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DAIRY WASTEWATER TREATMENT IN CONTINUOUS STIRRED TANK ELECTROCHEMICAL REACTOR (CSTER): PARAMETRIC OPTIMIZATION AND KINETICS

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Abstract

Dairy wastewater has been a major environmental concern because of massive effluents characterized by high pollution load. This study reports the influence of initial pH (pH_i), residence time (τ) and elapsed time (t) on the %COD removal (Y_1) and specific energy consumed (kWh per kg of COD removed, Y_2) for real dairy industry wastewater treatment in continuous stirred tank electrochemical reactor (CSTER) using aluminum electrodes. Central composite design (CCD) was applied for designing the experiments, analyzing the experimental data and optimizing the process parameters to maximizing Y_1 and simultaneously minimizing Y_2 . Important design parameters for continuous reactors like steady state time (t_s), mass transfer coefficient (k_m) and kinetic parameters were also estimated. Modified pseudo-first-order kinetic model was used for kinetic modeling with non-linear regression technique. Experiments conducted at optimal process parameters for CSTER ($pH_i = 4.5$, $\tau = 141$ min; $t = 52$ min) showed $Y_1 = 71.21\%$, $Y_2 = 4$.

Key words: aluminum electrode, COD removal, continuous electrochemical treatment, dairy wastewater, specific energy consumed

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1. Introduction

Increased demand in processed milk and milk products resulted enormous increase in dairy industries, consequently huge volume of wastewater is generated worldwide. Usually 0.2-10 liters of wastewater is generated for one liter of processed milk (Kushwaha et al., 2010a; Vourch et al., 2005). In dairy industry, various operational steps such as starting, equilibrating, stopping and rinsing the processing units (flushing water, first rinse water etc.) generates the wastewater (Kushwaha et al., 2011a; Vourch et al., 2008). However, large fraction of generated wastewater gets produced during cleaning operations. Dairy wastewater usually contains fat, lactose, nutrients, detergents and sanitizing agents, and loaded with high biochemical oxygen demand (BOD), chemical oxygen demand (COD) and

dissolved/suspended solids (Hepsen and Kyaya, 2012; Kushwaha et al., 2010a). Therefore, its disposal concern is at highest.

Various technologies for the treatment of dairy wastewaters have been reported in the literature such as membrane filtration (Frappart et al., 2006; Vourch et al., 2005), coagulation (Kushwaha et al., 2010b; Rusten et al., 1993), biological treatment (Demirel et al., 2005; Mohseni-Bandpi and Bazari, 2004; Sirianuntapiboon et al., 2005) and adsorption (Kushwaha et al., 2010c; Rao and Bhole, 2002; Sarkar et al., 2006). Aerobic process has been reported to be high energy intensive, whereas, anaerobic processes are inefficient to nutrients degradation and need high controls. Therefore, biological methods are very costly in terms of operating as well as fixed cost. On the other hand, the physical/chemical methods have been reported to generate huge volume of secondary

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pollutants, and are costly due to expensive adsorbents/coagulants/chemicals (Borbón et al., 2014; Chen and Liu 2012; Demirel et al., 2005; Kushwaha et al., 2011a).

Electrochemical (EC) treatment method is a feasible technique for wastewater treatment, including dairy wastewater (Bensadok et al., 2011; Borbón et al., 2014; Kushwaha et al., 2011b; Maiti et al., 2011; Qasim and Mane, 2013; Sangal et al., 2013a; Sharma, 2014; Sundarapandiyani et al., 2018; Tchamango et al., 2010; Un et al., 2014; Wang et al., 2017; Yavuz et al., 2011). EC treatment offers high removal efficiencies in compact reactors with simple equipment/instruments for control and operation of the process (Wang et al., 2017; Yavuz et al., 2011). Further, EC treatment produces lesser sludge as secondary pollutants due to involvement of electro-oxidation. Moreover, Kushwaha et al. (2010b) reported EC methods very cost effective in terms of operating cost.

Excellent assessment of the available literature on dairy wastewater treatment has been presented by Arvanitoyannis (2006) and Kushwaha et al. (2011a). In most of the reported studies, authors used batch EC reactor for the dairy wastewater treatment (Bensadok et al., 2011; Kushwaha et al., 2010b; 2011b; Qasim and Mane, 2013; Sharma, 2014; Tchamango et al., 2010; Yavuz et al., 2011).

Dairy industries generate strong and large volume of wastewater, generally 0.2-10 litre of effluent per litre of processed milk (Vourch et al., 2008) with high flow rate (Castillo et al., 2007; Hepsen and Kaya, 2012). This discourages the treatment in batch EC reactor. However, only two studies (Benazzi et al., 2016; Un et al., 2014) are available in open literature for continuous EC treatment of dairy wastewater, reporting the influence of current density, retention time and pH on treatment efficiency. Benazzi et al. (2016) used synthetic dairy wastewater (milk powder dissolved in distilled water) with Aluminium (Al) electrode, and Un et al. (2014) studied whey wastewater (liquid discharged from cheese production) treatment with iron electrode.

Conversely, for real dairy wastewater, the treatment performance may be restricted by presence of contaminants other than milk wastes such as: milk solids, detergents, sanitizers, cleaning water, phosphates, sequestering agents, surfactants and many other factors like turbidity, high chloride content, pH, etc. (Demirel et al., 2005; Grasshoff, 1997; Passeggi et al., 2009). Moreover, steady state time (t_s), mass transfer coefficient (k_m) and kinetic parameters, which

are important design parameters for the continuous reactors, and lacking in studies reported by Benazzi et al. (2016) and Un et al. (2014). Furthermore, energy consumption, which is an important operating cost parameter, is not reported in earlier studies. Therefore, in view of above lacking, more studies are needed to evaluate performance and applicability of continuous EC treatment to treat real dairy wastewater.

This study investigates EC treatment of real dairy industry wastewater in continuous stirred tank electrochemical reactor (CSTER). Experiments in CSTER were conducted to evaluate the influence of process parameters such as initial pH (pH_i), residence time (τ) and elapsed time (t) on the %COD removal (Y_1) and specific energy consumed (kWh per kg of COD removed, Y_2) using Aluminium (Al) electrode, and steady state time (t_s) and mass transfer coefficient (k_m) were estimated. Elapsed time is defined as the run time of the reactor after switching on the power supply to the reactor. Steady state time is defined as the time after which the treatment performance indicator (% COD removal) becomes constant. Central composite design (CCD) was applied for designing the experiments, analyzing the experimental data and optimizing the process parameters. Kinetic modeling was also performed using modified pseudo-first-order kinetic model through nonlinear regression technique.

2. Materials and methods

2.1. Wastewater and instrumentation

Dairy wastewater was collected from equalization tank of wastewater treatment plant of Verka Milk Plant, Patiala, Punjab, India, and was preserved at 4 °C. The dairy wastewater was characterized for COD, BOD (5-day BOD), total nitrogen (TN), total solids and Turbidity immediately after collection and three more times during the study. The detailed statistics with minimum, mean and maximum values with standard deviation have been provided in Table 1. Analytical reagent grade chemicals were used for analysis of wastewater samples before and after the treatment. To measure the COD, a digestion unit (Spectra lab, 2015D, India) and a double beam UV-visible spectrophotometer (HACH, DR 5000, USA) were used. BOD was measured using digital BOD-measurement system (WTW Oxitop IS 6, Germany), and turbidity meter supplied by Spectra lab India (NT 2000) was used to measure the turbidity. TN was determined using the standard Kjeldahl method.

Table 1. Dairy industry wastewater characteristics

Parameter	Values				EC Treated
	Untreated				
	Minimum	Mean	Maximum	SD	
COD (mg/L)	2675	2800	2930	109.77	806
BOD ₅ (mg/L)	2085	2285	2475	170.68	630
TN (mg/L)	14.07	15.12	15.84	0.759	3.92
Total solids (mg/L)	21140	22000	22310	573.8	2000
Turbidity (NTU)	811.6	844.9	858	23.69	1.3

2.2. Reactor and experimental procedure

Experiments were conducted in a cuboid shaped continuous stirred tank electrochemical reactor (CSTER) made of Perspex, having the actual working volume of 1.3 liter ($8.5\text{ cm} \times 8.5\text{ cm} \times 25.5\text{ cm}$) (Fig. 1). Two sets of Al electrodes, of 1 mm thickness with $21\text{ cm} \times 5\text{ cm}$ area were connected in parallel with inter-electrode spacing of 1 cm. Constant current/voltage digital direct current power supply (0-20 V, 0-5 A; Make Crown Electronics Delhi, India) was used for power supply. A magnetic stirrer was used to agitate the content in the CSTER reactor.

2 g/L of NaCl was introduced to the feed tank to increase the electrical conductivity (Kushwaha et al., 2011b). NaOH/H₂SO₄ were used to adjust pH as per the experimental condition required. To conduct the experiments, the dairy wastewater to the CSTER was continuously pumped from the feed reservoir with a flow rate equivalent to desired residence time (τ) by peristaltic pump (MICLINS PP- 30-EX). When the reactor was filled with wastewater, the power supply was switched on and the elapsed time (t) was measured. At pre decided various t values, treated wastewater samples were collected from the reactor, and analyzed for Y_1 and Y_2 .

2.3. Statistical methods and analysis

Central composite design (CCD) under response surface methodology (RSM) was applied to design experiments, modeling, analysis and optimization. RSM is a group of statistical techniques that are used in empirical study for mathematical modelling between a response and several independent input parameters of problems and

analysis (William & Gertrude 1962). Furthermore, CCD is five level full factorial experimental design method suitable for quadratic response model. This design method is augmented with center points and axial points allowing the assessment of the interaction parameters of the quadratic response model (Myers and Montgomery, 1995; Rakić et al., 2014). Since, CCD is five level design method, the design points fall at combination of high and low factor levels and their three mid points which produces high quality predictions. Moreover, CCD is capable of optimizing the process parameters within the study limits of process parameters.

The independent process parameters; τ : 30-150 min and t : 30-150 min were selected as input parameters for the CSTER treatment system, whereas, Y_1 and Y_2 were considered as responses of the system. Working range of independent variables (τ and t) were decided with the help of reported literature and preliminary experiments conducted (not shown here). Benazzi et al. (2016) and Körbahti and Tanyolac (2009) studied HRT effects in continuous EC reactor in the range of 30-90 min and 30-240 min, respectively. Electrolysis time study in the range of 30-75 min is reported for batch reactor (Sharma, 2014; Yavuz et al., 2011). Further, from the preliminary experiments conducted, no significant effect was observed for $\tau > 150$ min.

Therefore, in this study, the HRT (τ) was selected to be varied in range of 30-150 min. Elapsed time was also selected in range of 30-150 min, because preliminary experiments conducted revealed steady state time to be nearly 140 min at lower HRT (τ) value and 50 min at higher HRT (τ) values. However, Körbahti and Tanyolac (2009) varied elapsed time in the range of nearly 30-480 min.

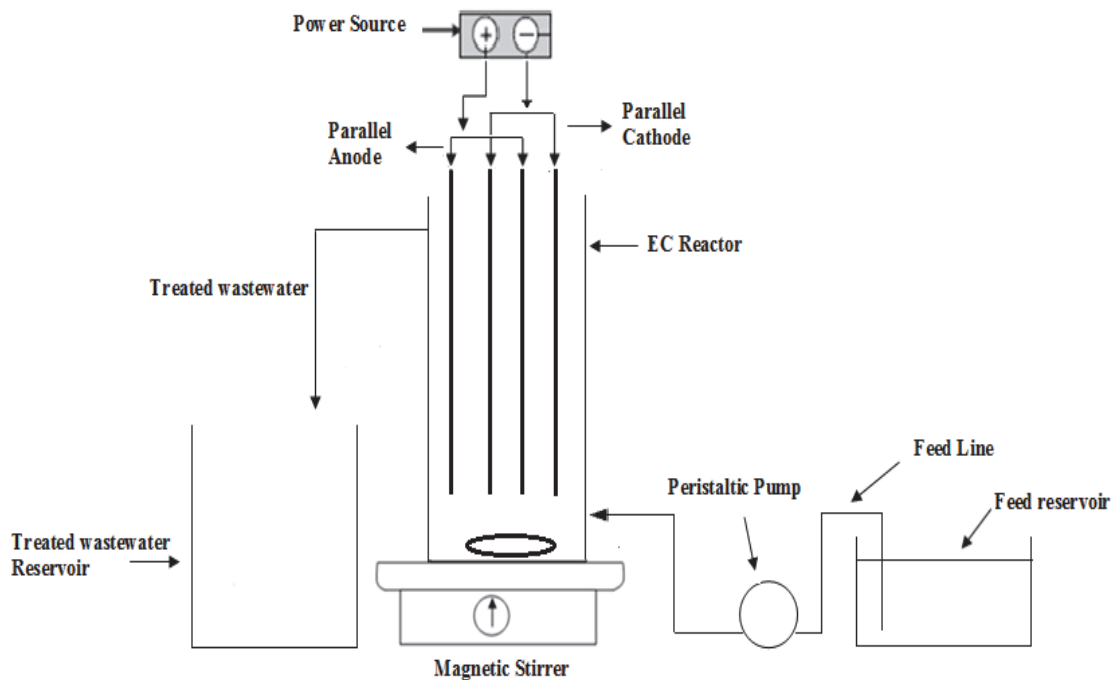


Fig 1. Continuous electrochemical reactor setup

To design experiments, the independent process parameters were coded at five levels between -2 to +2, and suggested number of experiments with experimental conditions by CCD has been presented in Table 2.

In our previous study (Kushwaha et al., 2011b), batch electrochemical treatment of synthetic dairy wastewater using Al electrodes was reported and current density was optimized. Therefore, in this study all the experiments suggested by the CCD were conducted at previously optimized current (i) = 3.7 A (Kushwaha et al., 2011b). To optimize pH_i , experiments were conducted for various pH_i : 4.5-9 at current (i) = 3.7 A, τ = 45 min and t =150 min, and Y_1 was measured.

The data obtained from the conducted experiments (Table 2) were fitted to quadratic equation (Eq. 1), and ANOVA was used to analyse the interaction between the process parameters and the responses.

$$Y = k_o + \sum_{i=1}^4 k_i X_i + \sum_{i=1}^4 k_{ii} X_i^2 + \sum_{i=j+1}^3 \sum_{j=1}^4 k_{ij} X_{ij} \quad (1)$$

where: Y is response; k_o , k_i , k_{ii} , k_{ij} are constant coefficients and X_i the independent process variables. The sequential F-test and other adequacy measures were used for selecting the best model (Sangal et al., 2013b). The fit quality of quadratic model was evaluated by the coefficient of determination, R^2 and adjusted R^2 . To come to a decision about the adequacy of the model for the % COD removal and specific energy consumed, two different tests such as the sequential model sum of squares and model summary statistics were carried out.

Since, there are two responses; Y_1 and Y_2 , Therefore, optimum process parameters must ensure maximizing Y_1 and at the same time minimizing Y_2 . For the purpose of optimization of process parameters, multi-response process optimization using desirability function approach of RSM was used (Kushwaha et al.,

2011b; Sangal et al., 2014). This approach transforms each individual response (Y_i) to an individual desirability measure (d_i), where d_i lies between 0-1, using a desirability transformation function. Depending on the preferred target (nominal-the-best: NTB; larger-the-best: LTB; and smaller-the-best: STB) of the response (Y_i), the individual desirability transformation function is varied. In this study, the preferred target for the responses Y_1 (%COD Removal) and Y_2 (specific energy consumed) were set as LTB and STB, respectively (Barman, 2016). The Eqs. (2) and (3) shows the desirability transformation function used to calculate the individual desirability measure for responses Y_1 and Y_2 with LTB and STB target set, respectively.

$$d_i = \begin{cases} 0 & ,if Y_i \leq Y_{i-min} \\ \left[\frac{Y_i - Y_{i-min}}{Y_{i-max} - Y_{i-min}} \right]^r & ,if Y_{i-min} < Y_i < Y_{i-max} \\ 1 & ,if Y_i \geq Y_{i-max} \end{cases} \quad (2)$$

$$d_i = \begin{cases} 1 & ,if Y_i \leq Y_{i-min} \\ \left[\frac{Y_i - Y_{i-max}}{Y_{i-min} - Y_{i-max}} \right]^s & ,if Y_{i-min} < Y_i < Y_{i-max} \\ 0 & ,if Y_i \geq Y_{i-max} \end{cases} \quad (3)$$

Here, Y_{i-min} and Y_{i-max} is minimum and maximum response values of i^{th} response, respectively, while Y_i is the i^{th} response values. r and s is weight assigned to responses and we take all as 1 in this study. Importance factor was also selected as 1 for both the responses; Y_1 and Y_2 .

The overall desirability (D) for the optimized system is explained by Eq. (4).

$$D = (d_1 \times d_2)^{\frac{1}{2}} \quad (4)$$

where, d_1 and d_2 are individual desirability for responses Y_1 and Y_2 , and $0 \leq D \leq 1$.

Table 2. Suggested experiments with process variables values and responses for EC treatment of dairy wastewater

Residence time, τ (min)	Elapsed time, t (min)	%COD Removal, Y_1		Specific Energy Consumed, Y_2	
		Actual	Predicted*	Actual	Predicted*
60	60	60.14	57.10	6.25	6.99
120	60	63.35	65.52	5.62	5.24
60	120	64.85	61.88	11.60	12.41
120	120	67.85	70.10	10.49	10.18
30	90	49.85	52.66	12.54	11.87
150	90	71.71	69.30	7.44	7.89
90	30	57.78	58.02	3.17	3.10
90	150	67.21	67.37	13.61	13.46
90	90	64.42	65.46	8.52	8.33
90	90	65.32	65.46	8.40	8.33
90	90	64.84	65.46	8.47	8.33
90	90	67.12	65.46	8.18	8.33
90	90	66.37	65.46	8.27	8.33
90	90	63.89	65.46	8.59	8.33

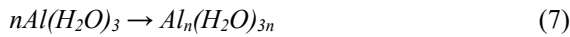
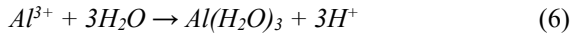
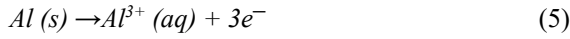
Predicted*: predicted by CCD

3. Result and discussions

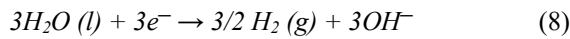
3.1. Effects of pH_i on Y_1

Effect of pH_i on Y_1 , were explored by conducting the continuous EC experiments at pH_i : 4.5-9 with $i=3.7$ A, $\tau = 45$ min (Fig. 2). Treated samples collected at various t were analyzed for Y_1 .

During EC treatment, Al^{3+} ions are generated due to anodic dissolution of anode. Subsequent processes result the formation of varieties of monomeric and polymeric aluminium hydrolyzed species depending on pH and Al^{3+} ions concentration (Duan and Gregory 2003; Zidane et al., 2008). Cationic and anionic monomeric and polymeric aluminium hydrolyzed species are formed at acidic pH and basic pH, respectively (Duan and Gregory, 2003; Singh et al., 2013). The anodic reactions are as follows (Eqs. 5-7) (Singh et al., 2013):



At cathode following reaction takes place



Various monomeric and polymeric aluminium hydrolyzed species destabilize the pollutants and/or form lower solubility particles which incarcerate the pollutants. Also, pollutants removal process is improved by generated hydrogen at cathode which is adsorbed on the pollutants resulting decrease in relative specific weight. In addition to this, generated $\cdot OH$ radicals at anode due to high oxygen overvoltage H_2O decomposition, and chlorine gas and various other chloro-oxidant species ($HOCl$ and ClO^-) destruct pollutants through mediated oxidation (Chen, 2004; Deborde and Von Gunten, 2008; K rbahti and Tanyolac, 2003; Lin et al., 1998). ClO^- ions dominate at highly basic pH, while $HOCl$ at highly acidic pH, and ClO^- ions has been reported to be a stronger oxidant (Zidne et al., 2008). The reactions involved are as follows (Eqs. 9-15)(Singh et al., 2013):

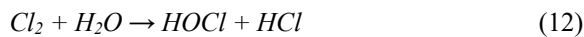
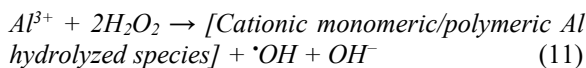
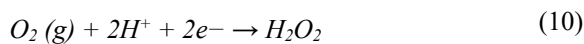
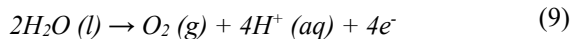


Fig. 2 illustrates effect of pH_i on Y_1 at various

t . Maximum Y_1 value of 60.36 was found at $pH_i = 4.5$ and $t = 150$ min. On increasing the pH_i upto 7.0, Y_1 value continuously decreased to 32.0 at $t = 150$ min. For all values of $pH_i > 7.0$, Y_1 value was found to increase up to ≈ 39.0 , and further no effect of increasing pH_i was observed. Dairy wastewater isoelectric point (pH_{iec}) is 4.2 (Selmer-Olsen et al., 1996). At $pH_i > pH_{iec}$ colloids and proteins present in the dairy wastewater are negatively charged and are destabilized by various hydrolyzed species; Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$ etc., and precipitation occurs. After precipitation, adsorption of organic substances on metal hydroxide precipitates reduces the COD. This may be the cause of higher Y_1 value at high acidic pH ($pH_i = 4.5$) EC treatment. Increase in pH_i to 7.0, decreases the concentration of Al^{3+} and its hydrolysed products (Duan and Gregory, 2003). Consequently, decreased Y_1 value was observed. Moreover, at $pH_i > 7.0$, $Al(OH)_4^-$ ions are formed which is incapable of removing COD. But it can be seen in the Fig. 2, Y_1 value was found to increase beyond $pH_i = 7.0$. This increase in Y_1 value is attributed to indirect oxidation of pollutants by ClO^- ions, H_2O_2 and $\cdot OH$ radicals which are generated via equation 8-11. Since, maximum Y_1 value of 60.36 was found at $pH_i = 4.5$, therefore, further study was conducted at $pH_i = 4.5$.

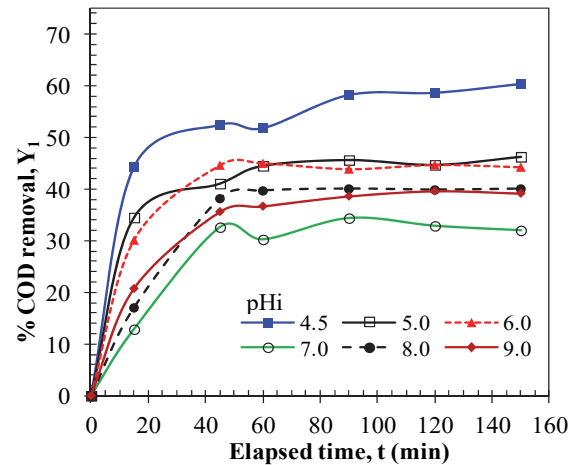


Fig. 2. Effect of pH_i on %COD removal by EC treatment of dairy wastewater (Current, $i = 3.7$ A, residence time, $\tau = 45$ min)

3.2. Effects of τ and t on Y_1 and Y_2 , Steady State Time, and Optimization

To explore the effect of τ and t , on Y_1 , the experiments were conducted at $pH_i = 4.5$ and current (i) = 3.7 A as per experimental condition suggested by the CCD, and COD value was monitored at the outlet of the reactor (Table 2). The experimental results were then fitted to quadratic model and it was evaluated by using sequential model sum of squares, model summary statistics and ANOVA were tested, and concluded that the quadratic model well fitted the experimental data. A normal probability plot of the residuals is shown in Fig. 3 a, b. The data points on

this plot lie reasonably close to a straight line, signifying that the underlying assumptions of the analysis were satisfied. In addition to above, other important statistical performance indicators such as root mean-squared error (RMSE), index of agreement (IA) and coefficient of variation (CV) were also calculated to see the statistical significance of the derived model. RMSE and IA for response Y_1 were found to be 1.873 and 0.962, respectively, advocating the actual data are in good agreement with predicted data. Furthermore, CV, which describes the degree of variation from actual values to predicted values, was found to be 8.2 and 7.62, respectively, implying good correlation.

ANOVA showed significant quadratic model fitting with model F-value, R^2 and adjusted R^2 being 10.03, 0.862 and 0.776, respectively (Table 3). Predicted Y_1 value was plotted against actual experimental values (not shown here), and it was found that the actual data are in good agreement with predicted. Values of “Prob>F” greater than 0.1 indicate that model terms are not significant. In the

present study, τ , t and τ^2 are significant terms (Table 3). Quadratic equation in terms of coded variable for %COD removal is given below (Eq. 14):

$$Y_1 = 65.46 + 4.16A + 2.34B - 1.12A^2 - 0.69B^2 - 0.052AB \tag{14}$$

The percentage contribution of each term in the equation 14 have also been calculated to evaluate the impacts of first-order (A, B), quadratic (A^2 , B^2), and interaction terms (AB) on Y_1 at the optimum process parameters values and found to be 69.43%, 30.1% and 0.00468%. It can be seen that the highest and least %contribution is of first-order terms and interaction terms, respectively, concluding first-order terms and quadratic terms highly impacts to the response Y_1 . However, the impact of interaction term is negligible.

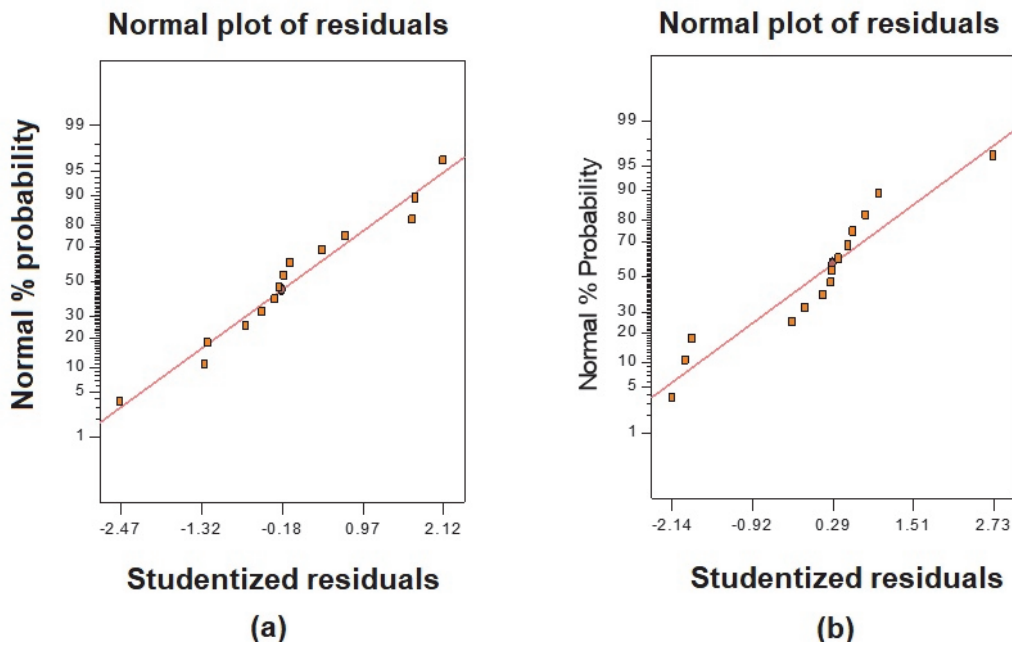


Fig. 3. Normal plot of residuals for (a) Y_1 (b) Y_2

Table 3. ANOVA for %COD removal and specific energy consumption

Source	%COD removal, Y_1 #					Specific Energy consumption, Y_2 \$				
	DF	Sum of Squares	Mean Square	F Value	Prob > F	DF	Sum of Squares	Mean Square	F Value	Prob > F
Model	308.23	5	61.65	10.03	0.0027	96.51	5	19.30	68.09	< 0.0001
A	207.75	1	207.75	33.81	0.0004	11.89	1	11.89	41.96	0.0002
B	65.66	1	65.66	10.69	0.0114	80.63	1	80.63	284.43	< 0.0001
A^2	30.33	1	30.33	4.93	0.0570	3.63	1	3.63	12.81	0.0072
B^2	11.55	1	11.55	1.88	0.2075	0.004	1	0.004	0.014	0.9074
AB	0.011	1	0.011	0.0018	0.9673	0.056	1	0.056	0.198	0.6678
Residual	49.16	8	6.14			2.27	8	0.288		
Lack of Fit	41.73	3	13.91	9.36	0.0171	2.15	3	0.715	29.45	0.0013
Pure Error	7.43	5	1.48			0.121	5	0.024		
Cor Total	357.39	13				98.78	13			

A: residence time, τ ; B: Elapsed time, t ; # R^2 : 0.862; Adjusted R^2 : 0.776; \$ R^2 : 0.98; Adjusted R^2 : 0.96

The classical 2-D and response surface 3-D plots for dependency of Y_1 on τ and t are shown in Figs. 4 and 5. It can be observed in Figs. 4 and 5, that for all values of τ increasing t value improves the Y_1 value. After 150 min of t , Y_1 values were found to be 56.07, 62.23, 64.86, 67.86 and 72.3 at 30, 60, 90, 120 and 150 min of τ (Fig. 4).

With increase in τ value, it can also be observed that steady state time (t_s) for COD removal is achieved earlier in CSTER. At $\tau = 30$ min, steady state was found at $t = 120$ min, while for all $\tau = 60$ min $t = 60$ min was observed. But for all the $\tau > 60$ min, steady state time (t_s) was observed after at $t = 50$ min. This variation in t_s may be due to fact that at higher τ value, higher amount of Al^{3+} and $Al(OH)_2^+$, $Al(OH)_2^+$ etc. are generated (Kumar et al., 2009; Thakur et al., 2009), and hence, maximum possible removable COD is removed at lower t value.

To investigate the effect of τ and t on Y_2 , experiments were conducted, and results are shown in Table 2. Actual Y_2 values from experiments were plotted against predicted values from CCD (not shown here). This showed that the actual data are in good agreement with predicted values. Furthermore, RMSE and IA values being 0.4033 and 0.994, implied actual data are in good agreement with predicted one. CV values: 8.2 and 7.62 for actual and predicted values, respectively, showed good correlation. Table 3 shows ANOVA for the quadratic model fitted for response Y_2 . Model F-value, R^2 and adjusted R^2 of 68.09, 0.98 and 0.96, respectively, implies quadratic model satisfactorily explain the response Y_2 . Also, τ , t and τ^2 were found noteworthy terms for response Y_2 . The approximating quadratic equation Y_2 is given below (Eq. 15):

$$Y_2 = 8.33 - 1.0A + 2.59B + 0.39A^2 - 0.13B^2 - 0.12AB \quad (15)$$

%contribution of first-order (A, B), quadratic (A^2 , B^2), and interaction terms (AB) in the equation 15, calculated at the optimum process parameters values, were found to be 66.72%, 29.91% and 3.56%, respectively. This implies that the first-order terms and quadratic terms highly impacts to the response Y_2 , as it was in the case of response Y_1 . However, the impact of interaction term is moderate opposite to the response Y_1 .

3-D response surface plot for dependency of Y_2 on τ and t are shown in Fig. 6. At any t value, it can be observed in Fig. 6 that Y_2 value is comparatively high at lower τ value, and decreased on increasing τ up to $\tau \approx 100$ min. Beyond $\tau = 100$ min, marginal change in Y_2 was observed.

At the low τ value, high steady state time (t_s) and low %COD removal are observed (as explained in above paragraph with the help of Figs. 4 and 5). Therefore, low %COD removal and higher steady state time (t_s) value are reasons for higher Y_2 value at lower τ . Beyond $\tau = 100$ min, due to nearly constant

steady state time (t_s) and small variation in %COD removal (Figs. 4 and 5), nearly constant Y_2 was observed. Further, at any τ , Y_2 value was always found to increase with increase in t value, obviously due to increase in treatment time.

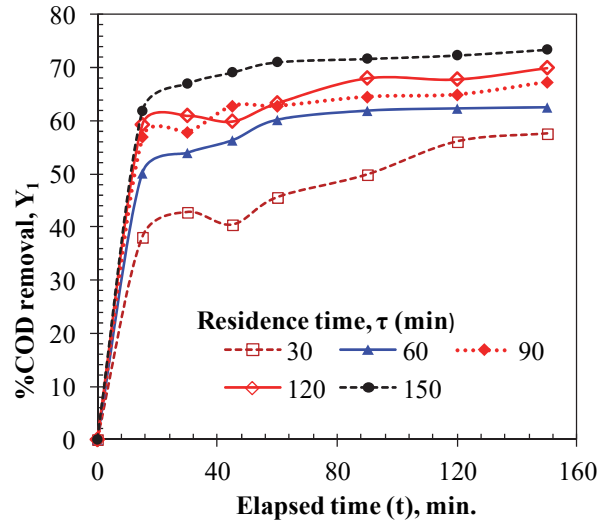


Fig. 4. Effect of residence time on %COD removal, Y_1 by EC treatment of dairy wastewater (Current, $i = 3.7$ A, $pH_i = 4.5$)

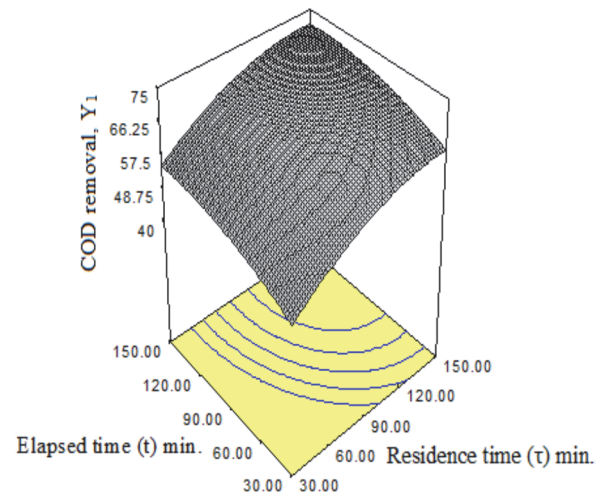


Fig. 5. 3-D response surface graph for %COD removal, Y_1 versus t and τ for the EC treatment of dairy wastewater at $pH_i = 4.5$ and $i = 3.7$ A

For optimization of EC treatment of dairy wastewater, residence time (τ) and Y_2 were set for being minimum within elapsed time, $t = 30$ -150 min, whereas Y_1 was set to be maximized. The applied constraints for this optimization is shown in Table 4. Suggested optimized values of τ , t , Y_1 and Y_2 by CCD were found to be 141 min, 52 min, 67% and 4.62 kWh/kg of COD removed, respectively. Three authentication runs were performed at these optimum condition, and the average values of responses Y_1 and Y_2 were observed to be 71.21% and 4.32 kWh/kg of COD removed, respectively. Other treated wastewater

characteristics at optimized parameters are shown in Table 1. Marginal error of 5.9% and 6.4% in Y_1 and Y_2 , respectively, showed good agreement between experimental and predicted values.

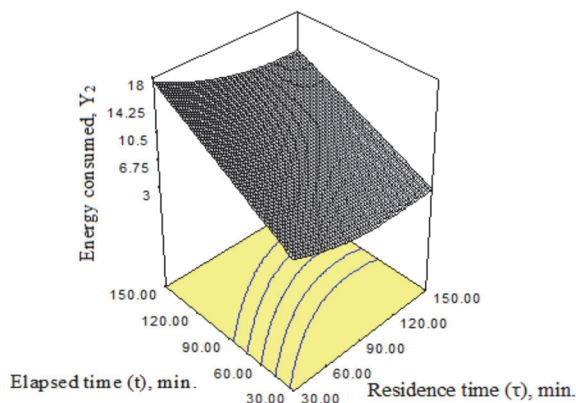


Fig. 6. 3-D response surface graph for specific energy consumed, Y_2 versus t and τ for the EC treatment of dairy wastewater at $pH_i=4.5$ and $i=3.7$ A

Table 4. Constraints used for the optimization of continuous EC treatment of dairy wastewater

Variables/ Responses	Goal	Lower Limit	Upper Limit
Residence time, τ	Minimize	30	150
Elapsed time, t	In range	30	150
%COD Removal, Y_1	Maximize	55	100
Energy Consumed (kWh/kg COD removed), Y_2	Minimize	3.17	13.61

3.3. Mass transfer coefficient

Electrochemical reactions are heterogeneous redox processes that occurring between an electrode and an electrolyte (wastewater in this case). In the present study, various aluminium hydrolyzed species and H_2 are produced in EC reactor via equation 5-6 at the surface of electrodes.

The rate of reaction depends only on the supply rate of reactant to the electrode if overpotential is sufficiently high, and the process becomes mass transport controlled.

In this condition, although the CSTER performance depends on parameters like electrode area, electrode length, electrode potential, electrolyte (wastewater in this case) properties and retention time (Trinidad et al., 1998), the process rate becomes highly dependent on the flow rate (Walsh, 1993). Due to the complexity involved in the CSTER and electrodes configuration, general correlations to express the mass transfer coefficient (k_m) in terms of Schmidt and Reynolds numbers may lead to unrealistic mass transfer coefficients (Korbahti et al., 2009).

For completely mixed (under complete mass transport control) and for single pass mode CSTER, mass transfer coefficient (k_m) can be represented by following equation (Eq. 16) (Trinidad et al., 1998).

$$k_m = \frac{COD_{fr} V_R}{(1 - COD_{fr}) A \tau} \quad (16)$$

where, k_m is mass transfer coefficient, COD_{fr} is fractional COD conversion, V_R is reactor volume, A is electrode area and τ is residence time.

The changes in k_m and COD_{fr} with change in τ is shown in Table 5. With increase in τ value COD_{fr} increases due to the increased mass transport to the electrodes and increased reaction time. Electrode passivation, which is due to film formed of Al^{3+} ions hydroxide species on electrode, limits the performance of EC treatment. With passage of time, thickness of this film increases, and performance of the EC treatment is affected. In this study, mass transfer coefficient (k_m) was found to decrease with increase in τ value. Increasing τ value provided increased reaction time. Hence, thicker film with higher resistance decreased the mass transfer coefficient (k_m) (Pletcher and Walsh, 1990).

Table 5. Mass transfer coefficient with specific energy consumption in CSTER

τ (min)	COD_{fr}	$k_m \times 10^{-6}$ m/s)	kWh/kg COD_R
30	0.576	46.6	18.097
60	0.625	28.6	15.044
90	0.672	23.5	13.611
120	0.700	20.0	12.706
150	0.734	19.0	12.113
141*	0.712	18.1	4.330

* τ value at optimum condition

3.4. Kinetic study

Kinetic study for the EC treatment of dairy wastewater was performed for COD removal at various residence times (τ) 30-150 min. The collected kinetic data were analyzed using pseudo-first order kinetics. The rate equation for pseudo-first order kinetics may be written as (Eq. 17):

$$\frac{-dCOD}{dt} = kCOD \quad (17)$$

The integration of the above equation with $t=0$ and $t=t$ yields (Eq. 18):

$$\ln \frac{COD_0}{COD} = kt \quad (18)$$

At any value of residence times (τ), the removal of COD with elapsed time (t) first increases and then becomes constant (Fig. 4). Therefore, a fraction of initial COD (COD_0) is present in the wastewater and is not removable at experimental condition. The elapsed time (t) at which the COD removal becomes constant can be called as steady state. Therefore, COD removed at any elapsed time (t) may be termed as COD_{Rt} and at steady state as COD_{Re} . Therefore, in more accurate way the Eq. (18) can be modified to Eq. (19) (Lucas and Peres, 2009):

$$\ln \frac{(COD_{Re} - COD_{Rt})}{COD_{Re}} = -kt \quad (19)$$

Above equation can be written as (Eq. 20):

$$COD_{Rt} = COD_{Re} [1 - \exp(-kt)] \quad (20)$$

Equation 20 was used to fit the experimental data through nonlinear regression technique using Marquardt's percent standard deviation (MPSD) error function (Marquardt, 1963) given by Eq. (19).

$$MPSD = 100 \sqrt{\frac{1}{n_m - n_p} \sum_{i=1}^n \left(\frac{COD_{Rt,i,exp} - COD_{Rt,i,cal}}{COD_{Rt,i,exp}} \right)^2} \quad (21)$$

In this equation, $COD_{Rt,i,exp}$ and $COD_{Rt,i,cal}$ are the experimental and calculated values of COD removed for any value of elapsed time (t), respectively, and n_m is the number of measurements, and n_p is the number of parameters in the model.

The fitting of pseudo-first-order kinetic model with experimental data is shown in Fig. 7, and the calculated kinetic parameters values along with the coefficient of determination (R^2) and MPSD values are given in Table 6. The R^2 and MPSD values shows that the kinetics of continuous EC treatment of dairy wastewater can be satisfactorily represented by the pseudo-first-order kinetic model using non-linear regression fit.

Table 6. Kinetic parameters for the COD removal (Current, $i = 3.7$ A, $pH_i = 4.5$)

τ	$COD_{Re, exp}$ (mg/L)	$COD_{Re, cal}$ (mg/L)	k (min^{-1})	R^2	MPSD
30	1612	1500	0.053	0.956	27.94
60	1750	1701	0.116	0.993	9.25
90	1882	1756	0.146	0.994	8.33
120	1960	1841	0.155	0.989	12.36
150	2056	1990	0.156	0.997	6.62

From Table 6, it can be seen that the rate constant (k) values increases with an increase in τ value, which indicates higher COD removal at higher τ value. It can also be observed that at higher τ value of 120 and 150 min the k values are nearly same indicating no effect of increasing τ value on COD removal. This is due to because of the COD removal from dairy wastewater by continuous EC treatment

method is limited by τ at lower values. At higher τ values maximum removable COD from the dairy wastewater limits the treatment.

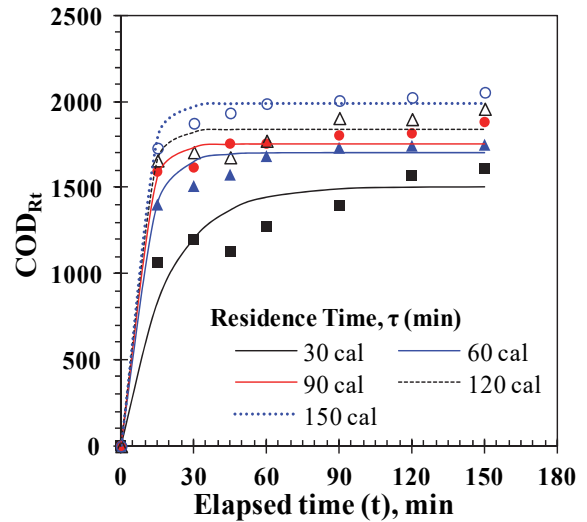


Fig. 7. Kinetics of the COD removal (Current, $i = 3.7$ A, $pH_i = 4.5$). Markers shows experimental data points and the lines calculated by the pseudo-first-order kinetic model (cal in the figure refers calculated values by pseudo-first-order kinetic model)

3.5. Comparison with literature data

Table 7 shows literature available on electrochemical treatment of dairy wastewater. Benazzi et al. (2016) reported 69% COD removal in continuous EC reactor using Al electrode with synthetic dairy wastewater, while in the present study, higher COD removal of 71.21% was achieved at optimum set of process parameters ($pH_i = 4.5$, $\tau = 141$ min; $t = 52$ min) with real dairy wastewater. However, Un et al. (2014) reported 86.4% COD removal in continuous EC reactor, but with iron electrode and cheese whey wastewater (liquid discharged from cheese production). Better performance of continuous EC treatment reported by Un et al. (2014) may be due to the iron electrode and whey wastewater characteristics. Furthermore, important design parameters for the continuous reactors such as steady state time (t_s), mass transfer coefficient (k_m) and kinetic parameters, and an important operating cost parameter, energy consumption, were not reported by Un et al. (2014) and Benazzi et al. (2016).

Table 7. Reported studies of electrochemical treatment of dairy wastewater

S. No.	Wastewater	Reactor	Electrode used	Result	References
1.	Real	Batch	Aluminium	COD removal=87%	Sharma (2014)
2.	Real	Batch	Aluminium and Iron	COD removal=79.2%	Yavuz et. al. (2011)
3.	Cheese whey	Continuous	Iron	COD removal=86.4%	Un et al. (2014)
4.	Synthetic	Continuous	Aluminium	COD removal=69% TOC removal= 65%	Benazzi et. al. (2016)
5.	Real	Continuous	Aluminium	COD removal=71.21% Energy consumed= 4.32 kWh/kg of COD removed	Present study

In the present study, t_s , k_m , k and specific energy consumed at optimum parameters were studied and found to be 50 min, 18.1×10^{-6} m/s, 0.156 min^{-1} and 4.32 kWh/kg of COD removed. In comparison to continuous EC treatment, higher COD removal has been reported in batch EC reactor.

Sharma (2014) and Yavuz et al. (2011) reported 87% and 79.2% of COD removal in batch EC treatment. However, the removed COD in the present study was found to be 1994 mg/L, while it was only 930 mg/L and 1228 mg/L in studies reported by Sharma (2014) and Yavuz et al. (2011), respectively. Furthermore, experiments were also conducted at optimized set of process parameters ($\text{pH}_i = 4.5$, $\tau = 141$ min; $t = 52$ min) to see the treatment performance without adding the NaCl.

The percentage of COD removal (Y_1) and specific energy consumed (Y_2) were observed very poor in comparison to the treatment with NaCl, being 30.2% and 25.13 kWh/kg of COD removed.

4. Conclusions

The following conclusions were drawn from the present study:

- Effect of process parameters; pH_i , residence time (τ) and elapsed time (t) on the %COD removal (Y_1) and specific energy consumed (Y_2) for real dairy wastewater by continuous EC process were studied and optimized successfully.

- At optimum set of process parameters ($\text{pH}_i = 4.5$, $\tau = 141$ min; $t = 52$ min) corresponding responses Y_1 and Y_2 , advocated by RSM and actual experiments conducted, were 67% and 4.62; 71.21% and 4.32 kWh/kg of COD removed, respectively.

- Both the mechanisms, electrocoagulation and electro-oxidation, were involved in removing COD. At highly acidic pH_i values, Al^{3+} and various hydrolyzed species; $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$ etc. removed COD by electrocoagulation method, while, at highly basic pH_i , ClO^- ions, H_2O_2 and $\cdot\text{OH}$ radicals indirectly oxidized the COD.

- Increased residence time (τ) reduced achieved steady state time (t_s), and for all the $\tau > 60$ min, steady state time (t_s) was observed at $t \approx 50$ min.

- From the kinetic study, rate constant (k) was found to increase with increasing τ value. It was also observed that the COD removal is limited by τ at its lower values, while at higher τ values maximum removable COD limits the treatment.

- From the disposal point of view, treated dairy wastewater will require further treatment by other physico-chemical and biological method to remove the remaining COD, BOD, TN and total solids.

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