Optimisation of Reactive Black 5 dye removal by electrocoagulation process using response surface methodology

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ABSTRACT

In this work, a regression model obtained from response surface methodology (RSM) was proposed for the electrocoagulation (EC) treatment of textile wastewater. The Reactive Black 5 dye (RB5) was used as a model dye to evaluate the performance of the model design. The effect of initial solution pH, applied current and treatment time on RB5 removal was investigated. The total number of experiments designed by RSM amounted to 27 runs, including three repeated experimental runs at the central point. The accuracy of the model was evaluated by the F-test, coefficient of determination ($R^2$), adjusted $R^2$ and standard deviation. The optimum conditions for RB5 removal were as follows: initial pH of 6.63, current of 0.075 A, electrolyte dose of 0.11 g/L and EC time of 50.3 min. The predicted RB5 removal was 83.3% and the percentage error between experimental and predicted results was only 3–5%. The obtained data confirm that the proposed model can be used for accurate prediction of RB5 removal. The value of the zeta potential increased with treatment time, and the X-ray diffraction pattern shows that iron complexes were found in the sludge.

Key words | electrocoagulation, iron complexes, optimisation, Reactive Black 5, response surface methodology

INTRODUCTION

Reactive dyes are widely used in the textile industry because of their vivid colours and easy attachment to textile fibres (Hassan et al. 2009). However, approximately 15% of unutilised dyes found in the dye bath effluent are the result of the low fixation of reactive dyes on fibres during the dyeing process (Wallace 2003). This amount is substantially dangerous for human beings and aquatic life, as well as the environment in general. Reactive dyes are recognised as recalcitrant compounds because of their high alkalinity, high concentration of organic compounds and strong colour compared to other dyes (Barka et al. 2010). Here, Reactive Black 5 (RB5) was selected as a reactive model dye because it is widely used in the textile industry and constitutes 50% of the total world demand of reactive dyes (Schumacher 2012).

Electrocoagulation (EC) is a popular technique used for the treatment of textile dyeing wastewater (Nandi & Patel 2013). The EC process has distinct advantages over conventional chemical coagulation. It is simple, uses low-cost equipment and is efficient where the coagulant is produced in situ through electro-oxidation of sacrificial anode (Garg & Prasad 2016). Furthermore, EC is characterised by low sludge generation and no secondary pollution, as the process is completed without adding any chemical coagulants (Mollah et al. 2004). The EC process typically involves three mechanisms: (i) production of coagulants by electro-oxidation of the sacrificial anode; (ii) destabilisation of the contaminants, particle suspension and breaking emulsions; and (iii) aggregation of the destabilised phases to form flocs (Gomes et al. 2007).

There is a large amount of literature on textile wastewater treatment using the EC process (Nandi & Patel 2013; Zodi et al. 2013; Kobya et al. 2016); however, limited information on RB5 removal using the EC technique with iron electrode is available. To date, the removal of RB5 using EC method and iron as the sacrificial anode has been reported only by Şengil & Özacak (2009) and Nandi & Patel (2013). A combination technique has been investigated by: (i) Chang et al. (2010) who used combined EC–granular activated carbon adsorption; and (ii) Raghu & Basha (2007) who used electrochemical technique followed by
ion exchange. To the best of our knowledge, RB5 treatment using the EC method with RSM design has only been reported by Mook et al. (in press). In general, one-factor-at-a-time is utilised in a multifactor experiment, but it involves a large number of experiments, and it is difficult to predict the optimum parameters on all responses. Response surface methodology (RSM) in Design Expert software is an efficient statistical tool to build models, and saves time due to the relatively small number of sets of experiments that need to be conducted. Furthermore, it can be used to investigate the interactive effects between parameters and to obtain the optimum conditions for desirable responses (Mook et al. 2015, in press). Hence, in this study, central composite design (CCD) was employed to investigate the interaction between parameters and to maximise the dye removal efficiency by the optimisation of the parameters.

Sodium chloride (NaCl) and sodium sulphate (Na₂SO₄) are common supporting electrolytes that are utilised to increase the electrical conductivity. NaCl is more favourable than Na₂SO₄ as it could generate strong oxidising agents, i.e. hypochlorite ions (Yildiz et al. 2007). This could enhance the oxidation of Fe²⁺ to Fe³⁺ and then the easier formation of Fe(OH)₃. However, using NaCl has the high possibility of forming hazardous by-products such as perchlorate, which has been recognised as carcinogenic (Bergmann & Rollin 2007). Hence, in this study, Na₂SO₄ was selected as a supporting electrolyte.

The aim of this study was to investigate the interaction between various parameters, initial pH, current, electrolyte dosage and EC time, and their effect on RB5 removal. The optimum operation condition was appraised with respect to higher RB5 removal efficiency. Special attention was given to the characterisation of EC sludge under optimum conditions.

METHODOLOGY

Materials and analytical methods

All the chemicals used were analytical grade and supplied by Sigma-Aldrich, Malaysia. The RB5 solution (40 mg/L) was freshly prepared and the pH was adjusted by 0.1 mol/L H₂SO₄ and NaOH. The anode used in the study was an iron woven mesh with a hole size of 0.5 cm × 0.6 cm, while the cathode was a round iron plate of diameter 9 cm. Both were purchased from KY Scientific, Malaysia. The electrodes were immersed in 0.01 mol/L H₂SO₄ for 24 hours and then rinsed with distilled water. Each electrode was polished by sandpaper to remove impurities.

Experimental design

The Design Expert Software (6.0.10) was used for the statistical design of experiments and data analysis. The CCD in RSM was utilised to investigate the interaction between four parameters: pH, current, EC time and electrolyte dose. These variables’ range was divided into five levels (−1, −0.5, 0, +0.5, +1), as shown in Table 1. The total set of experiments designed by CCD was 27 runs (Table 2), including three repeated runs at the central point.

Analysis of variance (ANOVA) was used for statistical analysis; it evaluates the significance of the model. The correlation coefficient (R²) and F-test were utilised to check the quality of the model and the statistical term significance.

Experimental setup and analytical methods

The EC experiments were carried out using a beaker containing 500 mL of RB5 solution with different pH and electrolyte dose according to Table 2. The configuration of the anode was double layer with a diameter of 2.6 cm and layer distance of 0.2 cm (Mook in press). The spacing between the anode and cathode was maintained at 3 cm. A programmable DC power supply (Gw Instek, Malaysia) was used to regulate the electric current of the reactor.

All collected samples were filtered through a 0.22 µm filter membrane to remove the suspended solids that could have affected the analysis process. The concentration of RB5 was determined using a Lambda 35 UV-Vis spectrophotometer (PerkinElmer, USA) at a wavelength of 597 nm.

The stability of the colloidal suspension during the EC process was measured using a zeta potential test (Malvern Nano ZS 90). The sludge produced during the EC process

| Experimental design matrix for experimental and predicted RB5 removal |
|---|---|---|---|---|---|
| Variables | Code | −1 | −0.5 | 0 | +0.5 | +1 |
| pH | X₁ | 4 | 5.5 | 7 | 8.5 | 10 |
| Current (A) | X₂ | 0.045 | 0.059 | 0.073 | 0.086 | 0.1 |
| EC time (min) | X₃ | 5 | 18.75 | 32.5 | 46.25 | 60 |
| Electrolyte dose (g/L) | X₄ | 0.05 | 0.08 | 0.1 | 0.13 | 0.15 |
Table 2 | Independent variables and coded levels

| Run | pH  | Current (A) | EC time (min) | Electrolyte dose (g/L) | R5 removal (%) |
|-----|-----|-------------|---------------|------------------------|---------------|
|     |     |             |               |                        | Experimental | Predicted    |
| 1   | 4   | 0.045       | 5             | 0.05                   | 15.1         | 16.7         |
| 2   | 10  | 0.045       | 5             | 0.05                   | 9.4          | 10.2         |
| 3   | 4   | 0.1         | 5             | 0.05                   | 17.8         | 16.1         |
| 4   | 10  | 0.1         | 5             | 0.05                   | 11.1         | 9.6          |
| 5   | 4   | 0.045       | 60            | 0.05                   | 46.9         | 44.7         |
| 6   | 10  | 0.045       | 60            | 0.05                   | 26.1         | 25.3         |
| 7   | 4   | 0.1         | 60            | 0.05                   | 67.3         | 68.4         |
| 8   | 10  | 0.1         | 60            | 0.05                   | 47.5         | 48.9         |
| 9   | 4   | 0.045       | 5             | 0.15                   | 7.0          | 5.0          |
| 10  | 10  | 0.045       | 5             | 0.15                   | 5.2          | 4.9          |
| 11  | 4   | 0.1         | 5             | 0.15                   | 13.4         | 14.9         |
| 12  | 10  | 0.1         | 5             | 0.15                   | 13.2         | 14.7         |
| 13  | 4   | 0.045       | 60            | 0.15                   | 46.4         | 48.0         |
| 14  | 10  | 0.045       | 60            | 0.15                   | 33.1         | 34.9         |
| 15  | 4   | 0.1         | 60            | 0.15                   | 82.8         | 82.1         |
| 16  | 10  | 0.1         | 60            | 0.15                   | 70.5         | 69.0         |
| 17  | 5.5 | 0.073       | 32.5          | 0.1                    | 65.2         | 64.6         |
| 18  | 8.5 | 0.073       | 32.5          | 0.1                    | 62.8         | 59.7         |
| 19  | 7   | 0.059       | 32.5          | 0.1                    | 61.4         | 63.8         |
| 20  | 7   | 0.086       | 32.5          | 0.1                    | 69.3         | 72.1         |
| 21  | 7   | 0.073       | 18.75         | 0.1                    | 57.0         | 57.7         |
| 22  | 7   | 0.073       | 46.25         | 0.1                    | 79.0         | 78.2         |
| 23  | 7   | 0.073       | 32.5          | 0.08                   | 61.3         | 63.8         |
| 24  | 7   | 0.073       | 32.5          | 0.13                   | 70.1         | 65.9         |
| 25  | 7   | 0.073       | 32.5          | 0.1                    | 69.5         | 67.9         |
| 26  | 7   | 0.073       | 32.5          | 0.1                    | 67.0         | 67.9         |
| 27  | 7   | 0.073       | 32.5          | 0.1                    | 69.2         | 67.9         |

was dried in an oven for 24 h and characterised by X-ray diffraction (XRD) analyses (PANalytical, Malaysia).

RESULTS AND DISCUSSION

Response and statistical analysis by CCD

CCD was employed to investigate the effect of and to optimise the four parameters on RB5 removal. Table 2 shows the experimental and predicted values of RB5 removal corresponding to the design matrix of four parameters by CCD. The analysis suggested quadratic model fitting for the response function. The regression model is presented in Equation (1), where $Y_{\text{act}}$ represents RB5 removal efficiency and $X_1$, $X_2$, $X_3$ and $X_4$ are pH, current, EC time and supporting electrolyte dosage, respectively, after excluding insignificant terms.

$$Y_{\text{act}} = 108.56062 + 34.90139X_1 - 145.13981X_2 + 0.17129X_3 + 744.63708X_4 - 2.59394X_1^2 - 5010.18351X_2^2 - 0.039205X_1X_3 + 10.54583X_1X_4 + 8.00248X_2X_3 + 1898.65636X_2X_4 + 2.70864X_3X_4$$ (1)

The quality and adequacy of the model is evaluated by the correlation coefficient value ($R^2$), adjusted and
The adjusted $R^2$ measures the proportion of the variation about the mean as explained by the model, whereas predicted $R^2$ is a measurement of the model to predict the response value. The discrepancy between predicted and adjusted $R^2$ should be less than 0.20 in order to confirm that the data or model is reliable (Mook et al. in press). Here, the adjusted and predicted $R^2$ are in good agreement, i.e. 0.9912 and 0.9808, respectively. The plot of predicted and actual RB5 removal efficiency (Figure 1) evaluates the accuracy and reliability of the predicted model (Equation (1)). The actual values were close to the predicted values, showing that the model is reliable to describe the effect of the parameters on RB5 removal efficiency.

The significance and adequacy of the model are determined by ANOVA. Table 3 summarises the ANOVA results for RB5 removal. The Fisher variance ratio, F-value, is a statistical valid measurement used to describe the variation in the mean of data (Tak et al. 2015). The probability F-value ($Prob. > F$) below 0.05 is considered as a significant term; insignificant model terms are required to be eliminated in order to improve the quality of the regression model. Here, the suggested quadratic regression model (Equation (1)) is highly significant, which is proven by the low probability value ($Prob. > F = 0.0001$). Table 3 shows that $X_1$ (pH), $X_2$ (current), $X_3$ (EC time), $X_4$ (electrolyte dose), $X_1^2$, $X_2^2$, $X_1X_3$, $X_1X_4$, $X_2X_3$, $X_2X_4$, $X_3X_4$ are the significant model terms, as each $Prob. > F$ was below 0.05.

‘Lack of fit’ is required to compare the deviation of actual points from the fitted surface relative to pure error. A non-significant lack of fit is required to demonstrate the applicability of the model in order to predict the response variables (Mook et al. 2015). The $Prob. > F$ of lack of fit for the quadratic model was 0.2385; this shows that the lack of fit was insignificant, and sufficient to be used to predict RB5 removal efficiency.

| Source          | Sum of squares | Degrees of freedom | Mean square | F-value | Prob > F | $R^2$  | Adj $R^2$ | Pred $R^2$ |
|-----------------|----------------|--------------------|-------------|---------|----------|--------|-----------|------------|
| Model           | 17,433.53      | 11                 | 1,584.87    | 267.13  | <0.0001  | 0.9949 | 0.9912    | 0.9808     |
| Residual        | 89             | 15                 | 5.93        |         |          |        |           |            |
| Lack of fit     | 85.34          | 13                 | 6.56        | 3.59    | 0.2385   |        |           |            |
| Pure error      | 3.65           | 2                  | 1.83        |         |          |        |           |            |
| $X_1$           | 396.16         | 1                  | 396.16      | 66.77   | <0.0001  |        |           |            |
| $X_2$           | 1,159.29       | 1                  | 1,159.29    | 195.4   | <0.0001  |        |           |            |
| $X_3$           | 6,979.71       | 1                  | 6,979.71    | 1,176.42| <0.0001  |        |           |            |
| $X_4$           | 73.12          | 1                  | 73.12       | 12.32   | 0.0032   |        |           |            |
| $X_1^2$         | 134.84         | 1                  | 134.84      | 22.73   | 0.0002   |        |           |            |
| $X_2^2$         | 38.82          | 1                  | 38.82       | 6.54    | 0.0219   |        |           |            |
| $X_1X_3$        | 167.38         | 1                  | 167.38      | 28.21   | <0.0001  |        |           |            |
| $X_1X_4$        | 40.04          | 1                  | 40.04       | 6.75    | 0.0202   |        |           |            |
| $X_2X_3$        | 586            | 1                  | 586         | 98.77   | <0.0001  |        |           |            |
| $X_2X_4$        | 109.05         | 1                  | 109.05      | 18.38   | 0.0006   |        |           |            |
| $X_3X_4$        | 221.94         | 1                  | 221.94      | 37.41   | <0.0001  |        |           |            |

Figure 1 | Predicted values from the response surface model versus actual data for RB5 removal efficiency.
Effect of variables

Interaction effect of pH and EC time

Figure 2 shows the effect of the four parameters on colour removal efficiency in a three-dimensional (3D) plot according to Equation (1). Figure 2(a) shows the effect of pH and EC time on RB5 removal at a constant current of 0.073 A and electrolyte dose of 0.1 g/L. The plot implies that the high removal of RB5 was achieved in weak acid to neutral conditions (pH 5.8–8.22) and longer process times (46–60 min). The RB5 removal decreased above pH 8.22 due to the formation of various iron hydroxides species that influenced the pH.

Iron ions (Fe$^{2+}$) are produced through anode dissolution. During water electrolysis, oxygen and hydroxide ions are produced at the anodic and cathodic region, respectively (Equations (2) and (5)). The Fe$^{2+}$ oxidised
spontaneously to Fe$^{3+}$ in the presence of oxygen species. Subsequently, the hydroxide ions further react with Fe$^{3+}$ to form Fe(OH)$_3$ as shown in Equation (4) (Zaroual et al. 2006). A solubility diagram for Fe(III) in water is presented in Figure 3 (Sengil & Özacar 2009).

Anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ \hspace{1cm} (2)

$2\text{Fe} \rightarrow 2\text{Fe}^{2+} + 4\text{e}^-$ \hspace{1cm} (3)

$2\text{Fe}^{2+} + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Fe(OH)}_3(\text{s}) + 4\text{H}^+$ \hspace{1cm} (4)

Cathode: $4\text{H}_2\text{O} + 2\text{e}^- \rightarrow 4(\text{OH})^- + 2\text{H}_2(\text{g})$ \hspace{1cm} (5)

Overall reaction: $2\text{Fe} + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 
\rightarrow 2\text{Fe(OH)}_3(\text{s}) + 4\text{H}_2(\text{g})$ \hspace{1cm} (6)

At low pH, H$^+$ ions become more prevalent in the solution and are reduced to H$_2$ at the cathode (Equation (7)); the hydroxide ions are then difficult to generate as the electrons are being used for H$^+$ reduction (Equation (5)). As shown in Figure 3, the soluble Fe(OH)$_2$ and Fe(OH)$_{2+}$ were produced, which are not capable of removing pollutant compounds. These species are transformed into Fe(OH)$_3$ in the pH aqueous solution of 6–9.5 (Sengil & Özacar 2009). Fe(OH)$_3$ is an insoluble metal hydroxide and removes the dye molecule through precipitation and adsorption (Mook et al. in press). When the initial pH of the solution is higher than 9.5, monomeric anions of Fe(OH)$_4$ are the dominant species that are formed via dissolution of Fe(OH)$_3$ (Equation (8); Kobya et al. 2006). The RB5 removal efficiency was found to be 89% at the initial pH of 6.3, which was the original pH of the dye solution. The obtained data are in a good agreement with the results presented by Daneshvar et al. (2006), who reported the maximum colour removal of Basic Red 46 and Basic Blue 3 between pH 5.5 and 8.5.

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ \hspace{1cm} (7)

$\text{Fe(OH)}_3 + \text{OH}^- \leftrightarrow \text{Fe(OH)}_4^-$ \hspace{1cm} (8)

During water electrolysis, hydrogen and hydroxide ions are produced as shown in Equations (2) and (5). The increasing of the final pH from acidic to alkaline is due to the presence of OH$^-$ ions, whereas the final pH of alkaline conditions (> pH 9) slightly decreases due to the consumption of hydroxide ions to form Fe(OH)$_4$ (Equation (8); Nandi & Patel 2013).

Interaction effect of pH and electrolyte dose

The supporting electrolyte is used to increase the conductivity of the solution in order to reduce the resistance between electrodes. As resistance decreases, the cell voltage decreases and contributes to the lower power consumption during the treatment process (Nandi & Patel 2013). Figure 2(b) shows the effect of pH and electrolyte dose on RB5 removal by maintaining current and EC time in the middle levels (0.073 A and 32.5 min). It was observed that the trend of RB5 removal was initially increased with increasing pH and then decelerated above pH 7 at any Na$_2$SO$_4$ concentration. Increasing the concentration of Na$_2$SO$_4$ from 0.05 to 0.1 g/L slightly increased the RB5 removal efficiency. In other words, the increased conductivity of the solution had a minor effect on the efficiency of dye removal. Moreover, among the four parameters of initial pH, current, EC time and electrolyte dose, the Prob. > F of electrolyte dose was the highest, indicating that the electrolyte dose has only a minor effect on RB5 removal.

The RB5 removal efficiency decreased above 0.1 g/L Na$_2$SO$_4$ concentration. This might be attributed to the excess of SO$_4^{2-}$ ions that interact with iron hydroxides via ligand exchange (Equation (9)). As a result, the amount of iron hydroxides required for dye removal decreased (Kleinhenz 1999). The removal trend is in a good agreement with the results presented by Tezcan Ün et al. (2009), who used EC to treat wastewater from a cattle slaughterhouse.
Interaction effect of electrolyte dose and current

The interactive effect of electrolyte dose and current on dye removal for a constant pH of 7 and treatment time of 32.5 min is illustrated in Figure 2(c). The higher removal of RB5 was obtained by the interaction between moderate electrolyte dosage and high current. The increase in applied current had a positive effect on dye removal for any given electrolyte dose. According to Faraday’s law (Equation (10)), the amount of Fe\(^{2+}\) formed from the anode is directly proportional to the current (Mollah et al. 2004). The increment quantity of Fe\(^{2+}\) enhances the formation of Fe(OH)\(_3\), which is the essential component to eliminate dye compounds. Furthermore, the bubble generation rate comprises oxygen (evaluated from the anode surface) and hydrogen gas (takes place in the cathode) and increases with current, which is beneficial for pollutants removed by flotation (Abdel-Gawad et al. 2012). However, increasing the current from 0.08 A to 0.1 A at a constant electrolyte dose of 0.1 g/L and pH 7 resulted in a slight improvement of RB5 removal, from 70.5% to 76.4%, respectively. The higher current might cause excessive production of oxygen and hydrogen gas, which disperses current usage for the generation of Fe\(^{2+}\) and OH\(^-\). Hence, current is one of the crucial parameters for EC treatment of wastewater.

\[
\text{Fe}^{2+}_{\text{theoretical}} = \frac{MI}{ZF} \tag{10}
\]

where \(M\) is the molecular weight of the iron (g/mol), \(I\) is the current (A), \(t\) is the operation time (s), \(Z\) is the number of electrons involved in the reaction (iron is +2) and \(F\) is the Faraday constant (96,485 C/mol).

Interaction effect of current and EC time

The effect of current and EC time, maintaining pH = 7 and electrolyte dose of 0.1 g/L, is shown in Figure 2(d). As the current and duration of the EC process increased, RB5 removal trend was growing. At constant current of 0.07 A, the RB5 removed as much as 86.6% after 60 min of treatment time. According to Equation (3), the production of Fe\(^{2+}\) increases with the time of the process. So, the formation of Fe(OH)\(_3\) was higher, and thus a sufficient amount of coagulants could react with dye compounds. Moreover, there was sufficient time for the coagulant to interact with RB5, and for the bubble generation that enhanced the flotation ability (Tezcan Ün et al. 2013).

Interaction effect of EC time and electrolyte dose

The interactive effect of EC time and electrolyte dose on RB5 removal at a constant pH 7 and current of 0.073 A is illustrated in Figure 2(e). The higher RB5 removal was obtained by a simultaneous higher electrolysis time and an intermediate range of Na\(_2\)SO\(_4\) of 0.08–0.12 g/L.

Optimisation operating conditions

The RSM software suggests a specific point that maximises desirability. The highest desirability value is 1.0, indicating that the response is close to the ideal value. The optimal operating conditions for the maximum RB5 removal were initial pH of 6.63, current of 0.075 A, electrolyte dose of 0.11 g/L and EC time of 50.3 min. Under the optimum conditions, the experimental removal efficiency of RB5 was 80.9%, close to the predicted value (83.3%). This proves that the proposed model (Equation (1)) is reliable and sufficient to predict the RB5 removal efficiency.

EC mechanism

The EC of RB5 is a complicated mechanism. The colour of the solution was removed by adsorption or complexation with iron hydroxides to form ionic bonds. Figure 4 shows the decolorisation of RB5 under optimum conditions (pH of 6.63, current of 0.075 A, electrolyte dose of 0.11 g/L and EC time of 50.3 min). The spectra of RB5 before treatment are characterised by two main peaks: a visible region with an absorbance peak at 597 nm, and an ultraviolet region with an absorbance peak at 312 nm. The peak at 597 nm corresponds to chromophoric group \(-\text{N}\equiv\text{N}-\), and the peak at 312 nm is related to benzene rings. As seen in
Figure 3, the peak at 597 nm decreased quickly within 20 min and the absorbance was reduced to 0.1825 after 50.3 min. This shows that the \(-\text{N}={\text{N}}-\) was cleavage, and the colour disappeared rapidly. As the EC process proceeds, the peak at 312 nm decreases concurrently with the reducing peak at 595 nm. During EC degradation, cleavage of \(-\text{N}={\text{N}}-\) and aromatic rings occurred, resulting in a decrease of the absorbance band of the dye solution. The obtained data are in good agreement with the results presented by Weng et al. (2013).

The colloid is recognised as a stable system, as the similar charges will repel each other and are difficult to aggregate. The charged colloidal particles attract opposite-charged ions to their surface to maintain their electroneutrality. The attraction of counter-ions leads to an electric double layer that includes the Stern and diffuse layers. However, it is difficult to determine the charge at the colloid surface, since the Stern layer is tightly bound to the colloid. Hence, the zeta potential is used as a measurement of the effective charge of the particle as it moves through the solution. In other words, zeta potential acts as an indicator of

Table 4 | XRD data of the sludge collected after the EC process

| \(2\theta\) (°) | Structure name | Molecular formula | Molecular structure |
|-----|----------------|------------------|--------------------|
| 8.22 | –              | \([\text{Fe}_4(\text{CO})_{13}C]\)^3^- | ![XRD diagram for 8.22°] |
| 11.82 | Amarantite | \(\text{Fe}^{3+}(\text{SO}_4)(\text{OH}).3\text{H}_2\text{O}\) | ![XRD diagram for 11.82°] |
| 21.32 | Ferrotychite | \(\text{Na}_6(\text{Fe}_2(\text{CO}_3)_4(\text{SO}_4) | ![XRD diagram for 21.32°] |

(continued)
solution stability. The function of the coagulant generated through electrolysis is to destabilise the colloidal suspension, which enables the destabilised particles to aggregate (Holt et al. 2002).

Figure 5 illustrates zeta potential measurements along with EC time for optimum conditions. The zeta potential values changed with time, which indicates that there was chemical interaction between the pollutants and iron hydroxide precipitates. The pollutants might be removed by hydrogen bonding and van der Waals interaction, but these types of attraction do not effect any change of zeta potential (Zaroual et al. 2006). During the first 3 minutes
of the EC process, there are no significant changes of zeta potential. This observation might be due to the low generation of iron, which limits the coagulation process. An increase in electrolysis time will increase the iron concentration, and as a consequence, the formation of coagulant will be greater. These cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids, in order to aggregate the pollutant. As the quantity of the coagulant increases, the dye removal efficiency and zeta potential increased (Emamjomeh 2006).

The final sludge produced during the EC process carried out under optimum conditions was analysed by XRD analysis in order to identify the residue obtained through the process. Table 4 summarises the chemical compounds observed from each peak in the XRD pattern. Iron complexes were present in the sludge. Körbahti proposed the possible mechanisms of formation of iron complexes in the EC process. Iron complexes were obtained through the surface complexation pathway, whereby the pollutant (RB5) acted as a ligand to bind with an iron hydroxide molecule followed by bond-dissociation; the iron complexes were formed during the precipitation and adsorption route, as shown in Equations (11)–(14) (Körbahti et al. 2011).

Precipitation: dye + monomeric Fe
→ [dye_monomeric Fe] (11)
dye + polymeric Fe → [dye_polymeric Fe] (12)
Adsorption: dye + Fe(OH)ₙ → [particle] (13)
[dye_polymeric Fe] + Fe(OH)ₙ → [particle] (14)

CONCLUSIONS

CCD in RSM was used for experimental design to achieve the optimum conditions for maximum removal efficiency of RB5. A quadratic model was suggested by CCD for fitting the response function. It was found that an initial pH of weak acid to neutral conditions, higher current, longer treatment time and intermediate electrolyte dose gave higher RB5 removal efficiency. The application of optimum conditions of EC treatment, i.e. initial pH of 6.63, current of 0.075 A, electrolyte dose of 0.11 g/L and EC time of 50.3 min, resulted in RB5 removal of 80.9%. The regression model can reliably predict EC in RB5 wastewater treatment. The zeta potential increased with electrolysis time, and the XRD indicated that the chemical compounds found in the sludge were iron complexes. The evaluation of intermediates (in solution) and sludge obtained at different treatment process times by gas chromatography–mass spectrometry and XRD is essential for future studies, to ensure that no toxicity compounds are presence in the effluent.

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