Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23619

146 (2019) 85–97
April

Optimization of batch electrochemical coagulation for treatment of real textile wastewater using stainless steel electrodes by CCD of RSM

Srikantha Hanumanthappa[a,*], Mahesh Shivaswamy[b], Sahana Mahesh[b]

[a]*Department of Civil Engineering, School of Engineering & Technology, Jain Global Campus, Jain University, Jakkasandra Post 562112, Bengaluru, India, email: sriki.env@gmail.com*
[b]*Department of Environmental Engineering, Sri Jayachamarajendra College of Engineering (JSS S&T University), Mysuru 570006, India, emails: maheshs@sjce.ac.in (M. Shivaswamy), sahanam@sjce.ac.in (S. Mahesh)*

Received 13 June 2018; Accepted 10 December 2018

ABSTRACT

The practicability and application of the batch electrochemical coagulation (ECC) for the treatment of real textile wastewater (TWW) was evaluated using stainless steel (SS) electrodes in sequence. The central composite design using response surface methodology was used to evaluate and optimize the effect of current density, electrolysis time and electrode numbers as independent variables on the color and chemical oxygen demand (COD) removal as the response function. The significance of the independent variables and their interactions was tested by means of analysis of variance (ANOVA) with 95% confidence level showing R^2 value of 91.48% for color and 92.08% for COD. An optimal current density 180 A/m^2, 45 min of electrolysis time and 4 SS electrodes in ECC showed minimal deviations of the observed values giving the predicted value of 93.60% color and 90.21% COD removal efficiency ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and thermo-gravimetric analysis (TGA) characterized the sludge generated after ECC treatment. SEM images showed vicissitudes on the anode plate with large dents and flake deposits. EDX results of post ECC sludge showed high amounts of metals because of electrode dissolution. TGA plots showed the completion of the oxidation process at higher temperature and the residue remained in it. The operating cost was found to be 2.97 Rs./m^3 (Indian Rupee) and the specific energy consumption was 8.1 kWh/m^3 of TWW treated for color and COD removal using 4 SS electrodes.

Keywords: Batch electrochemical coagulation (BECC); Central composite design (CCD); Response surface methodology (RSM); Color and COD removal; Operating cost; Specific energy consumption

1. Introduction

Textile industries are one of the major contributors to the economy of modern society with demand for variety of fabric materials. In India, textile industries are listed in the 'Red' category and marked as the most-polluted wastewater because a variety of dyes and chemicals are added during textile processing which confounds treatment before discharge into fragile delicate ecosystems. Wastewater treatment units in the textile industry consume ~1,000 m^3 of water every day [1]. High levels of chemical oxygen demand (COD), burly color, total dissolved solids (TDS), highly fluctuating pH, recalcitrancy and poor biological degradation make textile wastewater (TWW) carcinogenic, toxic and mutagenic/teratogenic to various aquatic species [2,3]. Local dyers in small towns in India produce large quantities of textile printing dye bath effluent during dyeing of textiles and woolen fabrics [4]. Removal of color and organics from TWW is a major environmental concern.

* Corresponding author.

Conventional treatment methods are too slow or ineffective in treating TWW and tend to generate large quantities of sludge [5]. Various treatment methods viz., segregation, pre- and post-aeration, neutralization, adsorption [6], coagulation–flocculation [7], mechanical filtration, biological treatment methods [8], ultrafiltration and advanced oxidation methods are in use for treatment of TWW but with wide limitations. Advanced research in treatment of TWW has several technical benefits for degradation of dyes but is high in cost requiring expensive equipment and high-energy requirements [9]. Social concerns of environmental impacts caused by the 'Red' and 'Orange' category industries demand new laws to implement strict mandates on environmental protection and a search for 'greener' and more efficient methods for wastewater treatment [10]. In this sense, electrochemical coagulation (ECC) as a treatment process for pollutants/contaminant removal is unique because it prevents the use of dilution, hazardous materials and does not require any added chemicals as additives to carry out oxidation/reduction reactions [11]. The ECC treatment process has found many applications in various types of contaminated water and industrial wastewaters such as oil mill effluent [12], textile dyes [13], electroplating [14], landfill leachate [15], distilleries [16], paper and pulp mill [10,17,18], poultry slaughterhouse [19], etc., proving its versatility and environmental compatibility giving small energy and spatial footprints.

Literature shows the promising results in treatment of textile wastewater using ECC technique. El-Ashtoukhy and Amin [20] studied removal of acid green dye 50 by anodic oxidation and ECC. Eight graphite rod anodes of diameter 1 cm were used as an anode and stainless steel (SS) mesh was used as cathode for current density (CD) 3.51 A/m^2 and 20 min electrolysis time (ET) achieving COD reductions of 68% and 87% proving that ECC is more economical than electrochemical oxidation. Ghanbari et al. [21] reported batch EC/ECF using Fe and Al electrodes as anodes in a cylindrical electrochemical reactor (ECR) made of Cu to serve as cathode for treating real TWW in 40 min ET achieving 98% and 87% color and COD removal for Fe-Al electrode combinations at neutral pH at 300 mA current. Kobya et al. [22] reported real dye house effluent treatment by continuous ECC using a 3.5 L ECR using Fe electrodes in monopolar parallel arrangement over an area of 660 m^2, CD 45 A/m^2 for 33 min ET. Removal efficiencies of COD and turbidity were 85% and 95% for Fe electrode and 77% and 95% for Al electrode. Recently, Mbacké et al. [23] studied crystal violet removal by batch ECC using Al and SS electrodes. The effectiveness of ECC was observed over a wide concentration range of 5–200 mg/L with color reductions over 70% at 15 min ET using Al electrodes. At about 60 min ET and an applied CD of 250 A/m^2 and an inter-electrode distance of 0.5 cm, SS electrodes achieved 99% color removal.

The aim of this research work was to optimize color and COD removal from real textile wastewater by adopting the ECC process and applying response surface methodology (RSM). RSM is an efficient experimental tool based on statistical analysis to determine optimal conditions for a multivariable system [24]. Statistical optimization before treatment can determine the role of each component and the interactions between the quality parameters that can save time, decrease the need for instrumentation and control on chemical additives and labor [25]. The application of RSM has demonstrated that this modeling can effectively optimize and predict the ECC processes [26] prior to experimentation. So, in this study RSM is employed to optimize and evaluate interlinks of influencing factors on the treatment efficiency of TWW with different number of experiments. For this purpose, a central composite design (CCD) was used to develop mathematical correlation between color and COD removal efficiency and three selected independent parameters such as CD, ET and number of electrodes.

The main intention of this study is to use SS electrodes in sequence (2, 4, 6, 8 and 10) in ECC of TWW because it involves the scale-up factor 'specific electrode area to volume (SEA/V) ratio'. The research objectives were set to study the electrochemical degradation levels using different electrode numbers (i.e., SEA/V) using SS electrodes for the treatment of raw TWW as is without dilution or modifications by any sort of adding salts/additives, etc. The sludge generated from the post-ECC treatment was characterized for physico-chemical characteristics, proximate and ultimate analysis, pH_{pzc}, surface morphology using scanning electron microscopy (SEM), elemental quantification using energy dispersive X-ray (EDX) spectroscopy and quantitative analysis of change in mass of sludge using thermo-gravimetric analysis (TGA) for reuse and recovery of the sludge. Finally, the operating cost and specific energy consumption (SEC) of the process at optimum conditions were also determined.

2. Materials and methods

The chemicals used for the estimation of water quality parameters were of analytical reagent grade purchased from Himedia Laboratories, Mumbai, India. The dimensional

Table 1
Cell characteristics of electrochemical reactor (ECR) and electrodes

Reactor		Electrodes	
Characteristics	Details	Characteristics	Details
Reactor type	Cubical shape of organic glass	Material	Stainless steel (SS 304 grade)
Dimensions (mm)	150 × 140 × 130		
Volume (L)	1.5	Shape	Rectangle
Electrode gap (mm)	10	Dimensions (mm)	100 × 50
Operating mode	Batch	Thickness (mm)	0.7–1.0
Stirring mechanism	Magnetic stirrer, 400 rpm	Connection	Bipolar
Power supply		Voltage range (V): 0–40	Current range (A): 0–5

characteristics of the reactor, electrodes and the configuration details are presented in Table 1. All the electrode plates were cleared off for scales and oxides on its surface using 15% hydrochloric acid and rinsed using distilled water.

2.1. BECC experiments

BECC experiments on raw TWW for removal of color and COD were carried out in duplicate and the test runs were performed at ambient temperature 25°C–27°C. Batch ECC experiments with applied cell voltages of 6, 12, 18, 24 and 30 V giving corresponding CDs of 20, 60, 180, 260 and 300 A/m^2 were carried out in a cuboidal 1.5 L ECR using SS electrodes for different electrode numbers or in sequence (2, 4, 6, 8 and 10) placed in parallel in a bipolar arrangement. The samples were retrieved at 15 min time intervals during treatment and at 75 min ET. The treated effluent samples were filtered and analyzed for pH, COD, color and other quality parameters. The electrode arrangements (4 SS) were set in bipolar mode and all BECC experiments lasted for 60–75 min ET (Fig. 1).

2.2. Instruments and analytical equipment

Water quality parameters were analyzed using various instruments and equipment following the Standard methods by APHA guidelines [27]. pH was measured using an inoLab WTW pH-meter, color by Platinum-Cobalt method and COD by closed reflux method using digestion unit (DRB200, HACH, USA). The surface morphology of electrodes and post ECC solid sludge residues was determined using SEM (SU3500, Hitachi, Japan) for the detailed characterization and to correlate the changes in electrode surface and also to observe solid residues. EDX spectroscopic analysis was carried out using EDX analyzer (QUANTA, Model 200 FEG, USA). The post-ECC dry sludge was subject to thermal analysis to measure and record the dynamics of sludge weight loss with increasing temperature and time using thermogravimetric (Pyris Diamond) analyzer.

2.3. Characteristics of raw textile wastewater

Raw textile wastewater for use in batch ECC was collected from an outfall conduit entering the equalization basin of a local textile mill. The dyes used on the fabric are acid dyes, direct dyes and vat dyes. The dye constituents that are unable to hug the fabric end up in the waste stream adding color to the effluent over 3000 PCU (Platinum-Cobalt unit). Raw TWW was characterized for various water quality parameters using procedures accorded to Standard methods [27] for analysis of wastewater. The initial characteristics of raw TWW used in the BECC are shown in Table 2.

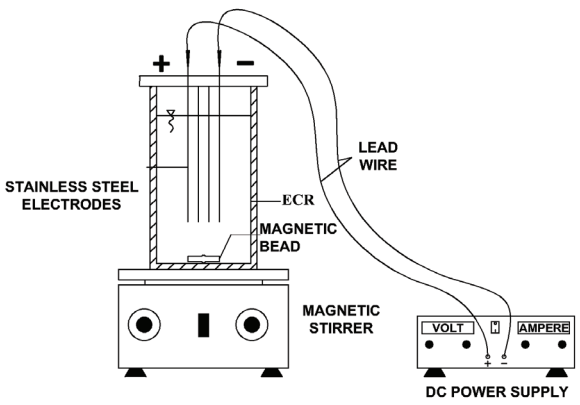

Fig. 1. Bipolar electrode arrangements using stainless steel (SS) electrodes.

2.4. Experimental design and data analysis

The CCD was used to create a set of designed experiments by STATISTICA software (StatSoft, USA) for the statistical design of experiments and data analysis performed in duplicate. The three most important operating variables such as CD, ET and number of electrodes were optimized and coded as x_1, x_2 and x_3. The study range chosen for selected parameters was as CD 20–300 A/m^2, ET 15–75 min and number of electrodes 2–10 for ECC using SS electrodes. CD, ET and number of electrodes were chosen as three independent variables in the ECC process with the range and levels are shown in Table 3.

Table 2
Physico-chemical characteristics of raw textile wastewater

Characteristics	Parameter value
pH	7.25–7.89
Color dark bluish purple, platinum-cobalt (PCU)	900–1,100
Oil and grease, mg/L	20–42
Chlorides, mg/L	760–1,320
Conductivity, mS/cm	2.4–2.9
Total hardness as $CaCO_3$, mg/L	10–14
Total alkalinity as $CaCO_3$, mg/L	20–28
Total solids (TS), mg/L	2,540–3,290
Total suspended solids (TSS), mg/L	980–1,230
Total dissolved solids (TDS), mg/L	1,560–2,060
Chemical oxygen demand (COD) as mg/L of O_2, mg/L	2,728–3,200
Biochemical oxygen demand (BOD_5), mg/L	820–890
COD/BOD	3.32–3.59
Nitrate, mg/L	18–28
Phosphate, mg/L	150–220
Sulfate, mg/L	55–78
Cl^-/SO_4^- (passivation factor)	13.81–16.92

Table 3
Coded and original factors

Original factors	Factor	Range of coded factors				
		–2	–1	0	+1	+2
x_1	Current density (CD), A/m^2	20	60	180	260	300
x_2	Electrolysis time (ET), min	15	30	45	60	75
x_3	Number of electrodes	2	4	6	8	10

For evaluation of experimental data, the response variable is fitted by second-order model in the form of quadratic polynomial model. In Table 3, the coded values for x_1, x_2 and x_3 are set at five levels –2, –1, 0, +1 and +2. Two dependent variables such as color and COD removals are analyzed as responses to obtain optimum CD, ET and number of electrodes for BECC treatment of real TWW as given in Eq. (1).

$$Y\left(\%\right) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (1)$$

2.5. Reaction mechanisms while treating real TWW

Two sorts of reactions occur in the ECC treatment process: (a) electrode-related reactions and (b) water quality–related reactions.

(a) Electrode-related reactions: The chemical reactions using SS electrodes are described using Eqs. (2)–(4) [28,29].

Stainless steel:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (2)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (3)$$

$$Fe \rightarrow Fe^{3+} + 3e^- \quad (4)$$

Metal ions such as Fe^{2+} and Fe^{3+} following the Pourbiax precipitate manifest curves combine with the negatively charged hydroxide ions (OH^-) to form respective hydroxides in the ECR. The real TWW used in BECC experiments was slightly alkaline with the initial pH values 7.25–7.89. During ECC, pH_0 value tends to change (increase or decrease) from its initial value depending on the electrode used. Under alkaline conditions of the bulk solution, electrolytic oxidation of SS produces Fe^{2+} and Fe^{3+} ions hydrolyze to produce insoluble $Fe(OH)_2$ presented in Eq. (5).

$$Fe^{2+} + 2OH^- \rightarrow Fe\left(OH\right)_2 \quad (5)$$

Under acidic conditions in the ECR, Fe^{2+} ions combine with oxygen to form a mild acid that lowers the bulk solution pH as shown in Eq. (6) [30].

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \quad (6)$$

When iron undergoes hydrolysis under acidic conditions preceding Eq. (5) and takes the form as shown in Eq. (7).

$$Fe + 6H_2O \rightarrow Fe(H_2O)_4(OH)_2 + 2H^+ + 2e^- \quad (7)$$

Triquetrahydroxy iron (III) begin to precipitate flocs displaying yellow color and rust forms on the SS electrodes ascribed to the reaction in Eq. (8) [31].

$$2Fe\left(H_2O\right)_3\left(OH\right)_3 \rightarrow Fe_2O_3 + 9H_2O \quad (8)$$

When the wastewater pH turns alkaline during ECC with pH values near 9, the precipitation occurs to form dark green floc. The so-formed flocs indicate the degradation byproducts of SS electrodes giving tetra aquadihydroxy iron (II) and Eq. (9) forms as reported by Thirugnanasambandham et al. [32].

$$Fe\left(H_2O\right)_4\left(OH\right)_2\left(aq\right) \rightarrow Fe\left(H_2O\right)_4\left(OH\right)_2\left(s\right) \quad (9)$$

(b) Water quality–related equations: water electrolysis is known as a process of electrically splitting water into oxygen and hydrogen. The overall electrolysis of water is represented by Eq. (10).

$$2\,H_2O - 4\,e^- \rightarrow O_2 + 4\,H^+ \quad (10)$$

3. Results and discussion

3.1. Scale-up parameter SEA/V control

The electrode numbers and the active area on the electrode face for a fixed volume of wastewater (SEA/V) have to be determined to overcome reported misconceptions that a larger number of electrodes give high removal of color and COD during ECC. Henceforth, a number of discrete BECC experiments were conducted to identify the number of electrodes to be used in a fixed working volume of 1.5 L. This analysis allows us to obtain a near to true SEA/V to be adopted which gives maximum removal of target pollutants/contaminants simultaneously keeping an eye on the electrode dissolution costs to control sludge production for minimum sludge volume index and to minimize running costs.

Through previous ECC experiments, over an operating voltage bandwidth of 5–40 V, a cell voltage of 18 V and corresponding CD of 180 A/m^2 was found optimum to achieve maximum removal of color and COD. Therefore, BECC experiments were conducted using 18 V cell voltage at different SEA/Vs. The SEA/V for 2, 4, 6, 8 and 10 electrodes was 6.6, 20, 33.33, 46.66 and 60 m^2/m^3, respectively. An SEA/V of 6.6 m^2/m^3, that is, two electrodes showed poor color and COD removals because of limited release of low charge M^+ ions into solution resulting in poor contaminant removal efficiencies. On the other extreme with increasing number of electrodes (8 and 10) or at much higher SEA/V, color and COD removals in the bulk solution were seen to decrease with the excess release of M^+ ions into solution bombarding and repelling with each other adding to the background COD values making the wastewater murky. Of the entire SS electrode sequences (2, 4, 6, 8 and 10), only 4 SS electrodes showed better color and COD removal efficiency. After the completion of each experiment, color and COD values were estimated using Standard methods [27].

The results obtained for color and COD removals after BECC of 75 min ET are shown in Fig. 2. The maximum color and COD removals of 94% and 89.64% were observed for 4 SS electrodes (SEA/V: 20 m^2/m^3). Similarly, maximum color and COD removals were 60 PCU from its initial color value of 1,000–1,100 PCU and COD of 312 mg/L from its initial value of 2,728–3,200 mg/L. This optimal operating condition

establishes that M^+ ions released in the solution that capture colloids is well synchronized with the color and COD removal from the bulk solution. During the ECC treatment process, the pH was observed to increase in all the experimental runs as the electrode numbers were increased. To avoid pH adjustment costs, the original pH value of 7.51 was retained and used in ECC treatment without any addition/modifications made to the wastewater.

3.2. Discrete time batch electrolysis for selected ET

Batch ECC using 4 SS electrodes for discrete ET of 15, 30, 45, 60 and 75 min was conducted to observe the pattern of COD and color removal. After each discrete BECC, water quality checks were made for color, COD, etc. When using 4 SS electrodes, COD residues in solution were observed to be 960, 768, 256, 768 and 1,280 mg/L with corresponding color removal of 800, 200, 20, 60 and 900 PCU after 15, 30, 45, 60 and 75 min ET. Several important water quality parameters of post ECC supernatant of 4 SS electrodes are shown in Table 4. The water quality parameters such as TDSs, chloride and total alkalinity were also reduced at 45 min ET; therefore, the optimal experimental condition was chosen as CD 180 A/m^2, 45 min ET and 4 SS electrodes.

The chlorine species formed in the ECR rely mainly on the type of wastewater and chlorines species that form when wastewater pH is between pH 6 and 9. During characterization of raw TWW high chloride concentrations of 760 mg/L was observed. During the ECC process, chlorine gas was generated at the anode and other chlorine species such as HOCl and ClO^- were formed depending upon the pH. The chlorine ions produced amid ECC treatment by the responses is exhibited in Eqs. (11)–(13).

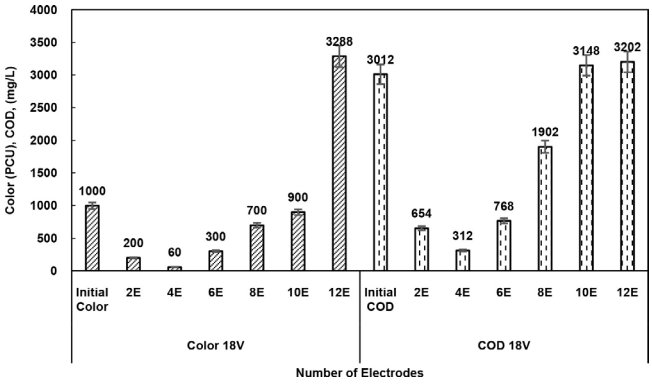

Fig. 2. Color and COD removals for different electrode numbers using SS plate electrodes. Operating conditions: ECR: 1.5 L; electrode arrangements: bipolar; color$_0$: 1,000 PCU; COD$_0$: 3,012 mg L^{-1}; ET: 75 min; agitation speed: 400 rpm; CD: 180 A/m^2.

$$2Cl^+ + 2e^- \rightarrow Cl_2 \uparrow \quad (11)$$

$$Cl_2 + H_2O \leftrightarrow HOCl + Cl^- + H_2^+ \quad (12)$$

$$HOCl \leftrightarrow ClO^- + H^+ \quad (13)$$

3.3. Statistical analysis of color removal using RSM and ANOVA

To check the accuracy of the data obtained (optimal operating condition) from BECC experiments and its relationship between three variables (CD, ET and number of electrodes or SEA/V) using SS electrodes was checked and analyzed by CCD using RSM. The design matrix with experimental and predicted (color and COD) removal efficiencies using SS electrodes is presented in Table 5. It shows CCD in the form of a 2^3 full factorial design with three additional experimental trials (run numbers 1, 5 and 6) as replicates of the central point.

Color and COD removal efficiencies were determined by performing optimization studies based on the corresponding operation studies. The optimized results for color and COD are given in Figs. 3 and 5 showing efficiency graphs for each of the three independent parameters CD, ET and number of electrodes or SEA/V.

Fig. 3 shows the effect of independent parameters such as CD, ET and number of electrodes (SEA/V) on the color removal efficiencies and the adequacy of RSM as justified through ANOVA. Response surface plots show the peaks for the optimum condition maximum values for the said independent variables. According to Fig. 3, the independent variables CD, ET and number of electrodes have positive effect on color removal. Therefore, from Table 5, it is shown that the observed color removal efficiency was 98% for CD 180 A/m^2, 45 min ET and number of electrodes is four; the average efficiency was 93.60% according to the predicted values with a deviation of 4.4%.

Analysis of variance (ANOVA) is used for graphical analysis of the data to fetch interactions between the process variables and the responses. The larger the value of F and the smaller the value of p, the more significant the corresponding

Table 4
Post BECC water quality for 4 SS electrode combinations for CD 180 A/m^2 at discrete 15, 30, 45, 60 and 75 min ET

Parameters	Post ECC values of 4 SS electrodes after BECC					
	Initial	15 min	30 min	45 min	60 min	75 min
pH	7.53 ± 0.3	8.17	8.18	8.3	8.41	8.84
Color, PCU	900–1,100	800	200	20	60	900
Total dissolved solids, mg/L	1,560–2,060	1,940	1,160	728	853	2,269
Total alkalinity, mg/L	20–28	99	98	98	98	98
Chloride, mg/L	760–1,320	616	489	356	388	702
COD, mg/L	2,728–3,200	960	768	256	768	1,280

Table 5
Actual design of experiments and responses (observed and predicted values) for ECC using SS electrodes

Exp. no.	CD x_1 (A/m^2)	ET x_2 (min)	Number of electrode x_3	Removal efficiency (%)			
				Color in % (observed)	Color in % (predicted)	COD in % (observed)	COD in % (predicted)
1	180	45	4	98	93.60	96	90.21
2	60	60	8	50	51.70	50	47.26
3	60	60	6	72	69.33	60	63.14
4	180	45	2	90	94.23	88	92.21
5	180	45	4	99	93.60	95	90.21
6	180	45	4	98	93.60	95	90.21
7	60	30	6	68	63.47	56	52.40
8	260	60	6	54	71.42	43	60.36
9	180	45	10	20	28.95	18	27.95
10	260	30	8	40	35.50	32	25.38
11	180	15	4	40	39.38	32	32.11
12	260	30	6	49	56.46	38	46.32
13	300	45	4	88	84.52	72	69.00
14	180	75	4	95	94.62	92	90.68
15	180	45	2	90	94.23	88	92.21
16	260	60	8	46	31.25	35	21.07
17	20	45	4	60	61.50	45	45.57

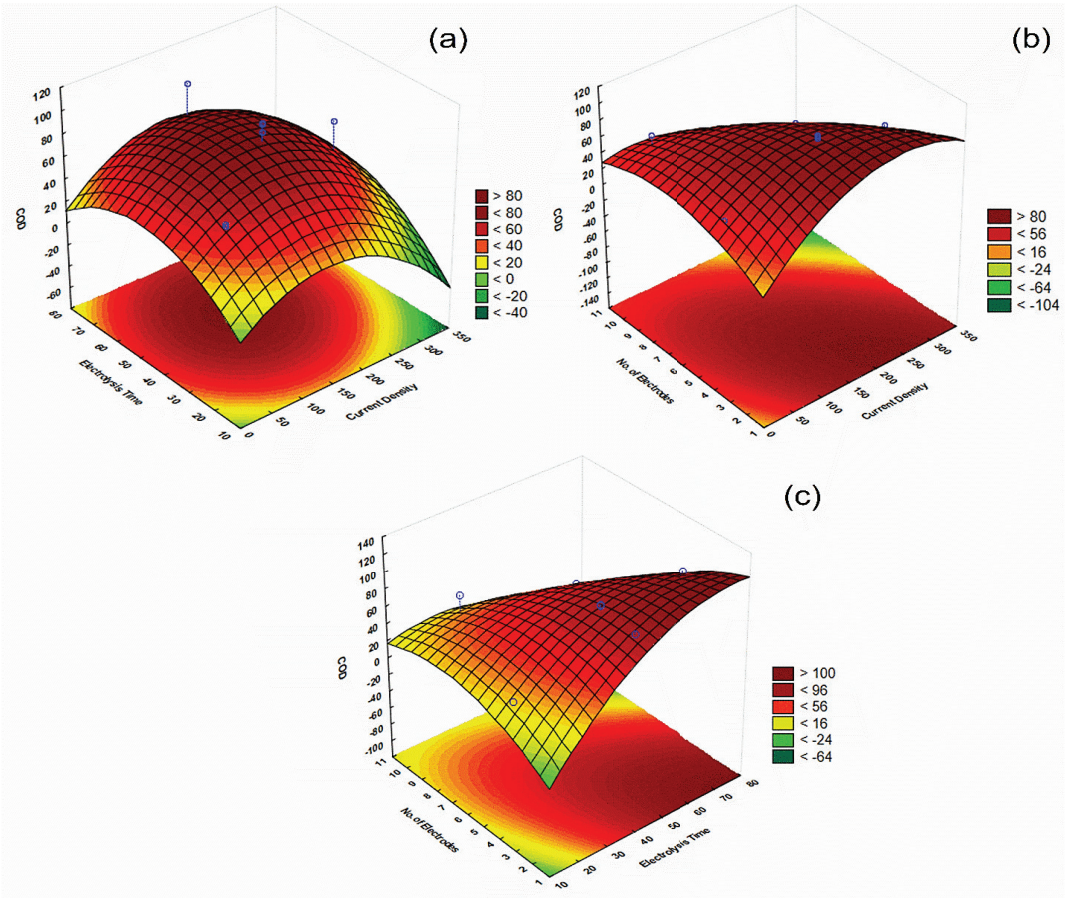

Fig. 3. Optimization of color removal with ECC.

coefficient is [33]. The quality of the fit polynomial model is expressed by the coefficient of determination R^2, adjusted R^2 and its statistical significance is checked by the *F*-test (Fischer's) in the same program. Model terms are evaluated by the *p*-value (probability) with 95% confidence level. The ANOVA results for response parameters for SS electrodes for color removal are given in Table 6.

From the ANOVA results, it may be observed that there exists a significant interaction with x_1 and x_3 (CD and SEA/V). High significance was observed between the CD-ET and SEA/V-ET within the experimental range. The actual values are the measured response data for a particular run and predicted values are evaluated from the model and generated using approximating functions. R^2 of the study was 91.48 and adjusted (Adj.) R^2 was 80.53 where the plot of observed and predicted values for color removal is shown in Fig. 4. The equation obtained from the model for color removal is given in Eq. (14).

$$Y\left(\text{Color}\right) = -132.660 + 0501x_1 + 4.370x_2 + 32.089x_3 - 0.001x_1^2 - 0.030x_2^2 - 1.308x_3^2 + 0.003x_1x_2 - 0.056x_1x_3 - 0.320x_2x_3 \quad (14)$$

3.4. Statistical analysis of COD removal using RSM and ANOVA

The second parameter analyzed with ECC was the COD removal efficiency. Fig. 5 shows the effects of CD, ET and number of electrodes or SEA/V on COD removal efficiencies obtained from the software and ANOVA is justified by the competence of RSM. COD removal efficiency of 95% was obtained for CD 180 A/m^2, ET 45 min and four number of electrodes, but the average efficiency was 90.21% according to the predicted values with a deviation of 4.79% that fell within an appropriate safety range and is quite satisfactory. The ANOVA results for response parameters for SS electrodes on COD removal are shown in Table 7.

Comparing the ANOVA results, highly significant interactions were observed for all the parameters such as CD-number of electrodes, CD-ET and number of electrodes-ET experimental range. R^2 of the study was 92.08 and adjusted (Adj.) R^2 was 81.89. The plot for COD removal for observed and predicted values is shown in Fig. 6 and the equation obtained from the model for COD removal is presented in Eq. (15).

$$Y\left(\text{COD}\right) = -166.700 + 0.780x_1 + 4.848x_2 + 30.323x_3 - 0.002x_1^2 - 0.032x_2^2 - 1.172x_3^2 + 0.001x_1x_2 - 0.058x_1x_3 - 0.306x_2x_3 \quad (15)$$

3.5. Characterization of ECC generated sludge

The ECC sludge generated after treating raw TWW operated at CD 180 A/m^2, 45 min ET with 4 SS electrodes (optimal condition) was analyzed for physico-chemical parameters, proximate and ultimate analysis, SEM, EDX and TGA. The physico-chemical parameters studied were pH, total solids, density, specific gravity and pH_{pzc}. Table 8 shows the results of physico-chemical analysis of TWW ECC sludge. TWW ECC dry sludge operated at CD 180 A/m^2 was amorphous in nature and dark brownish in color. The pH value of sludge was alkaline in nature and ranged pH of 8.12–8.59. Similar pH values of 8.02–8.78 were observed in a work reported by Patil and Pandey [34]. The alkaline nature of sludge would cause problems during handling and processing while using

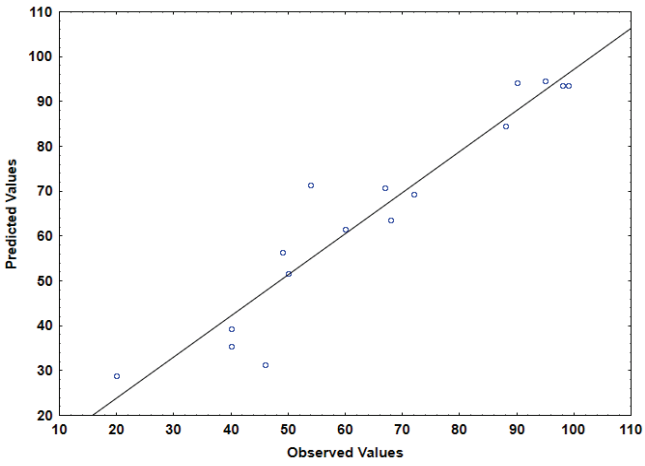

Fig. 4. Observed and predicted values for color removal in BECC.

Table 6
ANOVA results for response surface for color using SS electrodes

Factor	Sum of squares	Degree of freedom	Mean square	*F*-ratio	*p*-Value	Remarks
CD (L)	107.485	1	107.485	0.91466	0.0008	Highly significant
CD (Q)	469.809	1	469.809	3.99791	0.0285	Significant
ET (L)	162.933	1	162.933	1.38651	0.0006	Highly significant
ET(Q)	895.329	1	895.329	7.61895	0.0570	Significant
No. of electrodes (L)	3,579.358	1	3,579.358	30.45912	0.0008	Highly significant
No. of electrodes (Q)	457.428	1	457.428	3.89256	0.0491	Significant
1L by 2L	126.325	1	126.325	1.07499	0.0334	Significant
1L by 3L	1,228.833	1	1,228.833	10.45695	0.0143	Significant
2L by 3L	1,106.790	1	1,106.790	9.41841	0.0180	Significant
Error	822.595	7	117.514			
Total error	9,663.529	16				

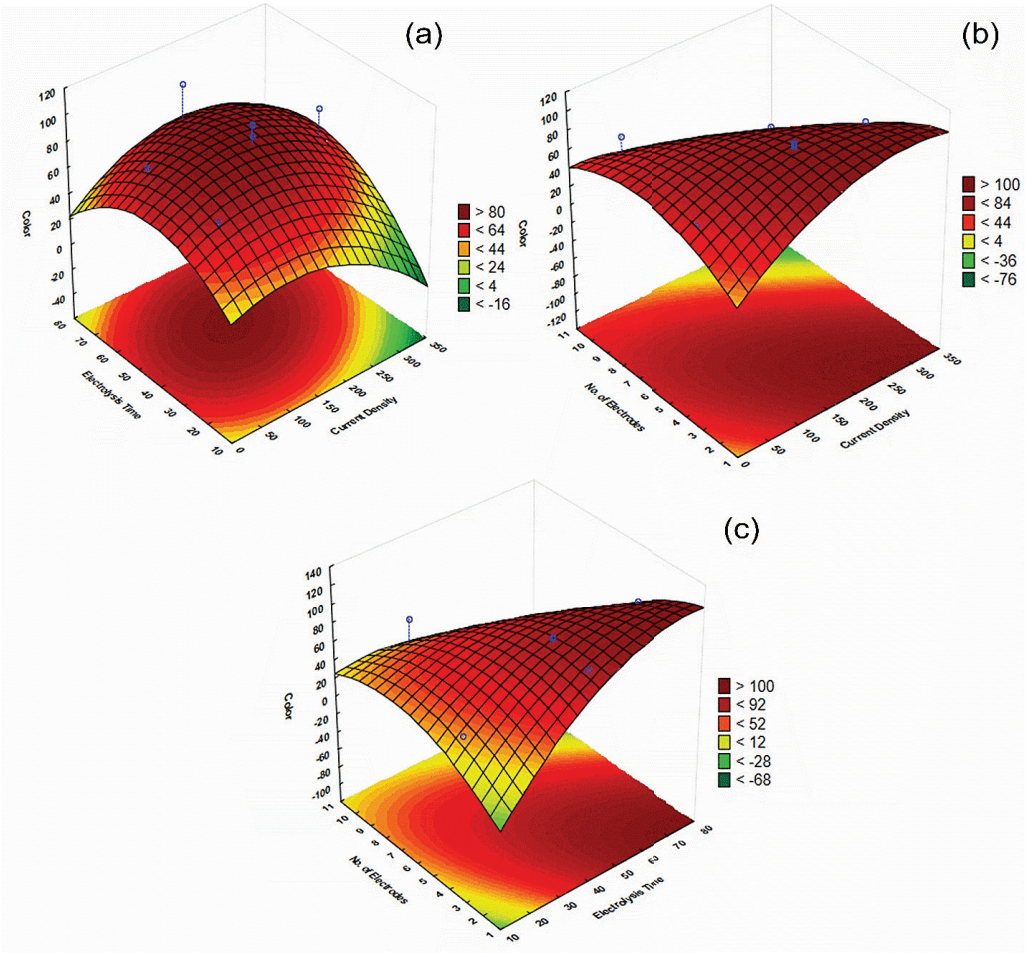

Fig. 5. Optimization of COD removal with BECC.

Table 7
ANOVA results for response surface for COD using SS electrodes

Factor	Sum of squares	Degree of freedom	Mean square	F-ratio	*p*-Value	Remarks
CD (L)	127.99	1	127.995	1.0490	0.0013	Highly significant
CD (Q)	1,277.01	1	1,277.014	10.4662	0.0143	Significant
ET (L)	367.41	1	367.406	3.0112	0.0126	Significant
ET(Q)	1,050.51	1	1,050.505	8.6097	0.0218	Significant
No. of electrodes (L)	3,407.98	1	3,407.976	27.9313	0.0011	Highly significant
No. of electrodes (Q)	367.54	1	367.539	3.0122	0.0126	Significant
1L by 2L	28.21	1	28.211	0.2312	0.0364	Significant
1L by 3L	1,323.69	1	1,323.691	10.8487	0.0132	Significant
2L by 3L	1,008.89	1	1,008.891	8.2687	0.0238	Significant
Error	854.09	7	122.013			
Total error	10,783.76	16				

sludge for subsequent thermo-chemical conversions. The specific gravity and bulk density of the solids content in the sludge are 1.08 and 2,120 kg/m^3, respectively. The volatile solids in TWW ECC sludge are 70.0% and the fixed solids content is 19.02% indicating a small quantity of inorganic solids in ECC generated sludge and hence, can be used as additive in cement [35].

3.6. Proximate and ultimate analysis of TWW ECC sludge

Proximate analysis of TWW ECC sludge comprises of moisture, volatile matter, ash content and fixed carbon. Table 9 shows the result of proximate analysis of TWW ECC sludge. The moisture content of TWW ECC dry sludge is 2.84%. The volatile matter in the sludge is 34.46% and

ash content of 49.86%. The fixed carbon value of 20.11% is ascribed to less free carbon in the TWW ECC sludge when compared with the Indian coal [17].

3.7. Point of zero charge (pH_{pzc})

The pH where the net particle charge is zero is called point of zero charge. pH_{pzc} is one of the characteristics to assess the use of ECC generated sludge as an adsorbent. The pH_{pzc} was determined using the standard procedure given by Mishra et al. [36]. pH_{pzc} for a given sludge is the pH at which that surface has a net neutral charge. Sludge generated using 4 SS electrodes at CD 180 A/m^2 and 45 min ET was used for the determination of pH_{pzc}. The pH_{pzc} of 4 SS electrode generated sludge is presented in Fig. 7 where the pH_{pzc} value of 4 SS generated sludge is 8.40 surmised for its suitability of sludge as an adsorbent for removing specific contaminants from other acidic wastewater streams.

3.8. Surface morphology of electrode and post ECC sludge

The surface morphology of electrodes and post ECC solid sludge residues of 4 SS electrode is shown in Figs. 8 and 9. SEM micrographs of the SS electrode (as anode) before and after use of 20 BECC cycles each of 45 min duration are shown in Figs. 8(a) and (b). New electrode has a smooth surface (Fig. 8(a)) and as the electrolysis progress, dents/pits (active areas) appear on the surfaces of the electrode. These corrosion pits extend across the width and depth of the electrode faces and more along the edges. After repeated discrete 20 cycles of BECC runs, SS anode plate surface turns rough shifting from pit corrosion to wave corrosion with large number of flake deposits and large-sized dents of ~100 to 200 μm size as shown in Fig. 8(b). Fig. 8(c) shows SEM micrographs of post ECC sludge of 4 SS electrode obtained after BECC treatment at 45 min ET showing amorphous nature with large number of pore spaces in the sludge marking the presence of locked gases.

EDX analysis of electrodes and sludge was observed using EDAX analyzer to determine the elemental composition when using 4 SS electrodes before and after BECC runs. Fig. 9(a) shows elemental composition of unused new SS electrode containing 65.65% Fe, 19.43% Cr, 5.41% C and 2.74% O by weight. Similarly, Fig. 9(b) shows EDX of SS electrode after 20 runs of ECC containing 62.42% Fe, 19.26% Cr, 9.45% C and 2.64% O. EDX analysis of sludge for 4 SS electrodes after 45 min ET shows the presence of 25.07% Fe, 37.52% C, 47.37% O, 0.28% Na, 0.90% Mg, 2.28% Al, 5.71% Si, 0.30% P, 0.72% S, 0.23% Cl and 3.28% Ca as shown in Fig. 9(c). The energy content in the sludge was determined using Dulong's equation [37] giving a calorific value of 85.427 kJ/kg for 4 SS electrodes sludge.

3.9. TGA of sludge

Fig. 10 shows the TGA and derivative thermogravimetric analysis (DTG) curves for 4 SS electrodes for the dry sludge obtained after 45 min ET. TGA on 10 mg sludge sample was

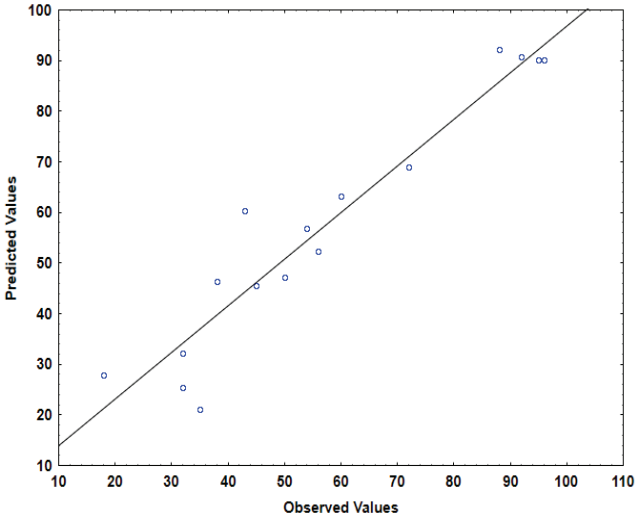

Fig. 6. Observed and predicted values for COD removal.

Table 8
Physico-chemical analysis of TWW ECC sludge obtained at optimal condition

Parameters	Values
pH	8.12–8.59
Solids content	
Total solids, %	96.72
Volatile solids, %	70.00
Fixed solids, %	19.02
Density, kg/m^3	2,120
Specific gravity	1.08
pH_{pzc}	8.70

Table 9
Proximate analysis of TWW ECC sludge obtained at optimal condition

Parameters	Values (%)
Moisture	2.84
Volatile matter	34.46
Ash content	49.86
Fixed carbon	20.11

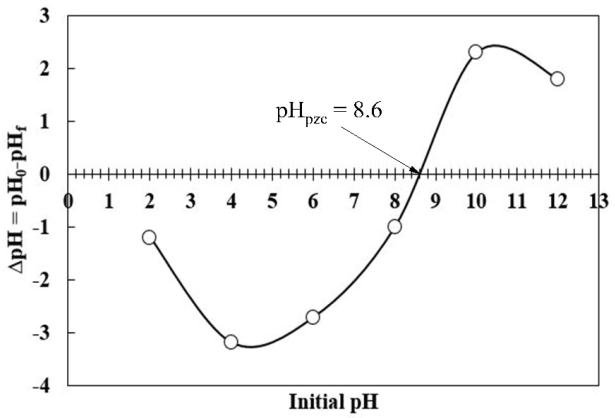

Fig. 7. Point of zero charge (pH_{pzc}) of ECC generated sludge using 4 SS electrodes.

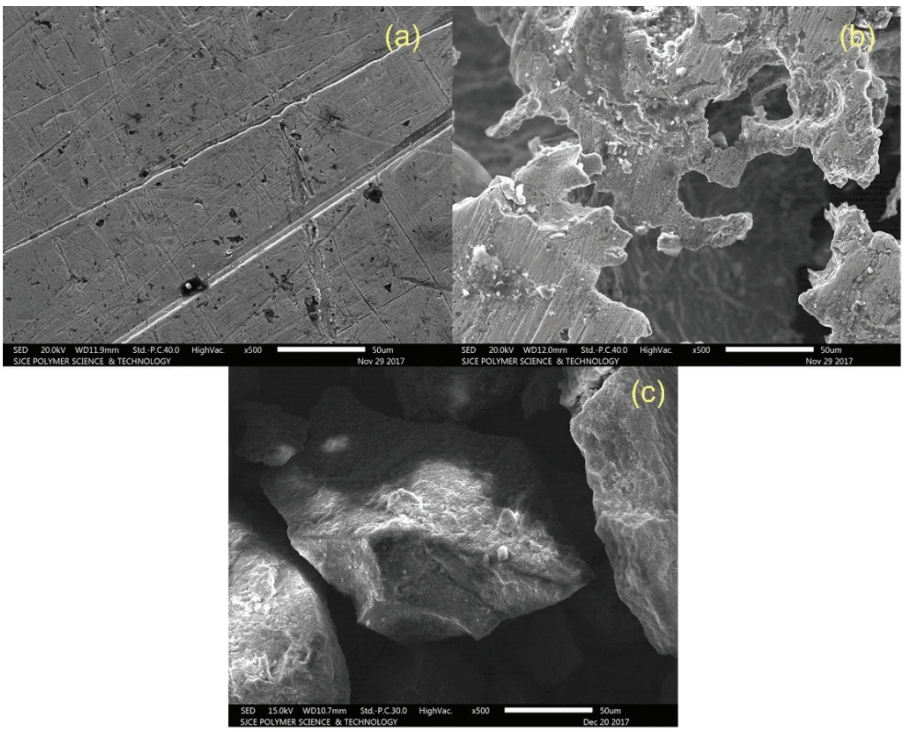

Fig. 8. SEM images of electrode and post ECC solid sludge residues of 4 SS electrodes. (a) SS electrode before use of ECC, (b) large dents after 20 runs of ECC and (c) 4 SS post ECC sludge.

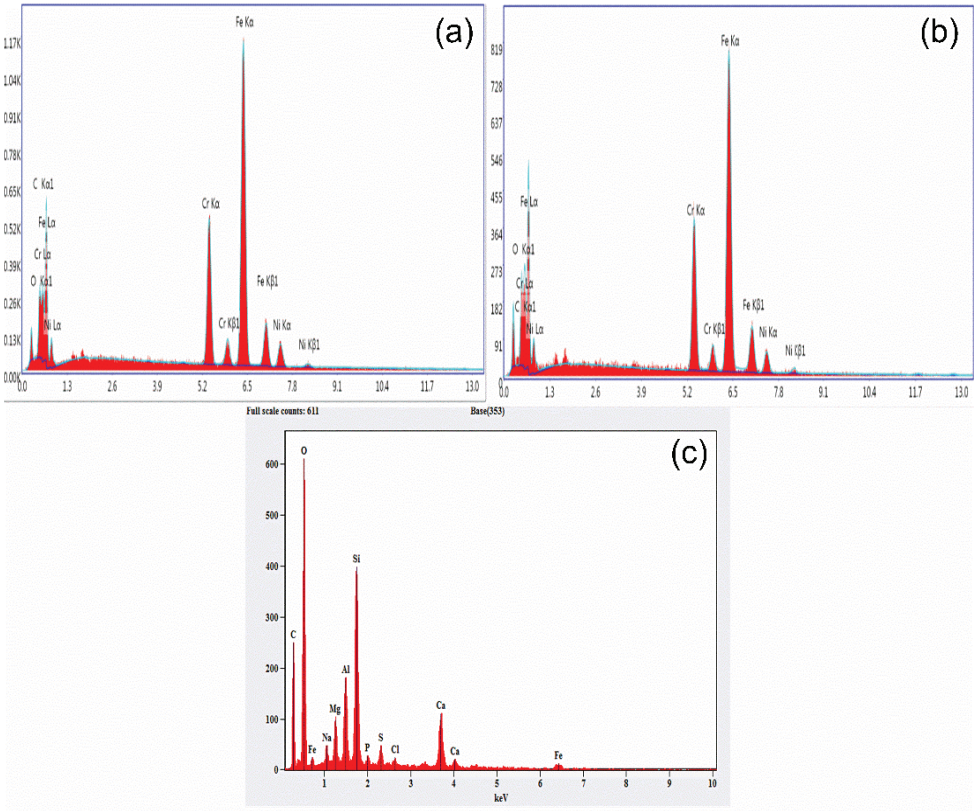

Fig. 9. EDX images of electrodes and post ECC solid sludge residues of 4 SS electrodes. (a) EDX images of SS electrode before use in ECC, (b) EDX of same SS electrode after 20 runs and (c) EDX of 4 SS electrode post ECC sludge.

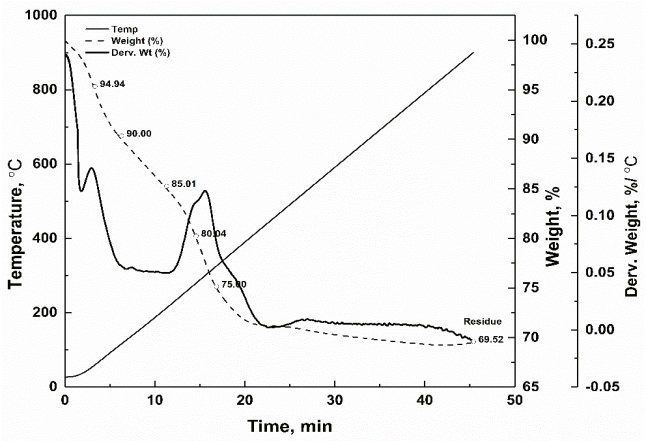

Fig. 10. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves for 4 SS post ECC sludge.

performed to understand the degradation kinetics of the sludge in the presence of air at the heating rate of 10 K/min. TGA of the sludge (Fig. 10) shows the stability of sludge up to 59.19°C with 5% reduction in weight. This weight loss is ascribed to the removal of moisture and bound water present in the samples [38]. The second step of weight loss took place between temperature 279.90°C and 325.58°C where 20%–25% of weight is reduced because of the evolution of oxides of carbon [39]. The third step of breakdown was observed stable between 400°C and 900°C and the residue remaining at 900°C was 3.754 mg (69.52% reduction). The DTG curve follows the TG curve between 300°C and 900°C except for a very small defused peak appearing at 301°C and may be neglected.

3.10. Operating cost and SEC

The success of choosing any wastewater treatment option is its 'Operating cost.' In the ECC treatment process, the operating cost (OC) includes material electrodes cost, utility cost (electrical energy), labor, maintenance and other fixed costs [40]. The major components such as energy cost, electrode material and chemicals for the treated water were taken into account to arrive at the 'operating cost' in Indian Rupee (INR) for each cubic meter of water treated. Eq. (16) shows the formula to calculate the OC of ECC.

$$\text{Operating cost} = a\ .C_{\text{energy}} + b.\ C_{\text{electrode}} + c\ .C_{\text{chemical}} \tag{16}$$

C_{energy} is the energy consumption in kWh/m^3 of water treated calculated using Eq. (17).

$$C_{\text{energy}} = \frac{v.I.t}{\text{Treated volume}(L)} \tag{17}$$

$C_{\text{electrode}}$ is the electrode consumption in kg/m^3 of wastewater treated which is calculated as shown in Eq. (18).

$$C_{\text{electrode}} = \frac{I.t.M_w}{Z.F.v} \tag{18}$$

where v is the cell voltage, I is the current (A) across the electrodes, t is the ET in seconds, M_w is the molecular mass of iron (0.05585 kg/mol), Z is the number of electrons transferred for iron (Z_{Fe} = 2), F is the Faraday's constant (96,485 C/mol), V is the volume of effluent treated in m^3 and $C_{\text{chemicals}}$ is the chemical consumption (optional) in kg per m^3 of water treated. The unit prices a, b and c for the Indian market are: a is the electrical energy prices of 0.66 Rs./kWh; b is electrode material price as 155 Rs./kg averaged for SS, respectively, c is price of chemicals which is zero Rs./kg, as no chemicals were used as additives in the ECC treatment process.

The OC for optimal condition was calculated using Eq. (16) for BECC of real TWW. An optimal operating condition of CD 180 A/m^2, 45 min ET and 4 SS electrodes (SEA/V: 20 m^2/m^3) gives a small OC of 2.97 Rs./m^3 (0.041 US $/m^3) for color and COD removal from real TWW excluding the values of water reclaimed.

SEC was also calculated for the aforesaid optimal operating condition applying Eq. (19) as also used by El-Ashtoukhy et al. [41] in the treatment of paper mill effluent.

$$\text{Specific energy consumption}\left(\frac{\text{KWh}}{\text{m}^3}\right) = \frac{v.I.t}{\text{Treated volume}(L)} \tag{19}$$

where t is the treatment time in h. The energy consumption was found to be 8.1 kWh for each cubic meter of real textile wastewater treated.

4. Conclusions

The ECC method was adopted to treat real TWW for different CDs, ETs and series of SS electrodes. After a number of experimental runs, the optimal conditions were obtained for CD 180 A/m^2, 45 min ET and 4 SS electrodes (SEA/V: 20 m^2/m^3). Experimental studies showed 98% color removal and 96% COD removal using ECC and the predicted values showed 93.60% color removal and 90.21% COD removal with minimal deviations from the experimental results using with CCD of RSM. The results obtained from the experimental studies and mathematical model indicate that BECC can be used as a novel option for the treatment of real TWW using SS electrodes. All the R^2 values obtained in the present research for the response variables were >0.80 showing that regression models explained the ECC process satisfactorily.

The SEM images showed changes in the morphology of the anode plate (SS) structure with large dents and flake deposits on repeated ECC cycles. EDX results showed that post ECC sludge contained higher amounts of metals discharged from TWW. The thermal analysis of the sludge showed the completion of the oxidation process at 900°C and residue remained was 1.463 mg for 4 SS post ECC sludge. Summarizing over the results, it was concluded that 4 SS electrodes could be used effectively to treat real TWW for small and large-scale applications giving reduced energy and spatial footprints. The ECC sludge from TWW may also be used as additives in Portland cement and as adsorbents to remove specific contaminants in tertiary treatment of select wastewaters.

Acknowledgments

The authors are thankful to Sri Jayachamarajendra College of Engineering (JSS S&T University), Mysuru, for giving the opportunity to carry out this research work and for providing permission to use the Central analytical facility for sludge analysis. Srikantha H is thankful for the Ministry of Human Resource Development (MHRD), Government of India, University Grant Commission (UGC) for providing fellowship throughout the research work.

References

[1] K. Govindan, Y. Oren, M. Noel, Effect of dye molecules and electrode material on the settling behavior of flocs in an electrocoagulation induced settling tank reactor (EISTR), Sep. Purif. Technol., 133 (2014) 396–406.
[2] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses, Colloids Surf., A, 264 (2005) 17–28.
[3] S. Singh, V.C. Srivastava, I.D. Mall, Multistep optimization and residue disposal study for electrochemical treatment of textile wastewater using aluminum electrode, Int. J. Chem. React. Eng., 11 (2013) 31–46.
[4] A.D. dos Santos, F.J. Cervantes, J.B. van Lier, Review paper on current technologies for decolorization of textile wastewaters: perspective for anaerobic biotechnology, Bioresour. Technol., 98 (2007) 2369–2385.
[5] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol., 98 (2007) 2243–2257.
[6] S.-H. Huo, X-P. Yan, Metal–organic framework MIL-100 (Fe) for the adsorption of malachite green from aqueous solution, J. Mater. Chem., 22 (2012) 7449–7445.
[7] S. Deng, Q. Zhou, G. Yu, J. Huang, Q. Fan, Removal of perfluorooctanoate from surface water by polyaluminium chloride coagulation, Water Res., 45 (2011) 1774–1780.
[8] C.-Y. Chen, J.-T. Kuo, C.-Y. Cheng, Y.-T. Huang, I.-H. Ho, Y.-C. Chung, Biological decolorization of dye solution containing malachite green by *Pandoraea pulmonicola* YC32 using a batch and continuous system, J. Hazard. Mater., 172 (2009) 1439–1445.
[9] D. Valero, J.M. Ortiz, E. Expósito, V. Montiel, A. Aldaz, Electrochemical wastewater treatment directly powered by photovoltaic panels: electrooxidation of a dye-containing wastewater, Environ. Sci. Technol., 44 (2010) 5182–5187.
[10] S. Mahesh, B. Prasad, I.D. Mall, I.M. Mishra, Electrochemical degradation of pulp and paper mill wastewater. Part 1. COD and color removal, Ind. Eng. Chem. Res., 45 (2006) 2830–2839.
[11] N. Drouiche, S. Aoudj, H. Lounici, H. Mahmoudi, N. Ghaffour, M.F. Goosen, Development of an empirical model for fluoride removal from photovoltaic wastewater by electrocoagulation process, Desal. Wat. Treat., 29 (2012) 96–102.
[12] U.T. Un, U.B. Ogutveren, Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes, J. Environ. Manage., 90 (2009) 428–433.
[13] C. O'Neill, F.R. Hawkes, D.L. Hawkes, N.D. Lourenco, H.M. Pinheiro, W.J. Delee, Colour in textile effluents-sources, measurement, discharge consents and simulation: a review, J. Chem. Technol. Biotechnol., 74 (1999) 1009–1018.
[14] M. Kobya, E. Demirbas, N.U. Parlak, S. Yigit, Treatment of cadmium and nickel electroplating rinse water by electrocoagulation, Environ. Technol., 31 (2010) 1471–1481.
[15] X. Li, J. Song, J. Guo, Z. Wang, Q. Feng, Landfill leachate treatment using electrocoagulation, Procedia Environ. Sci., 10 (2011) 1159–1164.
[16] V. Khandegar, A.K. Saroh, Treatment of distillery spentwash by electrocoagulation, J. Clean Energy Technol., 2 (2014) 244–247.
[17] S. Mahesh, B. Prasad, I.D. Mall, I.M. Mishra, Electrochemical degradation of pulp and paper mill wastewater. Part 2. Characterization and analysis of sludge, Ind. Eng. Chem. Res., 45 (2006) 5766–5774.
[18] S. Mahesh, K.K. Garg, V.C. Srivastava, I.M. Mishra, B. Prasad, I.D. Mall, Continuous electrocoagulation treatment of pulp and paper mill wastewater, operating cost and sludge study, RSC. Adv., 20 (2016) 16223–16233.
[19] M. Kobya, E. Senturk, M. Bayroglu, Treatment of poultry slaughterhouse wastewaters by electrocoagulation, J. Hazard. Mater., 133 (2006) 172–176.
[20] E-S.Z. El-Ashtoukhy, N.K. Amin, Removal of acid green dye 50 from wastewater by anodic oxidation and electrocoagulation--a comparative study, J. Hazard. Mater., 179 (2010) 113–119.
[21] F. Ghanbari, M. Moradi, A. Eslami, M.M. Emamjomeh, Electrocoagulation/flotation of textile wastewater with simultaneous application of aluminum and iron as anode, Environ. Process., 1 (2014) 447–457.
[22] M. Kobya, E. Gengec, E. Demirbas, Operating parameters and costs assessments of a real dyehouse wastewater effluent treated by a continuous electrocoagulation process, Chem. Eng. Process., 101 (2016) 87–100.
[23] M.K. Mbacké, M. Kane, N.O. Diallo, C.M. Diop, F. Chauvet, M. Comtat, T. Tzedakis, Electrocoagulation process applied on pollutants treatment- experimental optimization and fundamental investigation of the crystal violet dye removal, J. Environ. Chem. Eng., 4 (2016) 4001–4011.
[24] H. Hossini, P. Makhdoumi, S.O. Rastegar, F. Mohammadi-Moghadam, H.R. Ghaffari, A. Javid, Mirzaei, Optimization of the electrocoagulation process for sulfate removal using response surface methodology, Bulgar. Chem. Commun., 47 (2015) 63–71.
[25] H. Hossini, R. Rezaee, A. Ayati, A.H. Mahvi, Optimizing ammonia volatilization by air stripping from aquatic solutions using response surface methodology (RSM), Desal. Wat. Treat., 57 (2016) 11765–11772.
[26] O.M. Chavalparit, Ongwandee, Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology, J. Environ. Sci., 21 (2009) 1491–1496.
[27] R.B. Baird, A.D. Eaton, E.W. Rice, Standard Methods for the Examination of Water and Wastewater, 23rd edition APHA, Washington, D.C., USA, 2017.
[28] M. Kobya, A. Akyol, E. Demirbas, M.S. Oncel, Removal of arsenic from drinking water by batch and continuous electrocoagulation processes using hybrid Al-Fe plate electrodes, Environ. Prog. Sustain. Energy, 33 (2014) 131–140.
[29] J.R. Parga, G. González, H. Moreno, J.L. Valenzuela, Thermodynamic studies of the strontium adsorption on iron species generated by electrocoagulation, Desal. Wat. Treat., 37 (2012) 244–252.
[30] O. Larue, E. Vorobiev, C. Vu, B. Durand, Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions, Sep. Purif. Technol., 31 (2003) 177–192.
[31] S.W. Hasan, I. Ahamed, A.A. Housani, A. Giwa, Molecular and ionic-scale chemical mechanisms behind the role of nitrocyl group in the electrochemical removal of heavy metals from sludge, Sci. Rep., 6 (2016) 31828.
[32] K. Thirugnanasambandham, V. Sivakumar, M.J. Prakash, Evaluation of an electrocoagulation process for the treatment of bagasse-based pulp and paper industry wastewater, Environ. Prog. Sustain. Energy, 34 (2015) 411–419.
[33] S.L. Marco, A.P. José, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigm., 71 (2006) 236–244.
[34] H. Patel, S. Pandey, Evaluation of physical stability and leachability of Portland Pozzolona Cement (PPC) solidified chemical sludge generated from textile wastewater treatment plants, J. Hazard. Mater., 207–208 (2012) 56–64.
[35] M. Peces, S. Astals, J. Mata-Alvarez, Assessing total and volatile solids in municipal solid waste samples, Environ. Technol., 35 (2014) 3041–3046.
[36] S.K. Mishra, S.B. Kanungo, Rajeev, Adsorption of sodium dodecyl benzenesulfonate onto coal, J. Colloid Interface Sci., 267 (2003) 42–48.
[37] J.F. Nzihou, S. Hamidou, M. Bouda, J. Koulidiati, B.G. Segda, Using Dulong and Vandralek formulas to estimate the calorific

heating value of a household waste model, I. J. Sci. Eng. Res., 5 (2014) 1878–1883.
[38] C. Thakur, V.C. Srivastava, I.D. Mall, A.D. Hiwarkar, Mechanistic study and multi-response optimization of the electrochemical treatment of petroleum refinery wastewater, Clean – Soil, Air, Water, 46 (2018). doi:10.1002/clen.201700624.
[39] B.A. Fıl, R. Boncukcuoğlu, A.E. Yilmaz, S. Bayar, Electro-oxidation of pistachio processing industry wastewater using graphite anode, Clean Soil Air Water, 42 (2014) 1232–1238.
[40] J.C. Donini, J. Kan, J. Szynkarczuk, T.A. Hassan, K.L. Kar, The operating cost of electrocoagulation, Can. J. Chem. Eng., 72 (1994) 1007–1012.
[41] E.-SZ. El-Ashtoukhy, N.K. Amin, O. Abdelwahab, Treatment of paper mill effluents in a batch-stirred electrochemical tank reactor, Chem. Eng. J., 146 (2009) 205–210.