Studies on Electrochemical Treatment of Dairy Wastewater Using Aluminum Electrode

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This study reports results of electrochemical treatment to the synthetic dairy wastewater using aluminum electrode. Response surface methodology with four factors and five level full factorial central composite design has been used to design the experiments. Four operational parameters, namely current density (J)*: 61.73–308.64 A/m^2; dosage of sodium chloride (NaCl)* (m)*: 0–2 g/l; electrolysis time* (t)*: 10–90 min and initial pH (pH$_o$): 5–11, have been taken as input parameters and percentage chemical oxygen demand (COD) removal* (Y_1) *and the specific energy consumed (kWh per Kg of COD removed,* Y_2*) have been taken as responses of the system. Multiresponse optimization technique has been applied to find values of operational parameters which maximize the* Y_1 *and simultaneously minimize* Y_2*. The optimum values of operational parameters were found to be* $J = 123.46$ *A/m^2,* $m = 2.0$ *g/l,* $t = 74$ *min, and pH$_o$ = 6.5. Optimum* Y_1 *and* Y_2 *were found to be 70.91% and 1.32 kWh/kg COD removed.* © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 2589–2598, 2011

Keywords: RSM, dairy wastewater, electrochemical, COD removal, aluminum electrode

Introduction

Dairy industries are involved in the manufacturing of various types of milk products such as fluid milk, butter, cheese, yogurt, condensed milk, flavored milk, milk powder, ice cream, etc. Therefore, wastewater produced from dairy industry contains milk and milk products that have been lost in the process. Dairy industry wastewater are characterized by high chemical oxygen demand (COD), biological oxygen demand (BOD) and fats,[1] high concentrations of nutrients, variations in pH (4.2–11), and high load of suspended solids (0.024–4.5 g/l).[2] Due to high pollution load, dairy industry wastewater must be treated before their discharge in any water body.

Dairy wastewaters are generally treated using aerobic and anaerobic biological methods. Aerobic biological treatment methods are highly energy intensive,[3] whereas, anaerobic processes treatment partly convert the nutrient. Therefore, an additional process is needed for complete treatment of dairy wastewaters after anaerobic treatment.[4] Recently, Kushwaha et al.[5] studied the adsorptive treatment of dairy wastewater by activated carbon and bagasse fly ash.

Electrochemical (EC) treatment is an emerging water treatment technology. The major screened-off area in the EC treatment is electro-flotation, electro-coagulation and electro-oxidation. Electro-flotation is a simple process in which hydrogen and oxygen generated from water electrolysis move upwards and takes along with them the pollutant particles to the surface of a liquid body. In electro-coagulation process, the anode material undergoes oxidation and hence, various monomeric and polymeric metal hydrolyzed species are formed. These metal hydroxides remove organics from waste water by sweep coagulation and/or by aggregating with colloidal particles present in the waste water to form bigger size flocs and ultimately get removed by settling. Organics contained in wastewater are oxidized directly at the surface of the electrode or oxidizing agent is electrochemically generated to carry out oxidation in electro-oxidation process of waste water treatment.

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Table 1. Characteristics of SDW and Treated SDW by EC with Aluminum Electrode

	Value Range of SDW	
Parameters	Before EC treatment	After EC treatment at optimum condition
pH	6.3–6.8	8.61
COD (mg/l)	3900	1245
Total solids (mg/l)	3090	1410
Turbidity (NTU)	1744	2.0
Chloride (mg/l)	31	24.2
Total N (mg/l)	113.18	10.3

EC treatment technology has been utilized by various researchers for the treatment of various types of industrial wastewater.[6–14] Also, EC has been very successfully employed to restaurant and oily wastewaters.[15,16] However, only two studies are available in open literature for the EC treatment of dairy wastewater.[17,18] Sengil and Ozacar[17] studied the EC treatment of dairy wastewater with iron electrode and focused the study on COD and oil-grease removal. Tchamango et al.[18] used aluminum electrodes and reported COD, nitrogen content and turbidity removal efficiencies of 61, 81, and 100%, respectively. However, Tchamango et al.[18] did not optimized various operational parameters like current density (J), electrolysis time (t), and pH for the EC treatment of dairy wastewaters. Also, disposal aspect of residues (scum and sludge) were not dealt in any of the above two studies, which are very important from environmental point of view.

In this work, response surface methodology (RSM) has been used to design the experiments for the treatment of synthetic dairy wastewater (SDW) using aluminum (Al) electrodes. Effects of four operational parameters namely J, dosage of sodium chloride (m), t and initial pH (pH_o) were investigated for their effects on the percentage COD removal (Y_1) and specific energy consumed (KWh per kg of COD removed, Y_2). The major contribution of the article is in the application of multiresponse optimization technique for finding values of operational parameters which maximize the Y_1 and simultaneously minimize Y_2. A strategy for the disposal of EC treatment residues has also been proposed based on thermo-degradation analysis.

Materials and Methods

Wastewater and its characterization

The SDW was used in this study to prevent any change in wastewater composition throughout the experiments. For this purpose, milk powder of Amulya brand, manufactured by Banaskantha District Cooperative Milk producer's Union (Palanpur, Uttarakhand, India) was used. SDW was prepared by dissolving milk powder at the rate of 4 g/l of distilled water, and this concentration was maintained uniform throughout the study. Several investigators used same method for making SDW.[5,18–21] The characteristics of the SDW in this study are presented in Table 1. The SDW used in this study has similar characteristics as given by Rico Gutierrez et al.[22]; Koyuncu et al.[23]; Schwarzenbeck et al.[24]

Chemicals and analytical measurements

All the chemicals used in the study were of analytical reagent (AR) grade. COD was measured using digestion unit (DRB 200, HACH) and double beam UV-visible spectrophotometer (HACH, DR 5000). Turbidity meter supplied by Aqualytic (Germany), was used to measure turbidity. The chloride content was determined by standard titrimetric Volhard method and total nitrogen (TN) was determined using the standard Kjeldahl method. Energy dispersive X-ray (EDX) (SEM, QUANTA, Model 200 FEG) was used to study the distribution of the elements in the sludge generated by the coagulation of SDW. For the EDX, the samples were first ground to make the samples homogeneous and then spread on sample holders in such a manner to produce flat surfaces. After this, the samples were gold coated using sputter coater (Edwards S150) to provide conductivity to the samples, and then the EDX spectra were taken. Thermogravimetric analysis (TGA) of the residues was carried out using PerkinElemer (Pyris Diamond) TG Analyser. TGA scans were recorded from 20 to 1000°C at a heating rate of 10°C/min in the air atmosphere.

Reactor

Experiments were carried out in a rectangular reactor of 1.5 l ($108 \times 108 \times 130$ mm^3) made up of Perspex. Two pairs of aluminum plates of thickness 1 mm and dimensions, 10×8.5 cm^2, were used as electrodes. Area of electrodes dipped into the solution was 9.50×8.5 cm^2. The spacing of 1 cm between two electrodes in EC cell was maintained constant throughout the study. Current density was maintained constant by means of a precision digigtal direct current power supply (0–20 V, 0–5 A).

Experimental design

In this study, four factors and five levels full factorial central composite (CC) design based on RSM were used to design the experiments and data obtained from the experiments was analyzed using Design-Expert trial-version. Four operational parameters, namely J: 61.73–308.64 A/m^2; m: 0–2 g/l; t: 10–90 min and pH_o: 5–11, have been taken as input

Table 2. Process Parameters and Their Levels for EC Treatment of SDW Using Aluminum Electrodes

	Factors	Level				
Variable, unit	x_i	−2	−1	0	1	2
Current density, J (Am^{-2})	X_1	61.73	123.46	185.19	246.91	308.64
Mass of salt (NaCl), m (g/l)	X_2	0	0.5	1	1.5	2
Time of electrolysis, t (min)	X_3	10	30	50	70	90
pH_o	X_4	5	6.5	8.0	9.5	11

Table 3. Full Factorial Design Used for the EC Treatment of SDW by Aluminum Electrodes

Standard order	J (X_1)	m (X_2)	t (X_3)	pH_o (X_4)	% COD removal, Y_1 $Y_{1\ \mathrm{exp}}$(%)	$Y_{1\ \mathrm{pre}}$(%)	Specific Energy Consumed, Y_2 $Y_{2\ \mathrm{exp}}$	$Y_{2\ \mathrm{pre}}$
1	123.46	0.5	30	6.5	23.3	28.4	1.10	1.02
2	246.91	0.5	30	6.5	65.4	61.6	1.31	1.90
3	123.46	1.5	30	6.5	25.0	29.8	1.03	0.80
4	246.91	1.5	30	6.5	36.7	45.2	1.40	1.77
5	123.46	0.5	70	6.5	38.9	43.7	1.54	1.58
6	246.91	0.5	70	6.5	66.9	68.4	2.98	3.56
7	123.46	1.5	70	6.5	63.8	58.1	0.94	0.91
8	246.91	1.5	70	6.5	61.5	65.1	1.94	2.98
9	123.46	0.5	30	9.5	15.4	16.4	1.67	1.95
10	246.91	0.5	30	9.5	42.3	48.2	1.92	2.31
11	123.46	1.5	30	9.5	19.2	18.0	1.33	1.11
12	246.91	1.5	30	9.5	32.3	32.1	1.59	1.57
13	123.46	0.5	70	9.5	50.8	42.5	1.18	1.93
14	246.91	0.5	70	9.5	66.2	65.9	2.86	3.39
15	123.46	1.5	70	9.5	48.8	57.1	1.23	0.65
16	246.91	1.5	70	9.5	67.7	62.8	1.77	2.20
17	61.73	1	50	8	26.9	24.9	0.66	0.80
18	308.64	1	50	8	66.5	63.8	2.68	3.23
19	185.19	0	50	8	59.6	59.1	6.09	3.37
20	185.19	2	50	8	61.5	57.4	1.04	1.96
21	185.19	1	10	8	30.3	22.7	0.56	0.67
22	185.19	1	90	8	65.8	68.7	2.34	1.86
23	185.19	1	50	5	51.5	44.7	1.24	1.40
24	185.19	1	50	11	28.2	30.4	2.08	1.55
25	185.19	1	50	8	57.7	55.1	1.48	1.55
26	185.19	1	50	8	55.8	55.1	1.53	1.55
27	185.19	1	50	8	54.2	55.1	1.58	1.55
28	185.19	1	50	8	53.5	55.1	1.60	1.55
29	185.19	1	50	8	52.3	55.1	1.63	1.55
30	185.19	1	50	8	56.9	55.1	1.50	1.55

parameters and Y_1 and Y_2 have been taken as responses of the system. For this purpose, a total of 30 experiments were conducted. To decide the working range of operational parameters, preliminary experiments with varying operational parameters for COD removal were conducted (not shown here). Table 2 represents the variables and their levels whereas actual experimental design matrix is given in Table 3. For statistical calculations, the levels for the four parameters X_i [X_1 (J), X_2 (m), X_3 (t), X_4 (pH$_o$)] were coded as x_i according to the following relationship:

$$x_i = \frac{(X_i - X_0)}{\delta X}, \tag{1}$$

where x_i is coded (dimensionless) value of parameter X_i, X_0 is value of the parameter X_i at the center point and δX represents the step change. Based on this the levels were designated as −2, −1, 0, +1, and +2.

Since, there are more than one (two) responses in this study, therefore, multiresponse processes optimization by desirability function approach used to optimize the EC treatment of SDW. One-sided desirability d_i is used in the study given by:

$$d_i = \begin{cases} 0 & \text{if } Y_i \le Y_{i-\min} \\ \left[\dfrac{Y_i - Y_{i-\min}}{Y_{i-\max} - Y_{i-\min}}\right]^r & \text{if } Y_{i-\min} < Y_i < Y_{i-\max}, \\ 1 & \text{if } Y_i \ge Y_{i-\max} \end{cases} \tag{2}$$

where, Y_i is response values, $Y_{i\text{-min}}$ and $Y_{i\text{-max}}$ is minimum and maximum acceptable values of response i, and r is a weight and a positive constant, used to determine scale of desirability. The individual desirability functions are combined to obtain the overall desirability D, as follows:

$$D = (d_1 \times d_2 \times d_3 \ldots\ldots\ldots\ldots\ldots\ldots)^{\frac{1}{k}}, \tag{3}$$

where, $0 \le D \le 1$ and k is number of responses.

Experimental procedure

Experiments were conducted as per the conditions specified in the design matrix (Table 3). The pH$_o$ of the SDW was adjusted to desired level by adding 0.1 N NaOH or 0.1 N H_2SO_4 solutions. 1.5 l of SDW of known initial COD (C_o = 3900 mg/l) was fed into the reactor with addition of salt (NaCl) as per the condition. J was maintained constant during the run. After the appropriate time of electrolysis, samples were drawn from supernatant liquid, and its final COD was measured and the percentage COD removal was calculated.

Results and Discussion

Effects of J, m, t, *and pH$_o$ on* Y$_1$

The response (Y_1) by EC, were measured according to the conditions of various operational parameters as given in design matrix and the results are shown in Table 3. Sequential model sum of squares showed that quadratic model best fits the experimental data. The analysis of variance (ANOVA) result showed F-value of 13.48 implying that the

Table 4. ANOVA for Response Surface Quadratic Model for COD Removal

Source	Coefficient estimate	Sum of Squares	DF[#]	Mean Square	F-Value	Prob > F	
Model		7223.164	14	515.9403	13.48256	<0.0001	Significant
Intercept	55.06						
X_1	9.71	2264.192	1	2264.192	59.16794	<0.0001	Highly significant
X_2	−0.42	4.34554	1	4.34554	0.113558	0.7408	
X_3	11.5	3171.241	1	3171.241	82.87095	<0.0001	Highly significant
X_4	−3.57	305.7355	1	305.7355	7.989489	0.0128	Significant
X_1^2	−2.67	195.895	1	195.895	5.119134	0.0389	Significant
X_2^2	0.79	17.07855	1	17.07855	0.446297	0.5142	
X_3^2	−2.35	150.8985	1	150.8985	3.943283	0.0657	
X_4^2	−4.38	527.1822	1	527.1822	13.77634	0.0021	Significant
X_1X_2	−4.43	314.6801	1	314.6801	8.223229	0.0117	Significant
X_1X_3	−2.11	71.35035	1	71.35035	1.864529	0.1922	
X_1X_4	−0.32	1.671993	1	1.671993	0.043693	0.8372	
X_2X_3	3.26	169.7807	1	169.7807	4.436715	0.0524	
X_2X_4	0.046	0.033802	1	0.033802	0.000883	0.9767	
X_3X_4	2.72	117.9558	1	117.9558	3.082425	0.0995	
Residual		574.0083	15	38.26722			
Lack of Fit		552.2874	10	55.22874	12.71327	0.0059	Significant
Pure Error		21.72091	5	4.344181			
Cor Total		7797.172	29				

[#] Degree of freedom.

quadratic model is significant (Table 4). The model gives coefficient of determination (R-squared) value of 0.9263 and adjusted R-squared value of 0.8577, which advocates a good correlation between the observed and the predicted values. Values of "Prob $> F$" <0.05 indicate that model terms are significant and "Prob $> F$" lower than 0.0001 for the second-order polynomial fitting indicates that the model is statistically highly significant, and that the model terms are significant at 95% probability level.

The ANOVA table obtained from the response surface quadratic model shows that J and t are highly significant, whereas, $\mathrm{pH_o}$, J^2, $\mathrm{pH_o^2}$, and $J \times m$ are significant terms. The constant term in the quadratic model, which does not depend on any factors and interaction of factors, shows 55.06% average COD removal efficiency. The final quadratic equation in terms of coded factors for COD removal is given below:

$$Y_1 = 55.06 + 9.71X_1 + 11.5X_3 - 3.57X_4 - 2.67X_1^2 - 4.38X_4^2 - 4.43X_1X_2. \quad (4)$$

Three-dimensional response surface graphs for COD removal efficiency by various operational parameters J, m, t, and $\mathrm{pH_o}$ are shown in Figure 1.

Various reactions take place in the EC reactor during its operation. The anode material undergoes oxidation and cathode gets reducted. At anode, $\mathrm{Al^{3+}}$ ion generation takes place by the following reaction[14]:

$$\mathrm{Al(S)} \rightarrow \mathrm{Al^{3+}(aq)} + 3\mathrm{e^-}. \quad (5)$$

In addition, oxygen evolution can compete with aluminum dissolution at the anode via the following reaction:

$$2\mathrm{H_2O(l)} \rightarrow \mathrm{O_2(g)} + 4\mathrm{H^+(aq)} + 4\mathrm{e^-}. \quad (6)$$

At the cathode, hydrogen evolution takes place via the following reaction:

$$3\mathrm{H_2O(l)} + 3\mathrm{e^-} \rightarrow 3/2\mathrm{H_2(g)} + 3\mathrm{OH^-(aq)}. \quad (7)$$

Liberated $\mathrm{Al^{3+}}$ and $\mathrm{OH^-}$ ions react to form various monomeric and polymeric aluminum hydrolyzed species. The concentration of the hydrolyzed aluminum species depends on the aluminum concentration, and the solution pH.

The percentage of $\mathrm{Al^{3+}}$ hydrolytic products can be calculated from the following stability constant[25]:

$$\mathrm{Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+} \quad \mathrm{pK_1} = 4.95, \quad (8)$$

$$\mathrm{Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+} \quad \mathrm{pK_2} = 5.6, \quad (9)$$

$$\mathrm{Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+} \quad \mathrm{pK_3} = 6.7, \quad (10)$$

$$\mathrm{Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+} \quad \mathrm{pK_4} = 5.6. \quad (11)$$

In this study, the COD removal efficiency was found to increase with an increase in $\mathrm{pH_o}$ up to $\mathrm{pH_o} \approx 6.50$ and beyond that COD removal started to decrease (Figure 1a). This trend of COD removal was found to follow at every t (Figure 1a). Dairy wastewater has the isoelectric point ($\mathrm{pH_{iso}}$) around 4.2.[26] Thus, the milk proteins contained in the SDW are negatively charged at $\mathrm{pH} > \mathrm{pH_{iso}}$. These milk proteins get destabilized by positively charged hydrolyzed aluminum species like $\mathrm{Al^{3+}}$, $\mathrm{Al(OH)^{2+}}$, $\mathrm{Al(OH)_2^+}$, etc. Thus, the colloidal particles present in the SDW aggregate together to form bigger size flocs and ultimately get removed by settling. Also, from the speciation of Al (III), the $\mathrm{Al(OH)_3}$ species are formed in the pH range of 5–7, which help in the removal of colloids by sweep coagulation. Since the optimum $\mathrm{pH_o}$ was found to be ≈6.5, it seems that both charge neutralization of anionic colloids by monomeric cationic aluminum species and sweep coagulation with amorphous aluminum hydroxide help in maximum COD removal at $\mathrm{pH_o} \approx 6.5$.[27] However, for $\mathrm{pH_o} > 6.5$, formation of negatively charged $\mathrm{Al(OH)_4^-}$ causes the reduction in COD removal.

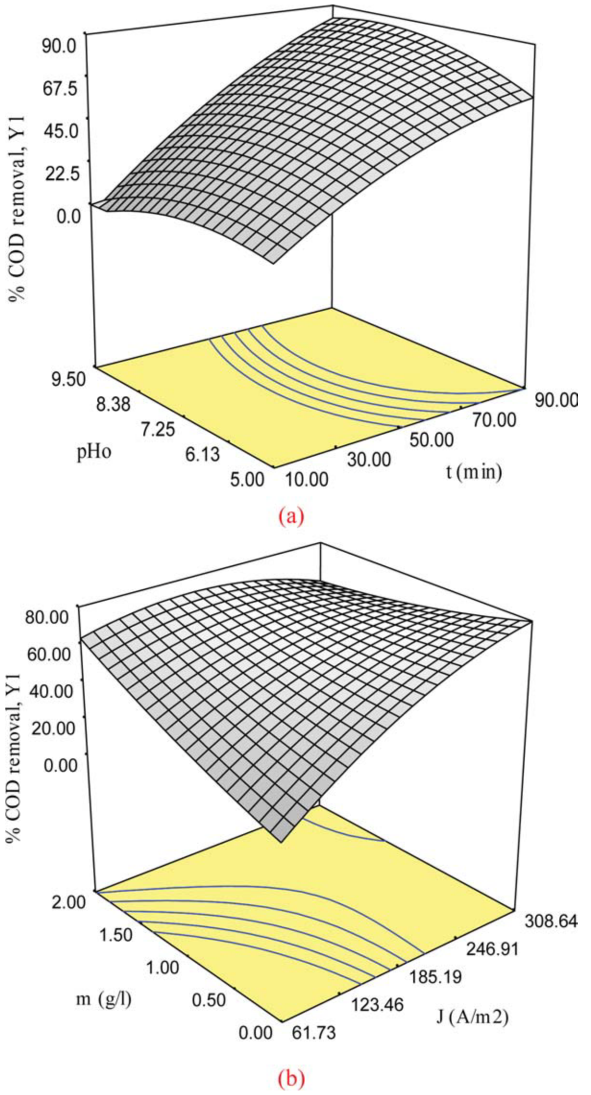

Figure 1. Three-dimensional response surface graphs for the EC treatment of SDW (a) %COD removal, Y_1 vs. t and pH_o at $m = 2.0$ g/l, $J = 123.46$ A/m^2; (b) %COD removal, Y_1 vs. J and m at $t = 74$ min, $pH_o = 6.5$.

[Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

Faraday's law describes the relationship between J and the amount of anode material that dissolves in the solution. It is given as;

$$w = \frac{MJt}{ZF}, \tag{12}$$

Where, w is the theoretical amount of ion produced per unit surface area (g/m^2) by current density J (A/m^2) passed for duration of time t (sec). Z is the number of electrons involved in the oxidation/reduction reaction; for Al, $Z = 3$. M is the atomic weight (g/mol) of anode material, for Al, $M = 26.9815$ g/mol; and F is the Faraday's constant (96,486 C/mol).

The COD removal efficiency depends directly on the concentration of Al^{3+} ions produced by the aluminum electrodes, which in turn as per Faradays law depends upon the t. When the value of t increases, an increase occurs in the concentration of aluminum ions and their hydroxide flocs. Consequently, an increase in t increases the COD removal efficiency. It may be seen in Figure 1a that the COD removal efficiency with t was found to be maximum at near about 70 min and then it remained constant with an increase in t. Figure 1b reveals the variation of the COD removal efficiency with J and m. It may be seen in Figure 1b that the COD removal efficiency increased with an increase in J upto 270 A/m^2 after which J had very marginal effect on the COD removal efficiency. Similar to t, an increase in J increase the amount of aluminum dissolved from the electrode for any constant t value. Consequently, higher amount of aluminum ions or hydroxides produced at higher J value resulted in higher COD removal efficiency.

It is observed that for $t > 70$ min and $J > 270$ A/m^2, an increase in t or J value did not improve the COD removal efficiency further. It is due to the fact that all the COD present in the SDW in the colloidal form gets removed at $t \approx 70$ min and $J \approx 270$ A/m^2, the remaining COD, which is due to the dissolved organics do not get removed despite an increase in t or J value. Figure 1b also shows the effect of m on the COD removal efficiency from SDW. The COD removal efficiency increased with an increase in m for lower J values ($J \leq 180$ A/m^2). However, for $J > 180$ A/m^2, increase in m value decreases COD removal efficiency (Figure 1b). The increase in COD removal efficiency with an increase in m at lower J value may be due to an increase in conductivity of the solution, which increases the aluminum dissolution rate and hypochlorite concentration in the reactor (formed by successive reaction from chlorine), which indirectly oxidize the COD. However, at higher J values, there is higher aluminum dissolution, and at this condition, increased m value helps in generation of large amount of aluminum ions. Excess aluminum ions cause charge reversal of the negatively charged colloidal particles present in the SDW,[28] which causes decrease in COD removal efficiency.

Effects of J, m, t, and pH_o on Y_2

The effect of various operational parameters on response, Y_2 by EC of SDW was measured and the results are shown in Table 3. The ANOVA for the quadratic model fitted for Y_2 is given in Table 5. The model F-value of 3.32 implies that the quadratic model is significant. The model gives coefficient of determination (R-squared) value of 0.7562 and adjusted R-squared value of 0.5286, implies quadratic model adequately described the response Y_2. The ANOVA table obtained shows that the model terms J, m, t, and m^2 are significant. The quadratic equation in terms of coded factors for Y_2 is given below:

$$Y_2 = 1.55 + 0.61X_1 - 0.35X_2 + 0.3X_3 - 0.28X_2^2. \tag{13}$$

Figure 2 shows the effect of J, m, t, and pH_o on energy consumed (kWh) and specific energy consumed (Y_2). It may be seen in Figure 2a that energy consumed always increased with t for all pH_o, however, Figure 2b shows that at higher pH_o (>6), specific energy consumed decreased with an increase in t. This is due to the fact that COD removal was

Table 5. ANOVA for Response Surface Quadratic Model for Specific Energy Consumed

Source	Coefficient estimate	Sum of Squares	DF	Mean Square	F-Value	Prob > F	
Model		19.165747	14	1.368982	3.323167	0.0137	significant
Intercept	1.55						
X_1	0.61	8.8720376	1	8.872038	21.53664	0.0003	significant
X_2	−0.35	2.983525	1	2.983525	7.242428	0.0168	significant
X_3	0.3	2.1204948	1	2.120495	5.147445	0.0385	significant
X_4	0.04	0.0324122	1	0.032412	0.07868	0.7829	
X_1^2	0.11	0.3627082	1	0.362708	0.880464	0.3629	
X_2^2	0.28	2.1002496	1	2.10025	5.0983	0.0393	significant
X_3^2	−0.07	0.1465394	1	0.146539	0.35572	0.5598	
X_4^2	−0.02	0.0113474	1	0.011347	0.027546	0.8704	
X_1X_2	0.02	0.0089998	1	0.009	0.021847	0.8845	
X_1X_3	0.27	1.2047451	1	1.204745	2.924487	0.1078	
X_1X_4	−0.13	0.272917	1	0.272917	0.662499	0.4284	
X_2X_3	−0.11	0.1995884	1	0.199588	0.484495	0.4970	
X_2X_4	−0.15	0.371765	1	0.371765	0.90245	0.3572	
X_3X_4	−0.14	0.3263124	1	0.326312	0.792115	0.3875	
Residual		6.1792643	15	0.411951			
Lack of Fit		6.1619061	10	0.616191	177.4926	<0.0001	significant
Pure Error		0.0173582	5	0.003472			
Cor Total		25.345011	29				

higher at $pH_o > 6$ and $t > 30$ min. Figure 2a also shows that energy consumed (kWh) first increased with an increase in pH_o and then decreased for $pH_o > 7$. It is known that hydroxides of aluminum get formed at pH ≈ 7. These hydroxide species stick on the electrode surface and grow like a film. Increase in resistance due to formation of this film increases the energy consumption at pH ≈ 7.[29]

It may be seen in the Figures 2c,d that an increase in J for any m increased the energy consumed (kWh) and specific energy consumed. Figures 2c,d also show that energy consumed and specific energy consumed first decreased with an increase in m value giving minimum values at $m \approx 1$ g/l, and thereafter they increased with an increase m. This trend was followed at every J. At a constant J, an increase in m value reduces the voltage between the electrodes, and hence energy consumed gets reduced for a given amount of COD removal. However, at high m (>1 g/l), chlorine species get formed during EC treatment, thus, consuming a high percentage of the applied current and increasing the energy consumed.[30]

Optimization analysis

For EC treatment of SDW, response Y_1 is to be maximized while Y_2 is to be minimized. Since the optimum conditions for responses Y_1 and Y_2 are not same, the desirability function approach could be utilized to get the maximum Y_1 and minimum Y_2 simultaneously. The constraints applied for the optimization of various operational parameters is given in Table 6.

For Y_1 and Y_2 the minimum acceptable values considered are 55% and 1.55 kWh/kg COD removed (minimum experimental value which does not depend on any factors and interaction of factors) and maximum values are 100% and 5.0 kWh/kg COD removed (the maximum value that may reach), respectively. Thus, one-sided desirability of Y_1 (d_1) is achieved as follow:

$$d_1 = \begin{cases} 0 & \text{if } Y_1 \le 55 \\ \left[\dfrac{Y_1 - 55}{100 - 55}\right] & \text{if } 55 < Y_1 < 100\,. \\ 1 & \text{if } Y_1 \ge 100 \end{cases} \qquad (14)$$

In a same way, one-sided desirability of Y_2 (d_2)

$$d_2 = \begin{cases} 1 & \text{if } Y_2 \le 0.56 \\ \left[\dfrac{5 - Y_2}{5 - 0.56}\right] & \text{if } 0.56 < Y_2 < 5\,. \\ 0 & \text{if } Y_2 \ge 5 \end{cases} \qquad (15)$$

In the above both equations $r = 1$. The overall desirability D is calculated by the following equation:

$$D = \sqrt{d_1 d_2}. \qquad (16)$$

By using D as a new desirability, the optimum values of operational parameters were found to be $J = 123.46$ A/m^2, $m = 2.0$ g/l, $t = 74$ min, and $pH_o = 6.5$, which produced overall $D = 0.515$. The responses Y_1 and Y_2 were 70.91% and 1.32 kWh/kg COD removed.

To verify the optimization result three verification run were conducted with the optimized set of operational parameters. The average value of responses Y_1 and Y_2 were found to be 68.08% and 1.22 kWh/kg COD removed, respectively, which are very close to predicted values. At optimized set of operational parameters, dissolved amount of aluminum electrodes after EC treatment was calculated and found to be 0.343 g. Dissolved mass of aluminum corresponded to 84% of the theoretical amount expected. The lower value of anode performance was probably due to the competition between Al^{3+} ions dissolution and O_2 and Cl_2 evolution at the anode.[31] Also, the formation of hydroxide film at the anode surface lowers the anode performance.[29]

The pH of the EC treatment system changes with time. Figure 3 shows the final pH_f with time (t) for the run carried out under optimum condition. It is clear from Figure 3 that pH_f increased from 6.5 to 7.85 within 5 min and after 30 min pH_f stabilizes to ≈ 8.5. This equilibrium pH_f is due to a dynamic balance between the complex chemical reactions involving a H^+ or OH^- donor and acceptor during EC treatment. This stable alkaline pH_f can be attributed to the cathodic water reduction, Eq. 7, being predominant over the

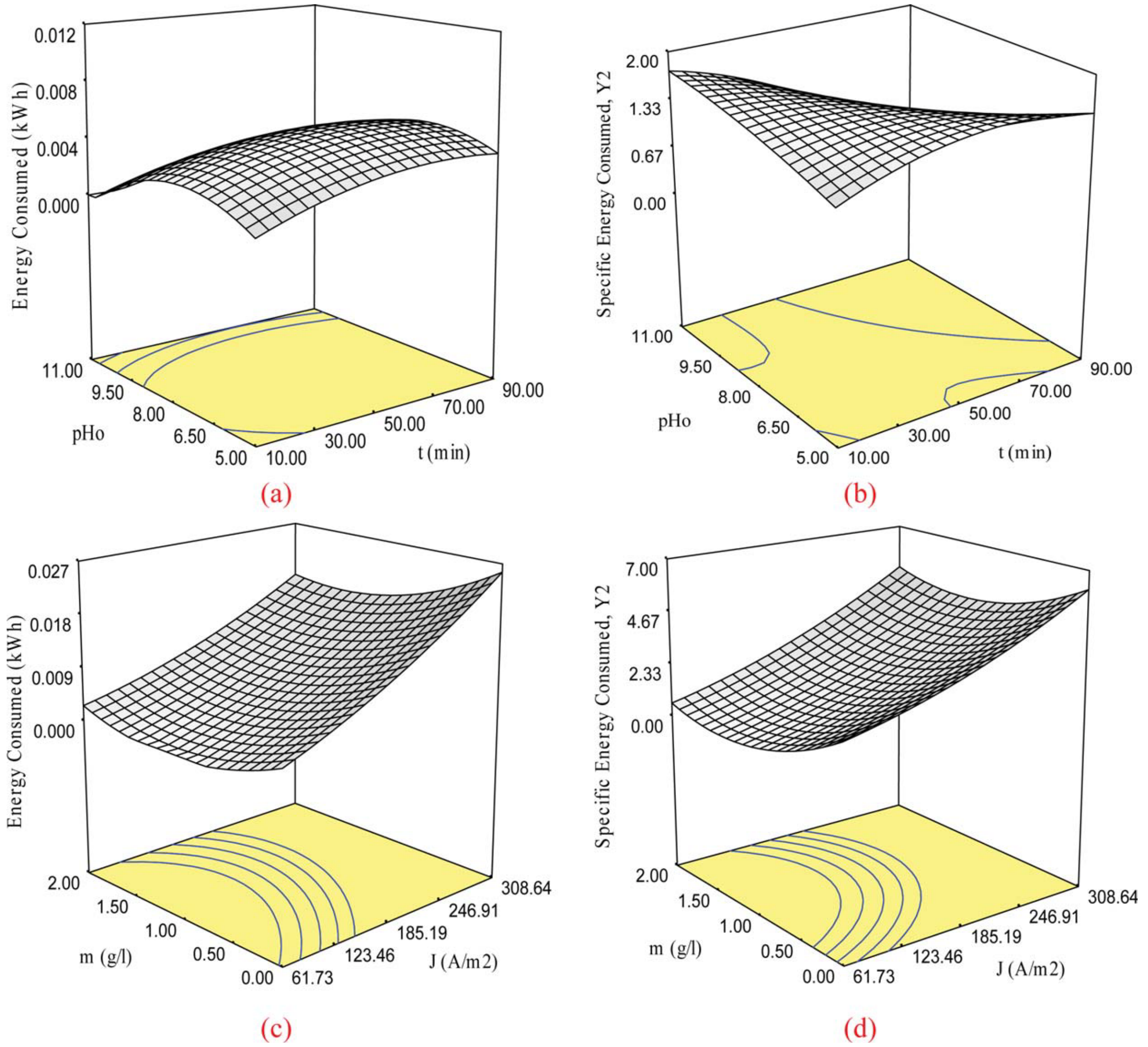

Figure 2. Three-dimensional response surface graphs for the EC treatment of SDW (a) Energy consumed (kWh) vs. t and pH$_o$ at $m = 2.0$ g/l, $J = 123.46$ A/m^2; (b) Specific energy consumed, Y_2 vs. t and pH$_o$ at $m = 2.0$ g/l, $J = 123.46$ A/m^2; (c) Energy consumed (kWh) vs. J and m at $t = 74$ min, pH$_o = 6.5$; and (d) Specific energy consumed, Y_2 vs. J and m at $t = 74$ min, pH$_o = 6.5$.

[Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

anodic water oxidation, Eq. 6 and aluminum hydroxylation reactions Eqs. 8–11.[32]

From the speciation of Al (III), Al(OH)$_4^-$ fully dominates after pH $\approx$ 7.5, which is not efficient to remove COD. Therefore, there should be no COD removal for pH $\geq$ 7.5, but, experimentally, it was seen that still there is COD removal. COD removal for pH $\geq$ 7.5 is due to the hypochlorite formation in the reactor (formed by successive reaction from chlorine) which indirectly oxidize the COD. For 6.5 $\leq$ pH $<$ 7.5, various positively charged hydrolyzed aluminum species are responsible for the COD removal (explained in Section "Effects of J, m, t, and pH$_o$ on Y_1").

Therefore, both electrocoagulation and electro-oxidation mechanisms are responsible for the SDW treatment, and

Table 6. Constraints Applied for the Optimization of EC Treatment of SDW

Variables	Objective	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
J (Am^{-2})	minimize	123.46	308.64	1	1	3
m (g/l)	is in range	0	2	1	1	3
t (min)	minimize	10	90	1	1	3
pH_o	is in range	5	7	1	1	3

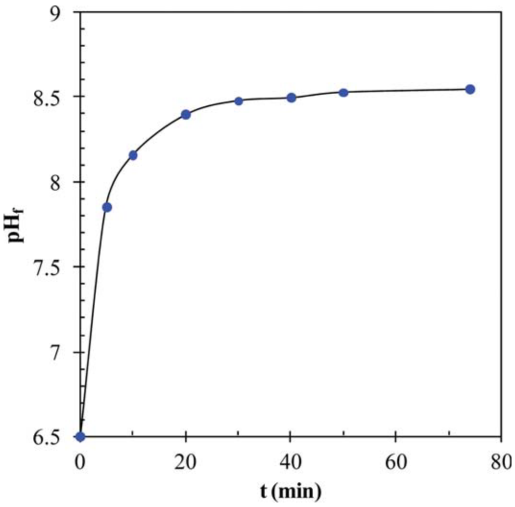

Figure 3. Graph of *t* vs. pH_f for the EC treatment of SDW at optimum condition.

[Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

hence, EC treatment is the real mechanism of SDW treatment.

Elemental analysis

EDX was conducted to study the distribution of the elements in sludge and scum generated at optimum condition by EC of SDW. EDX analysis showed the presence of 64.28 and 69.88% carbon, 23.8 and 19.31% oxygen, 9.10 and 8.34% aluminum, 0.34 and 0.77% sulfur, 0.12 and 0.52% potassium, 2.30 and 0.90% calcium, and 0.39 and 0.28% iron in sludge and scum, respectively. Thus, scum is found to contain higher amount of carbon as compared to sludge.

Aluminum mass balance was also performed for sludge and scum generated at optimum condition and calculation is shown in Table 7. Out of the total aluminum dissolved from the electrodes into the reactor, 27–29.21% goes to the scum, 71.1–73.33% goes into the sludge and rest goes to the treated SDW.

Treated SDW contained 9.54 mg/l of aluminum. No limit has been set by Government of India for discharge of aluminum containing effluents. EPA has also not given any maximum concentration limit on aluminum in its national primary drinking water regulations. However, it has prescribed a limit of 0.2 mg/l in national secondary drinking water regulations, which are not mandatory.[33] Obviously, the treated effluent will require further treatment by other physicochemical and biological method to remove the remaining COD, aluminum etc.

Disposal of residues

The generated sludge and scum by the EC treatment of SDW pose problems to their disposal. To check whether the generated sludge and scum could be oxidized as fuel in high temperature conditions such as those encountered in boilers and furnaces, thermal degradation characteristics of the sludge and scum were studied by TG instrument. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the sludge and scum for the heating rate of 10°C/min in the environment of air are shown in Figure 4. The TG traces can be divided in three oxidation zones. First oxidation zone describes loss of moisture and some volatile matter evolution and this is between 23 and 200°C for sludge and 20–250°C for scum. In this zone, there is loss of 9.4 and 11.7% mass of sludge and scum, respectively. Drying at higher temperature (>100°C) occurs due to loss of the bound moisture of the particles. The lack of endothermic peak in the first oxidation zone indicates the lack of any phase change during the heating process. The second oxidation zone lies between 200 and 550°C and

Table 7. Aluminum Mass Balance Calculation at Optimum Condition (*J*, *m*, *t*, pH_o = 123.46 A/m^2, 2.0 g/l, 74 min, 6.5) (Basis: 1.5 l of SDW)

Total aluminum introduced	
Aluminum in SDW (mg/l)	0.09
Total aluminum in SDW (g)	0.0001
Aluminum eroded by electrolysis (g) (Experimentally determined)	0.343
Total aluminum going in to the system (SDW feed + eroded) (g)	0.3431
Total aluminum in residues and treated SDW	
Sludge generated (g)	2.68
Total aluminum in sludge (g)	0.2439
Scum generated (g)	1.11
Total aluminum in scum (g)	0.0926
Al in treated SDW (mg/l)	9.54
Total aluminum in treated SDW (g)	0.0143
Total aluminum (residues + treated SDW) (g)	0.3508
% Error	−2.22

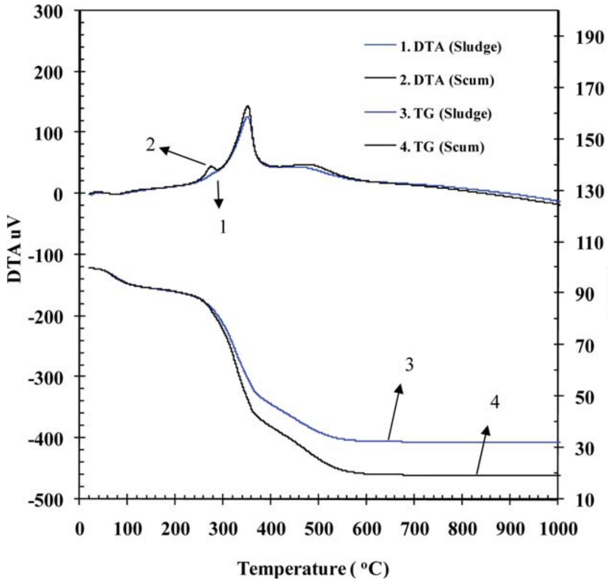

Figure 4. TG/DTA of sludge and scum generated by the EC treatment of SDW with aluminum electrodes at optimum conditions.

[Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

between 250 and 600°C for the sludge and scum, respectively. In this zone, the weight loss ~57.2 and ~68.3% was observed for sludge and scum, respectively. The strong exothermic peak for sludge and scum centered between 250 and 400°C shows the degradation by oxidation. It can also be seen that scum has higher exothermicity than sludge (Figure 4). This is due to higher carbon content of scum, which was confirmed by EDX analysis. The weight loss in this zone is mainly due to the carbon oxidation and evolution of CO_2 and CO. A third oxidation zone with weight loss ~1% can be envisaged at higher temperatures up to 1000°C. Overall, generated sludge and scum by EC treatment of SDW showed total weight loss of 68 and 80.8%, respectively. The higher oxidation of scum may be due to its higher carbon content.

The strong exothermic peak associated with oxidation of sludge and scum confirms the high energy evolution. Heating value of the sludge and scum generated by EC treatment of SDW were found to be 16.51 MJ/kg and 19.23 MJ/kg, respectively. Thus, the generated sludge and scum by EC treatment of SDW can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes. The bottom ash may be blended with clay to make fire bricks, thus, disposing of generated sludge and scum by EC treatment of SDW through chemical and physical fixation.[34]

Conclusion

Full factorial central composite (CC) design based on RSM has been successfully employed for the experimental design for electrochemical treatment of SDW using aluminum electrode. Multiresponse processes optimization by desirability function approach used to optimize the electrochemical treatment of SDW and give the combined $D = 0.515$. EC treatment process removed the COD, TS, TN and turbidity by 68.08, 54.3, 90.9, and 99.8%, respectively, at optimum condition set of parameters. Both, electrocoagulation (charge neutralization of anionic colloids present in the SDW by monomeric cationic aluminum species and sweep coagulation) and electro-oxidation by hypochlorite, which indirectly oxidize the COD were found to be the real mechanism of SDW treatment. The disposal study by TGA/DTA analysis showed that generated sludge and scum can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes.

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