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Organics removal from dairy wastewater by electrochemical treatment and residue disposal

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ABSTRACT

Dairy industry wastewater is characterized by high chemical oxygen demand (COD) and other pollution load. In the present study, the treatment of simulated dairy wastewater (SDW) was performed by electrochemical (EC) method using iron electrode. Full factorial central composite design (CCD) with four factors namely current density (J), dosage of sodium chloride (NaCl) (m), electrolysis time (t) and pH, with each factor at five levels, was used to optimize the factors for higher COD removal. Operational parameters J, m, t and pH were varied between 61.73–308.64 A/m^2, 0–2 g/l, 10–90 min and 5–11, respectively. Optimum value of J, t and pH were found 270 A/m^2, 50 min, and 7.0, respectively, while m was found to be zero. Optimum COD removal efficiency was found to be ≈70%. Physico-chemical analysis of iron electrodes and residues (scum and sludge) has been carried out to understand the EC mechanism as well as to study the disposal aspect of the residues generated during EC treatment. The mechanism of COD removal by EC seems to be a combination of electro-coagulation, electro-floatation and electro-oxidation.

1. Introduction

The dairy industries are associated with the generation of large volumes of wastewater [1] and this wastewater contains milk and milk products with wash water. In dairy industries water is used throughout all steps like cleaning, sanitization, heating, cooling and floor washing. Hence, large quantity of water is required in dairy industry [2]. Dairy wastewater biological oxygen demand (BOD), chemical oxygen demand (COD) and nutrients levels are very high. These wastewaters can cause environmental damage if discharged without treating. Therefore, dairy wastewater treatment is very important from environment and water requirement point of view for dairy industry [3].

Dairy wastewaters are generally treated usually using biological methods such as activated sludge process, aerated lagoons, trickling filters, sequencing batch reactor (SBR), anaerobic sludge blanket (UASB) reactor, anaerobic filters, etc. [4]. Aerobic biological processes are high energy intensive whereas, effluents treated by anaerobic biological processes need additional treatment [5]. On the other hand, the physical/chemical methods that have been proven to be successful are coagulation/flocculation [6,7]. Recently, Kushwaha et al. [8] studied the adsorptive treatment of dairy wastewater by activated carbon and bagasse fly ash.

Among physical/chemical methods, electrochemical (EC) treatment is one of the advanced processes which offers high removal efficiencies in compact reactors with simple equipments for control and operation of the process [9]. Various researchers have utilized it for the treatment of varieties of industrial wastewater [10–18]. Nutrient rich wastewater like restaurant wastewater has also been very successful treated by EC [19]. Also, there are few studies in the literature utilizing EC treatment successfully for food industries wastewaters [20–23].

EC treatment of dairy industry wastewater has been studied by Sengil and Ozacar [24] and Tchamango et al. [25]. Sengil and Ozacar [24] used iron electrode and reported significant COD and oil-grease removal, while, Tchamango et al. [25] used aluminium electrodes and reported COD, nitrogen and turbidity removal efficiencies of 61%, 81% and 100%, respectively. Only above two studies are reported in open literature for the EC treatment of dairy wastewater. Disposal aspects of residues (scum and sludge), which is a big issue, are missing in the previous two studies for the EC treatment of dairy wastewater.

In the classical method of optimization one parameter is varied at a time while other being constant. However, the classical method shows inability to understand complex interactions between the variables and the response [26,27]. Response surface methodology (RSM) is an effective statistical tool for collection of mathematical and statistical information useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main advantage of RSM is the reduced number of

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Table 1
Process parameters and their levels for EC treatment of SDW using iron (Fe) electrode.

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

experiments needed to provide sufficient information to optimize the process.

Present work investigates the suitability of iron (Fe) electrodes to treat simulated dairy wastewater (SDW). Central composite design (CCD) and response surface methodology (RSM) has been used to design the experiments, do statistical analysis and determine the optimum condition. Four factors; current density (J), electrolyte dosage as sodium chloride (m), electrolysis time (t) and pH were selected as variables, whereas, COD removal efficiency from SDW was the response. Detailed physico-chemical analysis of iron electrodes and residues (scum and sludge) has also been carried out to understand the EC mechanism. Thermo-degradation analysis of EC residues has also been proposed with respect to the disposal aspect.

2. Materials and methods

2.1. Feed

In the present study, simulated dairy wastewater (SDW) was prepared by dissolving 4 g of milk powder per litre of distilled water. Milk powder of Amulya brand, manufactured by Banaskantha District Cooperative Milk producer's Union Ltd., Palanpur, Uttarakhand, India, was used to prepare SDW. SDW was used in the present study so as to prevent any change in wastewater composition throughout the experiments. Several investigators used same method for making SDW [28–30,8]. The simulated wastewater was prepared freshly whenever required. The main characteristics of the used SDW were: COD = 3900 mg/l, total solids (TS) = 3090 mg/l, turbidity = 1744 NTU, conductivity = 220 μs/cm, chloride = 31 mg/l, total nitrogen (TN) = 113.18 mg/l and pH = 6.3–6.8. These characteristics were maintained uniform throughout the study.

2.2. Analytical measurements

All the chemicals used in the study were of analytical reagent (AR) grade. COD was measured using digestion unit (DRB 200, HACH, USA) and double beam UV visible spectrophotometer (HACH, DR 5000, USA). Total nitrogen (TN) and chloride content was determined using the standard Kjeldahl method and standard titrimetric Volhard method, respectively. Turbidity meter supplied by Aqualytic, Germany, was used to measure turbidity. Energy dispersive X-ray (EDX) analysis was used to study the distribution of the elements in the residues (sludge and scum). This was performed in EDX analyser QUANTA, Model 200 FEG, USA. Scanning electron microscope (SEM) was employed to understand the morphology of the electrode before and after the EC treatment of SDW; and to see the surface characteristics of the residues obtained after EC treatment. This was performed in the same equipment as EDX. Perkin Elmer (Pyris Diamond) thermo-gravimetric analyser (TGA) was used to analyse the residues.

2.3. Experimental design

Four factors and five level full factorial CCD based on RSM was used in this study, and a total of 30 experiments were conducted. Four operational parameters, namely J: 61.73–308.64 A/m^2; m: 0–2 g/l; t: 10–90 min and pH: 5–11 were taken as input parameters and percentage COD removal was taken as a response of the system (Y). Table 1 represents the variables and their levels whereas actual experimental design matrix is given in Table 2. For statistical calculations, the levels for the four parameters X_i (X_1 (J), X_2 (m), X_3 (t), X_4 (pH)) were coded as x_i according to the following relationship:

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

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

The data obtained were fitted to a second-order polynomial equation:

$$Y = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i=j}^{3} \sum_{i=j+1}^{4} b_{ij} X_{ij} \quad (2)$$

where Y is percentage COD removal; b_0, b_i, b_{ii}, b_{ij} are constant coefficients and X_i the uncoded independent variables.

2.4. Experimental set-up, procedure and data analysis

Cuboid shape batch reactor of dimension 108 mm × 108 mm × 130 mm having working volume 1.5 l was fabricated of Perspex sheet to conduct the EC experiments of SDW. Magnetic stirrer was used to agitate the SDW. Four iron electrodes, each having dimensions of 10 cm × 8.5 cm × 0.15 cm with inter-electrode spacing of 1 cm were connected in parallel in bipolar mode. The total submerged area of electrodes into the SDW was 9.50 cm × 8.5 cm. Current was maintained constant by means of a precision digital direct current power supply (0–20 V, 0–5 A) fitted with an ammeter and voltmeter.

Experiments were conducted as per the conditions specified in the design matrix (Table 2). The pH of the SDW was adjusted to desired level by adding 0.1 N NaOH or 0.1 N H_2SO_4 solutions. In the beginning of experiment, the SDW with initial COD concentration (C_0 = 3900 mg/l) and requisite m value was adjusted to desired pH, as per that particular run. Time, t, was measured when power supply was switched on. J was maintained constant during the run. After the desired t, samples were taken from the reactor and its final COD was measured. The percentage COD removal was calculated using the following relationship:

$$\text{Percent COD removal}\,(Y) = \frac{(C_0 - C_f)100}{C_0} \quad (3)$$

where C_f is the final COD concentration (mg/l) after t (min). The data obtained from the experiments was analysed using Design-Expert 6.0.8 trial version. Three analytical steps: adequacy of various models test (sequential model sum of squares and model summary statistics), analysis of variance (ANOVA) and the response surface plotting were performed to establish an optimum condition for the COD removal from the SDW.