Optimization of color and COD removal from livestock wastewater by electrocoagulation process: Application of Box–Behnken design (BBD)

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ABSTRACT

The present work aims to study the removal of color and COD from livestock wastewater by electrocoagulation (EC) process using Al electrodes. The Box–Behnken design and response surface methodology were used to investigate the effects of major operating variables and optimization conditions. The predicted values of responses obtained using the response function agree well with the experimental data. Economical operating conditions and removal efficiencies were found to be pH of 8, current density of 30 mA/cm^2, electrolysis time of 30 min and NaCl concentration of 1 g/L, and 95.2% (Y_1) and 93% (Y_2), respectively.

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Introduction

Discharge of livestock wastewater into the ecological system has negative impact on receiving water bodies. Livestock wastewater contains high-strength of COD, BOD$_5$, color, nitrogen, phosphorus and suspended solids. Large volumes of livestock wastewater are produced, and the wastewater is a primary pollution source of surface and ground waters. Much attention is paid to these problems in many countries as treatment of livestock wastewater is a difficult problem [1,2]. Issues include the intense odor, the possibility of pathogen dissemination, and the content of structured polymers toxic to microorganisms [3]. Therefore, several treatment processes are used to treat livestock wastewater. In recent years, strict environmental regulations have called for new processes for efficient and adequate treatment of various industrial wastewaters with relatively low operating costs. At this point, the electrocoagulation (EC) process has attracted a great deal of attention in treating industrial wastewaters due to its versatility and environmental compatibility. This method is characterized by simple equipment, easy operation, a shortened reactive retention period, a reduction or absence of equipment for adding chemicals, and decreased amount of precipitate or sludge which sediments rapidly. EC has been proved to be an efficient method for the treatment of wastewater. It was tested successfully for treating municipal wastewater [4], textile wastewater [5], poultry manure wastewater [6], landfill leachate [7], rose processing wastewater [8], chemical mechanical polishing wastewater [9], oily bilgewater [10], heavy metal contaminated groundwater [11], restaurant wastewater [12], dyeing wastewater [13,14], olive oil mill wastewater [15–17], and paper-recycling wastewater [18].

Despite the impressive amount of scientific research on the treatment of industrial wastewaters by EC, little research has been done on the treatment of livestock wastewater using EC process. Extensive literature survey shows that none of the researchers studied the optimization of the EC process using an aluminum electrode to treat livestock wastewater. To date, most of the studies on the optimization of wastewater treatment process have focused on the traditional one-factor-at-a time approach. However, this approach, which does not take into account the cross effects from the factors considered, is time consuming and has in poor optimization results [19,20]. Response surface methodology (RSM) is a powerful statistical-based technique for modeling complex systems, evaluating the simultaneous effects of several factors, and thus searching for the optimum conditions for desirable responses [21,22]. RSM also generates a mathematical model that can be used to predict the response of a system to any new condition. However, RSM has still not been used as a modeling and optimization tool for EC process to treat livestock wastewater in batch mode. Hence, in this study, Box–Behnken response surface design (BBD) coupled with Derringer's desired function methodology was used to

Table 1
Values of the livestock wastewater parameters.

Parameter	Unit	Value (mean ± S.D.)
Chemical oxygen demand (COD)	mg/L	2210 ± 29
Total organic carbon (TOC)	mg/L	420 ± 40
Biological oxygen demand (BOD)	mg/L	1140 ± 50
Total suspended solids (TSS)	mg/L	2340 ± 230
Total Kjeldhl nitrogen (TKN)	mg/L	3500 ± 420
Total phosphorus (TP)	mg/L	380 ± 30
pH	Dimensionless	8.4 ± 0.2
Alkalinity	maCO$_3$/L	1200 ± 210
Color	Absorbance at 287 nm	2.4

optimize and investigate the influence of the key process variables of EC such as initial pH, current density, electrolysis time, and initial electrolyte (NaCl) concentration (independent variables) on color removal and chemical oxygen demand (COD) removal (dependent variables).

Materials and methods

Livestock wastewater

Livestock wastewater used was supplied by the Pajucity Facilities Management Corporation, Gyeonggi do, Korea. The livestock effluent was sampled after the screening of coarser solids using a filter having a pore size of approximately 2.0 mm and sedimentation for 24 h. Samples were collected in polypropylene bottles, shipped cold, and kept at 4 °C before use. The length of the storage before starting experiments varied from one day to six weeks. During the course of this study, the effluent has been sampled at different times, and the initial characteristics varied with time (Table 1). This effluent initially contained high concentrations of soluble and undissolved organics (2210 ± 29 mg/L COD, 420 ± 40 mg/L TOC, 1140 ± 50 mg/L BOD$_5$, 2340 ± 230 mg/L TSS, 3500 ± 420 mg/L TN, 380 ± 30 mg/L TP, pH 8.4 ± 0.2, 1200 ± 210 mg CO$_3$/L alkalinity). The maximum color absorbance at 287 nm was 2.4 and the color was dark gray.

Electrocoagulation process

The experimental setup is shown in Fig. 1. EC experiments were conducted in a lab-scale EC cell having a total volume of 1 L. The EC cell was made from 6-mm transparent Plexiglas with the dimensions of 80 mm (width) × 80 mm (length) × 10 mm (height) and was equipped with four parallel monopolar electrodes: two

Fig. 1. Bench-scale EC reactor with monopolar electrodes in parallel connection.

anodes and two cathodes with the dimension of 50 mm × 60 mm × 3 mm, made of aluminum plate.

The total effective electrode area was 90 cm^2 and the spacing between the electrodes was 11 mm. A digital DC power supply (Smart Power, 1 kW SMART Programmable DC Power Supplies, TSP5020, 0 ∼ 50 V, 0∼20 A) was used to give regulated electricity current to the EC cell. Before each run, the electrodes were washed with acetone to remove surface matter; then, the impurities on the aluminum electrode surface were removed by dipping for 5 min in a solution freshly prepared by mixing 100 cm^3 of HCl solution (5% v/v) and 200 cm^3 of hexamethylenetetramine aqueous solution (2.80%), dried and weighted [23]. All runs were performed at constant temperature (25 °C), mixing speed (200 rpm), and with 1 L of wastewater solution. At the end of the run, the solution was filtered and then the filtrate was analyzed; the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried, and reweighted.

Analytical techniques

Different samples of 100 ml were taken at 5 min intervals for up to 0.5 h and filtered before being analyzed to determine BOD$_5$, COD, TSS and other parameters. COD, TOC, BOD$_5$, TSS, TKN, TP, pH, alkalinity, and color were determined according to the standard methods [24]. COD was measured using COD reactor and direct reading spectrophotometer (DR/5000, HACH, USA). The pH and conductivity were adjusted to a desirable value using NaOH or H$_2$SO$_4$, and NaCl, and measured using a pH meter model E520 (Metrohm Herisau, Switzerland) and a Conductivity Meter (Jenway Model 4200), respectively. The COD measurement was made according to the standard closed reflux and colorimetric methods, and the reactor and spectrophotometer were HACH DR/200 and DR 89, respectively. The TOC was measured using a Shimadzu TOC Analyser (Japan). The wastewater pH was measured with a laboratory bench Cyber Scan pH meter (Eutech, Thermo Fisher Scientific). The solution pH was monitored by a portable pH meter (Mettler Toledo S02, Germany). The removal efficiency (R) was calculated using the following equation:

$$R\,(\%) = \left[1 - \frac{Y}{Y_0}\right] \times 100 \tag{1}$$

where Y_0 and Y represent are the initial and final values of color and COD, respectively.

Experimental design

Response surface methodology (RSM) is a useful statistical tool for the optimization of different processes and widely used for experimental design. In this method, the leading objective is to optimize the response surface that is influenced by different parameters. RSM also identified the relationship between the controllable input parameters and the response variable. In this study, the optimization of experimental conditions for removal of livestock wastewater by electrocoagulation was conducted using Box–Behnken design (BBD) technique under RSM. In order to evaluate the influence of operating parameters on the color and COD removal efficiencies of livestock wastewater, four main factors to two levels each one were chosen: pH (X_1), current density (mA/cm^2) (X_2), electrolysis time (min) (X_3) and initial NaCl concentration (g/L) (X_4) as shown in Table 2. To consider the effectiveness of EC reactor, one of the important parameters for experimental design must consider the following variables: pH, current density, electrolysis time, and NaCl concentration. These variables would affect the overall treatment time, reaction rate, energy consumption, as well as the removal efficiency measured in the electrochemical processes.
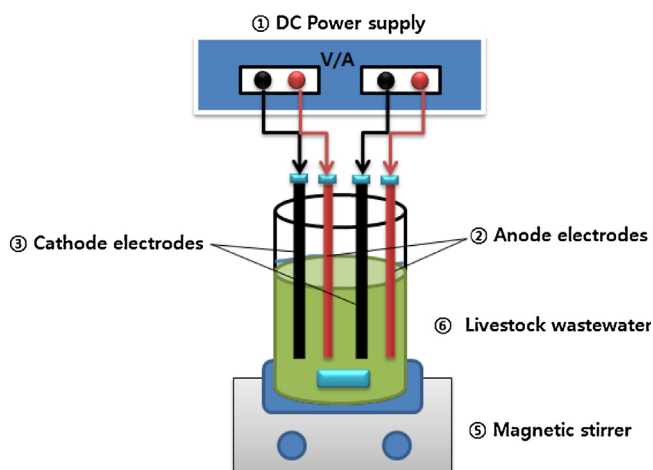
Table 2
Coded and actual values of the variables of the design of experiments for the overall electro-coagulation optimization.

Factor	Variables	Coded levels of variables		
		−1	0	+1
X_1	pH	4	6	8
X_2	Current density (mA/cm^2)	10	20	30
X_3	Electrolysis time (min)	10	20	30
X_4	NaCl concentration (g/L)	1	2	3

The experimental data (Table 3) were analyzed by the response surface regression (RSREG) procedure to fit the following second order polynomial model:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii}X_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k}\beta_{ij}X_iX_j + \varepsilon \quad (2)$$

where Y is response (color and COD removal efficiencies, %); β_0, β_i ($i = 1, 2, 3, 4$) and β_{ij} ($i = 1, 2, 3, 4$; $j = 1, 2, 3, 4$) are the model coefficients and X_i and X_j the coded independent variables. RSM was applied to the experimental data using statistical software, Minitable 14 (trial version).

Results and discussion

Response analysis and interpretation by Box–Behnken design (BBD)

In this present study, electrocoagulation process (EC) was investigated to treat livestock wastewater under different operating conditions such as initial pH (4–8), current density (10–30 mA/cm^2), electrolysis time (10–30 min), and electrolyte concentration (1–3 g NaCl/L) by using aluminum anode in batch mode. Four factors with three levels of Box–Behnken response surface design (BBD) were employed to optimize and investigate the effect of process variables on the responses such as color and chemical oxygen demand (COD) removal. The design matrix of the variables (pH (X_1), current density (mA/cm^2) (X_2), electrolysis time (min) (X_3), and initial NaCl concentration (g/L) (X_4)) in the uncoded and coded units by the Box–Behnken design (BBD) is shown in Table 3, along with the predicted and experimental values of the responses (color removal (Y_1) and COD removal (Y_2)). The predicted values of the responses were obtained from quadratic model fitting techniques for the percentage of color and COD removal using the software mimitab14 software. The response functions with the determined coefficients for color and COD removal are presented by Eqs. (3) and (4).

$$\begin{aligned}Y_1 \text{ (Color removal, \%)} =& \ 125.64 - 8.696X_1 + 0.155X_2 \\ & - 0.376X_3 - 10.925X_4 + 0.604X_1^2 \\ & + 0.008X_2^2 + 0.012X_3^2 + 1.979X_4^2 \\ & - 0.071X_1X_2 + 0.006X_1X_3 \\ & + 0.188X_1X_4 + 0.009X_2X_3 \\ & + 0.088X_2X_4 + 0.001X_3X_4 \end{aligned} \quad (3)$$

$$\begin{aligned}Y_2 \text{ (COD removal, \%)} =& \ 79.0 - 1.463X_1 + 0.16_1X_2 + 0.85X_3 \\ & - 4.258X_4 + 0.124X_1^2 + 0.007X_2^2 \\ & - 0.004X_3^2 + 1.246X_4^2 + 0.019X_1X_2 \\ & - 0.04X_1X_3 - 0.0875X_1X_4 \\ & - 0.0015X_2X_3 + 0.063X_2X_4 \\ & - 0.045X_3X_4 \end{aligned} \quad (4)$$

The analysis of variance (ANOVA) tests were also conducted for each response and presented in Table 4 indicating the fact that the predictability of the model is at 95% confidence level. Response function predictions agreed well with the experimental data ($R^2 = 98.3\%$ for Y_1 and $R^2 = 97.9\%$ for Y_2). To consider the relationship between the predicted values from the model

Table 3
Experimental design matrix and response based on the experimental runs and predicted values on color and COD removal (%) proposed by BBD design.

Run	Independent variables				Response (Y, %)			
	X_1	X_2 (mA/cm^2)	X_3 (min)	X_4 (g/L)	Experimental		Predicted	
	pH	Current density	Electrolysis time	NaCl concentration	Color removal	COD removal	Color removal	COD removal
1	4 (−1)	10 (−1)	20 (0)	2 (0)	88.6	84.2	88.8	84.7
2	8 (+1)	10 (−1)	20 (0)	2 (0)	81.9	82.1	82.1	81.6
3	4 (−1)	30 (+1)	20 (0)	2 (0)	98.5	92.1	99.3	91.8
4	8 (+1)	30 (+1)	20 (0)	2 (0)	86.1	91.5	87.0	90.3
5	6 (0)	20 (0)	10 (−1)	1 (−1)	85	83.1	86.3	83.1
6	6 (0)	20 (0)	30 (+1)	1 (−1)	92	90.2	92.5	90.6
7	6 (0)	20 (0)	10 (−1)	3 (+1)	85.5	86.2	86.0	85.1
8	6 (0)	20 (0)	30 (+1)	3 (+1)	92.5	91.5	92.2	90.8
9	4 (−1)	20 (0)	10 (−1)	2 (0)	91.6	83.2	91.5	83.7
10	8 (+)	20 (0)	10 (−1)	2 (0)	81.7	82.5	81.7	83.0
11	4 (−1)	20 (0)	30 (+1)	2 (0)	97.5	92	97.4	91.9
12	8 (+)	20 (0)	30 (+1)	2 (0)	88.1	88.1	88.2	88.0
13	6 (0)	10 (−1)	20 (0)	1 (−1)	87	84.2	86.0	84.0
14	6 (0)	30 (+1)	20 (0)	1 (−1)	92	90.9	91.9	90.6
15	6 (0)	10 (−1)	20 (0)	3 (+1)	84	83.2	84.0	83.8
16	6 (0)	30 (+1)	20 (0)	3 (+1)	92.5	92.4	93.4	93.0
17	4 (−1)	20 (0)	20 (0)	1 (−1)	96	89.1	95.7	88.7
18	8 (+)	20 (0)	20 (0)	1 (−1)	86	86.2	85.5	86.8
19	4 (−)	20 (0)	20 (0)	3 (+1)	95.2	90.3	94.7	90.2
20	8 (+)	20 (0)	20 (0)	3 (+1)	86.7	86.7	86.0	87.5
21	6 (0)	10 (−1)	10 (−1)	2 (0)	82.1	79.1	82.0	78.8
22	6 (0)	30 (+1)	10 (−1)	2 (0)	89.6	86.6	87.9	87.0
23	6 (0)	10 (−1)	30 (+1)	2 (0)	85.7	85.7	86.4	85.7
24	6 (0)	30 (+1)	30 (+1)	2 (0)	96.7	92.6	95.8	93.3
25	6 (0)	20 (0)	20 (0)	2 (0)	86.1	86.5	86.1	86.5
26	6 (0)	20 (0)	20 (0)	2 (0)	86.1	87	86.1	86.5
27	6 (0)	20 (0)	20 (0)	2 (0)	86.1	86.1	86.1	86.5

Table 4
ANOVA results for color and COD removal (%) by electrocoagulation process.

Response (Y, %)	Source	DF[a]	SS[b]	MS[c]	F-value[d]	Prob > F
Color removal	Model	14	616.332	44.0238	49.43	0.000
	Linear	4	561.2	140.3	157.5	0.000
	Quadratic	4	40.26	10.1	11.3	0.000
	Interaction	6	14.87	2.48	2.78	0.062
	Residual	12	10.6875	0.8906		
	Lack of fit	10	10.6875	1.0688		
	Pure error	2	0.000	0.000		
	Total	26	627.021	–		
	$R^2 = 98.3\%$, adjust $R^2 = 96.3\%$					
COD removal	Model	14	356.47	25.4622	44.44	0.000
	Linear	4	561.1	140.26	157.5	0.000
	Quadratic	4	40.26	10.1	11.3	0.000
	Interaction	6	14.88	2.48	2.78	0.062
	Residual	12	7.555	0.6296		
	Lack of fit	10	7.148	0.7148		
	Pure error	2	0.407	0.2033		
	Total	26	364.025	–		
	$R^2 = 97.9\%$, adjust $R^2 = 95.5\%$					

[a] DF: degrees of freedom of variance source.
[b] SS: sum of squares.
[c] MS: mean of squares (=SS/DF).
[d] F: F-value of variance source = MS/MSres; P: probability of error to be significant. The numbers indicated as subscript of F are degrees of freedom of variance source (i.e. regression, lack of fit) and degree of freedom of error, respectively.

calculated by Eqs. (3) and (4) and the observed values, the data obtained was very close to linear, indicating that both values were accurate and reliable, as shown in Fig. 2.

It is required to test the significance and adequacy of the model through the analysis of variance. The Fisher variance ratio, the F-value is a statistically valid measure to determine how well the factors describe the variation in the mean of data. The F-value indicates that the factors explain adequately the variation in the data about its mean, and the estimated factor effects are real. The corresponding analysis of variance (ANOVA) is presented in Table 4.

The quadratic regression model is highly significant [24] which is evident from the Fisher's F-test with a very low probability value (Prob > F = 0.0001). The significance of each coefficient of Eqs. (3) and (4) was determined by applying t-test and p-values of each as listed in Table 5. Since the p-values of all the coefficients are $p < 0.05$, it implies that these are significant. From Table 5, the model Y_1 terms X_1, X_4, X_1^2, X_3^2, X_4^2 and X_1X_2 had significant effects on the percentage of color removal whereas the model Y_2 terms X_3 and X_4^2 had significant effects on the percentage of COD removal, since each p-value was less than 0.05.

Effect of variables on color and COD removal efficiency

The interaction effects of pH and current density

The 2D contour plots in Figs. 3 and 4 which are simulations from Eqs. (2) and (3) describe the effect of the process variables on color and COD removal efficiencies. As shown in Figs. 3a and 4a, high removals of color (90–96%) and COD (86–90%) were achieved in acidic medium, at initial pH (X_1) values in the range of 6–4 and current density (X_2) in the range of 15–30 mA/cm². Especially, there is an obvious interaction between the initial pH (X_1) and the current density (X_2) on color removal (X_1X_2 for $p > 0.0001$), as shown in Table 5.

However, decolorization of livestock wastewater on an interaction between 8 of the initial pH (X_1) and 20 mA/cm² or 30 mA/cm² of current density (X_2) was lower. Furthermore, the color removal rate decreased at an initial pH of 8 even when the current density increased from 20 to 30 mA/cm². The 98.5% for high color removal efficiency was obtained with 20 min of electrolysis time (X_3) at pH 4 with current density (X_2) of 30 mA/cm² and NaCl concentration
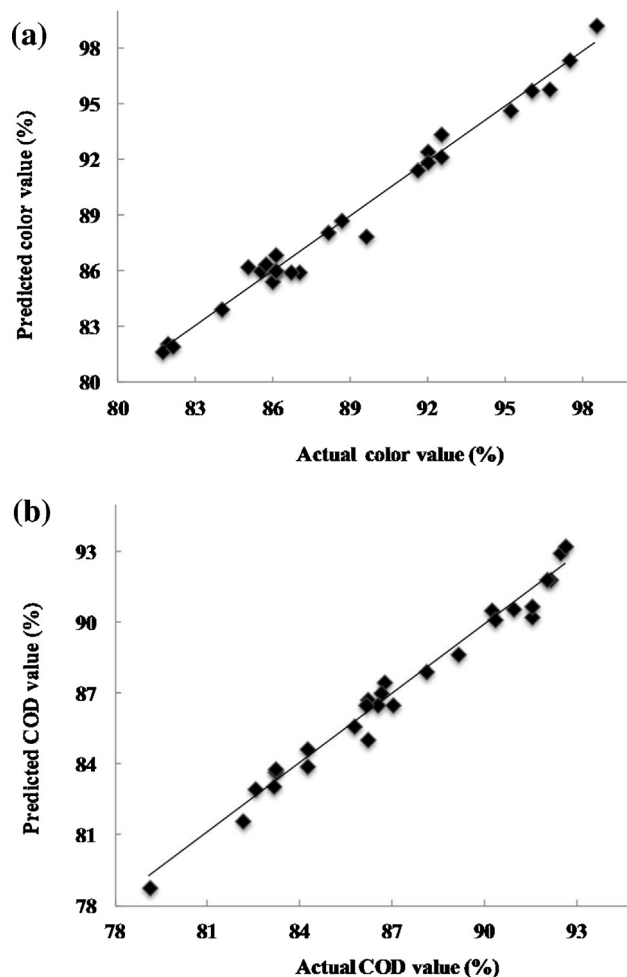

Fig. 2. Regression plots of the actual data against the predicted values from the response surface models describing (a) COD removal and (b) color removal efficiencies by the EC process.
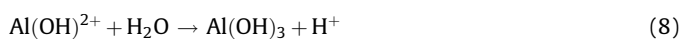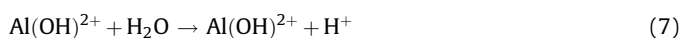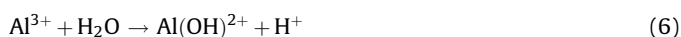
Table 5
Estimates of the model regression for color and COD removal by electrocoagulation process.

Relationship	Factor	Coeffi	SE coeffi	T value	Prob > F	Remark
	Model	125.642	8.322	15.1	0.000**	Significant
Linear	X_1	−8.696	1.480	−5.88	0.000**	Significant
	X_2	0.155	0.256	0.607	0.555	–
	X_3	−0.376	0.256	−1.471	0.167	–
	X_4	−10.925	2.556	−4.275	0.001**	Significant
Quadratic	X_1^2	0.604	0.102	5.914	0.000**	Significant
	X_2^2	0.008	0.004	1.876	0.085	–
	X_3^2	0.012	0.004	2.886	0.014*	Significant
	X_4^2	1.979	0.409	4.843	0.000**	Significant
Interaction	X_1X_2	−0.071	0.024	−3.02	0.000**	Significant
	X_1X_3	0.006	0.024	0.265	0.796	–
	X_1X_4	0.188	0.236	0.795	0.442	–
	X_2X_3	0.009	0.005	1.854	0.088	–
	X_2X_4	0.088	0.047	1.854	0.088	–
	X_3X_4	0.001	0.047	0.000	1.000	–
	Model	79.0	6.997	11.289	0.000	–
Linear	X_1	−1.463	1.244	−1.176	0.263	–
	X_2	0.161	0.215	0.749	0.469	–
	X_3	0.85	0.215	3.956	0.002**	Significant
	X_4	−4.26	2.149	−1.982	0.071	–
Quadratic	X_1^2	0.124	0.086	1.443	0.175	–
	X_2^2	0.001	0.003	0.206	0.840	–
	X_3^2	−0.004	0.003	−1.176	0.262	–
	X_4^2	1.246	0.344	3.626	0.003**	Significant
Interaction	X_1X_2	0.019	0.02	0.945	0.363	–
	X_1X_3	−0.04	0.02	−2.016	0.005**	Significant
	X_1X_4	−0.088	0.198	−0.441	0.667	–
	X_2X_3	−0.003	0.004	−0.378	0.712	–
	X_2X_4	0.064	0.040	1.575	0.141	–
	X_3X_4	−0.045	0.040	−1.134	0.279	–

* Significant at 5% (p-value).
** Significant at 1% (p-value).

(X_4) of 2 g/L (Run 3). However, similar results on COD removal showed four different run ranges (92.1% for Run 3, 92% for Run 11, 92.4% for Run 16 and 92.6% for Run 24) as shown in Table 3. This can be attributed to the fact that acid medium affects the mechanism of coagulation and leads to the formation of different chemical species in the bulk wastewater. Similar results have been reported in other studies using Al electrodes [25]. It can be concluded that an acidic initial medium was found to be beneficial to achieving the highest color and COD removals. In electrocoagulation process, pH is a crucial parameter that affects the performance of the treatment efficiency. Types of metal hydroxides formed in electrocoagulation process change depending on the initial pH. Aluminum ions (Al^{3+}) produced by dissolution of the anode (Eq. (5)) immediately undergoes spontaneous hydrolysis reactions that generate various monomeric species (Eq. (6)–(8)) over a wide pH range [26]. The dissolution of the aluminum anode produces Al^{3+} and $Al(OH)_2^+$ at low pH, which, at appropriate pH values, are transformed initially into $Al(OH)_3$. However, depending on the pH of the aqueous medium, other ionic species such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$, as well as polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{+4}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ may also be present in the system [27]. These intermediate species convert finally into $Al(OH)_3(s)$; the overall process of flocks formation may be described as:

$$Al \rightarrow Al^{3+} + 3e^- \quad (5)$$

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad (6)$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad (7)$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_3 + H^+ \quad (8)$$

These hydroxides ($Al(OH)_3$) compounds (Eq. (8)) have large surface area as coagulant, which are beneficial for a rapid adsorption of soluble organic compounds and metal ions [28]. Since $Al(OH)_3$ has higher weight and density, it settles faster [29] and it is easier to make the trapped colloidal separate from the aqueous medium by sedimentation or H_2 flotation [30]. When the initial pH was kept originally at 8.4, the removal efficiencies of color and COD were obtained to be 83.2% and 80.4%, respectively. This could be because the OH^- ion will accumulate in aqueous solution during the process. The increasing of pH at acidic conditions gives an attribute to hydrogen evolution at the cathodes.

The interaction effects of current density and electrolysis time

The effects of initial pH (X_1) and electrolysis time (X_3), while keeping current density (X_2) and initial NaCl concentration (X_4) in the middle levels (20 mA/cm^2 and 1.5 g NaCl/L), are shown in Figs. 3b and 4b. As the duration of the electrolysis treatment increased, a comparable increase in the removal efficiencies of color and COD was observed. It was also observed that as the reaction time increased from 10 to 20 min, the color and COD removal efficiencies increased from 90 to 93% and from 84 to 88.5%, respectively. This is due to the fact that, as the time of electrolysis increased, the mixing and reaction time also increased [31]. This is also ascribed to the fact as the time increased, more hydrogen bubbles were generated at the cathode; these bubbles improved the degree of mixing and enhanced the flotation ability of the cell with a consequent increased in the percentage removal [32,33]. However, the interaction effect at the initial pH (X_1) values in the range of 6–8 and at electrolysis time from 20 to 30 min is insignificant and very less change in color and COD removals (Figs. 3b and 4b).
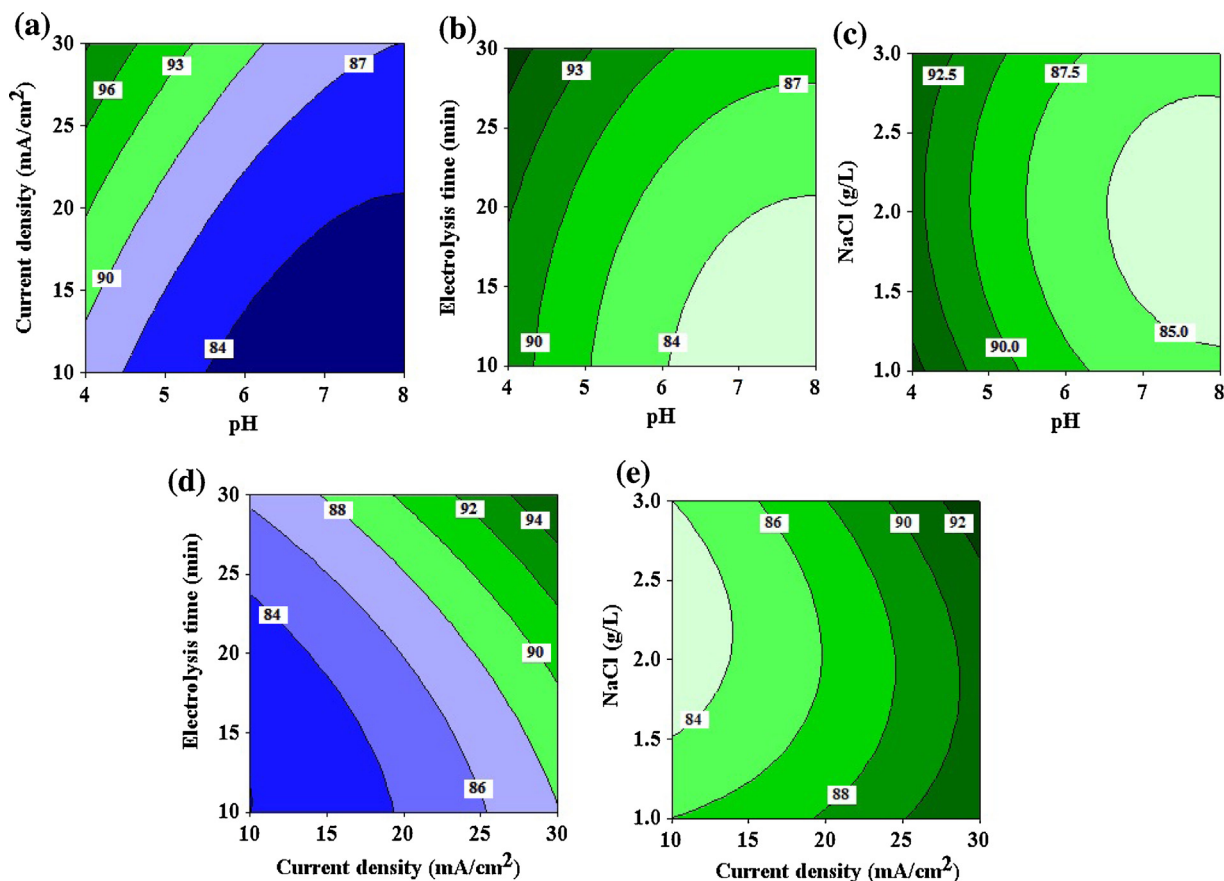
Fig. 3. Two-dimensional contour plots showing the effects of the initial pH (X_1), current density (mA/cm^2) (X_2), electrolysis time (min) (X_3), and the initial NaCl concentration (g/L) (X_4) on color removal efficiency (Y_1).

The interaction effects of initial pH and NaCl concentration

Electrolysis time is of vital importance to the performance of EC process. Generally, the organic concentration in wastewater reduces the increase in electrolytic time. In molten sodium chloride (NaCl), there are two ions, namely, cation Na$^+$ and anion Cl$^-$. At the anode, the oxidation of chloride ion takes place by depositing two electrons and forming a pure chlorine gas. At the same time, the reduction of sodium ion takes place at the cathode forming a pure sodium metal. With the addition of NaCl to the medium, the following reactions take place in the wastewater [34,35] as shown in the following Eqs. (9)–(11).

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{9}$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \tag{10}$$

$$HOCl \rightarrow OCl^- + H^+ \tag{11}$$

2D counter plots for electrocoagulation process in Figs. 3c and 4c were shown to visualize the effects of the initial pH (X_1) and the initial NaCl concentration (X_4) on the removal efficiencies of color and COD responses, while keeping current density (X_2) and electrolysis time (X_3) in the middle levels (20 mA/cm^2 and 20 min), respectively. Increasing NaCl concentration (X_4) to 2 g/L at a range from 4 to 8 for the initial pH (X_1) decreased the color and COD removal efficiencies from 90% to 85% and from 88% to 86%, whereas further increase in NaCl concentration (X_4) increased the color and COD removal efficiencies from 85% to 92.5% and from 86% to 89%, respectively. Increasing the electrolyte concentration from 0.5 g/L to 1.0 g/L slightly increased color and COD removal rates, and a further addition of NaCl up to 2 g/L or beyond 1 g/L of NaCl

resulted in a moderate but significant retardation of treatment efficiencies both in terms of color and COD removals. Previous works show similar results of various electrolytes like NaCl, KCl, NaNO$_3$, NaNO$_2$, NaSO$_4$, etc., that are available [36,37]. But, due to low cost and easy availability, NaCl has been selected as the best electrolyte [38].

The interaction effects of current density and electrolysis time

The effects of current density (X_2) and electrolysis time (X_3) as an estimate of percent color and COD removals are shown in Figs. 3d and 4d, respectively. As can be understood from Figs. 3d and 4d, increasing the electrolysis time (X_3) had a positive effect on color removal at an electrolysis time from 20 to 30 min and COD removal at all selected electrolysis times from 10 to 30 min. Also, the color removal rate on an interaction between 10 mA/cm^2 of current density (X_2) and from 20 to 30 min of electrolysis time (X_3) decreased (Fig. 3d). However, increasing current density (X_2) to 20 mA/cm^2 at a constant 20 min of electrolysis time (X_3) enhanced the removal rate, whereas further increase in current density (X_2) lowered the removal efficiency. As expected, increasing the current density (X_2) from 20 to 30 mA/cm^2 and the electorlysis time (X_3) from 15 to 30 min resulted in a dramatic increase in percent COD removals from 81 to 92%. As it is clear from the response contour plot, COD removal had its peak value while both of the process variables were kept at the maximum (Fig. 4d). This trend can be attributed to greater production of sludge by aluminum hydroxides. Al^{3+} ions undergo hydrolysis and the resulting aluminum hydroxides produce more sludge with a consequent significant removal of color and COD as described by Eqs. (5)–(8). Also, by increasing the current density of the cell, the amount of hydrogen
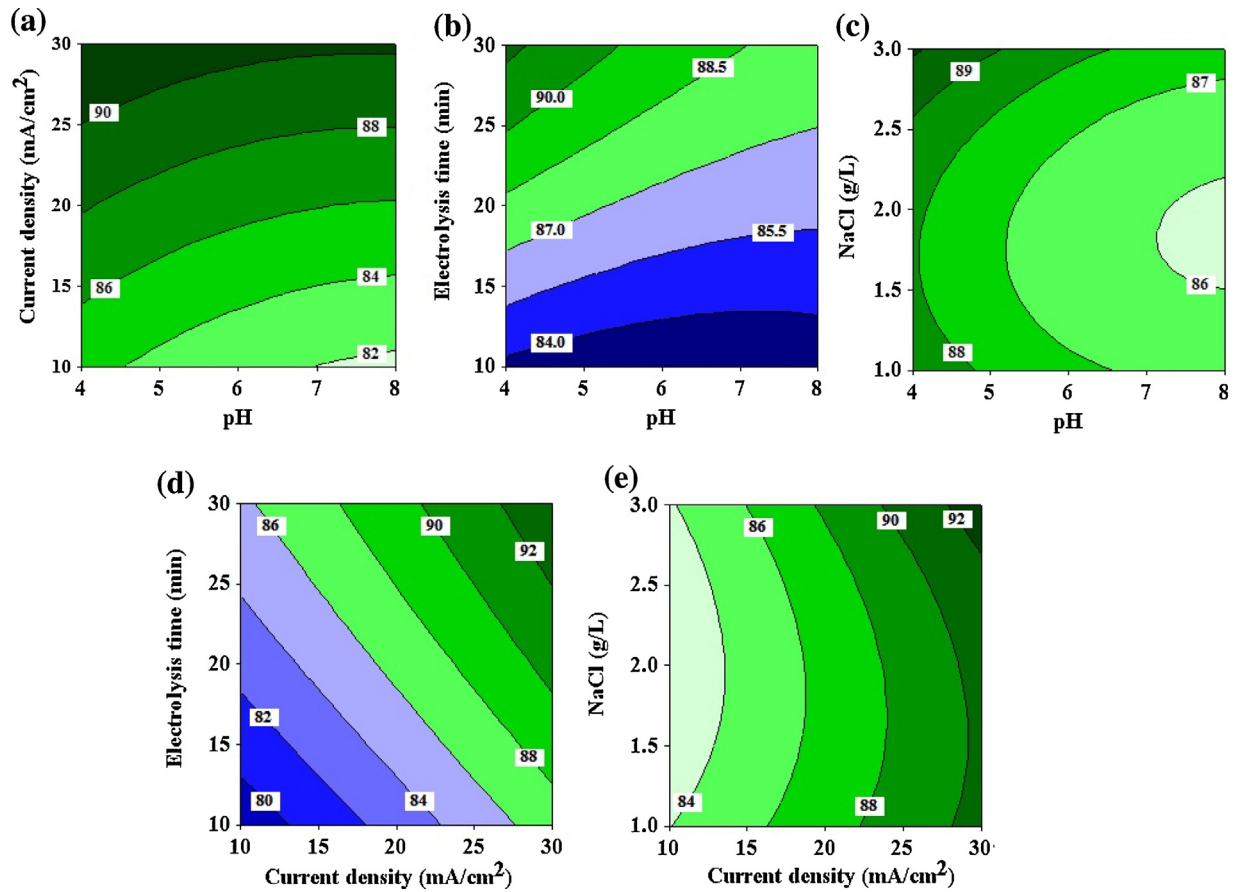
Fig. 4. Two-dimensional contour plots showing the effects of the initial pH (X_1), current density (mA/cm^2) (X_2), electrolysis time (min) (X_3), and the initial NaCl concentration (g/L) (X_4) on COD removal efficiency (Y_2).

bubbles at the cathode increased, resulting in a greater upward flux and a faster removals of color and COD [39,40].

The interaction effects of initial pH and electorlysis time

By keeping the initial pH (X_1) and electrolysis time (X_3) at the central level (6, 20 min), the interaction effects of current density (X_2) and the initial NaCl concentration (X_4) on the color and COD removals are shown in Figs. 3e and 4e. Increasing NaCl concentration (X_4) to 2 g/L at a range from 10 to 30 mA/cm^2 for current density (X_2) decreased the removal efficiency, whereas further increase in NaCl concentration (X_4) increased the color and COD removal efficiencies (Figs. 3e and 4e).

Optimization and economic conditions using desirability functions

The numerical optimization of the software has been chosen in order to find the specific point that maximizes the desirability function. The desired goal was selected by adjusting the weight or the importance that might alter the characteristics of a goal. The goal fields for response have five options: none, maximum, minimum, target, and within range. In order to determine the optimum process parameters for the maximum or economic color and COD removal efficiencies, Derringer's desired function methodology optimization was used in this present study. This numerical optimization technique evaluates a point that maximizes the desirability function [41–43].

According to the BBD results, the optimal operating conditions for the maximum color and COD removals based on Derringer's desired function methodology are found to be the initial pH (X_1) of 4, current density (X_2) of 30 mA/cm^2, electrolysis time (X_3) of 30 min, and electrolyte concentration (X_4) of 3 g NaCl/L. Under these conditions, the predicted removal efficiency of color and COD is found to be 99.1 and 94.9%, respectively. Experiments were performed under the optimized conditions, which shows the removal efficiency of color and COD close to the predicted values (98.5 and 93.2% respectively). An experimental test was conducted using the predicted values. The experimental findings for all response parameters agreed well with the model predictions indicating color and COD removal efficiencies. Based on the discussion above and the data available, the economical condition of the input parameters can be summarized with respect to the desired levels of output. The economical values of the dependent variables (Y_1 and Y_2) in the electrocoagulation process were determined from the analysis of the removal efficiency and energy consumption. Electrical energy consumption and current efficiency are very important economical parameters in electrocoagulation process. Electrical energy consumption can be calculated by using the following relationship [28]:

$$E = U \times I \times t \tag{12}$$

where E is the electrical energy (Wh), U is the cell voltage (V), I is the current intensity (A), t is the time of electrolysis process (h). The electric energy consumed to removal of 1 g of color and COD was calculated with following equation [44]:

$$E\,(\text{Wh/g}) = \frac{E}{C_0 - C} \tag{13}$$

E (Wh/g) is the electric consumption for removing 1 g of color and COD, C_0 is the initial color or COD concentration (mg/L), and C is final color or COD concentration (mg/L). The economical

Table 6
Optimum conditions and experimental verification for electrocoagulation process.

Condition	Independent variables				Response (Y_1 and Y_2)					
	pH	Current density	Electrolysis time	NaCl concentration	Color removal (%)		COD removal (%)		Energy consumption (Wh/g)	
	X_1	X_2 (mA/cm^2)	X_3 (min)	X_4 (g/L)	Actual	Predicted	Actual	Predicted	Color-removed	COD-removed
Optimum	4.0	30	30	3	98.5	99.1	93.2	94.9	5.3	4.2
Economic	8.0	30	30	1	94.2	95.3	92.4	93.0	6.2	3.2

conditions for the maximum color and COD removals were the initial pH (X_1) = 8, current density (X_2) = 30 mA/cm^2, electrolysis time (X_3) = 30 min, and electrolyte concentration (X_4) = 1 g NaCl/L. It can be concluded that an initial pH 4 was found to be beneficial to achieving the highest color and COD removals. However, it is noted that acceptable treatment levels in terms of both removal efficiency and energy consumption can also be achieved at the initial pH or original pH. Since the best COD removal can be obtained at the range of 4–8 of the initial pH, it can be suggested that the EC condition can be performed without the initial pH modification. This is because the actual pH of the livestock wastewater is about 8.3 and close to neutral pH. From the statistical analysis, the results show that the initial pH ($p < 0.05$) significantly affects the COD reduction in livestock wastewater. The concentration of supporting electrolyte was adjusted to the desired level by adding a suitable amount of NaCl to the solution. The solution resistance decreases when the concentration of the supporting electrolyte in solution increases. The higher ionic strength generally decreases the cell voltage with increasing solution conductivity at constant current density. Accordingly, the necessary voltage for attaining a certain current density decreases and thus, so does the consumed electrical energy [27].

However, when the concentration of the supporting electrolyte was increased from 1 to 3 g NaCl/L, the COD removal efficiency increased slightly from 94.9% to 93%, while the corresponding specific energy consumption decreased from 4.3 to 3.2 Wh/g-COD removed. From the specific energy consumption shown in Table 6, 1.0 g NaCl/L was regarded as the optimum balance, providing reasonable removal efficiency and relatively low specific energy consumption. As shown in Table 6, the difference of color and COD removal efficiencies between the optimum and economical conditions was also low, and the actual difference values of 4.2 and 2.3%, respectively, were achieved for the two responses (Y_1, Y_2). Verification experiments were conducted under the optimum operational. The three replicate experiments yielded an average maximum and economical color and COD removal efficiencies. The good agreement between the predicted and the experimental results verified the validity of the model and existence of an optimal point. This indicated that the RSM was a powerful tool for determining the exact optimal values of the individual factors.

Conclusions

The performance of electrocoagulation (EC) technique for decolorization and chemical oxygen demand (COD) reduction of livestock wastewater was investigated in a laboratory batch study. In this study, experimental conditions were optimized by observing the effects of interactions among the variables on color and COD removal efficiencies using a response surface methodology (RSM). The RSM results demonstrated significant effects of four operating variables (initial pH, current density, electorlysis time and initial NaCl concentration) as well as their interactive effects on two responses (color and COD removals by electrocoagulation). Box–Behnken design (BBD) was used to determine the optimal removal efficiency for both color and COD. High R^2 value of 98.3%

for color removal and 97.9% for COD removal through ANOVA verified that the accuracy of the proposed polynomial model is acceptable. The maximum predicted color and COD removal were 99.1% and 94.9%, respectively, using optimized ratios of the initial pH: current density (mA/cm^2): electrolysis time (min): initial NaCl (g/L) of 4, 30, 30, and 3, respectively. The optimized data for the economical removals of COD and color were around 95.3% and 93%, respectively, at pH of 8, current density of 30 mA/cm^2, electrolysis time of 30 min, and NaCl concentration of 1 g/L. The optimal variables resulted in experimental values that were in close agreement with the model predictions. Our results imply that the response surface methodology (RSM) with a Box–Behnken design (BBD) can help identify the most significant operating factors for treating color and COD from livestock wastewater during an electro-coagulation reaction.

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