 solution was continuously pumped into the system and caused insufficient time for the coagulant to precipitate and adsorb RB5. Thus, the effluent RB5 concentration was found higher.

RB5 removal shows better efficiency in the batch system, but it has limitation applied for wide range capacity in commercial. As discussed, high amount of textile industrial wastewater about 160,000 tons were discharged annually in Malaysia. Hence, it is advisable to use continuous mode to treat dye effluent. Parameters in continuous system were then optimized by using RSM.

### 3.3. Optimization continuous process by RSM

#### 3.3.1. Development of regression equation

The parameters and RB5 removal were examined using CCD to establish a correlation between them. The analysis recommended a quadratic model for the response function. Table 4 presents the experimental and predicted results corresponding to different variable combinations. The regression model was achieved according to Eq. (22), where \(Y_{\text{act}}\) represents RB5 removal efficiency and \(X_1, X_2, X_3\) and \(X_4\) are pH values, current density, supporting electrolyte dosage and flow rate, respectively after excluding insignificant terms.

\[
Y_{\text{act}} = 6.65698 + 52.87547X_1 - 37.49992X_2 - 356.50288X_3 - 3.19012X_4 - 16.8625X_1X_3 + 144.3991X_1X_4 + 1.56932X_2X_4 - 3.9175X_1^2.
\]

#### 3.3.2. Statistical analysis

The correlation coefficient value was used to evaluate the quality of the model. The adjusted \(R^2\) is the measurement of the amount of variation about the mean as explained by the
model and the predicted $R^2$ is the quality measurement of the model to predict the response value. The predicted and adjusted $R^2$ should be within approximately 0.20 of each other to be in reasonable agreement. Either the data or the model may be problematic if the two values are out of this limited range (Mook et al., 2013). In this study, the value of the adjusted and predicted $R^2$ were 0.9749 and 0.9490, respectively, which indicates good agreement between the experimental and predicted values. Fig. 7 presents the predicted versus actual RB5 removal percentage values. The actual values were close to the predicted values, showing that the model can be used to describe the interaction between parameters and RB5 removal efficiency.

ANOVA was used to determine the significance and adequacy of the model. Table 5 summarizes the ANOVA results for RB5 removal. The $F$-value for a model is the ratio of the model mean square to the mean square for the residual (Anderson and Whitcomb, 2004). In this study, the model $F$-value was 127.33 indicating that the model is significant. There is only a 0.01% chance that a “Model F-Value” this large could occur due to noise. In general, a probability $F$-value (Prob. > $F$) less than 0.05 is considered significant, whereas a value greater than 0.10 shows that the model term is insignificant. Eliminating insignificant model terms (excluding those which are required to support the hierarchy) is required to improve the regression model. Table 5 shows that $X_1$ (pH), $X_2$ (current density), $X_3$ (electrolyte dose), $X_4$ (flow rate), $X_1, X_3, X_2, X_3, X_2 X_4$ and $X_1^2$ are the significant model terms.

Model suitability could also be analyzed by residual data. This is checked by diagnostic plots such as normal probability and residual plots. The points in the normal probability plot should adhere to a straight line to indicate that the residuals follow a normal distribution (Hassani et al., 2014). This can be seen in Fig. 8 where the normal probability against the residual plot is in normal distribution. “Lack of fit” is a test to compare the deviation of actual points from the fitted surface relative to pure error (Anderson and Whitcomb, 2004). The Prob. > $F$ of “lack-of-fit” for the model was 0.5398; this shows that the lack of fit was insignificant relative to the pure error. A non-significant lack of fit is required to demonstrate the applicability of the model for predicting the response variables within the range of parameters being studied.

### 3.3.3. Effects of variables

A perturbation plot was used to study the individual effect of these parameters, initial pH (A), current density (B), electrolyte dose (C) and flow rate (D) on RB5 elimination. The effect of each parameter over its range can be observed on the plot by

<table>
<thead>
<tr>
<th>Table 3 – Comparison between different anode configurations for electrocoagulation of RB5.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrode configuration</strong></td>
</tr>
<tr>
<td>A: Iron plate</td>
</tr>
<tr>
<td>C: Iron plate</td>
</tr>
<tr>
<td>A: Iron plate</td>
</tr>
<tr>
<td>C: SS plate</td>
</tr>
<tr>
<td>A: Iron mesh double layer</td>
</tr>
<tr>
<td>C: Iron plate</td>
</tr>
</tbody>
</table>

SS: stainless steel.
making the other factors constant. Design-Expert software sets the reference point at code 0 (midpoint) for all the parameters. A steep slope or curvature indicates that the response is sensitive, whereas a flat line shows an insensitive response to change for that particular variable (Hassani et al., 2014). Based on Fig. 9, it was apparent that the electrolyte dose exerts the highest effect on RB5 removal as indicated by the steep slope. The relatively flat line for the flow rate parameter showed that RB5 removal was in this case insensitive.

Fig. 10 shows the interactions between four variables in a three-dimensional surface plot for RB5 removal according to Eq. (20). Fig. 10a depicts the relationship of initial pH and electrolyte dose on RB5 removal at a constant current density (1.5 mA/cm²) and flow rate (11.5 ml/min). The plot implies that RB5 removal is lower at acidic and base condition. At a lower pH, the H⁺ reduced to hydrogen gas (H₂) at the cathode, which reduced the amount of hydroxide ions generated (Sengil and Ozacar, 2009). The maximum RB5 removal was observed in the pH range 5.5–7.4 since this is close to the optimal pH for Fe(OH)₃ solid formation which is able to adsorb the soluble organic compounds and trap the colloidal particles (Bayramoglu et al., 2004). Beyond a pH of 7.4, Fe(OH)₃ dissolves to form Fe(OH)₄⁻ and migrates to the anode surface to undergo oxidization. Consequently, the formation of iron hydroxide coagulant decreased and thus RB5 removal was reduced (Thirugnanasambandham et al., 2015).

NaCl is commonly used to increase the conductivity of the solution; this resulted in a lower voltage being required to achieve a certain current. In this respect, the power consumption can be reduced. Moreover, Cl⁻ ions are able to destroy the passivation layer on the iron electrode leading to a higher anodic dissolution rate (Kuokkanen et al., 2013). The expected result is that RB5 removal increases with a higher NaCl concentration due to the prevalent Cl⁻ formation (Bayramoglu et al., 2004; Daneshvar et al., 2006; Mollih et al., 2004). However,

Table 4 – Central composite design for experimental and predicted RB5 removal.

<table>
<thead>
<tr>
<th>Run</th>
<th>pH</th>
<th>Current density (mA/cm²)</th>
<th>Electrolyte dose (g/L)</th>
<th>Flow rate (ml/min)</th>
<th>Actual (%)</th>
<th>Predicted (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>1.00</td>
<td>0.3</td>
<td>15</td>
<td>11.31</td>
<td>9.80</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
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<td>0.23</td>
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<td>61.47</td>
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<td>3</td>
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<td>2.01</td>
<td>0.15</td>
<td>8</td>
<td>60.21</td>
<td>59.76</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>1.76</td>
<td>0.23</td>
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<td>68.83</td>
<td>66.16</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
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<td>0.15</td>
<td>8</td>
<td>75.97</td>
<td>76.42</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>2.01</td>
<td>0.3</td>
<td>8</td>
<td>43.43</td>
<td>42.93</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>1.00</td>
<td>0.3</td>
<td>8</td>
<td>27.29</td>
<td>24.37</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>2.01</td>
<td>0.15</td>
<td>8</td>
<td>70.69</td>
<td>73.11</td>
</tr>
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Fig. 10a shows that a high NaCl concentration seems to be disadvantageous for the electrocoagulation of RB5 solution which diverges from the expectation. This might be explained by the over consumption of electrode at a higher NaCl dosage during the elimination of the passivation layer (Shankar et al., 2013). Moreover, excess Cl\(^{-}\) in the solution could form transitory compounds such as Fe(OH)\(_2\)Cl, Fe(OH)\(_2\)Cl\(_2\), FeCl\(_2\), and FeCl\(_3\), which compete with RB5 to use Fe(OH)\(_n\) and Fe\(^{2+}\). The obtained data trend is in good agreement with the result presented by Jotin et al. (2012), who found that more NaCl added would reduce the coagulant forming. It’s advisable to add proper NaCl dosage in order to limit the current usage because a high current would enhance oxygen evolution and heat generation, which would then negatively affect dye removal (Mollah et al., 2004).

Fig. 10b shows the combined effect of current density and flow rate on RB5 dye removal at a constant pH 6 and 0.225 g/L NaCl. As can be seen, RB5 removal efficiency increases with increasing current density. An increase in current density improves the formation of Fe(OH)\(_3\) from Fe\(^{2+}\), which is the essential species to remove dye compounds. The production rate of Fe\(^{2+}\) from the anode occurs according to Faraday’s law (Eq. (23)) in which the amount of iron ion formation is directly proportional to current (Mollah et al., 2004). The results are in agreement with those reported in the literature (Patel et al., 2011; Song et al., 2007; Thirugnanasambandham et al., 2015). RB5 removal efficiency decreases with increasing feed flow rate, which is attributable to the increased RB5 dye loading (Mook et al., 2013). Hence, there was insufficient reaction time for iron hydroxide and dye compounds. Low current density and high flow rate could not remove dye significantly due to the inadequate quantity of iron hydroxide and lack of reaction time. At a higher current density, changes in RB5 removal were insignificant at any given flow rate. This likely occurs because there is sufficient iron hydroxide generated to remove even high amounts of dye.

\[
\text{Fe}_{\text{theoretical}}^{2+} = \frac{MI}{ZF},
\]

The interactive effect of current density and electrolyte dose on dye removal for the constant pH of 6 and flow rate of 11.5 mL/min is illustrated in Fig. 10c. The higher values of RB5 removal were obtained by a simultaneously lower electrolyte dose and higher current density.

### 3.3.4. Validation of the model

The desirability value indicates that the response is close to the ideal value. The highest value (1.0) shows a response within the

![Fig. 8 - Normal probability plot for RB5 removal efficiency.](image)

![Fig. 9 - Perturbation plot: A, pH; B, current density; C, electrolyte dose; D, flow rate.](image)

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
<th>DF</th>
<th>MS</th>
<th>F value</th>
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ANOVA: analysis of variance.
SS: Sum of Squares; DF: Degrees of Freedom; MS: Mean Square.
ideal intervals or that it achieves its ideal value (Hassani et al., 2014). The desirability of optimum conditions suggested by RSM was 1.0. To verify the proposed model and optimization result, an experiment was carried out according to the optimum conditions, namely an initial solution pH of 6.29, current density of 1.6 mA/cm², electrolyte dose of 0.15 g/L and flow rate of 11.47 mL/min. RB5 removal efficiency under the optimum conditions was 78.19%, which was previously predicted by the model to be 81.62%. This indicates that the proposed model can sufficiently predict RB5 removal. Additionally, the sludge was found to be black in color as RB5 was being adsorbed or precipitated by iron hydroxides.

4. Conclusion

An iron mesh single and double layer electrodes were employed in the electrocoagulation process to remove RB5. The double layer electrode showed a better performance exhibiting higher RB5 and COD removal efficiency. It was found that the smaller diameter and separating distance of the double layer increase the diffusion coefficient, kinetic rate constant and lower electrical energy consumption. Under optimum conditions of continuous mode, the initial solution pH of 6.29, current density of 1.6 mA/cm², electrolyte dose of 0.15 g/L and flow rate of 11.47 mL/min resulted in an RB5 removal efficiency of 81.62%. From these results, the iron mesh double layer electrode could become a novel alternative electrode for electrocoagulation in wastewater treatment.

Acknowledgments

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REFERENCES


Fig. 10 – Response surface plot of RB5 removal efficiency (a) interaction between pH and electrolyte dose, (b) interaction between current density and flow rate, (c) interaction between current density and electrolyte dose.


