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Electrochemical treatment of simulated beet sugar factory wastewater

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ABSTRACT

Electrochemical treatment of simulated beet sugar factory wastewater was studied as an alternative treatment method for the first time in literature. Through the preliminary batch runs, appropriate electrode material was determined as iron due to high removal efficiency of chemical oxygen demand, COD, and turbidity. The effect of operational conditions, applied voltage, electrolyte concentration and waste concentration on COD removal percent and initial COD removal rate were investigated through response surface methodology, RSM. In the set of runs, highest COD removal and COD initial removal rate were realized as 86.36% and 43.65 mg/L min, respectively, after 8 h at the applied voltage of 12 V, 100% waste concentration with 50 g/L NaCl. Treatment conditions were optimized by RSM where applied voltage was kept in the range, electrolyte concentration was minimized, waste concentration, COD removal percent and COD initial removal rate were maximized at 25 °C. Optimum conditions at 25 °C were estimated as 12 V applied voltage, 100% waste concentration and 33.05 g/L electrolyte concentration to achieve 79.66% and 33.69 mg/L min for COD removal and COD initial removal rate, respectively. Kinetic investigations denoted that reaction order of electrochemical treatment reaction was 1.2 with the activation energy of 5.17 kJ/mol. These results support the applicability of electrochemical treatment to the beet sugar factory wastewater as an alternative advanced wastewater treatment method with further research.

1. Introduction

The beet sugar factory wastewater with high organic load has a strong potential to create serious environmental pollution problems if discharged before treatment. Typical levels of biochemical oxygen demand, BOD_5, are 4000–7000 mg/L in untreated effluent from beet processing, while wastewater has chemical oxygen demand, COD, of up to 10,000 mg/L. In addition to the sugars and organic materials arriving with the beet, wastewater resulting from the washing of incoming raw materials may also contain crop pests, pesticide residues, and pathogens [1].

Conventional treatment methods of sugar factory wastewater include preliminary filtration of solids, sedimentation for suspended solids reduction, flow and load equalization and advanced biological treatment, which is typically anaerobic followed by aerobic treatment and nutrient removal [1,2]. Utilization of wastewater ponds (lagooning) [3–5] is commonly preferred as an economic process for the sugar factory wastewater, since the discharge of treated water takes place only when the required degree of removal is reached [6]. However, large space requirements [3], risk of unpleasant and annoying odor emissions in the spring and nearly summer [7], contamination risk of ground water in the event of inadequate sealing of the pond's floor [3,8,9] and undesirable massive development of algal production during the vegetative period [3] are main disadvantages of the lagooning. Aerated ponds are also considered for the treatment of sugar factory wastewater requiring less space and residence time than lagooning, but oxygen consumption and hydraulic retention time, HRT, can be high and excess land requirement may still exist [3].

In last two decades, combined anaerobic and aerobic treatments of sugar industry wastewater have been approved as an acceptable process due to high performance of COD removal, relatively small energy requirements, an almost insignificant production of excess sludge, low odor emissions, less land usage, compact system structure and energy recovery [3,10]. However, high rate systems especially upflow anaerobic sludge blanket, UASB, expanded granular sludge blanket, EGSB, and fluidized bed reactor, FBR, systems started to be preferable anaerobic technologies for soluble wastewater because of the increased pollution loading rate and relatively decreased HRT [11–14]. Nevertheless, all conventional biological treatment systems for sugar factory wastewaters may not be appropriate and feasible due to large land space requirement as well as high capital and operational costs [3,10,15].

Conversion of sugar wastewater to produce energy in fuel cells currently represents an alternative way for wastewater treatment. However, existing transition metal-catalyzed fuel cells

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cannot be used to generate electrical power from carbohydrates [16]. Microbiological fuel cells, MFC, with a life time of more than 5 years [17] can use carbohydrates, but limited electrochemical COD removal efficiency around 20%, low current (<0.1 A) and voltage output (0.5–0.7 V) and low power density (40 W/m^3) are the current disadvantages of MFCs implying that MFC technology needs to be improved for industrial applications [18,19].

Electrochemical treatment may be considered as an economical alternative process under the conditions when conventional treatment methods fail to reduce pollution [20]. The electrochemical treatment is considered as one of the advanced oxidation processes, potentially a powerful method of pollution control, offering high removal efficiencies in compact reactors with simple equipments for control and operation of the process. Electrochemical processes generally have lower temperature requirement than those of other equivalent non-electrochemical treatments and adding electrolyte solutes to increase the conductivity of wastewater is usually preferred. The treatment process would be relatively non-specific, that is, applicable to a variety of contaminants but capable of preventing the production of unwanted side-products [21]. In recent years there has been a growing interest in the treatment of industrial effluents by electrochemical methods as an alternative to traditional biological treatments [22]. Many researchers had investigated the electrochemical oxidation of various types of wastewater containing phenol [23–25], cyanides [26], nuclear wastes [27], human wastes [28], cigarette industry wastewater [29], textile wastewater [30] and tannery wastewater [31]. Nevertheless, there are few studies dealing with electrochemical treatment of food-processing industrial wastewaters such as deproteinated whey wastewater [32], coke-plant wastewater [33], coffee curing wastewater [34], olive oil wastewater [35], olive mill wastewater [36–42], green table olive processing wastewater [43], starchy wastewater [44], distillery industry wastewater [45–47], beer brewery wastewater [48] and vinasse wastewater from beet molasses [49].

In recent years, studies have been carried out to determine the feasibility and to optimize the electrochemical treatment technologies with response surface methodology, RSM. The RSM is an important branch of experimental design and a critical technology in developing new processes, optimizing their performance, and improving design and formulation of new products. The most popular class of RSM is second order central composite design, CCD. The CCD is an effective design that is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points [50–52]. In the optimization process, the responses can be simply related to chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is given as

$$\eta = \beta_0 + \sum_{j=1}^{k}\beta_j x_j + \sum_{j=1}^{k}\beta_{jj} x_j^2 + \sum_{i}\sum_{<j=2}^{k}\beta_{ij} x_i x_j + e_i \tag{1}$$

where η is the response, x_i and x_j are variables ($i = 1$ to k), β_0 is the constant coefficient, β_j, β_{jj} and β_{ij} (i and $j = 1$ to k) are interaction coefficients of linear, quadratic and the second-order terms, respectively, k is the number of independent parameters (=3 in this study) and e_i is the error. RSM has already been used to optimize the electrochemical treatment of deproteinated whey wastewater [32], industrial paint wastewater [53], textile dye wastewater [54,55], electrochemical removal of mercury ions from wastewater [56], sodium from fermented food composts [57], chromium from industrial wastewater [58] and chromium-contaminated waters [59]. Kaminari et al. [60] have also used RSM to study the effects of operational parameters involved in designing fluidized-bed electrochemical reactors for the electrochemical removal of lead from industrial wastewater [60].

Generally, two mechanisms are considered to be responsible for electrochemical degradation of organic matter, *R* [35]:

(a) Direct anodic oxidation where the pollutants are adsorbed on the anode surface, *S*, and destroyed by the anodic electron transfer reactions.

(b) Indirect oxidation in the liquid bulk mediated by the oxidants that are formed electrochemically; such as chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide. Anodic water discharge results in the formation of hydroxyl radicals which are adsorbed on the anode surface and can then oxidize the organic matter [35]:

$$\mathrm{H_2O + S \rightarrow S[OH^\bullet] + H^+ + e^-} \tag{2}$$

$$\mathrm{R + S[OH^\bullet] \rightarrow S + RO + H^+ + e^-} \tag{3}$$

In the presence of NaCl, chlorohydroxyl radicals are also formed on the anode surface and then oxidize the organic matter:

$$\mathrm{H_2O + S + Cl^- \rightarrow S[ClOH^\bullet] + H^+ + 2e^-} \tag{4}$$

$$\mathrm{R + S[ClOH^\bullet] \rightarrow S + RO + H^+ + Cl^-} \tag{5}$$

Reactions between water and radicals near the anode can yield molecular oxygen, free chlorine and hydrogen peroxide [35]:

$$\mathrm{H_2O + S[OH^\bullet] \rightarrow S + O_2 + 3H^+ + 3e^-} \tag{6}$$

$$\mathrm{H_2O + S[ClOH^\bullet] + Cl^- \rightarrow S + O_2 + Cl_2 + 3H^+ + 4e^-} \tag{7}$$

$$\mathrm{H_2O + S[OH^\bullet] \rightarrow S + H_2O_2 + H^+ + e^-} \tag{8}$$

Furthermore, hypochloric acid can be formed during electrochemical reaction by

$$\mathrm{H_2O + Cl^- \rightarrow HClO + H^+ + 2e^-} \tag{9}$$

Therefore, direct anodic oxidation of organics through reactions (3)–(5) results in reduced COD as well as the formation of primary oxidants such as oxygen, chlorine, hypochloric acid and hydrogen peroxide [35].

In neutral to moderate pH solutions, a cycle of chloride–chlorine–hypochlorite–chloride occurs, causing the initial concentration of chlorides to remain stable. In strong alkaline solutions, the cycle of chloride–chlorine–chloride is blocked due to the production of stable $\mathrm{ClO_3{}^-}$. At low pH, chlorides are reduced with the production of free chlorine; while at high pH, the chlorides are oxidized and chlorates are produced [49,61].

Tasaka and Tojo [62] have suggested that in alkaline solution the anodic oxidation of $\mathrm{ClO^-}$ proceeds under the consecutive first order reactions:

$$\mathrm{ClO^- + 2OH^- \rightarrow ClO_2{}^- + H_2O + 2e^-} \tag{10}$$

$$\mathrm{ClO_2{}^- + 2OH^- \rightarrow ClO_3{}^- + H_2O + 2e^-} \tag{11}$$

where the rate constant of Eq. (10) is much less than the one of Eq. (11). The electrochemical oxidation of hypochlorous acid is difficult to investigate due to its high oxidation potential and the conversion of HClO into $\mathrm{Cl_2}$ [63]. The electrochemical oxidation reaction of HClO and $\mathrm{HClO_2}$ are

$$\mathrm{HClO + H_2O \rightarrow HClO_2 + 2H^+ + 2e^-} \tag{12}$$

$$\mathrm{HClO_2 + H_2O \rightarrow ClO_3{}^- + 3H^+ + 2e^-} \tag{13}$$

A related oxidation reaction, the electrochemical oxidation of $\mathrm{ClO_3{}^-}$ has been studied extensively [64]:

$$\mathrm{ClO_3{}^- + H_2O \rightarrow ClO_4{}^- + 2H^+ + 2e^-} \tag{14}$$

Table 1
Characteristics of beet sugar factory wastewater.

Characteristics	Mean value of real wastewater
COD (mg/L)	6300
Total nitrogen (mg/L)	53.23
Total phosphorus (mg/L)	4.77
Calcium (mg/L)	906

Analogous to chlorate formation in alkaline solution, it is likely that a bimolecular reaction of HClO is responsible for chlorate formation in acidic solution. The proposed reactions are [63]:

$$\text{a slow reaction}: \quad 2\text{HClO} \rightarrow \text{ClO}_2{}^- + 2\text{H}^+ + \text{Cl}^- \tag{15}$$

and

$$\text{a fast one}: \quad \text{HClO} + \text{ClO}_2{}^- \rightarrow \text{ClO}_3{}^- + \text{H}^+ + \text{Cl}^- \tag{16}$$

Free chlorine and oxygen can further react on the anode yielding secondary oxidants such as chlorine dioxide and ozone, respectively:

$$\text{H}_2\text{O} + \text{S}[\text{ClOH}^\bullet] + \text{Cl}_2 \rightarrow \text{S} + \text{ClO}_2 + 3\text{H}^+ + 2\text{Cl}^- + \text{e}^- \tag{17}$$

$$\text{O}_2 + \text{S}[\text{OH}^\bullet] \rightarrow \text{S} + \text{O}_3 + \text{H}^+ + \text{e}^- \tag{18}$$

Primary and secondary oxidants are quite stable and migrate in the solution bulk where they indirectly oxidize the pollutants [35]. On the other hand, the main cathodic reaction is the evolution of hydrogen but as a side reaction, there is a possibility of the cathodic reductions of hypochlorite and chlorate to form chloride radical [65].

In this study, an attempt was made to achieve electrochemical treatment of simulated beet sugar factory wastewater in the presence of supporting electrolyte with adequate electrode material, being first in literature. The operational conditions were then optimized using RSM by Design-Expert® 6 (trial version). The batch runs were designed in accordance with the CCD and sugar factory wastewater was simulated for the standardization of the wastewater throughout the study. Three factors; waste concentration, applied voltage and electrolyte concentration were selected as the primary independent variables, while COD removal percent and COD initial removal rate were the responses (dependent variables) in the design and optimization of the treatment process. Reaction kinetics of the treatment have also been studied at different waste concentrations and temperatures so as to fine-tune the process.

2. Materials and methods

2.1. Chemicals and materials

In order to standardize the beet sugar factory wastewater in the runs, the beet sugar factory wastewater was synthetically prepared based on the real process information from the Turkish Sugar Factories Corp., Ereğli Sugar Factories Campaign Report of years 2000/2002 [66]. Average parameter values of the generated wastewater for the period of two campaign years are presented in Table 1, which are also similar to those of 1995/1996 campaign [2]. As given in Table 1; COD (sugar), nitrogen, phosphorus and calcium are the main contaminants of the real wastewater. 6000 mg saccharose (99.9% purity, Ankara Sugar Factory, Turkish Sugar Factories Corporation, Turkey) as a readily soluble COD source, 310.4 mg ammonium carbonate (NH_4HCO_3, Merck) as the nitrogen source, 22 mg potassium dihydrogen phosphate (KH_2PO_4, Merck) as the phosphorus source and 1674 mg calcium hydroxide ($Ca(OH)_2$, Merck) as the calcium source of wastewater are dissolved in 1 L distilled water to simulate the generated wastewater of the sugar processing. Original composition is regarded as 100% waste concentration.

Different waste concentrations were prepared from standard wastewater (100% waste concentration) by dilution with distilled water. For the investigation of order of reaction kinetics at 25 °C, waste concentration was changed in the range of 10–100% of the standard. NaCl (Merck) in high purity was used as supporting electrolyte. Carbon electrodes were obtained from Meteor, Germany. Iron and stainless steel (SS304) electrodes were manufactured in Ankara Mechanical Factory, Turkish Sugar Factories Corporation (Turkey). All electrodes were of cylindrical shape with OD = 13 mm and 6 cm immersed length.

2.2. Experimental set up

The electrochemical reactor designed in our laboratory [67] was used batch-wise in all experiments. The reactor was made of glass having a net working volume of 2 L immersed in a temperature controlled water bath. The electrodes (in three pairs) were used as anode and cathode and placed tightly 8 cm apart on a Plexiglas® reactor cover. A glass stirrer with a single 4.5 cm paddle was used for homogenization with a Heidolph-RZR1 (Germany) model mixer at constant 360 rpm, which provided adequate mixing. Temperature of the water bath was controlled with a temperature-controlled heating-cooling unit (Selecta P Digiterm 100, Spain) to maintain a constant reaction temperature of 25 °C. For the investigation of activation energy and Arrhenius constant, electrochemical treatment runs were carried out at different temperatures in the range 25–45 °C in a constant temperature water bath. The reaction temperature was monitored with a glass thermometer immersed. The current was applied by a constant voltage/current controlled DC power source; NETES NPS-1810 D (China). Experimental set-up is shown in Fig. 1.

2.3. Analysis

The pH was measured with a WTW 320 model pH meter (Germany) and a Hach 2100AN IS turbidimeter (USA) was used to determine turbidity. COD of the wastewater was determined by the oxidation with chromosulfuric acid method, analog to

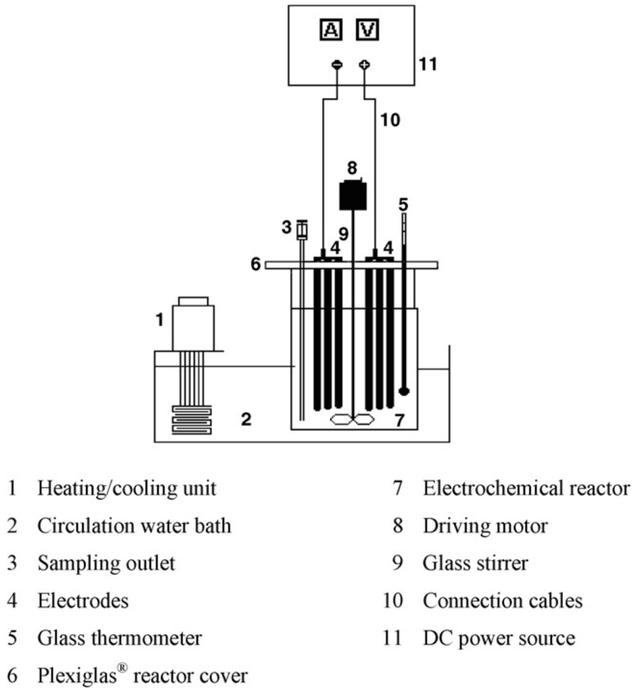

Fig. 1. Schematic diagram of the experimental set up.

DIN 38409 H41, ISO 6060-1989. Dr. Lange (Germany) COD kits (LCK 014, 1000–10,000 mg/L; LCK 114, 150–1000 mg/L; LCK 314, 15–150 mg/L; LCK 614, 50–300 mg/L), a MDA spectrophotometer (ISIS 9000) and a thermostat (LT 100) were used for COD measurements. Simulated beet sugar factory wastewater was loaded into the reactor and the reaction under predetermined conditions started with the application of specified voltage and continuous agitation. At appropriate time intervals, samples of 10 mL were taken from the reactor and analyzed to determine the COD, turbidity and pH.

2.4. Experimental design and optimization

The CCD was employed in the experimental design. The CCD with three factors at three levels was applied using Design-Expert 6.0 (trial version) with the limits of the independent variables. Each independent variable was coded at three levels between −1 and +1 in the ranges determined by the preliminary experiments, whereas waste concentration, 20–100%; applied voltage, 2–12 V and electrolyte concentration, 0–50 g/L.

The total number of experiments was 20 (=2^k+2k+6), where k is the number of factors (=3). 14 experiments were augmented with six replications at the design center to evaluate the pure error and were carried out in randomized order. Experimental conditions of CCD runs and corresponding results (responses) are presented in Table 2. First four columns of Table 2 show run number and experimental conditions of the runs. Performance of the process was evaluated by analyzing the responses; COD removal percent and COD initial removal rate.

The dependent variables, COD removal and COD initial removal rate were processed for Eq. (1) with Design-Expert 6.0 program including ANOVA to obtain the interaction between the process variables and the response. The fitting quality of polynomial models was expressed in terms of R^2 and R^2_{adj}, and statistical significance was checked by the F-test in the program. A module in Design-Expert® software searched and optimized the factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. The desired goals were selected as maximum COD removal percent and COD initial removal rate whereas applied voltage was set within the range, pollution load was kept maximum and electrolyte concentration was set to minimum. In the program, for all of the dependent and independent variables corresponding importances of goals were selected the highest. These individual goals were combined into an overall desirability function by Design-Expert® to find the best local maximum [68].

3. Results and discussion

3.1. Selection of electrode material

The efficiency and end products of electrochemical waste treatment are profoundly dependent on the nature of anodic material [29,69,70]. In the study, iron, carbon and stainless steel SS304 were tried for electrode material due to their low cost and commercialized features.

The COD and turbidity percent, and pH time profiles of batch experiments were presented in Fig. 2(a), (b) and (c), for carbon, stainless steel and iron electrodes, respectively, at 25 °C, 8 V applied voltage, 100% waste concentration with 50 g/L NaCl. After 8 h of reaction time, overall values of COD removal for iron, stainless steel and carbon electrodes were achieved as 59.42%, 42.86% and 15.15%, respectively. Turbidity removals for iron and stainless steel electrodes were realized as 30.64% and 0.96%, respectively, after 8 h while an increase in turbidity was experienced for the carbon electrode most likely due to the slow erosion of the electrode material during the reaction.

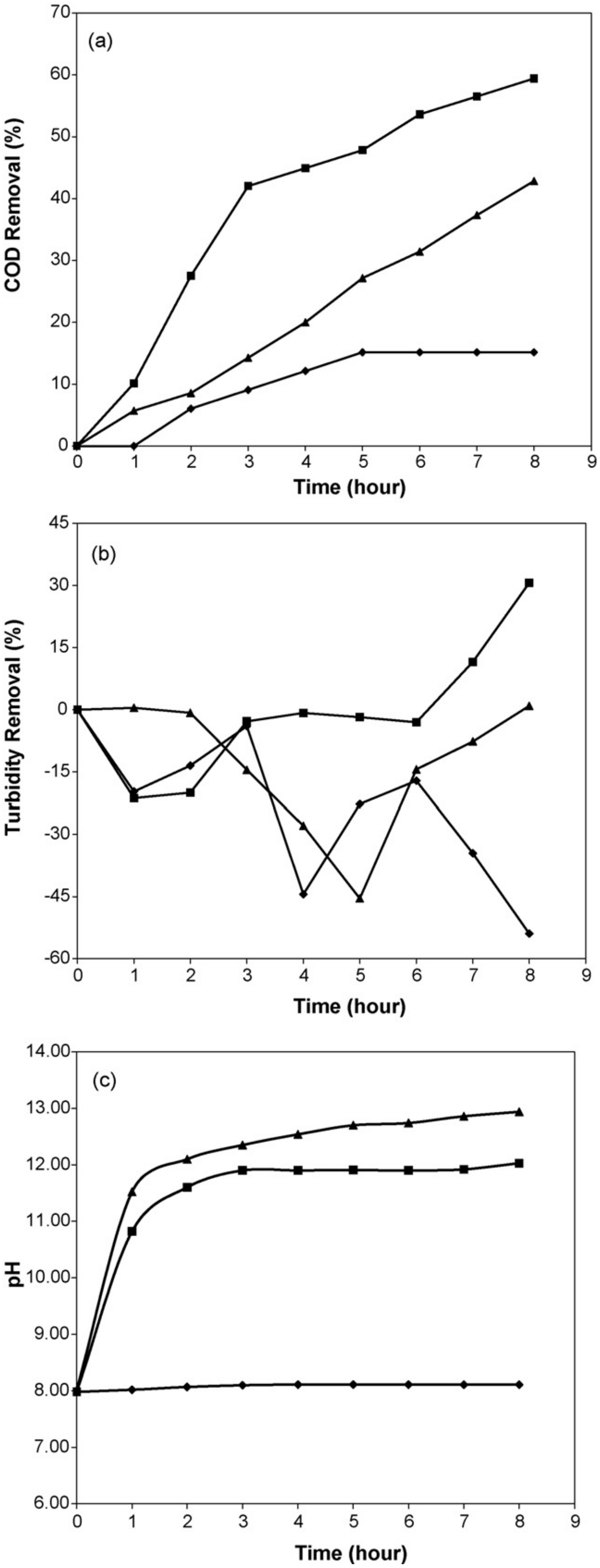

Fig. 2. (a) COD removal percentage–time profile during batch experiments for carbon, stainless steel and iron electrodes at 25 °C, 50 g/L electrolyte and 100% waste concentration, and 8 V applied voltage ((♦) carbon; (■) iron; (▲) stainless steel). (b) Turbidity removal percentage–time profile during batch experiments for carbon, stainless steel and iron electrodes at 25 °C, 50 g/L electrolyte and 100% waste concentration, and 8 V applied voltage ((♦) carbon; (■) iron; (▲) stainless steel). (c) pH–time profile during batch experiments for carbon, stainless steel and iron electrodes at 25 °C, 50 g/L electrolyte and 100% waste concentration, and 8 V applied voltage ((♦) carbon; (■) iron; (▲) stainless steel).

Table 2
Experimental conditions of CCD runs of Design Expert® and the corresponding results (responses).

Runs	Waste concentration (%)	Applied voltage (V)	Electrolyte concentration (g/L)	COD removal (%)	COD initial removal rate (mg/L min)
1	20	12	0	8.10	0.38
2	60	7	25	62.50	13.17
3	60	12	25	75.61	25.83
4	100	2	50	23.53	2.74
5	60	7	25	68.18	15.68
6	20	2	50	33.33	2.15
7	60	7	25	62.79	11.32
8	60	2	25	9.09	3.23
9	20	12	50	78.57	9.08
10	60	7	25	64.29	14.17
11	100	12	0	8.57	3.33
12	20	7	25	66.67	4.95
13	60	7	0	6.98	0.65
14	60	7	25	60.47	9.54
15	100	7	25	65.71	23.43
16	60	7	50	78.57	24.50
17	100	12	50	86.36	43.65
18	60	7	25	61.90	10.83
19	20	2	0	7.14	0.82
20	100	2	0	7.51	4.85

The indirect oxidation efficiency depends on the diffusion rate of oxidants into the solution, pH and temperature of the reaction medium [35]. The medium pH was stabilized at 8.11 for carbon electrode, while pH gradually increased and remained constant at 12.03 and 12.94 for iron and steel electrodes, respectively. The pH rise was likely due to Fenton reaction where hydroxyl ion is produced in the presence of Fe^{2+} and hydrogen peroxide available in the reaction medium [71]. Moreover, under alkaline conditions hydroxyl ions are produced at the cathode and reactions involving hypochlorite, chloride ions, oxygen, hydrogen peroxide and hydroxyl radicals are dominating [35].

Due to slow but net oxidation of iron anode, the formation of some $Fe(OH)_3$ is inevitable in the solution as experienced in the form of small precipitate at the end of the reaction. The adsorption of COD bearing chemicals onto $Fe(OH)_3$ is quite possible up to some extent which of course would cause a drop in COD content of the reaction medium as soon as the $Fe(OH)_3$ is formed. Carbon electrode is rather inert and does not produce metal ions while stainless steel does not produce that much of Fe^{3+} ions.

Due to high removal of turbidity and COD, iron was chosen as the appropriate electrode material for the electrochemical treatment reactions of simulated beet sugar factory wastewater and utilized throughout the runs.

3.2. Experimental results

Twenty batch runs were carried out to determine the effects of independent factors on responses and the results were presented with corresponding experimental conditions in Table 2. More than 60% COD removal was realized in twelve runs of the table. As a general trend, increasing electrolyte concentration and applied voltage resulted in enhanced COD removal and COD initial removal rate in every run. In each run at the end of 8 h, a low volume precipitate was formed (4–6%, v/v, after 15 min centrifuge at 4500 rpm). For several experiments, after 8 h the precipitate was washed with pure sulphuric acid successively twice and collected extracts were analyzed. The COD values of the extracts were found to be 3–6% more than those of the supernatants proving insignificant contribution of adsorption onto the precipitate.

In Table 2, run 17 gave the highest COD removal percent and COD initial removal rate as 86.36% and 43.65 mg/L min, respectively, after 8 h at 12 V with 50 g/L electrolyte concentration. Fig. 3 depicts COD removal percent and pH time profiles in this run. In Fig. 3, 69.70% of COD removal was achieved in the first hour of reaction time indicating a relatively high COD initial removal rate and efficient overall removal of COD. In Fig. 3, pH increased from 8.03 to 12.50 within the 3 h of reaction due to production of hydroxyl ions [35].

3.3. Evaluation of results with Design-Expert®

Experimental results were evaluated with Design-Expert 6.0 to yield approximating functions for dependent variables; COD removal percent, y_1, and COD initial removal rate, y_2. These approximating functions are presented in Eqs. (19) and (20):

$$\begin{aligned} y_1 = & -7.65728 - 0.47824x_1 + 10.54805x_2 + 1.76905x_3 \\ & + 3.37045E-003x_1^2 - 0.73789x_2^2 - 0.028836x_3^2 \\ & + 0.011056x_1x_2 - 3.56250E-004x_1x_3 + 0.10605x_2x_3 \end{aligned} \quad (19)$$

$$\begin{aligned} y_2 = & +7.96080 - 0.080450x_1 - 1.10915x_2 - 0.27159x_3 \\ & + 0.020563x_1x_2 + 3.52250E-003x_1x_3 + 0.049800x_2x_3 \end{aligned} \quad (20)$$

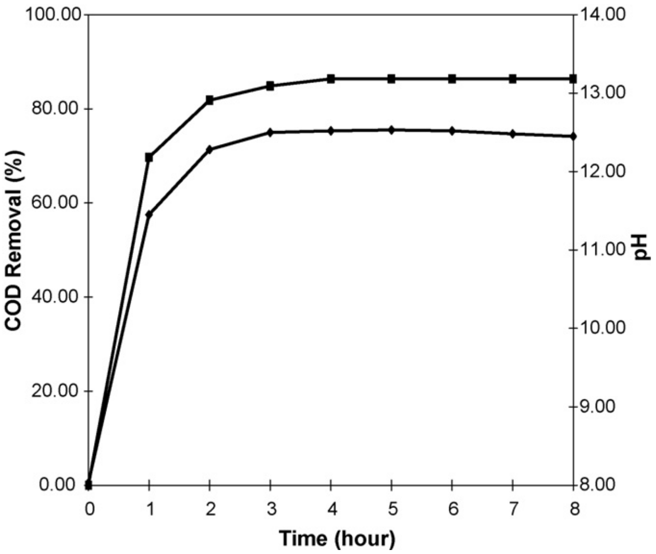

Fig. 3. COD removal percent and pH profiles with the reaction time for run 17 at 25 °C, 50 g/L electrolyte and 100% waste concentration, and 12 V of applied voltage ((■) COD removal; (♦) pH).

Table 3
Regression analysis and response surface fitting (ANOVA) for COD removal percentage and COD initial removal rate.

Source	Sum of squares	Degrees of freedom	Mean square	*F* value	Prob > *F*
COD removal percentage					
Model	15718.74	9	1746.53	18.70	<0.0001
Residual	933.84	10	93.38		
Lack of fit	898.20	5	179.64	25.20	0.0015
Pure error	35.65	5	7.13		
$R^2 = 0.9439$, $R^2_{\mathrm{adj}} = 0.8935$, Adeq Precision = 13.382					
COD initial removal rate					
Model	1900.70	6	316.78	9.64	0.0004
Residual	427.41	13	32.88		
Lack of fit	401.13	8	50.14	9.54	0.0118
Pure error	26.28	5	5.26		
$R^2 = 0.8164$, $R^2_{\mathrm{adj}} = 0.7317$, Adeq Precision = 13.919					

In Eqs. (19) and (20); x_1, x_2 and x_3 correspond to independent variables of waste concentration, applied voltage and electrolyte concentration, respectively. The CCD of Design-Expert® produced quadratic and two factor interaction, 2FI, equations for COD removal and COD initial removal rate, respectively. Quadratic model has the significance of adding squared terms to the mean, block, linear and 2FI terms already in the model. Consequently, the quadratic model comes out best as it exhibits low standard deviation and high R^2 values [72]. ANOVA results for COD removal percent and COD initial removal rate are presented in Table 3. In the table, model *F*-value of 18.70 and 9.64 imply that the models are significant for COD removal percent and COD initial removal rate, respectively. “Adeq Precision” measures the signal to noise ratio and a ratio greater than 4 is desirable [68,73]. Therefore, the ratios of 13.382 and 13.919 for the models of COD removal percent and COD initial removal rate, respectively, indicate that adequate signals for the models can be used to navigate the design space. The values of Prob > *F* less than 0.0500 indicated that model terms are significant. Prob > *F* values are less than 0.0001 for COD removal percent and 0.0004 for COD initial removal rate which indicate that terms are significant in the model. The “Lack of Fit” *F* values of 25.20 and 9.54 imply the lack of fit values are also significant for the models of COD removal percent and COD initial removal rate, respectively. Coefficients of determination, R^2, were found as 0.9439 and 0.8164 whereas adjusted R^2, R^2_{adj}, were determined as 0.8935 and 0.7317 for COD removal percent and COD initial removal rate, respectively, indicating a good fit for both dependent variables. The model of COD initial removal rate has a relatively lower coefficient value than that of COD removal percent due to the non-linear influences between 2FI and quadratic models.

3.4. Optimization of treatment conditions

The experimental outcomes were optimized by Design-Expert® software using the approximating functions of COD removal percent and COD initial removal rate in Eqs. (19) and (20), respectively. A cost driven approach was used for optimization in 2–12 V applied voltage range; electrolyte concentration was minimized to save electrolyte, whereas waste concentration, COD removal percent and COD initial removal rate were maximized. The results of optimization are shown in Table 4 in descending desirability.

Optimum conditions bound with specified constraints were obtained for highest desirability of 0.732 at 100% waste concentration, 33.05 g/L electrolyte concentration and 12 V applied voltage. Under these conditions, 79.66% COD removal and 33.69 mg/L min COD initial removal rate were predicted after 8 h of reaction time. In order to validate the optimization, a specific batch run was performed under these optimum conditions. In this run, COD removal was realized as 85.29% whereas COD initial removal rate was 20.83 mg/L min, proving fair predictive power of the model.

3.5. Reaction kinetics

Reaction kinetics of electrochemical oxidation of simulated beet sugar factory wastewater with iron electrodes have been investigated under optimum conditions determined before. In a batch reaction, rate term is usually expressed with respect to initial COD removal rate if the reaction medium is of complex structure. The oxidation of wastewater can then be described in terms of COD concentration:

$$-\frac{d[\mathrm{COD}]}{\mathrm{d}t}\bigg|_{t=0} = k[\mathrm{COD}]^n \tag{21}$$

which can be linearized in the form:

$$\ln\left(-\frac{d\,[\mathrm{COD}]}{\mathrm{d}t}\right) = \ln(k) + n\ln([\mathrm{COD}]) \tag{22}$$

From the slope of the plot in Fig. 4(a), showing ln([COD]) versus ln(−d[COD]/d*t*), reaction order was calculated as 1.2 and from the intersection point, the specific reaction rate constant at 25 °C was calculated as $0.057\,\mathrm{L}^{0.2}/(\mathrm{g}^{0.2}\,\mathrm{h})$ with a reasonably good fit ($R^2 = 0.9947$).

When overall reaction rate is expressed with Eq. (21), then the specific reaction rate constant, *k*, can be expressed by the Arrhenius equation:

$$k = A\ \exp\left(-\frac{E_a}{RT}\right) \tag{23}$$

which can be linearized in the form:

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \tag{24}$$

The activation energy value, E_a, was calculated 5.17 kJ/mol whereas Arrhenius constant was found $0.36\,\mathrm{L}^{0.2}/(\mathrm{g}^{0.2}\,\mathrm{h})$ in Fig. 4(b) from the slope and intersection points of the graph, respectively. Since E_a for a diffusion-controlled homogeneous reaction is typically less than 40 kJ/mol, the limiting step of electrochemical treatment of simulated beet sugar factory wastewater is probably of a diffusional nature [74–76].

Although there is no study to date that compares the reaction rate and activation energy of electrochemical treatment for sugar factory wastewaters, there are some electrooxidation studies including reaction kinetics. Samet et al. studied the electrochemical oxidation of 4-chloroguaiacol (4-CG) at Nb/PbO_2 anodes under different experimental conditions and activation energy of the reaction was found as 15 kJ/mol [75]. In another study for the electrochemical oxidation of phenol on Pt electrode in 1 M NaOH and 0.5 M H_2SO_4 solutions, activation energy has been calculated

Table 4
Optimization results.

Solution no.	Waste concentration (%)	Applied voltage (V)	Electrolyte concentration (g/L)	COD removal (%)	COD initial removal rate (mg/L min)	Desirability
1	100.00	12.00	33.05	79.66	33.69	0.732
2	100.00	12.00	29.61	75.48	31.36	0.719

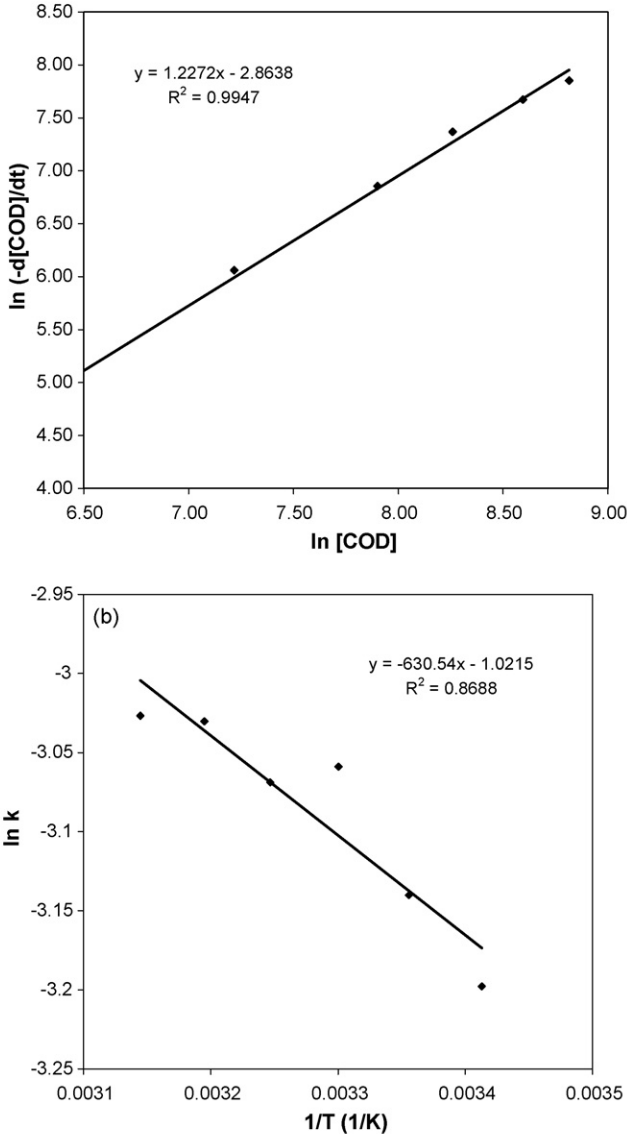

Fig. 4. (a) ln([COD]) versus ln(−d[COD]/d*t*) graph at 25 °C, 12 V of applied potential and 33.05 g/L electrolyte concentration. (b) 1/*T* versus ln(*k*) at 100% waste concentration, 12 V of applied potential and 33.05 g/L electrolyte concentration.

as 14.6 and 15.2 kJ/mol, respectively [77]. In some other studies for the electrocatalytic degradation of phenol, the activation energies were calculated as 23.8 kJ/mol and 10.9 kJ/mol when β-PbO_2 [76] and carbon [24] electrodes were used, respectively. Szpyrkowicz et al. studied the treatment of a wastewater containing dilute copper(I) cyanide using stainless steel electrodes and an activation energy value of 15 kJ/mol was found for cyanide depletion reaction under mass transfer controlled conditions [78]. In our work, the activation energy value is smaller than values published in the literature [24,75–78], which implies that the electrochemical destruction of beet sugar factory wastewater is catalyzed more easily and less sensitive to temperature changes.

Textile wastewater was also tried for electrochemical treatment in a single-cell reactor under different operating conditions and the kinetics of decolourisation were found of second order, with the highest apparent rate constant (k = 0.523 L/(mol s)) achieved at 40 °C [79]. The high value of the activation energy, 24.13 kJ/mol, found in this study indicated that decolourisation is highly temperature sensitive and experimental results proved that the decrease in solubility of Cl_2 at elevated reaction temperatures influenced the reaction rate to a minor degree [79].

3.6. *Effects of operational parameters under optimum conditions*

Eqs. (19) and (20) have been used to visualize the effects of independent variables on responses under optimized conditions in 3D graphs of Figs. 5–7. The effects of waste and electrolyte concentration on COD removal percent and COD initial removal rate at 25 °C reaction temperature and 12 V applied voltage after 8 h of reaction time are shown in Fig. 5(a) and (b), respectively. In Fig. 5(a) the COD removal percent increased by increasing electrolyte concentration and was not significantly affected by waste concentration. Elevated electrolyte concentration resulted in enhanced conductivity and in return increased the electrochemical reaction rate. Moreover, excess electrolyte in reaction medium increased the secondary oxidants such as hypochlorite, oxygen and hydrogen peroxide under

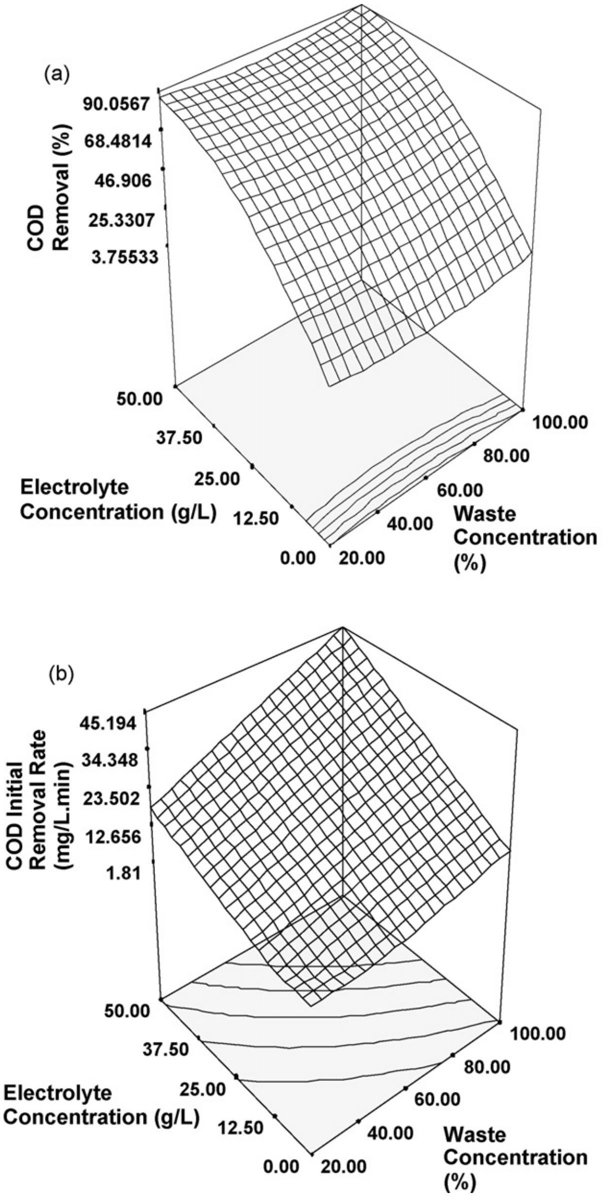

Fig. 5. (a) The effects of waste and electrolyte concentrations on COD removal percent at 25 °C of reaction temperature and 12 V of applied voltage. (b) The effects of waste and electrolyte concentrations on COD initial removal rate at 25 °C and 12 V of applied voltage.

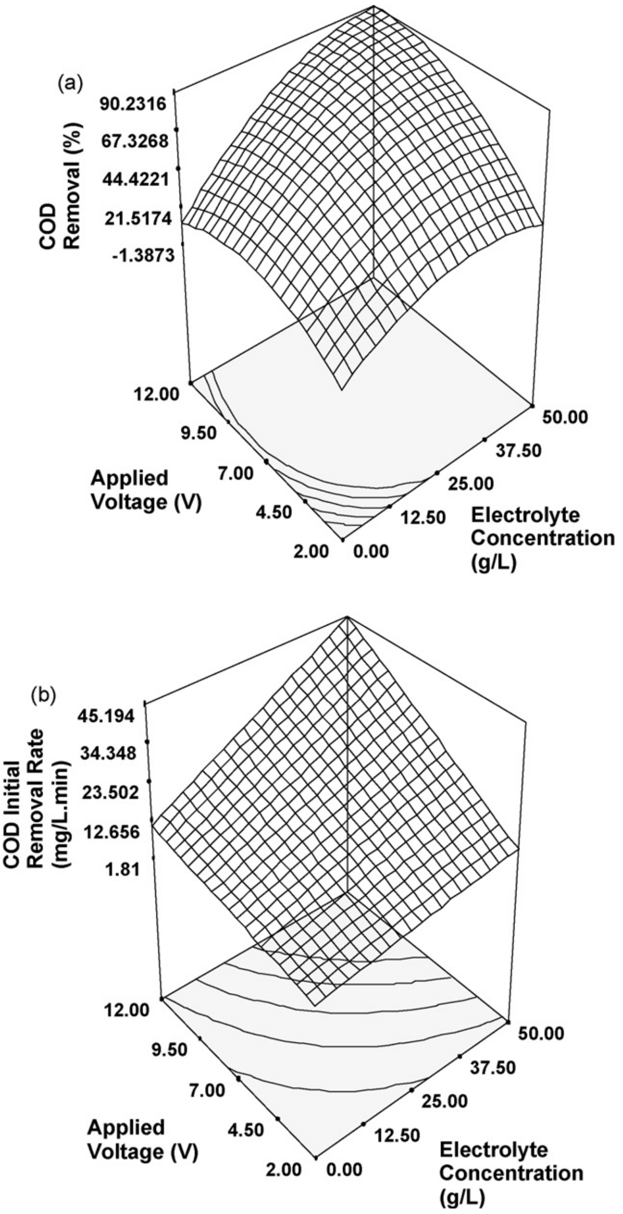

Fig. 6. (a) The effects of applied voltage and electrolyte concentration on COD removal percent at 25 °C and 100% waste concentration. (b) The effects of applied voltage and electrolyte concentration on COD initial removal rate at 25 °C and 100% waste concentration.

alkaline conditions to oxidize the wastewater indirectly [35,80]. In Fig. 5(b), COD initial removal rate increased linearly both with high concentrations of electrolyte and waste. From Fig. 5(a) and (b), it is clear that increasing waste concentration increases the COD initial removal rate but does not affect the overall COD removal percent implying almost first order destruction kinetics.

The effects of applied voltage and electrolyte concentration on COD removal percent and COD initial removal rate at 25 °C reaction temperature and 100% waste concentration are shown in Fig. 6(a) and (b), respectively. In Fig. 6 (a), below 10 V applied voltage, it is evident that COD removal percent increases with the increase in applied voltage, but above this value applied voltage does not affect COD removal efficacy. Applied potential is the major driving force in electrochemical reactors, because increased voltage promotes the availability of new reactions by enabling higher half cell voltage and current density increase for oxidation reactions [81]. Moreover, enhanced voltage increases the current simultaneously, which directly amplifies the rate of the electrochemical reactions. Electrolyte concentration is also effective on COD removal percent, decrease in electrolyte levels results in ineffective treatment. In Fig. 6 (b), it is clear that COD initial removal rate increased with increasing applied voltage and electrolyte concentration, proving that faster electrochemical reactions are enabled both with increased conductivity and potential.

The effects of waste concentration and applied voltage on COD removal and COD initial removal rate at 25 °C reaction temperature and 33.05 g/L electrolyte concentration are presented in Fig. 7(a) and (b), respectively. In Fig. 7(a), COD removal increased with increasing applied voltage as observed in previous graphs. The mechanism of COD destruction of wastewaters of complex structure in saline medium is still an unresolved issue. Nevertheless, the mechanisms thought to be responsible for organic matter degradation can be stated not only accomplished by the oxidants that are formed electrochemically but also by direct anodic oxidation where the pollutants are adsorbed on the anode surface and destroyed by the anodic electron transfer reaction. Waste concentration did not

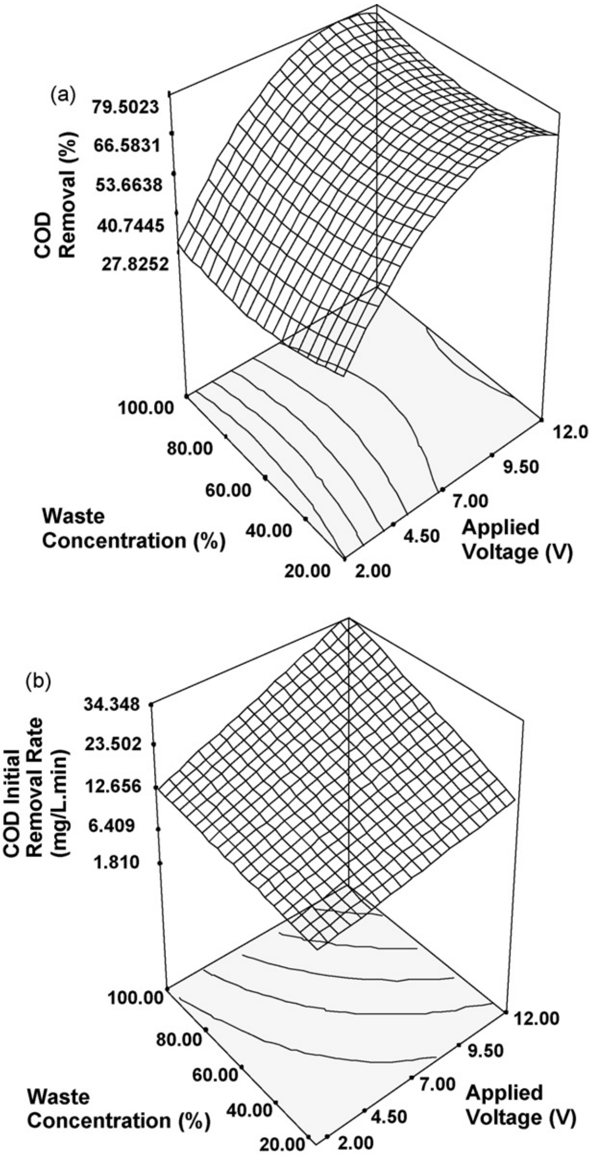

Fig. 7. (a) The effects of applied voltage and waste concentration on COD removal percent at 25 °C and 33.05 g/L electrolyte concentration. (b) The effects of applied voltage and waste concentration on COD initial removal rate at 25 °C and 33.05 g/L electrolyte concentration.

have an influence on COD removal percent due to first order reaction kinetics as observed in Fig. 7(b). Apparently, for higher COD removal rates and overall conversion it is better to start with highly concentrated wastewater.

Although there has not been any literature work done yet to compare the results of this study, there are other studies of conventional treatment methods for sugar factory wastewater. The conventional method of sugar factory wastewater treatment is based on biological methods; the commercial application comprises anaerobic treatment followed by activated sludge process. Of anaerobic treatments, contact process, UASB, anaerobic fixed bed, ANFB, and fluidized bed have been applied for treating beet sugar factory wastewater. Huss and Pascual [82] reported 99% COD removal for 27,000 kg/day total COD loading with the anaerobic methane production plant, ANAMET, with a HRT value of 2.43 days [82]. Yang et al. [83] quoted that 10.2 L UASB reactor fed with sugar mill wastewater demonstrated a COD removal of 85% at 6.7 kg COD/m^3 day OLR with 4.3 h HRT [83]. Ramjeawon [84] achieved 91% COD removal with a HRT of 6 h at 12.5 kgCOD/m^3 day OLR stating the feasibility of an 1 m^3 UASB reactor for treating sugar factory wastewater under industrial conditions [84]. A 500 m^3 fluidized bed reactor was tested at several sugar factories in Germany and Italy and approximately 95% COD removal was realized [14,85]. In the investigation of the treatment of molasses-based synthetic sugar factory wastewater using 10 L UASB process, COD removal was 78% at an OLR of 4.2 kg COD/m^3 day with HRT of 6 h with initial COD of 1000 mg/L [15]. Farhadian et al. [86] obtained 75–93% COD removal from the pilot scale upflow anaerobic fixed bed reactor with the influent COD concentration 2000–8000 mg/L with 20 h of HRT [86]. Of our study, considering run 17, 86.36% COD removal of initial 6300 mg/L COD was achieved after 8 h of electrochemical treatment at 12 V using 50 g/L NaCl electrolyte and 43.65 mg/L min initial COD removal rate was realized. On the basis of reaction time and OLR, electrochemical treatment in our work had a much better performance than most of the biological treatment processes above, besides does not have the drawbacks of large land necessity, high investment and operational costs, lime precipitation and deposition in units and nutrient requirements; the characteristics of the biological one. Moreover, reaction rate can be increased in the same volume of the electrochemical reactor by increasing electrode surface area/current or narrowing the gap between electrodes, which is not possible at all in biological reactors.

With our study, it has been demonstrated that beet sugar factory wastewater could be successfully treated by electrochemical oxidation and a final effluent with reduced pollution can be obtained. For practical applications of the electrochemical treatment of beet sugar factory wastewater, further investigation and optimization are needed in order to achieve higher COD removals for the required environmental regulations.

4. Conclusion

The electrochemical treatment of simulated beet sugar factory wastewater was investigated with iron electrodes in the presence of NaCl electrolyte, for the first time in literature. The effects of operating parameters of applied voltage, waste and electrolyte concentrations on COD removal percent and COD initial removal rate were elucidated through batch runs. COD removal percent and COD initial removal rate changed in the range 6.98–86.36% and 0.38–43.65 mg/L min, respectively, depending on experimental conditions of the treatment. The highest reduction in COD concentration was achieved 5441 mg/L in the treatment of beet sugar factory wastewater, which did not necessitate a pre-treatment process. This reduction in COD concentration is not lower than the conventional combined biological treatment and the electrolysis time of 8 h and higher OLR are the main advantages of this method over biological treatments. For the generalization of electrochemical treatment in industrial applications, treatment process was experimentally designed and treatment conditions were optimized through response surface methodology, where a cost driven approach was followed. In this respect, maximization of process responses of COD removal percent and COD initial removal rate were pursued while applied voltage was kept in the range, electrolyte concentration was minimized and waste concentration was maximized at 25 °C of reaction. The optimum conditions were satisfied at 100% waste concentration, 33.05 g/L supporting electrolyte concentration and 12 V applied voltage realizing 79.66% COD removal and 33.69 mg/L min COD initial removal rate, respectively. Kinetic investigations proved that the reaction order for the electrochemical oxidation of beet sugar factory wastewater is of 1.2 with an activation energy of 5.17 kJ/mol. Outcomes of this study reveal the applicability of electrochemical treatment of beet sugar factory wastewater as a strong alternative method to previous conventional solutions with further research.

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