CONTINUOUS ELECTROCHEMICAL TREATMENT OF DAIRY INDUSTRY WASTEWATER

Thesis submitted in partial fulfillment of the requirement for the award of
degree of

Master of Technology
in
Chemical Engineering

By

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CERTIFICATE

This is to certify that the thesis entitled **"Continuous Electrochemical Treatment of Dairy Industry Wastewater",** is an authentic record of my own work carried out as requirements for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, under the supervision of Dr. V. K. Sangal, Assistant Professor, Department of Chemical Engineering and Dr. J. P. Kushwaha, Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala, during January to July 2013.

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ABSTRACT

Dairy industry generates a vast amount of wastewaters and is characterized by high chemical oxygen demand (COD) and nutrient due to their high level of organic contents. The amount of wastewater generated is approximately 0.2 liter to 10 liter of waste per liter of processed milk. It may be either extremely acid or alkaline. The dairy wastes usually contain inert, organic or toxic materials and possibly pathogenic bacteria. Europe has the largest market in the dairy industry. US have the second largest market. Global: 1.9%, APAC: 3.5%, Western Europe: 0.2%, Africa: 2.2%, Eastern Europe: 2.4%, Latin America: 2.8%. India is one of the largest milk producers in the world with a market size of US$4.4 billion CAGR (2005-2009).

Different method for the treatment of dairy wastewater is Aerobic, Anaerobic, Sequential batch reactor, trickling filter, oil filter separation, electrochemical method etc. Present work reports the dairy wastewater treatment by continuous electrochemical treatment method with aluminum electrodes. The effect of various parameters like pH, current (I), flow rate (F) and treatment time (t) on % COD removal (Y_1) and specific energy consumed (Kwh/kg of COD removed) Y_2 were observed through experimental design and analysis of data using central composite design (CCD) based on response surface methodology (RSM). For this four factors and three level full factorial CCD based on RSM have been used for the experimental design.

Variables current (I); 0.5–2.5 A; electrolysis time (t): 30–120 min, pH: 5–10 and wastewater flow rate (F); 0.8-1.8 l/h have been considered as input parameters and % COD removal (Y_1) and specific energy consumed (KWh per kg of COD removed) (Y_2) have been taken as a responses of the system. A total of 30 experiments were suggested by RSM. The data obtained from the experiments was analyzed using Design-Expert 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 responses.The data obtained by the experiments set suggested were fitted to a second-order polynomial model equation.

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ABBREVIATION

APAC	Asia-Pacific
BFBR	Buoyant filter bioreactor BOD
	Biological Oxygen Demand
CAGR	Compound Annual Growth Rate
COD	Chemical oxygen demand
DF	Dairy Factory
ECT	Electrochemical treatment
HUASB	Hybrid upflow anaerobic sludge blanket reactor.
SDW	Synthetic Dairy wastewater

CHAPTER-1

Introduction

In agro-industries the wastewater are characterized by high chemical oxygen demand (COD) due to their high level of organic contents. A major concern in dairy industry is that it generates a vast amount of wastewaters: approximately 0.2 liter to 10 liter of waste per liter of processed milk (Balannec et al., 2005). In addition, they may be either extremely acid or alkaline and may have high or low concentrations of colored matter. The dairy wastes usually contain inert, organic or toxic materials and possibly pathogenic bacteria. The effluents from dairy waste are concentrated in nature, and the major contributors these effluents are carbohydrates, proteins and fats originating from milk. Treatment of dairy effluents has a great significance in recycling water for use in industrial processes (Hamdani et al., 2005). In numerous latest cases, if the effluents from dairy are not treated properly and thrown in the river which will result in the eutrophication due to phosphorous and nitrogen compounds(Chimenos et al., 2006). Pollutants from dairy wastewater contain a spectrum of organic and inorganic chemicals which are released in the form of solids, slurries and liquid effluents which have very harmful effects on environment. The majority of the wastewater quantity is generated from cleaning of transport lines, tank trucks, washing of milk silos and other cleaning agent which have a significant influence on discharged levels of nutrients. In general the biological treatment are favored over the chemical treatment as the biological process is more cost effective and much environment friendly as compare to the chemical processes also the COD removal efficiency and the reagent cost is high in the chemical process.

The wastewater generated by the dairy industries includes:

1. Washing and cleaning operations in the tanks, trunks, pipes etc.
2. Spillage by leaks and overflow.
3. Processing loss include, sludge discharge from clarifiers, discharge from bottles and washer, evaporator entrainment, splashing and container breakage in automatic packing equipment.
4. Spoiled products, returned products or by products.

5. Detergent and other compound used in washing and sanitizing solution that are discharge as waste.
6. Waste constituents may be present in raw water which ultimately go to waste.
7. Entrainment of lubricants from conveyers, stackers and other equipment. Milk products are some time deliberately wasted sometime whey and butter milk.

1.1 Minimal national standard (MINAS) for dairy effluents

The Central Pollution Control Board (CPCB) Delhi by the authority resides in it through the Environment (Protection) Act 1986 has provided effluents standards for various quality parameters. For the dairy wastewater the BOD limit is 100 mg/l .Different parameter for dairy effluents are given below in Table 1.1

Table 1.1 Standards for emission or discharge of environmental pollutants from dairy industries

Parameters (Effluents)	value	Quantum per product processed
pH	6.5-8.5	-
BOD [3 days at 27^0C]	100 mg/l	-
Suspended solid	150 mg/l	-
Oil and grease	10 mg/l	-
Wastewater generation	-	3 m^3/kl of milk

Source: http://cpcb.nic.in/Industry_Specific_Standards.php

1.2 Global scenario of dairy industry

Europe has the largest market in the dairy industry. US has the second largest market after Europe in preference to the rich, prepared, fat-specific, and organic variants of a variety of dairy products in the market CAGR (2011-2014) drinking milk sector: Global: 1.9%, APAC: 3.5%, Western Europe: 0.2%, Africa: 2.2%, Eastern Europe:

2.4%, Latin America: 2.8%. India is going to be a main market for international markets as the growing population provides a lot of growth opportunities. It is proposed India will account over 1/3 of the global milk consumption by 2020.

1.3 Indian scenario of dairy industry

India is one of the largest milk producers in the world .Market size of Indian Dairy Industry stands at around US$4.4 billion CAGR (2005-2009): 11.9% domestic market 50% in fluid form, 35% in traditional products (cheese, yogurt and milk based sweets), and 15% is consumed for production of butter, ghee, milk powder and other processed dairy products Forecast 2014: increase by 49.4% to take market value to US $ 6.5bn.(Sneha et al., 2011).

1.4 Characteristics of dairy wastewater

Organic and nutrient concentrations varied significantly, because of the daily and weekly frequency of production in the factory and often as a result of washing procedures during the production cycle. Wastewaters from the dairy industry are usually generated in an intermittent way, so the flow rates of these effluents change significantly. High season variation is also encountered which is typically high in summer and low in the winter months. The use of acid and alkaline cleaners and sanitizers in the dairy industry additionally influences wastewater characteristics and typically results in a highly variable pH. The dairy industries produces various products so each product has its own characteristics so its depend on the system and method of operation used. Dairy industry wastewaters are characterized by their high content in nutrients, especially nitrogen (400 mg/l TKN and 20-50 mg/l TP). High COD concentrations indicate that dairy industry wastewaters are strong and fluctuating in nature. In industrial dairy wastewaters, nitrogen originates mainly from milk proteins, and is present in various forms; either an organic nitrogen (proteins, urea, nucleic acids), or as ions such as NH^{4+}, NO^{2-} and NO^{3-}. Particularly high Na concentrations point out the use of large amount of alkaline cleaners at dairy plants and conc. The concentrations of heavy metals, such as copper (Cu), nickel (Ni) and zinc (Zn) were reported to be in a range that would not affect adversely the performance of a biological treatment. Phosphorus is found mainly in inorganic forms; as orthophosphate (PO_4^{3-}) and polyphosphate ($P_2O_7^{4-}$), as well as organic forms. Concentrations of suspended solids (SS) and volatile suspended solids (VSS) are also used to evaluate wastewater strength and treatability. Dairy wastewater is composed of easily degradable carbohydrates, mainly lactose, as well as less biodegradable proteins and lipids. In cheese-processing wastewater, 97.7% of total COD was accounted for by lactose, lactate, protein and fat lactose is the main carbohydrate in dairy wastewater and is a readily available substrate for anaerobic bacteria. The effluents generated by the dairy waste are given in Table 1.2

Table 1.2:- Characteristic of overall effluents generated in dairy industry

Origin	BOD	COD	Fats	Nt	Pt	Ph	Ts	Vs	TSS	VSS
DF	4000	2600	400	55	35	8-11			675	635
DF	4000	2160		200	60	5-9	5100	4300		500
DF	2926	1580	294	36	21	6.7	710	1880		
DF	633	260		106		8.9		447	240	
DF	2209	1112	60		33	7.2	2540		278	
DF	4500	2300		56		7.2		1093	816	
DF	______	285		296		8.1	1500		943	
DF	2125	1250		70	100	9.8			280	250
DF		241		191	50.9	8,5				804
DF	4500	2300	350	60	50				800	
DF	4000	2000		60					800	
DF	1750			75	9.5				400	355

Source: Pooja et al., 2008.

1.4.1 Physical characteristics

The principal physical characteristics of wastewater include solids content, colour, odour and temperature. –

1.4.2 Total Solids: The total solids in a wastewater consist of the insoluble or suspended solids and the soluble compounds dissolved in water. The suspended solids content is found by drying and weighing the residue removed by the filtering of the sample. Between 40 and 65 % of the solids in an average wastewater are suspended. Settle able solids, expressed as millilitres per litre, are those that can be removed by sedimentation. Usually about 60 % of the suspended solids in a municipal wastewater are settleable (Ron et al., 1998).

1.4.3 Color: It is a qualitative characteristic that can be used to assess the general condition of wastewater. Wastewater that is light brown in color is less than 6 h old, while a light-to-medium grey color which shows that the wastewater undergone some degree of decomposition. Lastly, if the color is dark grey or black, the wastewater is typically septic, having undergone extensive bacterial decomposition under anaerobic conditions.

1.4.4 Temperature: The temperature of wastewater is commonly higher than that of the water supply because warm municipal water has been added. Due to the addition of the biological processes it is necessary to measure the temperature of wastewater as the biological processes are temperature dependent.. The temperature of wastewater will vary from season to season and also with geographic location. In cold regions the temperature will vary from about 7 to 18 °C, while in warmer regions the temperatures vary from 13 to 24 °C (Ron et al.; 1998).

1.5 Chemical characteristics

Inorganic chemicals: The principal chemical tests include free ammonia, organic nitrogen, nitrites, nitrates, organic phosphorus and inorganic phosphorus. Nitrogen and phosphorus are important because these two nutrients are responsible for the growth of aquatic plants. Different test such as pH, chloride, sulphate and alkalinity are conducted to check whether the treated wastewater is suitable to reuse and in controlling the various treatment processes (Munter et al, 2005).

Organic chemicals: Different test are developed over the years to determine the organic content of wastewater. In general, the tests may be divided into those used to measure gross concentrations of organic matter greater than about 1 mg/l and those used to measure trace concentrations in the range of 10-12 to 10-3 mg/l. Laboratory methods commonly used today to measure gross amounts of organic matter (greater than 1 mg/l) in wastewater include (1) Biochemical oxygen demand (BOD), (2) chemical oxygen demand (COD) and (3) total organic carbon (TOC). Trace organics in the range of 10-12 to 10-3 mg/l are determined using instrumental methods including gas mass spectroscopy and chromatography. Specific organic compounds are determined to assess the presence of priority pollutants. The BOD, COD and TOC tests are gross measures of organic content and as such do not reflect the response of the wastewater to various types of biological treatment technologies.

1.6 Dairy Wastewater Treatment

Different techniques for treating the dairy industry wastewater include grease traps, oil water separation of floatable solids. Biological treatment consists of the aerobic and anaerobic process. Sometimes both anaerobic treatment and aerobic treatment are employed one after another. Advantages and disadvantages of various treatment process for dairy wastewater given in Table 1.3.

Table 1.3 Advantage and disadvantage of various treatment processes for dairy wastewater

Treatment	Disadvantage	Advantage
Anaerobic	• Optimal process temperature is about 30^{o}C. • Post treatment of BOD removal is often required	• Energy production is Possible • No need of land • No energy consumption • The production of excess sludge is less. • The system will not be affected in case of shutdown or power failure.
Aerobic	• Energy required for aeration • High land requirement • System will be affected by the shutdown and power failure • Post treatment of further nutrient is often required • High production of Excess sludge	• Low process temperature • End treatment of waste water
SBR(Sequencing batch reactor)	• High sludge volume index. • During selected operating cycles plugging of aeration in devices take place. • Sophisticated controls, automated valves require High maintenance.	• Simple and cost effective. • It is highly flexible in terms of cycle time and sequence. • More resistant to fluctuating influent loading. • Aerobic and anoxic phases can be combined in

		single reactor • Near ideal quiescent settling condition
Electro coagulation	• Simple equipment and is easy to operate. • Sludge is readily settable and easy to de. • No use of chemicals ad The EC process avoids uses of chemicals • no possibility of secondary pollution caused by checmical substances. • EC produces effluent with less TDS content as compared with chemical treatments. • Flocs are much larger , contain less bond water., is acid-resistant and more stable, and therefore, can be separated faster by filtration. • It is acid resistant and more stable so filtration process can be used. • No moving parts so maintenance cost is less.	• 'Sacrificial electrode' are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced. • The use of electricity may be expensive in many places. • An impermeable oxide layer may be formed over the cathode leading to the loss of efficiency of EC unit. • High conductivity o the wastewater suspension is required. • Gelatinous hydroxide may be tending to solubilize in some cases.

Source: Yang et al.; 1991

CHAPTER-2

Theory

2.1 ELECTROCHEMICAL TREATMENT (ECT)

ECT process can be another alternative process for treating dairy wastewaters. The major screened-off area in the ECT is electro-coagulation (EC), electro-flotation (EF) and electro-oxidation (EO). An ECT unit consists of anodes and cathodes in parallel mode. When electric power is applied from a power source, the anode material gets oxidized and the cathode is subjected to reduction of elemental metals and due to further reactions depending on conditions applied, removal of various pollutants takes place by EC and/or EF and/or EO mechanisms.

2.2 Electro-flotation (EF)

EF is a simple process in which buoyant gases bubbles generated during electrolysis take along with them the pollutant materials to the surface of liquid body. The bubbles of hydrogen and oxygen which are generated from water electrolysis move upwards in the liquid phase. A layer of foam, containing gas bubbles and floated particles is formed at the surface of water. The rate of flotation depends on several parameters such as surface tension between the water particles and gas bubbles; the bubble size distribution and bubble density; size distribution of the particles; the residence time of the solution/liquid in the EC cell and the flotation tank; the particle and gas bubble zeta potentials; and the temperature, pH of the solution (Koren et al., 1995).

2.3 Electro-oxidation (EO)

Decomposition of organic materials through EO treatment means the oxidation of organics present in wastewater to carbon dioxide and water or other oxides. The electrochemical oxidation of wastewater is achieved in two ways. First, by direct anodic oxidation, in which organics are adsorbed at the electrode and oxidized at the surface of the electrode and second, by indirect oxidation in which some oxidizing agents are generated electrochemically which are responsible for oxidation of organics present in the solution. The schemes of these two processes are illustrated in Fig.2.1

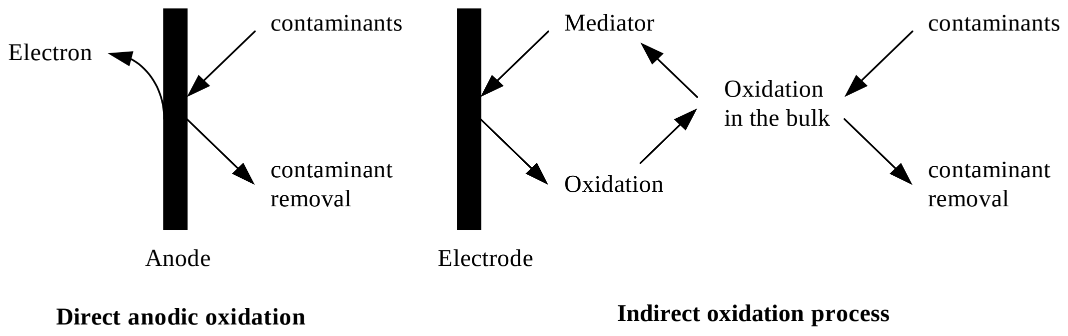

Fig.2.1. Direct and indirect oxidation processes in ECT (Juttner et al., 2000).

Organic pollutants are adsorbed on the anode surface in direct anodic oxidation process, where active oxygen (adsorbed hydroxyl radicals) or chemisorbed "active oxygen" is accountable for the oxidation of adsorbed Organics pollutants. The mechanism of oxidation of organic matter on oxide anode (MO_X) was suggested by Comninellis (1994). The reactions involve are as follows:

$$H_2O + MO_X \longrightarrow MO_X[OH] + H^+ + e^- \qquad (2.1)$$

The adsorbed hydroxyl radicals may form chemisorbed active oxygen $MO_X[OH]$

$$\longrightarrow MO_{X+1} + H^+ + e^- \qquad (2.2)$$

The liberated chemisorbed active oxygen is responsible for the oxidation.

During the EO treatment process, two types, of oxidation is possible. In one way, toxic and non-biocompatible pollutants are converted into bio-degradable organics, so that further biological treatment can be initiated. In contrast, in other way, pollutants are oxidized to water and CO_2 and no further purification is necessary.

In an indirect oxidation process, strong oxidant such as hypochlorite/chlorine, ozone, and hydrogen peroxide are regenerated during electrolysis. Following reaction shows the formation of hypochlorite:

$$H_2O + Cl^- \longrightarrow HOCl + H^+ + 2e^- \qquad (2.3)$$

High voltage can led to formation of hydrogen peroxide and other molecules as follows:

$$H_2O \longrightarrow OH, O, H^+, H_2O_2 \qquad (2.4)$$

These oxidants oxidize many inorganic and organic pollutants in the bulk solution (Abuzaid et al., 1999).

2.4 Electro-coagulation (EC): EC, like coagulation, is the process of destabilization of colloidal particles present in wastewater and can be achieved by two mechanisms: one in which an increase in ionic concentration, reduce the zeta potential, and adsorption of counter ions on colloidal particles neutralizes the particle charge; and other by well known mechanism of sweep flocculation Various reactions take place in the EC reactor during its operation. As the current is applied, the anode material undergoes oxidation and cathode gets reduced. If iron or Al electrodes are used, Fe^{2+} and Al^{3+} ion generation takes place at anode by the following reaction

$$Fe\ (S) \rightarrow Fe^{2+}\ (aq) + 2e- \qquad (2.5)$$

$$Al\ (S) \rightarrow Al^{3+}\ (aq) + 3e- \qquad (2.6)$$

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

$$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e- \qquad (2.7)$$

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

$$3H_2O\ (l) + 3e- \rightarrow 3/2H_2\ (g) + 3OH^-\ (aq) \qquad (2.8)$$

Liberated Fe^{2+}/Al^{3+} and OH^- ions react to form various monomeric and polymeric hydrolyzed species. The concentration of the hydrolyzed metal species depends on the metal concentration, and the solution pH. These metal hydrolyzed products are responsible for the coagulation of pollutants from solution.

Application of electro coagulation for the treatment of several effluent types has been considered a competitive means of wastewater treatment, especially for removing metals, anions, dyes, organic matter (BOD, COD), total suspended solids and colloids in wastewater from different sources. Among physico-chemical methods, electro coagulation technique is one of the processes which offer high removal efficiencies in compact reactors, with simple equipments for control and relatively moderate operating cost Compared to the chemical coagulation treatment with aluminum sulphate, the efficiency of the electro coagulation technique was almost identical. However the wastewaters treated by electro coagulation differed by the fact that they exhibited a lower conductivity and a neutral pH value (by contrast to the acid nature of the solution treated by the chemical coagulation). This result (low conductivity, neutral pH) tends to show that it may be possible to recycle the treated water for some industrial uses. Moreover, the electro coagulation process uses fewer reagents: the mass of the aluminum anode dissolved during the treatment is lower compared to the quantity of the aluminum salt used in chemical coagulation.

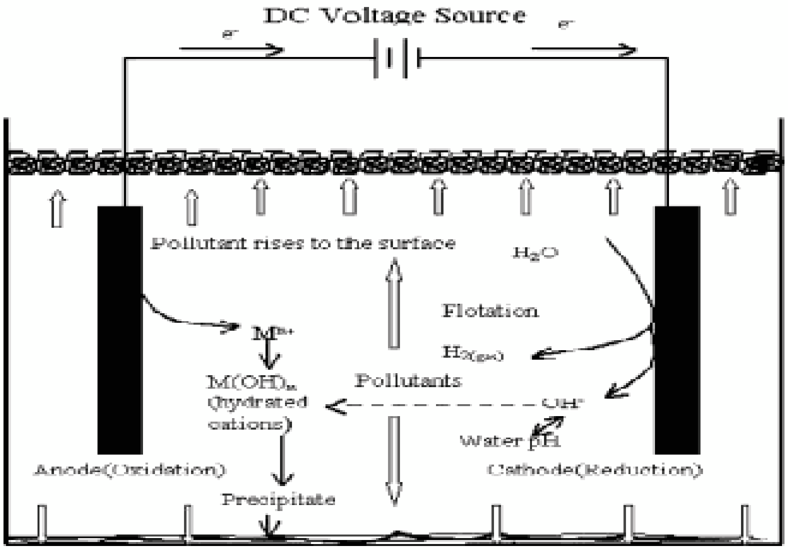

Figure 2.2: Schematic diagram of bench scale two electrode EC cell (Pretorius et al., 1991)

2 .5 Types of arrangement of EC

2.5.1 Monopolar electrode in parallel connection: The parallel arrangement essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a

DC power source as shown in Figure 2.3. In a monopolar arrangement, each pair of 'sacrificial electrodes' is internally connected with each other, and has no inter-connections with the outer electrodes. The experimental set-up also requires a resistance box to regulate the flow of current and a multimeter to read the current values. The conductive metal plates or rods used in EC fabrication are commonly known as 'sacrificial electrodes' (Pretorius et al., 1991).

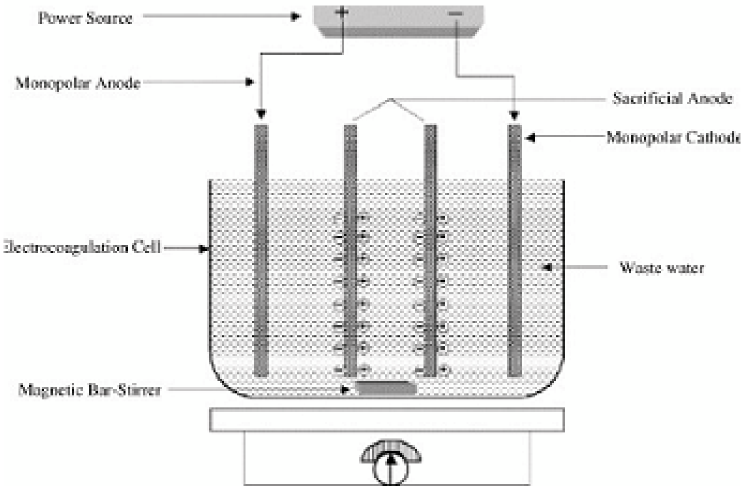

Figure 2.3: Bench-scale EC electrode with monopolar electrode in parallel connection (Pretorius et al., 1991).

2.5.2 Monopolar Electrode in Series Connection: An arrangement of EC with monopolar electrode in series as shown in Figure 2.4. Each pair of 'sacrificial electrodes' is internally connected with each other. , and has no inter- connections with the outer electrodes. This Arrangement of Monopolar electrode with cell is series is electrically similar to single cell with many electrode and interconnection

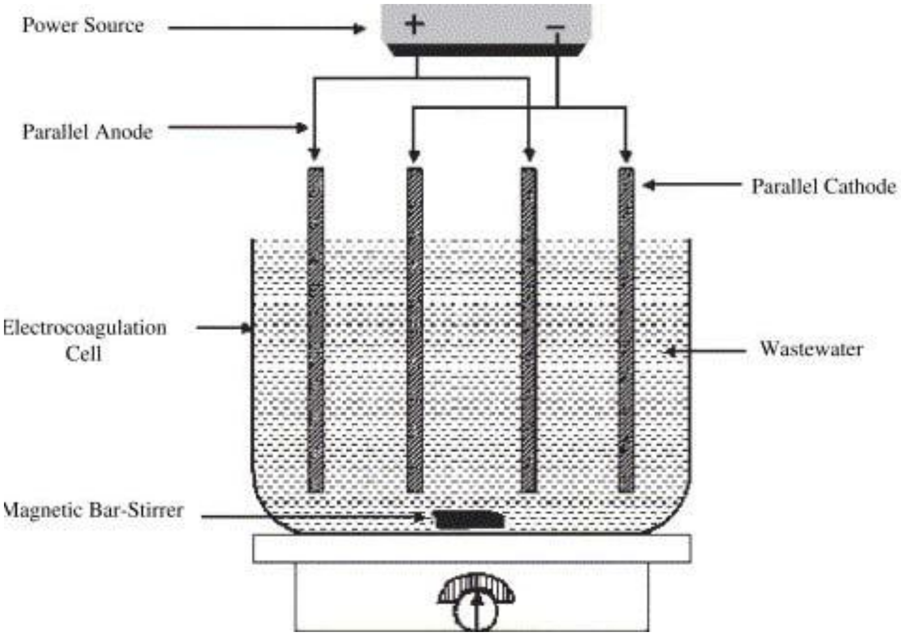

Figure 2.4: Bench-Scale EC Electrode with Monopolar Electrode in Series Connection (Pretorius et al.,1991).

In series Cell Arrangement, a higher potential Difference is required for a given current to flow because the cells connected in series have a higher Resistance. The same current would however, flow through all the electrodes. On the other hand, in parallel the electric current is divided between all the electrodes in relation to resistance of the individual cells.

2.5.3. Bipolar Electrode in Parallel Connection: The sacrificial electrodes are placed between the two parallel electrodes without any electrical connection as shown in Figure 2.5. Only the two monopolar electrodes are connected to the electric power source with no interconnections between the sacrificial electrodes**.** When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared to the parallel side beside it. The sacrificial electrodes in this case are also known as bipolar electrodes (Pouet et al., 1995,).

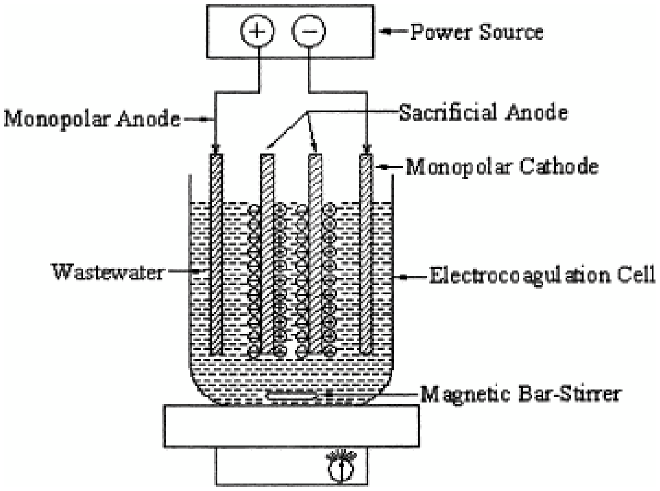

Figure 2.5: Bench-Scale EC Electrode with bipolar Electrode in Parallel Connection (Pretorius et al., 1991).

2.6 Factors Affecting Electro coagulation:

2.6.1. Current density (*J*), electrolysis time (*t*) and anodic dissolution: Faraday's law describes the relationship between current density (*J*) and the amount of anode material that dissolves in the solution. It is given as:

$$w = \frac{MJt}{ZF} \tag{2.9}$$

Where, w is the theoretical amount of ion produced per unit surface area by current density J passed for duration of time, t. Z is the number of electrons involved in the oxidation/reduction reaction, M is the atomic weight of anode material and F is the Faraday's constant (96486 C/mol). The pollutants removal efficiency depends directly on the concentration of aluminum ions produced by the metal electrodes, which in turn as per Faradays law depends upon the t and J. When the value of t and J increases, an increase occurs in the concentration of metal ions and their hydroxide flocks. Consequently, an increase in t and J increases the removal efficiency.

2.6.2. pH: The initial pH of the wastewater will have a significant impact on the efficiency of the ECT. The effluent pH after ECT would increase. The incremental increase in pH with an incremental increase in the amount of current applied tends to decrease at higher current The general cause of the pH increase can be explained from the following equation:

$$2\ H_2O + 2e^- \longrightarrow H_2\ (g) + 2OH^-\ \text{(cathode)} \qquad (2.10)$$

At the cathode, generated hydrogen gas (which attaches to the flocculated agglomerates, resulting in flocks flotation to the surface of the water) and this causes the pH to increase as the hydroxide-ion concentration in the water increases. This reaction is one of the dominant reactions that occur in the electro-flocculation system (Koren and Syversen, 1995).

Also, due to the following reaction, pH is affected:

$$2\ H_2O \longrightarrow O_2\ (g) + 4H^+ + 4\ e^- \qquad (2.11)$$

These two reactions tend to neutralize pH. This is the reason, which, however, prevents larger pH increases due to larger hydroxides formations at higher current densities

2.6.3. Conductivity and the effect of salts: Feed conductivity is an important parameter in ECT, since it directly affects the energy consumed per unit mass of pollutants removed. If conductivity is low, higher amount of energy is consumed per unit of mass of pollutants removed and vice versa. Due to this, some salts (commonly NaCl) are added to increase the conductivity of feed. When, salt is added to the solution, it reduces the solution resistance and hence, voltage distribution between the electrodes reduces. However, a too high conductivity may lead to secondary parasite reactions, diminishing the main reaction of the electrolytic decomposition. Additionally, the presence of chlorides can enhance the degradation of organic pollutants in the wastewaters due to the formation of various species (Cl_2, HOCl and ClO^-) formed as function of the pH (Deborde et al., 2008). ClO^-, which is dominating at higher pH, has been reported as better oxidant among all chlorine species (Deborde et al., 2008). Moreover, the type and concentration of salt also influences the effectiveness of the treatment. Salts of bi- and tri-valent metals are more effective than monovalent salts because of their high ionic strengths. Cl_2 and OH^- ions are generated on the surface of the anode and the cathode, respectively, when NaCl is used as an electrolyte in ECT. The organics are destroyed in the bulk solution by oxidation reaction of the regenerated oxidant. In an ECT cell, Cl_2/hypochlorite formation may take place because chloride is widely presented in many wastewaters.

CHAPTER-3

Literature Review

Numerous studies have already been done in electro coagulation of dairy wastewater therefore an overview of it; in the form of literature review is must.

Silva et al., (2012) studied the efficiency of electro coagulation on dairy wastewater by using Iron Electrode. Electrolysis time, pH, current density and distance between electrodes were considered to assess the removal efficiency of chemical oxygen demand (COD), total solids (TS) and their fractions and turbidity. By using the iron electrode a problem occurred in the form of undesirable colour and increases in number of dissolved solids in the treated effluents. Reported significant reduction in COD by 58%; removal of turbidity, suspended solids and volatile suspended solids by 95%; and a final treated effluent pH of approximately 9.5.The electric current applied for 15 minutes, a sample with an initial pH close to neutral (pH 7.0) and a current density of 50 A.m−2 .

Bensadok et al., (2011) studied the batch electrochemical treatment of dairy effluents using Al and Ti/Pt as electrodes system. The greater removal efficiency was obtained cathode and anode both with Al when the values of current density, electrolysis time, pH and NaCl Conc. Where respectivalely at 50 A/M^2, 2 min, 6.6, and 2.5 .Removal efficiency of COD, phosphate and turbidity attained respectively 80%, 59% and 96%. Corresponding energy consumption was very low and equal 0.03 kWh/kg and 0.04 kWh/kg, for COD and phosphate removal. The obtained results shows that the phosphates could be removed by coagulation and electrochemically by the same order but turbidity related to suspended solid and colloidal material are eliminated by coagulation process.

Bhatti et al., (2011) studied the RSM modelling for electro coagulation of copper from simulated wastewater. The reactor was made up of prexiglass sheet having a area of 4 x 7 cm^2 and a height of 40 cm. The electrode has a clear spacing of 15 mm and was rested on a support of 3 cm above the base. The removal of copper from synthetic wastewater was investigated using aluminium electrode pair at four operational parameters: copper concentration (2.5-32.5 mg/l), pH (5-9), voltage (6-18 V) and treatment time (5-25 min). The copper removal efficiency is 99.3% and the energy consumption is 87%. The main effects model indicated the pH has highest negative effect on the copper removal efficiency.

Tchamango et al., (2010) studied the dairy wastewater treatment by electro coagulation using aluminium electrodes. Chemical oxygen demand (COD) was reduced by up to 61% while the removal of phosphorus, nitrogen contents, and turbidity were 89%, 81% and 100%, respectively. A different treatment method is also applied to phosphate and lactose solution revealed that lactose is not completely removed and account for rather low degradation of COD. Electro coagulation result shows that in some industries the treated water can also be recycled .Electro coagulation process uses fewer reagents: the mass of the aluminium anode dissolved during the treatment is lower compared to the quantity of the aluminium salt used in chemical coagulation.

Passeggi, et al., (2009) studied the integrated anaerobic treatment of dairy industrial wastewater and sludge. It consists of comprising two anaerobic sludge-blanket reactors in parallel arrangement with upward flow, internal fat-separation by flotation. Using loading rates up to a maximum 5.5kgCOD/m3.d–hydraulic residence time of 17hours- reactor efficiency was found to remain stable around 90% of COD. Average sludge digester efficiency using a loading rate of 3.5kgVS/m3.d with a lipid content of 47% of COD amounted to 78% of VS 87% of lipid removal.

Banu, et al., (2008) studied the treatment of dairy wastewater using anaerobic and photo catalytic methods. The anaerobic process treatment is carried out in a HUASB reactor. By the integration of the biological and photo catalytic the removal of 95% and 96% of COD and BOD is achieved. Secondary oxidation process of photo catalytic shows the enchanted organic removal.

Shaylinda et al., (2008) studied the effect of electricity of the dairy wastewater. he samples were prepared by using different concentration, which was 1.0 g/1, 2.0 g/1, 3.0 g/l, 4.0 g/l and 5.0 g/1. Size of electrode plate is 75 mm x 75 mm x 1 mm and 3 cm distance between electrodes were used. NaCl with 10 g/L doses was added into sample as electrolyte substance. Electrolyte is a chemical dissolve that able to conduct electricity. The ranges of current density that was used are between 32 A/m^2 to 54 $A/m^{2.}$ The amount of current density, duration of electric current flow and concentration of the sample does affecting the percentage of turbidity and BOD removal. Electricity was able to remove turbidity more than 99.0%. While for BOD, the removal rate was below than 80.0 %.

Sengil et al., (2006) studied the electro coagulation of dairy wastewater by mild steel electrode.it studied; the effects of initial pH, electrolysis time, initial concentration of COD, conductivity and current density were examined. The optimum operating range for each operating variable was experimentally determined. The batch experimental results revealed that COD and oil-grease in aqueous phase was effectively removed. The overall COD and oil-grease removal efficiencies reached 98 and 99%, respectively. The optimum current density, pH and electrolysis time for 18,300 mg COD/l and 4570 mg oil-grease/l were 0.6 mA/cm^2, 7 and 1 min, respectively. Mean energy consumption was 0.003 kWh/kg of COD.

Stephanie et al., (2006)., studied the removal of nutrients from dairy wastewater from ecological treatment system. The ETS system consists of series of aerobic and anaerobic reactor and wetlands. It effectively treat the dairy wastewater with a overall efficiency of 99% ammonium removal and COD and 79% removal of the orthophosphate. Nitrate was produced and treated with in the system with an effluent conc. of 0.53%. The Nh_4-N conc. was reduced to less than 0.05mg/l. It eliminates the need to dilution before the treatment. However the treatment of solid separation on a large scale is to investigated.

Schwarzenbeck et al., (2005) studied the effect of Aerobic granular sludge sequencing batch reactor for removal of dairy effluents. After the removal of biomass from effluents and the granulation the removal efficiency is 90% COD_{total} , 80% N_{total}, 67% P_{total} is achieved at volumetric exchange ratio of 50 %for a cycle duration of 8 h. Effluents values stabilize at around 125 mg/l $COD_{dissolved}$. The stability of the granules depends on the presence of distinct feast. The real wastewater show slower kinetic degradation than the synthetic wastewater.

Haridas et al.,(2005) studied the buoyant filter bioreactor: a high – rate anaerobic reactor for complex wastewater- process dynamics with dairy effluents. The BFBR is used to treat dairy effluents without the fat removal of the pre treatment and COD removal efficiency of 90% at loading rate of 9.85 g COD/m^3d. The residual COD in BFBR is very low and methane yield of 0.371 CH_4/g COD removed.

Bandpi et al., (2004) studied the effect of Biological Treatment of Dairy Wastewater by Sequencing Batch Reactor. The reactor was made up of prexi glass sheet with volume 22.5 liter. The COD removal efficiency is achieved is more than 90% but the conc. varied from 400 to 2500 mg/l. the optimum oxygen in the reactor is 2-3 mg/l and ML VSS was around 3000 mg/l.

Omil et al., (2003) studied anaerobic filter reactor performance for the treatment of a complex dairy wastewater at industrial scale. The process is operated at 20 kg COD/m^3d with no inhibition effect detected. Inhibition occurs at when sample conc. is increased by 10 times and COD removal efficiency of 90%. No sludge flotation was observed. The biomass is feed in to SBR with a waste sludge generated is about 2-3 kg VSS/d.

Yu et al., (2002) studied the acidogenesis of dairy wastewater at various pH levels. The effect of pH range 4.0-6.5 is studied at acidification of dairy wastewater at 37^{o}C for 12 hours results in a 69-99% of carbohydrate in dairy wastewater, 37-84% protein; 16-50% lipid is acidified. The degradation in the dairy pollutants increased with pH 4.0-5.5. Based on COD 48% dairy pollutants are converted in to volatile fatty acids.

Vidal et al., (2000) studied the Influence of the content in fats and proteins on the anaerobic biodegradability of dairy wastewaters. COD concentrations between 3 and 5 kg COD/m3 was recommended, because these conditions ensure the highest levels of biodegradability and methanisation of both wastewaters and eliminate flotation problems. Ammonia production is significant in carbohydrate- rich wastewaters when the COD is high

Carta et al., (1999) studied Aerobic purification of dairy wastewater in Continuous regime reactor. Continuous flow pattern s used to have a low effluents COD and minimum ammonium concentration. The system is aerated by air injection. The COD removal is 92%-98%, with stabilized pH of 8.5. By increasing the inlet flow the quality of the effluents is increased but a solid residue was generated which is enriched in nutrients . The conc. of the nitrogen, nitrate-nitrogen and ammonium is relatively low. Nitrification and denitrification occurs under aerobic condition.

Ince et al,; (1998) studied the effect two-phase anaerobic digestion system when treating dairy wastewater. After the hydraulic retention time (HRT) of 2 days the overall, 90% COD and 95% BOD removal efficiencies at an organic loading rate (OLR) of 5 kg COD/m3 d and were achieved. In the pre-acidification reactor, a maximum of 60% conversion rate of COD to volatile fatty acids (VFAs) was achieved at an OLR of 12 kg COD/m3 d after which the conversion rate remained reasonably constant while a 60% removal of total fatty matter was obtained.

Michael et al., (1997) studied the treatment of milk powder wastewater using the AAO activated sludge configuration. With a HRT of 7 days and sludge 20 days and another system with a HRT of 48 min the overall nitrogen removal remain unchanged at 66%, sludge volume index (SVI) doesn't not improve. Phosphorous removal efficiency is reduced from 49%-20% which may lead to higher nitrate value. COD removal efficiency shows a excellent 90% removal rate.

Cordobo et al., (1995) studied the Improved Performance of a Hybrid Design over an Anaerobic Filter for the Treatment of Dairy Industry Wastewater at Laboratory Scale. A combined system of an anaerobic filter into an UASB resulted in an increased efficiency of removal of organic matter of 92% at the highest organic loading rate tested compared with that of the unmodified anaerobic filter. Both reactors were tested using dairy industry wastewater at identical operating conditions al 30°C.

Venkataraman et al.,(1992) studied the Determination of Kinetic Constants for a Two-Stage Anaerobic Upflow Packed-Bed Reactor for Dairy Wastewater. A two-stage upflow packed-bed (reactors in series) system was used for the treatment of dairy wastewater. Loadings that applied to reactor I and reactor H were 14.29 and 5"0 kg of chemical oxygen demand (COD) per m 3 per day. COD removal efficiencies at various loading rates were in the ranges of 93"8-98"5% and 72"5-84% for the two reactor systems, respectively. The combined biogas yield was between 0.196 and 0"386 m 3 gas/kg COD.

Warburton[a] et al., (1981) studied the treatment of dairy shed wastewater by anaerobic/aerobic process. On increasing the loading rate of anaerobic range (0.63-1.35 kg COD $m^{-3}d^{-1}$) has a low effect on the COD and TS removal at 71% for both parameters.

By increasing the HRT 5-10 days the BOD of anaerobic is increased by 30%. It shows that the hydraulic residence time plays a critical role in the anaerobic system.

Warburton[b] et al., (1981) studied the treatment of dairy shed wastewater by anaerobic/aerobic process. Stone media trickling filter is used after the anaerobic pre treatment.BOD effluent discharge is 160 mg/l at high recycle ratio and residence time of 3 days shows 72% removal in the aerobic phase. By changing the plant configuration the influence of the aerobic residence may be reduced and the overall final discharge of BOD is less than 80 mg/l. The solid accumulation rate of 56% of the BOD removed, or 250 g TS/m3 of influent would necessitate the removal or recycling provides a accumulated back solid phase to the anaerobic phase.

Warburton[c] et al., (1981) studied the treatment of dairy shed wastewater by anaerobic/aerobic process. A 2 stage system was developed for the treatment process for dairy wastewater. The overall average COD removal is 70% in the anaerobic phase was unaffected by the loading rate but in the aerobic phase 66% is removed at the optimum condition. The final discharge from aerobic tank is 700 mg/l COD. An overall treatment efficiency of 89.5% is achieved.

Research Gap

- Only a very few studies has been reported on the continuous electrochemical treatment process.
- A very less work on RSM modeling of Dairy wastewater treatment by continuous electrochemical method.

CHAPTER-4

Objectives

In the present work following objectives have been set to study the dairy wastewater treatment by continuous electrochemical treatment method with aluminum electrodes.

- To study the effect of various parameters like pH, current (I), flow rate (F) and treatment time (t) on % COD removal and specific energy consumed (kWh/kg of COD removed).
- RSM modeling and optimization of continuous electrochemical treatment method.

CHAPTER-5

Experimental setup and procedure

This chapter reports electrochemical treatment of dairy wastewater with aluminum electrodes. Experiments were conducted in a continuous setup to investigate the effect of current (I), pH, Flow rate (F) and and time (t) on % COD removal (Y_1) and specific energy consumed (Kwh/kg of COD removed) (Y_2).

5.1 Lab Scale Experimental setup

EC reactor with mono-polar electrode is connected in parallel. The reactor having a volume of 1.7 liter (l) (8cm x 8cm x 25cm) with working volume of 1.5 l, was fabricated with the plexi glass sheet. Aluminum electrodes having thickness of 1 mm, and length and width of 15 and 5 cm, respectively, were used as electrode for the experiments. The regulated direct current power supply (Make crown electronics Delhi India) was used to supply the current during the experiments. The experimental setup is shown in Fig. 5.1.

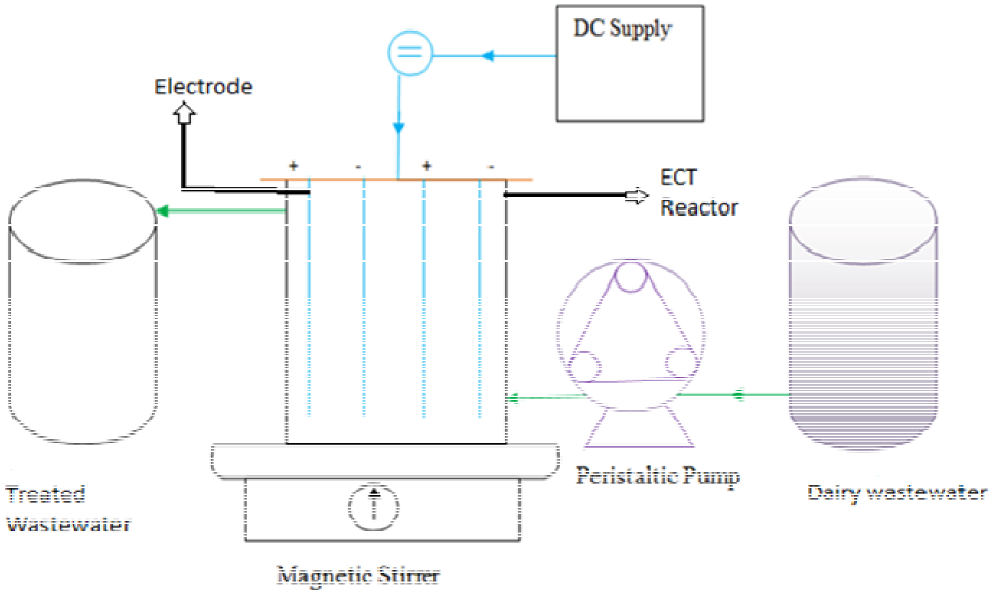

Fig 5.1 Experimental set-up of Continuous ECT System.

5.2 Wastewater

Dairy wastewater contain high amount of nutrients and carbon sources which provides favourable conditions for microbial growth. Due to this, the COD and nutrients concentration of dairy wastewater alters during storage. Therefore, to avoid this alteration in COD, simulated dairy wastewater (SDW) was prepared in this study. SDW was prepared in the laboratory by dissolving 4 g of milk powder of Nestle brand in one litre of distilled water in order to make constant wastewater composition throughout the experiments.

Several investigators used same method for making SDW (Ramasamy et al., 2004; Balannec et al., 2005; Leal et al., 2006, Kushwaha et al., 2010a; 2010b). The prepared SDW showed COD of 4320 mg/l. The SDW was prepared freshly whenever required and concentration was maintained uniform throughout the study.

4.2.3. Experimental Design and Experimental Procedure

Four factors and three level full factorial central composite design (CCD) based on response surface methodology (RSM) have been used for the experimental design, and data obtained from the experiments were analyzed by Design-Expert trial version. RSM is an effective statistical tool for collection of mathematical and statistical information useful for optimizing processes and can be used to evaluate the relative significance of several affecting parameters even in the presence of complex interactions. The main advantage of RSM is the reduced number of experiments needed to provide sufficient information to optimise the process.

Variables current (I); 0.5–2.5 A; electrolysis time (t): 30–120 min, pH: 5–10 and wastewater flow rate (F); 0.8-1.8 l/h have been considered as input parameters and % COD removal (Y_1) and specific energy consumed (KWh per kg of COD removed) (Y_2) have been taken as a responses of the system. Table 4.1 shows various operational variables and their levels whereas actual experimental design matrix is given in Table 4.2.

A total of 30 experiments, designed by RSM (Table 4.2), were conducted to study the effects of the four parameters on responses Y_1, $_{\text{and}}$ Y_2. The pH of the SDW was adjusted to desired level by adding 0.1 N NaOH or 0.1 N HCl solutions.

At the start of experiment, the SDW was adjusted to desired pH level as per experimental condition shown in table 4.2. Time, t, was measured when power supply was switched on. Current (I) was maintained constant during the run. After the desired t, samples were taken from the reactor and its final was measured using titration method. The percentage COD removal was calculated using the following relationship:

$$\text{Percent COD removal}\,(\mathrm{Y}_1) = \frac{(COD_0 - COD_f)100}{COD_0} \qquad \textbf{4.1}$$

where, COD_o is the initial COD concentration, and COD_f is the final COD concentration (mg/l) after *t* (min).

Table 4.1. Range of Variables and levels of the design model for Al electrode

Factor	Variable	Range of actual and coded variables		
		-1	0	1
A	Initial pH	5	7.5	10
B	Time of electrolysis, *t* (min)	30	75	120
C	Current, *I* (A)	0.5	1.5	2.5
D	Flow rate (F) (l/h)	0.8	1.3	1.8

Table 4.2. Full Factorial Design Used for the ECT of STW by Aluminum Electrodes

pH	Time, t (Minute)	Current (i)	Flow rate (liter/hour)
10	30	2.5	0.8
7.5	75	1.5	1.3
7.5	75	1.5	1.8
7.5	75	0.5	1.3
7.5	75	1.5	0.8
7.5	75	2.5	1.3
10	30	0.5	0.8
7.5	75	1.5	1.3
10	120	0.5	0.8
5	30	0.5	1.8
10	120	0.5	1.8
5	30	2.5	0.8
5	120	0.5	1.8
7.5	75	1.5	1.3
7.5	75	1.5	1.3
5	120	2.5	1.8
5	30	0.5	0.8
10	75	1.5	1.3
7.5	75	1.5	1.3
7.5	75	1.5	1.3
10	120	2.5	1.8
10	30	0.5	1.8
5	120	2.5	0.8
5	75	1.5	1.3
7.5	30	1.5	1.3
5	120	0.5	0.8
10	30	2.5	1.8
5	30	2.5	1.8
7.5	120	1.5	1.3
10	120	2.5	0.8

The data obtained from the experiments was analyzed using Design-Expert 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 responses.The data obtained by the experiments set suggested were fitted to a second-order polynomial model equation:

$$Y = b_o + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i=j}^{3} \sum_{i=j+1}^{4} b_{ij} X_{ij} \qquad \textbf{4.2}$$

Where, Y is Response; b_o, b_i, b_{ii}, b_{ij} are constant coefficients and X_i the uncoded independent variables. The significant terms in the model were found by analysis of variance (ANOVA) for each response. The model adequacies were checked by R^2, adjusted-R^2, predicted-R^2 and prediction error sum of squares (PRESS). A good model will have a large predicted R^2, and a low PRESS.

CHAPTER-6

Results and Discussion

6.0 GENERAL

The experimental results of COD removal from the synthetic dairy wastewater (SDW) by continuous electrochemical (ECT) method with Aluminum (Al) electrode have been discussed in this chapter. The treatment process for simulated dairy wastewater (SDW) shows a considerable reduction in the COD, and the results and their interpretations have been discussed in detail.

The ECT process was optimized using central composite design based on response surface methodology (RSM), for the responses % COD removal (Y_1) and specific electrical energy consumption (Kwh/kg of COD removed) (Y_2). Analysis of variance (ANOVA) has also been mentioned.

6.1 RESULTS AND DISCUSSION

6.1.1 Statistical Analysis

The responses (Y_1, Y_2) by continuous ECT of SDW by the Al electrode were calculated according to the setting of various operational parameters as given in design matrix of experiments (Table 6.1) and the results are shown in Table 6.1. Linear, interactive, quadratic and cubic models were fitted to the experimental data to obtain the regression equations. Sequential model sum of squares and model summary statistics were also tested to decide the adequacy of various models and results are given in Table 6.2 and Table 6.3 for responses Y_1, and Y_2, respectively. Sequential model sum of squares showed that quadratic model best fits the experimental data for responses Y_1, and Y_2. Cubic model was found to be aliased for all two responses.

The model gives coefficient of determination (R-squared) value of 0.9713 and 0.9948 for Y_1 and Y_2, respectively, and adjusted R-squared value of 0.9445 and 0.99 for Y_1 and Y_2, respectively, and predicted R-squared value of 0.9382 and 0.9662, respectively, which advocates a good correlation between the observed and the predicted values. Figure 6.1 and 6.2 also shows that actual values and predicted values are close to each other.

The analysis of variance (ANOVA) table shows model F-value of 36.24 and 206.42, for Y_1 and Y_2, respectively. This implies that models considered are significant (Table 6.4 and Table 6.5). For model terms to be significant, “Prob>F” values should be less than 0.05. “Prob>F” values larger than 0.100 indicate that the model term are insignificant. ANOVA table obtained from the response surface models shows that pH, t, I and F are significant terms for Y_1; and pH, t, i, pH x t, pH x I, and t x i are significant terms for Y_2.

The final quadratic equation in terms of coded factors for COD removal (Y_1) and energy consumption per litre of effluent treated are given below:

$$Y_1 = 84.21 + 3.60A + 7.91B + 2.98C - 2.06D - 0.15AB - 0.41AC - 0.040AD - 0.21BC - 0.62BD - 0.60CD + 0.83A^2 + 0.92B^2 + 0.78C^2 - 2.06D^2 \qquad \textbf{6.1}$$

$$Y_2 = 1.00 + 0.14A + 0.5B + 0.84C - 0.037D + 0.077AB + 0.092AC - 0.015AD + .47BC - 0.032BD - 0.040CD + 0.055A^2 + 7.311E\text{-}3B^2 - 0.043C^2 + 0.012D^2 \qquad \textbf{6.2}$$

Table 6.1. Full factorial Design used and responses for the ECT of STW by aluminum electrodes

pH	Time, t (Minute)	Current (i)	Flow rate (liter/hour)	%COD removal (Y_1)		Specific Energy Consumed (Y_2)	
				Actual	Predicted	Actual	predicted
10	30	2.5	0.8	85.18	85.40	0.996	1.070
7.5	75	1.5	1.3	82.3	84.21	1.031	0.999
7.5	75	1.5	1.8	78.19	80.09	0.999	0.974
7.5	75	0.5	1.3	79.27	82.01	0.170	0.112
7.5	75	1.5	0.8	84.57	84.20	0.958	1.048
7.5	75	2.5	1.3	89.16	87.96	1.677	1.799
10	30	0.5	0.8	81.43	81.06	0.104	0.051
7.5	75	1.5	1.3	85	84.21	1.031	0.999
10	120	0.5	0.8	96.43	95.74	0.352	0.445
5	30	0.5	1.8	67.38	66.18	0.063	0.175
10	120	0.5	1.8	91.78	91.58	0.319	0.358
5	30	2.5	0.8	78.58	78.64	0.786	0.727
5	120	0.5	1.8	84.43	83.96	0.201	0.131
7.5	75	1.5	1.3	88.2	84.21	1.031	0.999
7.5	75	1.5	1.3	86.54	84.21	1.031	0.999
5	120	2.5	1.8	91.28	91.52	2.451	2.484
5	30	0.5	0.8	72.93	72.66	0.063	0.076
10	75	1.5	1.3	87.97	88.63	1.217	1.196
7.5	75	1.5	1.3	84.19	84.21	1.031	0.999
7.5	75	1.5	1.3	83.6	84.21	1.031	0.999
10	120	2.5	1.8	97.48	97.50	3.087	3.079
10	30	0.5	1.8	74.48	74.42	0.114	0.092
5	120	2.5	0.8	93.29	93.10	2.647	2.673
5	75	1.5	1.3	80.56	81.43	0.826	0.911
7.5	30	1.5	1.3	75.38	77.22	0.461	0.453
5	120	0.5	0.8	87.43	87.96	0.212	0.160
10	30	2.5	1.8	81.84	81.18	0.919	0.951
5	30	2.5	1.8	74.14	74.58	0.755	0.666
7.5	120	1.5	1.3	93.34	93.03	1.488	1.559
10	120	2.5	0.8	98.18	99.25	3.458	3.326

Table 6.2. Sequential model Sum of Square for % COD removal (Y_1)

Source	Sum of square	DF	Mean Square	F Value	prob > F
Mean vs Total	214128.1	1	214128.1		
Linear vs Mean	1593.449	4	398.3622	128.2845	< 0.0001
2FI vs Linear	15.78165	6	2.630275	0.807995	0.5763
Quadratic vs 2FI	13.87058	4	3.467644	1.084083	0.3993
Cubic vs Quadratic	17.08223	8	2.135279	0.48375	0.8349
Residual	30.89811	7	4.414016		
Total	215799.2	30	7193.305		

Table 6.3. Sequential Model Sum of Square for specific Energy Consumption (Y_2)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Mean vs Total	31.03065	1	31.03065		
Linear vs Mean	18.68948	4	4.672369	30.14523	< 0.0001
2FI vs Linear	3.743582	6	0.62393	90.28639	< 0.0001
Quadratic vs 2FI	0.014785	4	0.003696	0.475865	0.7529
Cubic vs Quadratic	0.101306	8	0.012663	5.828196	0.0157
Residual	0.015209	7	0.002173		
Total	53.59501	30	1.7865		

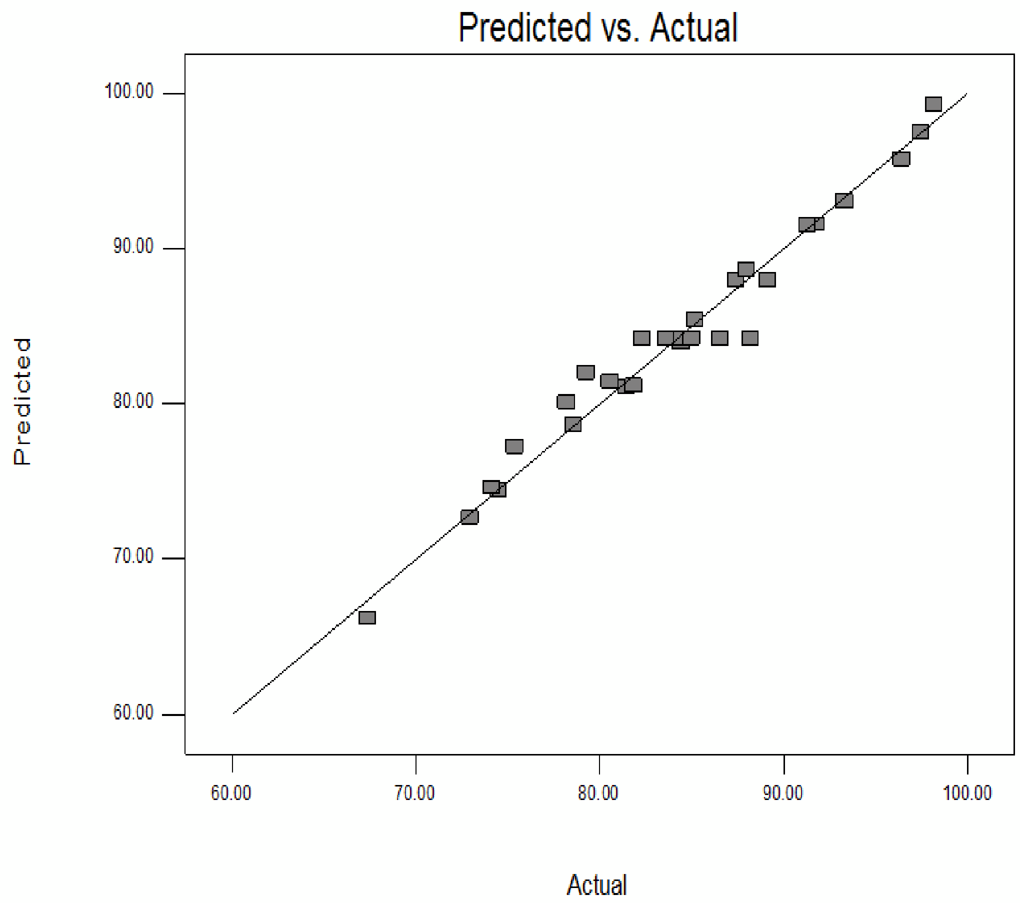

Figure 6.1. Comparison of Actual result with Predicted result for % COD Removal

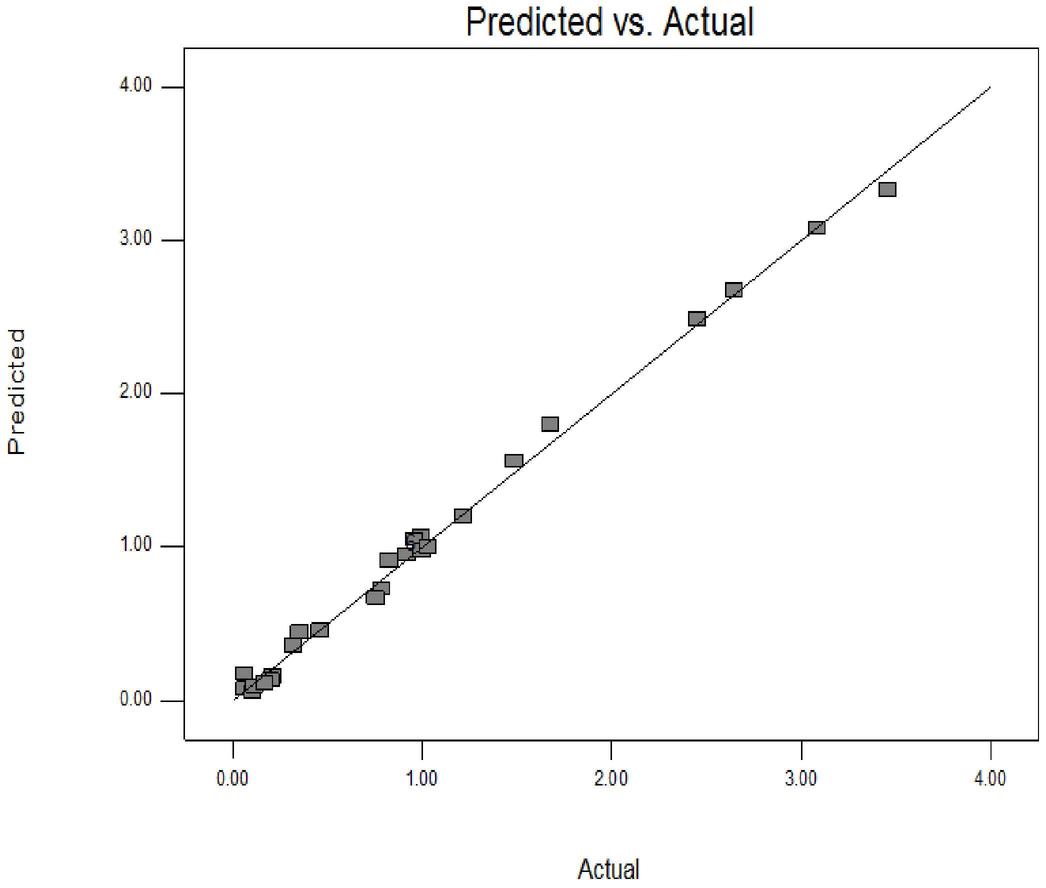

Figure 6.2. Comparison of Actual result with Predicted Result for Specific Energy Consumption

Table 6.4. ANOVA for % COD Removal

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	1623.101	14	115.9358	36.24478	< 0.0001	significant
A-pH	232.9201	1	232.9201	72.81736	< 0.0001	
B-t	1124.961	1	1124.961	351.6942	< 0.0001	
C-I	159.4303	1	159.4303	49.84237	< 0.0001	
D-rate	76.1378	1	76.1378	23.80281	0.0002	
AB	0.378225	1	0.378225	0.118244	0.7357	
AC	2.6896	1	2.6896	0.840844	0.3737	
AD	0.0256	1	0.0256	0.008003	0.9299	
BC	0.7056	1	0.7056	0.22059	0.6453	
BD	6.1504	1	6.1504	1.922787	0.1858	
CD	5.832225	1	5.832225	1.823317	0.1969	
A^2	1.769067	1	1.769067	0.55306	0.4686	
B^2	2.199223	1	2.199223	0.687539	0.4200	
C^2	1.561453	1	1.561453	0.488154	0.4954	
D^2	10.98074	1	10.98074	3.432887	0.0837	
Residual	47.98034	15	3.198689			
Lack of Fit	25.46746	10	2.546746	0.56562	0.7928	not significant
Pure Error	22.51288	5	4.502577			
Cor Total	1671.081	29				

Table 6.5 ANOVA for Specific Energy Consumption

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	22.44784	14	1.603417	206.4214	< 0.0001	significant
A-pH	0.365282	1	0.365282	47.0258	< 0.0001	
B-t	5.504561	1	5.504561	708.6484	< 0.0001	
C-I	12.79493	1	12.79493	1647.199	< 0.0001	
D-rate	0.024707	1	0.024707	3.180686	0.0948	
AB	0.09577	1	0.09577	12.32933	0.0031	
AC	0.135342	1	0.135342	17.42369	0.0008	
AD	0.003395	1	0.003395	0.437044	0.5186	
BC	3.467086	1	3.467086	446.3472	< 0.0001	
BD	0.016332	1	0.016332	2.1026	0.1676	
CD	0.025656	1	0.025656	3.302956	0.0892	
A^2	0.007712	1	0.007712	0.992823	0.3349	
B^2	0.000138	1	0.000138	0.017828	0.8956	
C^2	0.004893	1	0.004893	0.629903	0.4398	
D^2	0.000348	1	0.000348	0.04479	0.8352	
Residual	0.116515	15	0.007768			
Lack of Fit	0.116515	10	0.011652			
Pure Error	0	5	0			
Cor Total	22.56436	29				

6.2 Effects of I, F, t and pH on Y_1, and Y_2

To study the interactions of various parameters (I, F, t and pH) on responses Y_1, and Y_2 for the ECT of SDW by Al electrode, 3-D response surface graphs were considered (Fig. 6.3 and Fig. 6.4).

During the electrochemical treatment, anode is oxidized and Al^{3+} and OH^{-} ions are generated.

$Al\ (s) \rightarrow Al^{3+}\ (aq) + 3e$ **6.3**

$3H_2O\ (l) + 3e \rightarrow 3/2\ H_2\ (g) + 3OH^{-}$ **6.4**

Generated Al^{3+} and OH^{-} ions react to form various monomeric species such as $Al\ (OH)^{2+}$, $Al\ (OH)_2^{+}$, $Al_2\ (OH)_2^{4+}$ and $Al\ (OH)_4^{-}$ and various polymeric species such as $Al_6\ (OH)_{15}^{3+}$, $Al_7\ (OH)_{17}^{4+}$, $Al_8\ (OH)_{20}^{4+}$, $Al_{13}O_4\ (OH)_{24}^{7+}$, and $Al_{13}\ (OH)_{34}^{5+}$ [Bayramoglu et al. 2003] depending on the pH of the solution. The concentration of these species depends on the aluminum concentration in the solution. Percentage of various aluminium hydroxides products can be calculated from the following stability constants: [Duan et al., 2003]

$Al^{3+} + H_2O \rightarrow Al\ (OH)^{2+} + H^{+}$ $pK_1=4.95$ **6.5**

$Al\ (OH)^{2+} + H_2O \rightarrow Al(OH)_2^{+} + H^{+}$ $pK_2=5.6$ **6.6**

$Al\ (OH)_2^{+} + H_2O \rightarrow Al(OH)_3 + H^{+}$ $pK_3=6.7$ **6.7**

$Al\ (OH)_3 + H_2O \rightarrow Al(OH)_4^{-} + H^{+}$ $pK_4=5.6$ **6.8**

Above equations confirms that the hydrolysis constants cover a very narrower range and are compressed into pH region approximately 5-6. The dominant soluble species are Al^{3+} and $Al\ (OH)_4^{-}$ at low and high pH, respectively Duan et al., 2003].

Dairy wastewater has the isoelectric point (pH_{iso}) around 4.2 (Selmer-Olsen et al., 1996). Therefore, the milk proteins contained in the SDW are negatively charged at $pH > pH_{iso}$. These milk proteins get destabilized by positively charged hydrolysed aluminum species like Al^{3+}, $Al\ (OH)^{2+}$, $Al\ (OH)_2^{+}$, $Al_2\ (OH)_2^{4+}$, $Al_6\ (OH)_{15}^{3+}$, $Al_7\ (OH)_{17}^{4+}$, $Al_8\ (OH)_{20}^{4+}$, $Al_{13}O_4\ (OH)_{24}^{7+}$, and $Al_{13}\ (OH)_{34}^{5+}$ etc. which are dominating in acidic pH range. Due to this, the colloidal particles present in the SDW aggregate together and form bigger size flocs and are removed by settling. Also, the speciation of Al (III) shows that the $Al(OH)_3$ species are formed in the *pH* range of 5-7, which help in the removal of colloids by sweep coagulation.

In the present study, the % COD removal was found to increase with an increase in pH from 5-10 (Fig. 6.3 a). This trend of COD removal was also found true at every t (Fig. 6.3a). Therefore, coagulation and sweep coagulation is the true mechanism for the COD removal up to neutral pH.

Since, at alkaline pH range, Al $(OH)_4^-$ is dominates which is not a effective coagulant. Therefore, there should not be charge neutralization and destabilization of SDW in alkaline pH range. But Fig. 6.3 shows increased %COD removal at alkaline pH range.

During the electrolysis, at anode chlorine gas generated from NaCl (which is used in preparation of SDW). This generated chlorine, depending on pH of SDW, forms different chlorine species (Cl_2, HOCl and ClO^-). These generated species are capable of oxidizing the organics present in the SDW indirectly. ClO^-, which is fully dominating at higher pH ($pH \geq 10$) has been reported as superior oxidant among all chlorine species. At lower pH ($3 \leq pH \leq 5$) HOCl is fully dominating species (Deborde and Gunten 2008; Bansal et al., 2013). Thus, COD removal for alkaline pH range is attributed to electro-oxidation by formation HOCl and ClO^- which indirectly oxidize the COD from SDW.

Faraday's law describes the relationship between current density (J=I/A, A= area of electrrodes), time (t) and the quantity of anode material that dissolves in the solution. It is given as:

$$w = \frac{MJt}{ZF} \qquad \mathbf{6.9}$$

Where, w is the theoretical amount of ion produced per unit surface area by current density J passed for duration of time, t**.** Z is the number of electrons involved in the oxidation/reduction reaction, M is the atomic weight of anode material and F is the Faraday's constant (96486 C/mol). for Al, Z =3. M is the atomic weight (g/mol) of anode material, for Al, M =26.9815 g/mol; and F is the Faraday's constant (96486 C/mol).

Higher the amount of coagulants generated, higher is the % COD removal. The coagulants concentration depends directly on the concentration of aluminum ions generated by Al electrodes, which depends upon the t and I as per Faradays law. Therefore, concentration of coagulants are increased by increasing the value of t and I.

Fig. 6.3 b shows that increasing I increases % COD removal at all F value. Higher I, higher amount of coagulants are generated, and hence higher COD removal is achieved.

Also, with increase in t, % COD removal was found to increase (Fig.6.3a). This is due to the reason that at higher time higher amount coagulants and oxidants are generated, which remove higher amount of COD from SDW.

With increase in F value, % COD removal was found to increase up to F=1.3. For F>1.3, % COD removal was found to decrease.

Fig. 6.4 shows the effect of I, t, pH, and F on specific energy consumed (Y_2, kWh/Kg of COD removed). It may be seen in Fig. 6.4 that energy consumed always increased with t and I at all pH. Increasing t and I at lower pH showed lower specific energy consumed. However, at higher values of t and I increasing pH showed rapid increase in specific energy consumed.

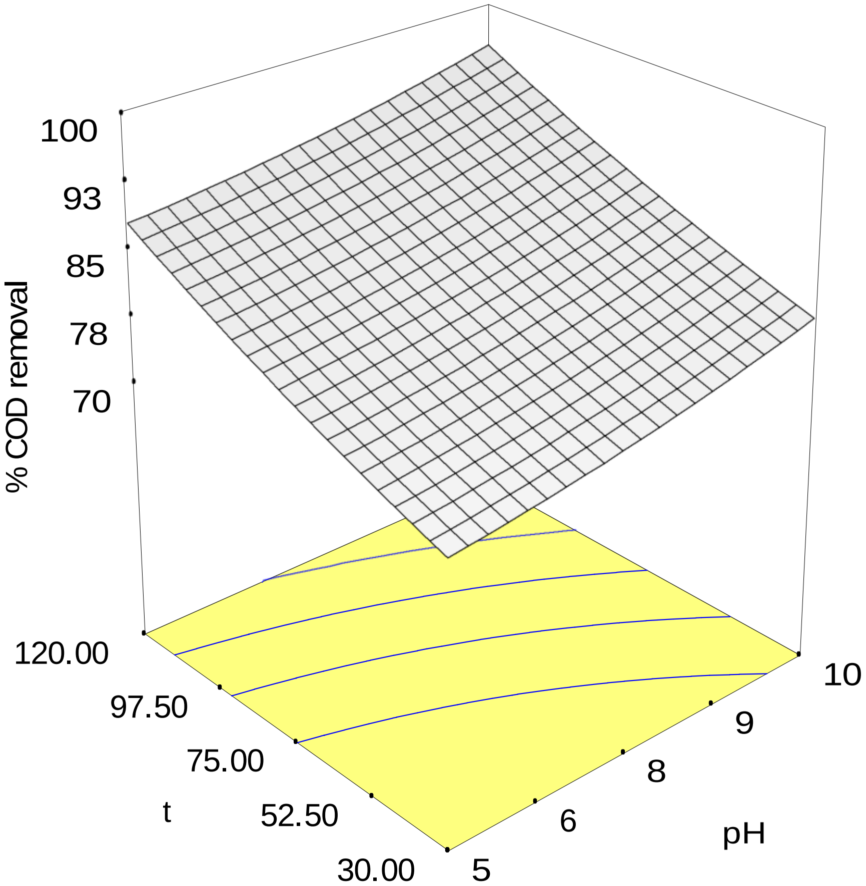

Fig. 6.3 (a) Three-dimensional response surface graphs for the continuous ECT of SDW. % COD Removal, versus *t* and *pH*

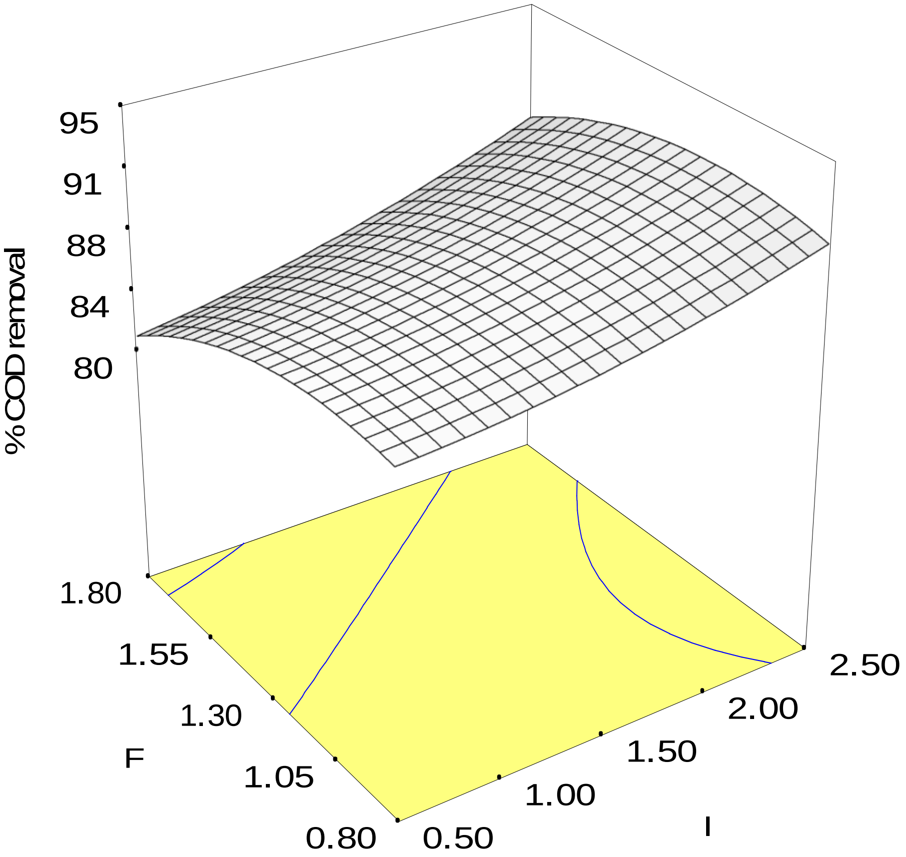

Fig. 6.3 (b) Three-dimensional response surface graphs for the continuous ECT of SDW. %COD Removal versus flow rate (F) and I

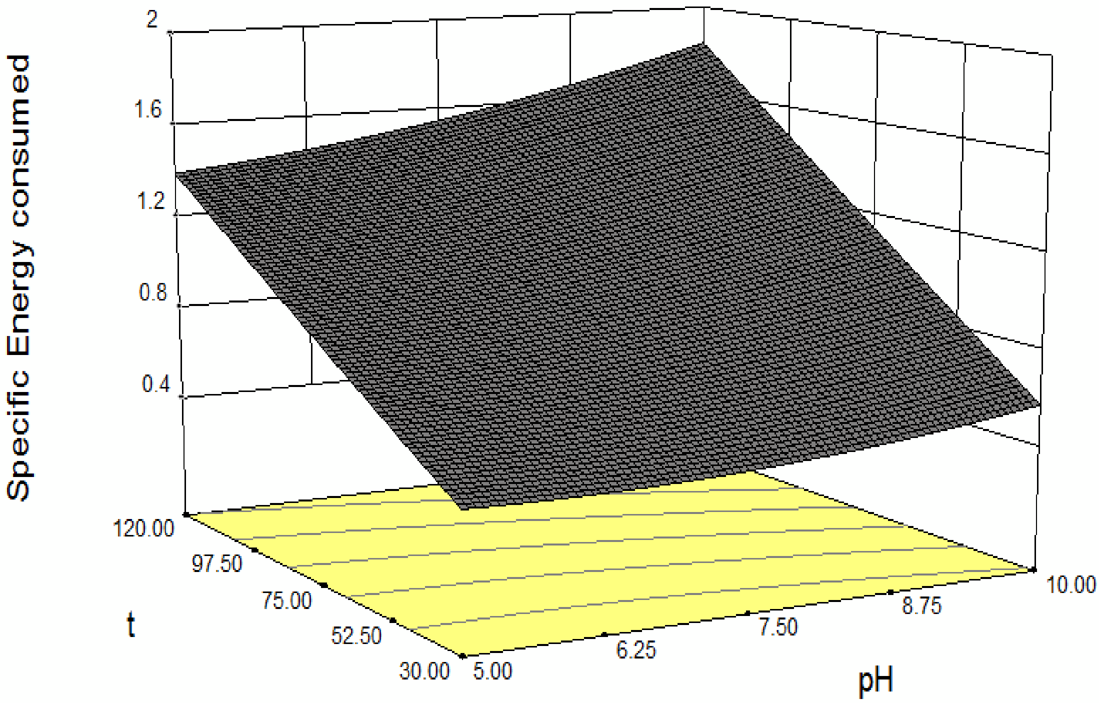

Fig. 6.4. (a) Three-dimensional response surface graphs for the ECT of SDW, Specific Energy Consumed (Y_2), versus *t* and *pH*

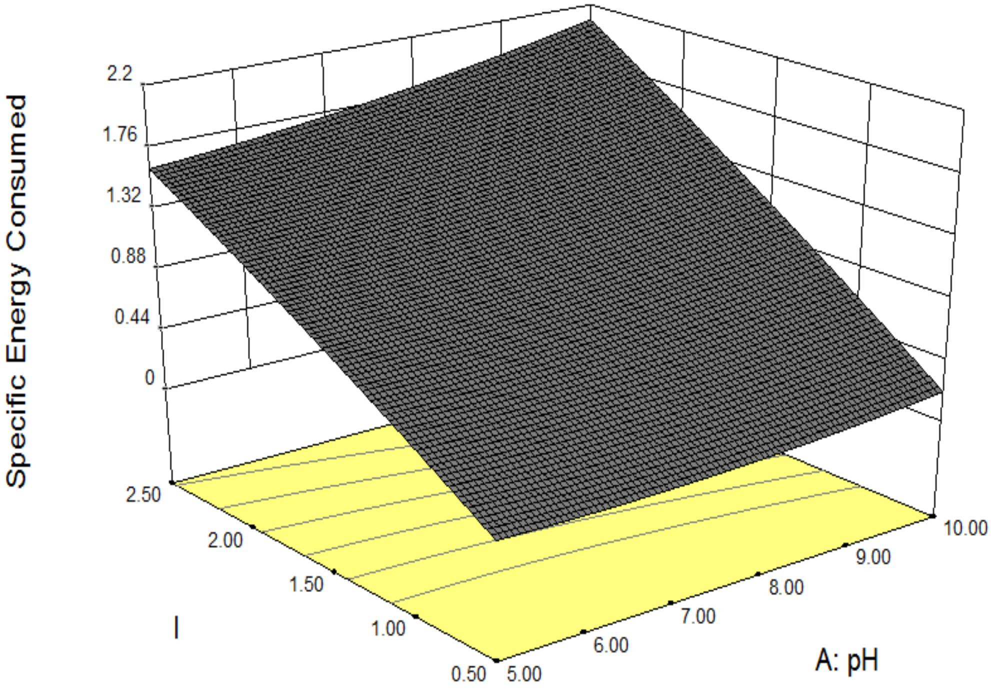

Fig. 6.4. (b) Three-dimensional response surface graphs for the ECT of SDW, Specific Energy Consumed (Y_2), versus *pH* and *I*

6.3 Optimization Analysis

ECT of SDW was also optimized by RSM in terms of maximization of response Y_1 and minimization of response Y_2 simultaneously with the help of desirability (D) function approach. For this purpose some constraints for operational parameters were applied (Table 6.6).

Table 6.7 shows the optimum values of operational parameters suggested by RSM. These optimized values of parameters are I = 0.5 A, t = 120 min, F= 1.08 l/h and pH = 6.75 which produced overall *D* = 0.883. The responses Y_1, and Y_2 were 90%, and 0.2 kWh/Kg of COD removed, respectively.

Table 6.6. Constraints applied for the optimization of ECT of STW by Al electrode.

Variables	Objective	Lower Limit	Upper Limit
I (A)	is in range	0.5	2.5
t (min)	is in range	30	120
pH	is in range	5	8
F (l/h)	is in range	0.8	1.8

Table 6.7. Optimum condition for ECT of STW by Al electrode.

Variables	Optimum values
I (A)	0.5
t (min)	120
pH	6.75
F (l/h)	1.08

CHAPTER-7

Conclusion

From the result and discussion for the treatment of simulated dairy wastewater (SDW) by continuous electrochemical treatment (ECT) following major conclusions were found:

- Sequential model sum of squares showed that quadratic model best fits the experimental data for responses Y_1, and Y_2.
- The model gives coefficient of determination (R-squared) value of 0.9713 and 0.9948 for Y_1 and Y_2, respectively, and adjusted R-squared value of 0.9445 and 0.99 for Y_1 and Y_2, respectively, and predicted R-squared value of 0.9382 and 0.9662, respectively.
- The analysis of variance (ANOVA) table shows model F-value of 36.24 and 206.42, for Y_1 and Y_2, respectively. This implies that models considered are significant.
- Optimum values of the process variables for the ECT of SDW were found to be pH=6.75, I=0.5 A, t=120 minute and F=1.08 l/h.
- The responses % COD removal Y_1, and specific energy consumed (kWh per kg of COD removed) Y_2 were 90%, and 0.2 kWh/Kg of COD removed, respectively.
- Hydrolysed aluminum species like Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al_2(OH)_2^{4+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$ etc. were found to be responsible for coagulation and subsequent adsorption of COD from the SDW in the acidic pH range of SDW
- COD removal for alkaline pH range is attributed to electro-oxidation by formation HOCl and ClO^- which indirectly oxidize the COD from SDW.

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