DAIRY WASTE WATER TREATMENT BY CONTINUOUS ELECTROCHEMICAL PROCESS

Dissertation

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by

Poonam Kumari
(Regn. No. 601211005)

Under supervision of

Dr. J. P. Kushwaha	Dr. V. K. Sangal
Assistant Professor	Assistant Professor
Department of Chemical Engineering	Department of Chemical Engineering

Department of Chemical Engineering
Thapar University
Patiala-147004, Punjab

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Certificate

This is to certify that the thesis entitled **"Dairy waste water treatment by continuous electrochemical process"**, 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 2014.

Date: 18/7/14

Poonam Kumari
(Roll No: 601211005)

It is certified that the above statement made by the student is correct to the best of our knowledge and belief.

18/07/13

Dr. V. K. Sangal
Assistant Professor
Department of Chemical Engineering
Thapar University, Patiala

18.07.14

Dr. J. P. Kushwaha
Assistant Professor
Department of Chemical Engineering
Thapar University, Patiala

Countersigned by

Dr. Rajeev Mehta
Professor and Head
Department of Chemical Engineering
Thapar University, Patiala

Dr. S. K. Mohapatra 18/7
Dean, Academic Affairs
Thapar University, Patiala

Abstract

Increased demand in processed milk products globally directed rapid growth of dairy industries. Subsequently, the discharged wastewater volume has also been increased. Due to high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), high load of dissolved and suspended solids, together with fats and nutrients, dairy wastewater must be treated before discharge.

Existing technologies for the treatment of dairy wastewaters includes biological and physico-chemical methods. Biological treatment methods showed significant COD removal, but these methods require high energy and/or operational controlling. Among physico-chemical methods coagulation/ flocculation are generally used, however, high reagent costs and low soluble COD removal are major drawback of these methods. Electrochemical (EC) treatment has been reported as a feasible method for the treatment of various type of wastewater including dairy wastewater. However, no study reports continuous EC treatment of dairy wastewater.

In the present work, actual dairy wastewater treatment by means of continuous electrochemical (EC) treatment was investigated using aluminum electrode. The effects of independent variables such as initial pH (pH_i), residence time (τ) and elapsed time (t) on the %COD removal (Y_1) and specific energy consumed (kWh per kg of COD removed, Y_2) were explored. In highly acidic pH values, Al^{3+} and various hydrolyzed species; $Al(OH)^{2+}$, $Al(OH)_2^+$ etc. were found responsible for COD removal. While, at highly basic pH ClO^- ions indirectly oxidized the COD.

Five level full factorial central composite design (CCD) of response surface methodology (RSM) was applied to design experiments and modeling. For optimization of the EC treatment of dairy wastewater, multi-response process optimization utilizing desirability function of RSM was used, and for this purpose, residence time (τ) and Y_2 were set to be minimized within elapsed time studied, whereas Y_1 was maximized.

ANOVA showed significant quadratic model fitting showing R^2 and adjusted R^2 of 0.862 and 0.776, respectively, for response Y_1, while respective values for Y_2 were found to be 0.98 and 0.96, respectively.

Optimized values of τ, t, Y_1 and Y_2 by RSM were found to be 141 min, 52 min, 67% and 4.62 kWh/kg of COD removed, respectively, with desirability value of 0.464. At this optimized set of variables actual experiment showed Y_1 and Y_2 values being 71.21% and 4.32 kWh/kg of COD removed, respectively.

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Poonam

Poonam

(601211005)

Table of Content

References

List of Figures

List of Tables

Nomenclature

AR	Analytical Reagent
AS	Activated Sludge
BOD	Biological Oxygen Demand
CCD	Central Composite Design
CIP	Clean in Place
COD	Chemical Oxygen Demand
CPCB	Central Pollution Control Board
EC	Electrochemical
ECF	Electro-Coagulation/Flotation
EF	Electro Flotation
Fig.	Figure
GCMMF	Gujarat Co-operative Milk Marketing Federation
HRT	Hydraulic Retention Time
IF	Impeller Flotation
Ref	Reference
RSM	Response Surface Methodology
SBR	Sequential Batch Reactor
SDW	Simulated Dairy Wastewater
TDS	Total Dissolved Solids
Ti/BDD	Titanium-based Boron-Doped Diamond film electrodes
TKN	Total Kjeldahl Nitrogen
TN	Total Nitrogen
TS	Total Solids
TSS	Total Suspended Solids

CHAPTER-1

INTRODUCTION

1.1 General

"Water is life to all living and non-living". It is a unique variety of natural resource among all sources available on earth. Every life requires water to sustain on the planet. Water is essential for all the important activities similar to food production, industries like energy, manufacturing and production. It plays a vital role in economic development and the general well being of the country.

United Nations stated that water is a social and cultural good, not only an economic commodity. Water is chemically a compound of oxygen and hydrogen. It is having highly distinctive physical and chemical properties. It has chemical formula: H_2O. Out of all the water available on the Earth, 97% of water is saline and is in oceans, 3% of water is freshwater available in rivers, glaciers and streams.

1.2 Dairy Industries

Industrialization is backbone for development of any country. But pollution caused by industries is a serious concern in the entire world. Of all industries, the food sector has one of the highest consumptions of water and is one of the biggest producers of effluent per unit of production. In addition to this, it generates a large volume of sludge in biological treatment. The dairy industry is this kind of example. Dairy technology has been defined as that branch of diary science which deals with processing of milk and the manufacture of milk products on an Industrial scale. During the past few years, the number of the diary plants of medium and large size has increased. Dairy industry is one of the biggest food industries in India, and India ranks first for producing milk. The dairy industry is one of a major source of waste water generation. The dairy industry in India has been reported to generate 6-10 litres of waste water per litre of the milk processed and generates between 3.739 and 11.217 million m^3 of waste per year (Monroy et.al, 1995). Depending upon the process employed, product manufactured and housekeeping exercised. Waste water is generated in milk processing unit, mainly in homogenization, pasteurization of fluid milk and the production of dairy products such as butter, cheese, milk powder etc. The details has been shown in **Table 1.1**

Table 1.1 Details of source of waste generation in dairy process

Dairy processes	Sources of waste	
Preparation stages		
Milk receiving/ storage	Poor drainage from tankers	Foaming
	Spills and leakages from hoses and pipes	Cleaning operations
	Spills from storage silos/ tanks	
Pasteurisation/ ultra heat treatment	Liquid losses/ leaks	Foaming
	Recovery of downgraded product	Deposits on the surfaces of pasteurisation and heating equipment
	Cleaning operations	
Homogenisation	Liquid losses/ leaks	Cleaning operations
Separation / clarification (centrifuge, reverse osmosis)	Foaming	Pipe leaks
	Cleaning operations	
Product processing stages		
Market milk	Foaming	Sludge removal from clarifiers/ separators
	Product washing	Leakages
	Cleaning operations	Damaged milk packages
	Overfilling	Cleaning of filling machinery
	Poor drainage system	
Cheese making	Overfilling vats	Spills and leaks
	Incomplete separation of whey from curd	Cleaning operations
	Use of salt in making cheese	
Butter making	Cleaning operations	Vacreation (reduced pressure pasteurisation using steam) and salt use
	Product washing	
Powder manufacture	Spills of powder handling	Stack losses
	Start-up and shut-down losses	Cleaning of evaporators and driers
	Plant malfunction	Bagging losses

Ref: http://www.water.wa.gov.au/PublicationStore/first/104028.pdf

The waste water of dairy industry contain large quantities of milk constituents such as casein, lactose, fat, inorganic salt with detergents & sanitizers used for washing. Process flow chart of a particular dairy industry is shown in Fig. 1.1

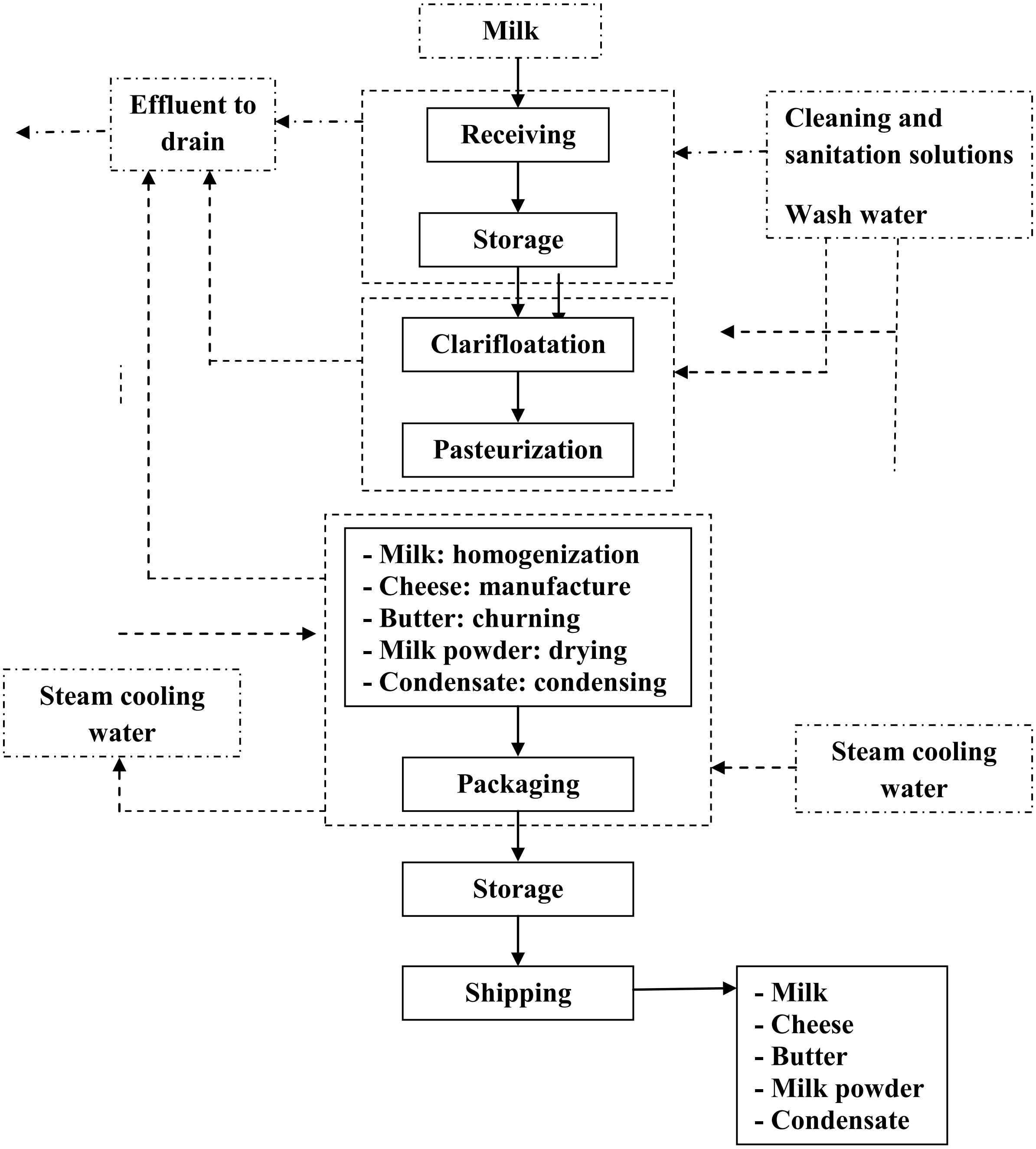

Fig 1.1 Process flow chart of dairy industry

Source: http://www.fao.org/wairdocs/lead/x6114e/x6114e06.htm

Many milk processing unit use “clean in place” (CIP) system. It pumps cleaning solutions through all equipment in this order ; caustic solution (sodium hydroxide) wash, water rinse, acid solution (phosphoric or Nitric acid) wash, water rinse, and sodium hypo-chlorite disinfectant (Tikariha and Sahu, 2014). These chemicals by default become a part of waste water. Lots of water is used to clean dairy processing plants. The resulting waste water can include detergent, salts, sanitizers, base and organic matter. Waste water volume and strength fluctuated from day to day. This is due to partly differences in production. The data of effluent or waste water volume per unit of product processed (litres waste water/kg product), waste water concentration (mg/litre) and weight of waste generated per unit of product processed (g waste/kg product) also changes. Another two major reasons are Climate of the area and production of the dairy plant. These factors are also responsible for changing waste water character. This variation is due to many reasons e.g. from one industry to another dairy industry, from season to season and from hour to hour and from handling person to person.

Waste water affects the soil quality and soil structure. Some part of waste water can also leach is to underlying groundwater and affect its quality. The problem is more severe, when it concerns waste water discharge before treatment from dairy or milk processing industry. It is one of the biggest sources of industrial effluents in many countries like India and Europe. A typical European dairy factory generates approximately 50m^3 waste water daily. It contains considerable concentration of organic matter (fat, protein and carbohydrates) and nutrients mainly (Nitrogen and phosphorous) originating from the milk and the milk products (Omil et al., 2002; Demirel et al., 2005). The annual cost of treatment and disposal for the typical plant are in million dollars.

Disposal of untreated water is rapidly becoming a major economic and social problem. Every dairy industry is facing the problem of water treatment, utilization and disposal of the waste water. Disposal of waste water into rivers, fields, land and other aquatic bodies without or with partial treatment will soon offer a serious problem to health and hygiene.

It is a big challenge to find solution for cheaper treatment, utilization and easy disposal of waste water from milk processing unit, worldwide. The sludge of Dairy characterized by low heavy metal content and high amounts of degradable carbon can prevent the depletion of soil nutrients that results harvesting in forest plantation (Omil et al., 2007). Anaerobic bi hydrogen production as a source of energy from dairy industry waste water treatment in sequencing batch reactor was studied also (Venkata et al., 2007). Dairy industry sewage sludge can be used as a fertilizer for an acid soil (Suarez et al., 2004). The dairy waste effluent provides nutrients and water for crop growth (Macoon et al., 2002). 5% dairy waste solids in feeding diet of sheep and swine is another means for combating solid disposal problem of dairy industry (Thompson et al., 1998).

Water recycling is very important these days due to increased water demand. The urbanization and industrialization, leads to increased standard of living, reduced rainfall, depletion in natural water resources. Reed bed treatment method can be used for the treatment of dairy waste water and microbes (Mantovi et al., 2002). The present research on study of waste water quality may become very useful for milk processing industry to plan its appropriate disposal, recycling and utilization strategy in order to avoid pollution as well as keeping environment clean.

Indian Dairy Industry overview: The packaged milk segment is dominated by the dairy cooperatives. Gujarat Co-operative Milk Marketing Federation (GCMMF) is the biggest (supplier http://www.aavinmilk.com/dairyprofile.html). All other local dairy cooperatives have their local brands named as e.g. Warana in Maharashtra, Gokul, Verka in Punjab, Vijaya in Andhra Pradesh, Saras in Rajasthan, Aavin in Tamil Nadu, etc. Other private players include J K Dairy, Indiana Dairy, Heritage Foods, Dairy Specialties, etc. Amrut Industries, once a leading player in the sector has turned bankrupt and is facing liquidation.

There are a large variety of traditional Indian milk products such as (http://www.aavinmilk.com/dairyprofile.html)

Makkhan - unsalted butter.
Ghee - butter oil prepared by heat clarification, for longer shelf life.
Kheer - a sweet mix of boiled milk, sugar and rice.
Basundi - milk and sugar boiled down till it thickens.
Rabri - sweetened cream.
Dahi - a type of curd.
Lassi - curd mixed with water and sugar/ salt.
Channa/Paneer - coagulate milk mixed with lactic acid.
Khoa - evaporated milk, used as a base in most of sweets.

Western milk products such as butter, cheese, and yogurt have gained popularity in the Indian market. The consumption has been expanding with increasing urbanization. The list of major player in dairy industry along with products is given below

Table 1.2 Some of the major dairy products manufacturers in the country

Company	Brands	Major Products
Nestle India Limited	Milkmaid,Cerelac, Milo, Lactogen, Everyday	Sweetened condensed milk, milk powder, malted foods and Dairy whitener
Milkfood Limited	Milkfood	Ghee, ice cream, and other milk products
SmithKline Beecham Limited	Horlicks, Viva, Maltova	ghee, Malted Milk food, butter, powdered milk, milk fluid and other milk based baby foods.
Punjab State Cooperative Milk Producers' Federation Ltd (Milkfed)	Verka	Liquid milk, skimmed milk powder, whole milk powder, ghee, infant food, butter, cheese, lassi, sweetened flavoured milk, ice cream, malted food, vigour
Indodan Industries Limited	Indana	Condensed milk, skimmed milk powder, dairy milk whitener, whole milk powder, chilled and processed milk
Gujarat Co-operative milk Marketing Federation Limited	Amul	Butter, Cheese and other milk products
H.J. Heinz Limited	Farex, Complan, Glactose, Bonniemix, Vitamilk	Infant Milk food, malted Milk food
Britannia	Milkman	Flavoured milk, cheese, Milk Powder, Ghee
Cadbury	Bournvita	Malted food

1.3 Health and Ecological Effect

Dairy wastewater, both raw and treated, include pathogens that may re-infect the herd. It can cause disease in humans also. Proper management during reuse and the use of exclusion periods before grazing are necessary to prevent infection in both human and animals.

Faecal and other wastes like urine, respiratory secretions, sloughed skin etc. collected by waste management systems contain large numbers of pathogens. Such pathogens can cause diseases in animals grazing on the pasture or crops to which manure and effluent have been applied, and to humans via occupational exposure, or via exposure to contaminated water, food, air or soil. The term zoonoses is used. It means those microorganisms of animal origin that can cause diseases in humans".

The list of pathogens found in dairy shed wastewater is long and described in the Table 1.3

Table 1.3 List of Pathogens found in dairy industry

	Pathogen	Disease in dairy cattle	Disease in humans	Transmission
Bacteria	*Salmonella* spp.	May be asymptomatic	Yes	Food, water, and clothing
	Escherichia coli	No	Yes (pathogenic strain O157:H7)	Food and water
	Listeria monocytogenes	May be asymptomatic	Yes	Food, water, and clothing
	Mycobacterium paratuberculosis	Yes (Johne's disease)	Uncertain (possible link to Crohn's disease)	Respiratory
	Campylobacter jejuni	No	Yes (gastroenteritis)	Food and water
	*Leptospira*spp.	Yes	Yes	Urine
Protozoa	*Cryptosporidium parvum*	May be asymptomatic	May be asymptomatic	Ingestion of water
	Giardia spp.	May be asymptomatic	May be asymptomatic	Ingestion of water

(Ref: Sobsey et al. 2006).

1.4 Wastewater Characteristic

Dairy effluent contains soluble organics, suspended solids, trace organics. Dairy wastewaters are characterised by high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), high load of dissolved and suspended solids together with fats and nutrients (Kushwaha et al., 2010a; Hepsen and Kaya, 2012). The suspended matter content of milk waste is considerable mainly due to fine curd found in cheese waste. The pollution effect of dairy waste is attributed to the immediate and high oxygen demand. Casein decomposition leads to the formation of heavy black sludge's and strong butyric acid odours and characterize milk waste pollution.

It's quality and quantity depends largely on the quantity of milk processed and type of product manufactured. The waste water of dairy contains large quantities of milk constituents such as casein, inorganic salts, besides detergents and sanitizers used for washing. It has high sodium content from the use of caustic soda for cleaning. Typical Characteristics of dairy industry wastewaters reported by various authors are given in Table 1.4.

Table 1.4 Characteristics of dairy industry wastewater

Waste Type	COD	BOD	pH	TSS	TS	References
Milk & Dairy Products factory	10251.2	4840.6	8.34	5802.6		Cristian, 2010
Dairy effluent	1900 - 2700	1200 - 1800	7.2 - 8.8	500 -740	900 - 1350	Deshannavar et al., 2012
Arab Dairy Factory	3383 ± 1345	1941± 864	7.9 ± 1.2	831 ± 392		Tawfik et al., 2007
Dairy waste water	2500 - 3000	1300 - 1600	7.2 - 7.5	72000 - 80000	8000 - 10000	Qazi et al., 2011
Dairy effluent (CPCB 1993)	1120 - 3360	320 - 1750	5.6 - 8	28 - 1900		Lata et al., 1999
Bhandara Co-operative dairy industry wastewater	1400 - 2500	800 - 1000	7.1-8.2	1045 - 1800	1100 - 1600	Gotmare et al., 2011
Aavin dairy industry washwater	2500 - 3300		6.4 -7.1	630 -730	1300 - 1400	Sathyamoorthy et al., 2012
Dairy industry wastewater	2100	1040	41858	1200	2500	Arumugam, 2008

1.4.1 Discharge Standard

Indian government have decided discharge standard for every industry. The list contain discharge standard almost for every industry. Every Indian industry, small or big, needs to follow these discharge standards strictly for our environment and better climate. Table 1.5 shows discharge standard decided by central pollution control board for particularly dairy industry and Table 1.6 shows discharge standard in general.

Table 1.5 Standards for emission or discharge of environmental pollutants from dairy industries

S.No	**Parameter**	**Concentration in mg/l except Ph**	**Quantum per product processed**
1	pH	6.5-8.5	-
2	*BOD [3 days at 27oC]	100	-
3	Suspended Solids	150	-
4	Oil and Grease	10	-
5	Waste Water generation	-	3m3/Kl of milk

(Ref: http://cpcb.nic.in/Industry_Specific_Standards.php)

BOD may be made stringent upto 30 mg/l if the recipient fresh water body is a source for drinking water supply. BOD shall be upto 350 mg/l for the chilling plant effluent for applying on land provided the land is designed and operated as a secondary treatment system with suitable monitoring facilities. The drainage water from the land after secondary treatment has to satisfy a limit of 30 mg/l of BOD and 10 mg/l of nitrate expressed as _N‘. The net addition to the groundwater quality should not be more than 3 mg/l of BOD and 3 mg/l of nitrate expressed as _N‘. This limit for applying on land is allowed subject to the availability of adequate land for discharge under the control of industry, BOD value is relaxable upto 350 mg/l, provided the wastewater is discharged into a town sewer leading to secondary treatment of the sewage.

Suspended solids limit is relaxable upto 450 mg/l, provided the wastewater is discharged into town sewer leading to secondary treatment of the sewage.

Table 1.6 General Standards for discharge of environmental pollution

Sl. No.	Parameter	Standards			
		Inland surface water	Public sewers	Land of irrigation	Marine / coastal areas
1.	Colour and odour	All efforts should be made to remove colour and unpleasant odour as far practicable.	--	All efforts should be made to remove colour and unpleasant odour as far practicable.	All efforts should be made to remove colour and unpleasant odour as far practicable.
2.	Suspended solids mg/l, max.	100	600	200	a. For process waste water 100 b. For cooling water effluent 10 per cent above total suspended matter of influent
3.	Particle size of suspended solids	Shall pass 850 micron IS Sieve	--		a. Floatable solids, solids max. 3 mm. b. Setleable solids. Max 856 microns
4.	pH value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
5.	Temperature	Shall not exceed 5°C above the receiving water temperature.	--	--	Shall not exceed 5°C above the receiving water temperature.
6.	Oil and grease, Mg / l max.	10	20	10	20
7.	Total residual chlorine, mg/l max	1.0	--	--	1.0
8.	Ammonical	50	50	--	50

	nitrogen (as N), mg/l, max.				
9.	Total nitrogen (as N); mg/l, max.	100	--	--	100
10.	Free ammonia (as NH3), mg/l, max	5.0	--	--	5.0
11.	Biochemical oxygen demand (3 days at 27^{o}C), mg/l, max.	30	350	100	100
12.	Chemical oxygen demand, mg/l, max.	250	--	--	250
13.	Arsenic (as As) mg/l, max	0.2	0.2	0.2	0.2
14.	Mercury (As Hg), mg/l, max.	0.01	0.01	--	0.01
15.	Lead (as Pb) mg/l, max.	0.1	0.1	--	2.0
16.	Cadmium (as Cd) mg/l, max.	2.0	1.0	--	2.0
17.	Hexavalent chromium (as Cr + 6), mg/l, max.	0.1	2.0	--	1.0
18.	Total chromium (as Cr) mg/l, max.	2.0	2.0	--	2.0
19.	Copper (as Cu) mg/l, max.	3.0	3.0	--	30
20.	Zinc (as Zn) mg/l,	5.0	15	--	15

	max.				
21.	Selenium (as Se) mg/l, max.	0.05	0.05	--	0.05
22.	Nickel (as Ni) mg/l, max.	3.0	3.0	--	50
23.	Cyanide (as CN) mg/l, max.	0.2	2.0	0.2	0.2
24.	Fluoride (as F) mg/l, max.	2.0	15	--	15
25.	Dissolved phosphates (as P), mg/l, max.	5.0	--	--	--
26.	Sulphide (as S) mg/l, max.	2.0	--	--	5.0
27.	Phenolic compounds (as C_6H_5OH) mg/l, max.	1.0	5.0	--	5.0
28.	Radioactive materials :				
	a. Alpha emitters micro cure mg/l, max.	10^{-7}	10^{-7}	10^{-8}	10^{-7}
	b. Beta emitters micro cure, mg/l, max.	10^{-6}	10^{-6}	10^{-7}	10^{-6}
29.	Bio-assay test	90% suivival of fish after 96 hours in 100% effluent	90% survival of fish after 96 hours in 100% effluent	90% survival of fish after 96 hours in 100% effluent	90% sunfival of fish after 96 hours in 100% effluent.

30.	Manganese (as Mn)	2 mg/l	2 mg/l	2 mg/l	2 mg/l
31.	Iron (as Fe)	3 mg/l	3 mg/l	3 mg/l	3 mg/l
32.	Vanadium (as V)	0.2 mg/l	0.2 mg/l	--	0.2 mg/l
33.	Nitrate Nitrogen	10 mg/l	--	--	20 mg/l

(Ref: http://cpcb.nic.in/GeneralStandards.pdf)

1.5 Treatment Method for Dairy Wastewater

Existing technologies for the treatment of dairy wastewaters includes biological and physico-chemical methods (Vourch et al., 2008; Kushwaha et al., 2010b; Demirel et al., 2005; Mohseni-Bandpi et al., 2004; Sirianuntapiboonet al., 2005; Rusten et al. 1993). Various biological methods such as activated sludge process, trickling filters aerated lagoons, anaerobic sludge blanket (UASB) reactor, anaerobic filters, sequencing batch reactor (SBR), etc are generally used for the dairy industry wastewaters (Demirel et al., 2005). Whereas, Physico-chemical treatment methods consisting of coagulation/flocculation, electro-chemical treatment (ECT) adsorption and membrane processes like nanofiltration (NF) and/or reverse osmosis (RO) have also been reported (Arvanitoyannis and Giakoundis, 2006).

Biological treatment methods showed significant COD removal, but these methods require high energy and/or operational controlling (Chen and Liu, 2012; Kushwaha et al., 2011a). Among physico-chemical methods coagulation/ flocculation are generally used, however, high reagent costs and low soluble COD removal are major drawback of these methods (Borbón et al., 2014; Demirel et al., 2005). Electrochemical (EC) treatment has been reported as a feasible method for the treatment of various type of wastewater including dairy wastewater (Kushwaha et al., 2010a; Borbón et al., 2014; Mahesh et al., 2006; Feng et al., 2007; Raju et al., 2008; Maiti et al., 2011; Kushwaha et al., 2011b; Sengil and Ozacar, 2006; Tchamango et al., 2010; Qasim et al., 2013; Sharma, 2014; Yavuz et al., 2011). Assesment of the current research on dairy wastewater treatment is available in open literature (Arvanitoyannis 2006; Kushwaha et al., 2011a). Table 2.1 tabulates reported studies for electrochemical treatment of dairy wastewater.

1.6 Objectives

In the present work, continuous electrochemical (EC) treatment of actual dairy industry wastewater was evaluated using aluminum (Al) electrode. Following objectives were set:

- To study the effects of three variables, namely initial pH (pHi), residence time (τ) and elapsed time (t) on the %COD removal and specific energy consumed (kWh per kg of COD removed).
- Modeling and optimization of continuous EC treatment of dairy wastewater using five level full factorial central composite design (CCD) under response surface methodology (RSM).

CHAPTER-2

LITERATURE REVIEW

The dairy industries are considered as most polluting industries because generation of wastewater is very large in terms of volume and contamination level. Dairy effluent contains soluble organics, suspended solids, trace organics. All these components contribute largely towards their high biological oxygen demand (BOD_5) and chemical oxygen demand (COD). Dairy wastewaters are generally treated using aerobic and anaerobic biological methods. In past few years, there are so many people who are doing research work on electrochemical treatment methods. In this chapter, review of literature on the electrochemical treatment technologies for wastewater treatment is presented.

Bensadok et al. (2011) investigated electrochemical treatment of synthetic dairy wastewater in batch reactor using aluminium electrode. The removal of COD, phosphate and turbidity was observed, and it was reported that the removal efficiency of COD, phosphate and turbidity attained respectively 80%, 59% and 96% at optimal values of current density, initial pH, NaCl concentration and electrolysis time were 0.5 mA/cm^2, 6.6, 1.5 g/L and 2 minute respectively.

Tchamango et al. (2010) used artificial dairy effluents. The experiments were carried out using a soluble aluminium anode. Additional experiments related to the mass variations of electrodes were also carried out from which it appeared that the anode and the cathode were consumed during the electrolysis. The flocks were separated by filtration. The analysis of the filtrates showed that the 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.

The poor lowering of the COD due to lactose was not eliminated properly during electrocoagulation. This result (low conductivity, neutral pH) tends to show that it may be possible to recycle the treated water for some industrial uses. The mass of the aluminium anode dissolved during the treatment is lower compared to the quantity of the aluminium salt used in chemical coagulation. These two observations clearly show that the electro-coagulation technique is more performing.

Sengila et al. (2006) used wastewater which was obtained from a tank containing a mixture of exhaust solutions at a dairy factory in Turkey (Sakarya). They used bench-scale EC reactor with bipolar electrodes in parallel connection. The results of experiments showed that COD and oil–grease was effectively removed at initial pH 6–7 when the initial concentration of COD and oil–grease was 18,300 and 4570 mg/L, respectively. The results also indicated that the removal efficiency of the COD and oil–grease was raised to 98 and 99%, respectively after treatment. The optimal current density was 0.6 mA/cm^2 for an operating time of 1 min. Under these conditions, the electrode consumption is 0.0204 g electrode/kg COD removed. At the optimal conditions the power requirement was 0.003 kWh/kg COD. The experimental results showed that optimal NaCl amount was 0.3 g/L. The gelatinous charged hydroxo cationic complexes generated in EC can effectively remove pollutants by adsorption. The equilibrium data fit well in the Freundlich adsorption isotherm model. The predictions of Freundlich adsorption isotherm model are in very good agreement to the experimental data.

Chen (2004) reviewed electrochemical methods for treatment of wastewater. This paper reviews the development, design and applications of electrochemical technologies in water and waste water treatment. Particular focus was given to electrode position, electrocoagulation, electroflotation (EF) and electrooxidation. Over 300 related publications were reviewed with 221 cited or analyzed. Electrode position is effective in recover heavy metals from waste water streams. It is considered as an established technology with possible further development in the improvement of space-time yield. EC has been in use for water production or wastewater treatment. It is finding more applications using either aluminum, iron or the hybrid Al/Fe electrodes. The separation of the flocculated sludge from the treated water can be accomplished by using EF. The EF technology is effective in removing colloidal particles, oil & grease, as well as organic pollutants. It is proven to perform better than dissolved air flotation, sedimentation, impeller flotation (IF). The newly developed stable and active electrodes for oxygen evolution would definitely boost the adoption of this technology. Electrooxidation is finding its application in wastewater treatment in combination with other technologies. It is effective in degrading the refractory pollutants on the surface of a few electrodes. Titanium-based boron-doped diamond film electrodes (Ti/BDD) show high activity and give reasonable stability. Its industrial application calls for the production of Ti/BDD anode in large size at reasonable cost and durability.

Kushwaha et al. (2010) used simulated dairy wastewater (SDW). The main characteristics of the used SDW were: COD= 3900 mg/l, total solids (TS) = 3090 mg/l, turbidity = 1744 NTU, conductivity = 220s/cm, chloride = 31mg/l, total nitrogen (TN) = 113.18 mg/l and pH = 6.3–6.8. These characteristics were maintained uniform throughout the study. In this 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 parameter values J,m,t and pH were varied between 61.73–308.64A/m^2, 0–2 g/l, 10–90 min and 5–11, respectively. Optimum value of J, t and pH were found 270A/m^2, 50 min, and 7.0, respectively, while m after analysis was found to be zero. Optimum COD removal efficiency was found ≈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.

Qasim et al. (2013) made an attempt to study the characterization and effect of electrocoagulation, alum and powdered activated charcoal on three selected food industrial effluents. The treatments were studied in relation with important water quality parameters mainly associated with estimation of pH, EC, TDS, COD, Turbidity and Hardness of the treated effluents. In this, thorough treatment studies were carried out on diary, sweet-snacks and ice-cream industrial effluents. Characterization of the effluents was also carried out to check the pollution potential of these effluents. The electrocoagulation was performed with the help of aluminium electrodes at different time intervals in order to check the variations in effluent parameters. The studies revealed that electrocoagulation and adsorption have better ability to reduce the water parameters.

Kushwaha et al. (2013) investigated treatment of simulated dairy wastewater (SDW) in terms of COD and total Kjeldahl nitrogen (TKN) removal by aerobic sequential batch reactor (SBR). Main characteristics of the prepared SDW were: COD = 3900 mg/L, total Kjeldahl nitrogen (TKN) = 113.18 mg/L, turbidity = 1744 NTU, conductivity = 220 μs/cm, chloride = 31 mg/L, and pH = 6.5.

They optimized SBR for various operating parameters and four phase study was carried out by varying hydraulic retention time(HRT), filling time of SDW to the reactor, anoxic phase introduction after filling phase and react phase. Kinetic study has also been performed at various HRT. Optimum HRT (HRT opt) of 1 d with volume exchange ratio of 0.5 was found to sufficient to treat SDW. The problem of disposal of wasted activated sludge (AS) during the SBR cycle, elemental and thermo-degradation analysis of sludge was performed to understand its thermal degradation characteristics and possibility to utilize wasted fuel.

Moussavi et al. (2011) were examined various operating variables for their effects on TPH removal; these variables included electrode materials (aluminum, iron, and steel), water pH (4 to 11), current density (2 to 18 mA/cm^2), reaction time (2 to 60 min), aeration, and the mode of operation (batch and continuous). They used petroleum contaminated groundwater. Batch experiments indicated that the maximum TPH removal was achieved using steel-iron as the anode–cathode electrode arrangement. A pH level was neutral. The increase in current density from 2 to 18 mA/cm^2 at optimum electrode and pH increased TPH removal from 71.7 to 95.1% during the ECP. The rate of TPH removal followed a pseudo second-order reaction. Aeration process increased the reaction constant of TPH removal from 0.477 to 0.078 L/g· min. Increasing the hydraulic retention time from 10 to 60 min in the continuous operation mode of the ECP led to an increase in the TPH removal from 67.2 to 93.4%. Therefore, batch and continuous experiments showed that the ECP could be efficient in eliminating TPH from water and thus may be a promising technique for treating petroleum-contaminated groundwater.

Korbahti et al. (2009) investigated the continuous electrochemical treatment of industrial textile wastewater in a tubular reactor. They used synthetic wastewater. The effects of residence time on chemical oxygen demand (COD), color and turbidity removals and pH change were studied under response surface optimized conditions. Temperature was 30^{0}C, electrolyte concentration was 25 g/L and was COD feed concentration 3505 mg/L with 123.97 mA/cm^2 current density. They increased residence time resulted in steady profiles of COD and color removals with higher treatment performances. The best column performance was realized at 3 h of residence time as 53.5% and 99.3% for COD and color removals, respectively, at the expense of 193.1 kWh/kg COD with a mass transfer coefficient of $9.47\times10{-}6$ m/s.

Linares-Hernández et al. (2010) used a synergistic combination of electrocoagulation and electrooxidation. This study addresses the elimination of persistent organic compounds in industrial wastewater. After experiments only half of the COD was eliminated from wastewater and an oxidation peak in the cyclic voltammetry scan remained. Electrooxidation is very effective in breaking down organic compounds through oxidation as reflected in the elimination of COD, BOD_5, and oxidative peak in cyclic voltammetry, but requires so much time (21 hr.) that it has very limited practicality, especially when colloidal and suspended particles are present. Electrooxidative mineralization of electrocoagulated wastewater, in which most of the colloids and charged species have been removed, took less than 2 hr. In the coupled technique, electrocoagulation quickly coagulates and removes the colloidal and suspended particles, as well as many charged species, then electrooxidation oxidizes the remaining organics. The coupled process eliminates COD, BOD_5, color, turbidity, and coliforms in a practical amount of time (2 h).

Chopra et al. (2011) used different technologies is to get high quality water in sufficient quantity at an affordable price from the unused ravage water. Electrodes with Aluminum (Al), Iron (Fe), Steel (St) and graphite are generally the best suited to electrochemical water treatment. In the present review, the applications of electrochemical treatment as well as electro-coagulation (EC), electro-flotation (EF) and electro-coagulation/flotation (ECF) to the treatment of wastewater and their operating parameters (reactor design, current density, time and electrode type and arrangement) affecting these processes have been discussed. Among the electrochemical processes, EC process should be the best choice, not only because it can achieve more satisfactory removal but also due to the fact that the process is cost-effective and simple in technological aspect. The major research efforts in the future could be focused on physicochemical and/or biological treated wastewater for the optimization of electrolytic technology in order to meet the requirement of the desirable/permissible limits of discharged wastewater for its reuse.

Canizares et al. (2007) studied the influence of the main parameters (electrical charge passed, pH, electrolyte, oil content and operation mode) in the efficiency of these processes, when aluminium electrodes are used. Removal efficiency was good between 5-9 pH. Increases in the electrical charge lead to increase in the COD removal. The influence of the oil concentration is related to that of the electrical charge passed: for a given dose of aluminium, the higher the oil content the lower the COD-removal efficiency. To produce the break-up of the emulsion it is required a minimum dose of aluminium (electrical charge passed), lower doses do not attain the rupture of the emulsion. The type of electrolyte and its concentration were also found to influence the process efficiency. Better efficiencies were obtained in the treatment of chloride-containing wastes and for low concentration of electrolyte. The destabilization of the O/W emulsion was found to be favoured in the discontinuous operation mode. Bridging flocculation is a primary destabilization mechanism that can explain the experimental results obtained in this work.

Shanthi et al. (2011) study the domestic sewage treatment using an electrochemical technique. They were carried out experiments at different current densities and different volume in a batch electrochemical reactor using Ti/RuO2 as anode and stainless steel as cathode. The characteristic such as pH, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Phosphorous and colour of the domestic sewage before and after treatment has been critically examined. The results showed that electrochemical chloride mediated indirect oxidation is a relevant, neat and possible solution for the treatment of domestic sewage water. The maximum COD reduction and colour removal efficiencies were 97.8% and 100%, respectively. Further a critical review is made on the various treatment methodologies and a note on their advantages and disadvantages are highlighted.

Electrochemical (EC) treatment has been reported as a feasible method for the treatment of various type of wastewater including dairy wastewater (Kushwaha et al., 2010a; Borbón et al., 2014; Mahesh et al., 2006; Feng et al., 2007; Raju et al., 2008; Maiti et al., 2011; Kushwaha et al., 2011b; Sengil and Ozacar, 2006; Tchamango et al., 2010; Qasim et al., 2013; Sharma, 2014; Yavuz et al., 2011). Assesment of the current research on dairy wastewater treatment is available in open literature (Arvanitoyannis 2006; Kushwaha et al., 2011a).

Qasim et al. (2013) reported that electrocoagluation is effective technology to treat dairy wastewater. Sharma (2014) studied batch EC treatment of dairy wastewater, and reported 87% COD removal in 75 min of electrolysis. Yavuz et al. (2011) observed 79.2% COD removal from dairy wastewater by EC treatment using iron and aluminum as sacrificial electrodes with addition of H_2O_2. Kushwaha et al. (2010a; 2011b) studied the treatment of dairy wastewater by EC method using different type of electrodes and reported 70% and 68.08% COD removal with iron and aluminium (Al) electrode, respectively. COD and oil-grease removal by EC treatment from dairy wastewater with iron electrode were reported by Sengil and Ozacar (2006). 61%, 81% and 100% COD, nitrogen and turbidity removal, respectively, with Al electrode were reported by Tchamango et al. (2011).

Even though literature is rich in elucidating EC treatment of dairy wastewater (Kushwaha et al., 2010a; 2011b; Sengil and Ozacar, 2006; Tchamango et al., 2011; Qasim et al., 2013; Sharma, 2014; Yavuz et al. 2011), none of the study reports continuous EC treatment of dairy wastewater to the best of authors knowledge. However, few studies explaining continuous EC treatment for the other type of industrial wastewater are available in the literature (Lin et al., 1994; Sonoyama et al., 2001; Alfafara et al., 2004; Sakalis et al., 2005 ; Körbahti and Tanyolac¸ 2003, 2009).

From the assessment of literature for electrochemical treatment of dairy waste water, the following comparison was drawn and reported in Table 2.1.

Table 2.1: Reported studies of electrochemical treatment of dairy waste water

S. No.	Waste water	Parameter	Operating Mode	Operating condition	Reactor used	Electrode used	Result	References
1	Commercial milk powder which was diluted in distilled water(4g /L)	COD Phosphate Turbidity	Batch	current density was 0.5 mA/cm^2, initial pH was 6.6, NaCl concentration 1.5 g/L and electrolysis time was 2 mins 0.5	cylindrical vessel	Aluminum Platinized titanium electrode	the removal efficiency of COD was 80%, phosphate was 59% and turbidity was 96%	Bensadok et al., 2011
2	artificial wastewater derived from solutions of milk powder	chemical oxygen demand (COD) phosphorus, nitrogen contents, and turbidity	Batch	current density was 0.43Adm^{-2}, electrolysis time was from 15 to 210 min quantity of the dissolved milk was 2.5 to 20 gL^{-1}	2 L beaker	Aluminium	chemical oxygen demand (COD) was reduced by up to 61%, removal of phosphorus was 89% nitrogen was 81%.turbidity was 100%	Tchamango et al., 2010
3	Wastewater was obtained from a tank containing a mixture of	COD and oil–grease in the aqueous phase	Batch	The optimum current density, pH and electrolysis time for 18,300	Bench-scale EC reactor	Iron	COD removal efficiencies was 98 and oil–grease was 99%,	Sengil and ozacar, 2006

	exhaust solutions at a dairy factory in Turkey (Sakarya)			mg COD/L and 4570 mg oil–grease/L were 0.6 mA/cm^2, 7 and 1 min, respectively				
4	simulated dairy wastewater (SDW)	COD	Batch	current density (J), dosage of sodium chloride (NaCl) (m), electrolysis time (t) and pH were varied between 61.73–308.64A/m^2, 0–2 g/l, 10–90 min and 5–11	Cuboid shape batch reactor	Iron	COD removal efficiency was found to be ≈70%.	Kushwaha et al., 2010
5	Three wastewater samples were collected from three food industries namely dairy, sweet-snacks and ice-	pH, EC, TDS, COD, Turbidity and Hardness	Batch	current was 3 A,constant temperature was 25 ^{0}C, All solutions were magnetically stirred at 500 rpm and DC	Beaker	aluminum electrodes	COD was reduced by 61%, phosphorus by 89%, nitrogen 81%, and 100% turbidity.	Qasim and Mane, 2013

	cream wastewater of Pune city			power supply was 30 V				
6	simulated dairy wastewater (SDW)	COD, total Kjeldahl nitrogen	Batch	COD = 3900 mg/L, total Kjeldahl nitrogen (TKN) = 113.18 g/L, turbidity = 1744 NTU, conductivity = 220 µs/cm, chloride = 31 mg/L, and pH = 6.5	cylindrical glass reactor	N.A.	COD and TKN removal were found to be 96.7 and 76.7%	Kushwaha et al., 2013

CHAPTER-3
THEORY OF ELECTROCOAGULATION

3.1 General

In electrocoagulation, cations are produced electrolytically from iron and/or aluminium anodes. These cations are responsible for increasing the coagulation of contaminants from an aqueous medium. Electrophoretic motion occurs there which tends to concentrate negatively charged particles in the region of the anode and positively charged particles in the region of the cathode. The consumable metal anodes are used to continuously produce polyvalent metal cations in the region of the anode. The cations produced neutralize the negative charge of the particles moved towards the anodes by production of polyvalent cations from the oxidation of the sacrificial anodes (Fe and Al). The electrolysis gases like Hydrogen evolved at the anode and oxygen evolved at the cathode. Electrocoagulation technology is an enigmatic technology.

3.2 Theory

In EC process of destabilization of colloidal particles is achieved by two mechanisms: In one method an increase in ionic concentration reduces the zeta potential and in subsequent process 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. When current is applied to the electrode, the anode gets oxidized 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

$$Fe\,(S) \rightarrow Fe^{2+}\,(aq) + 2e^- \qquad (1)$$

$$Al\,(S) \rightarrow Al^{3+}\,(aq) + 3e^- \qquad (2)$$

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

$$2H_2O\,(l) \rightarrow O_2\,(g) + 4H^+\,(aq) + 4e^- \qquad (3)$$

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

$$3H_2O\,(l) + 3e^- \rightarrow 3/2H_2\,(g) + 3OH^-\,(aq) \qquad (4)$$

Liberated Al^{3+} and OH^{-} ions react to form various monomeric and polymeric hydrolyzed species like $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al(OH)^{4-}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$ $Al_{13}(OH)_{34}^{5+}$(Johnson et al., 1983). 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.

3.3 Different Types of Arrangement of Electrodes

There are three different kinds of arrangements of electrode reported in Bench-scale electrocoagulation reactor.

(i) Mono polar electrodes in parallel connection
(ii) Mono polar electrodes in series connection
(iii) Bipolar electrodes in parallel connection

(i) Mono polar electrodes in parallel connection

Fig. 3.1 shows a simple arrangement of an EC cell consisting of a pair of anodes and a pair of cathodes in parallel arrangement. A direct current power source is applied to a pair of conductive metal plates placed between two parallel. The experimental set up also consists of a resistance box to regulate the current density and a multi meter to read the current values. The conductive metal plates, which are commonly known as ‘sacrificial electrodes’, may be made up of the same or of different materials (Pretorius et al., 1991).

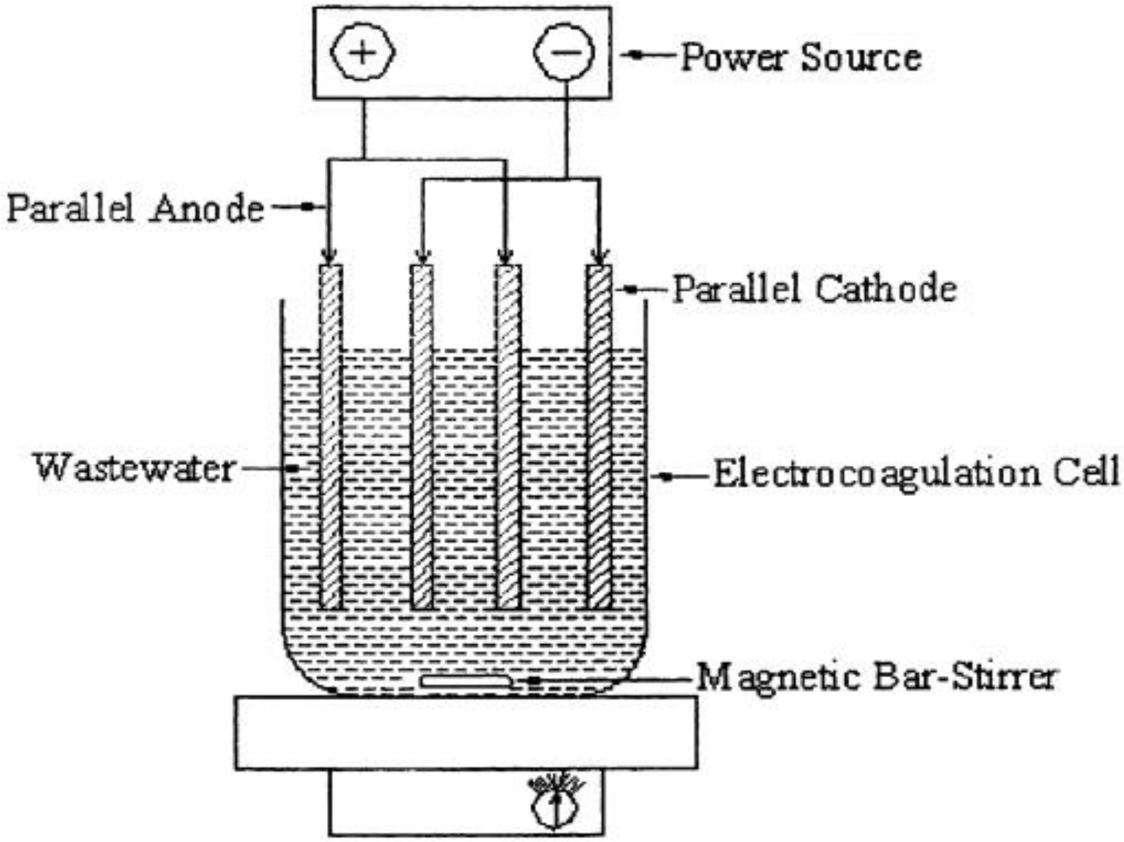

Fig. 3.1: Bench-scale Electrocoagulation reactor with mono polar electrodes in parallel connection

(ii) Mono polar electrodes in series connection

An arrangement of an EC cell with monopolar electrodes in series is shown in Fig. 3.2. It can be seen from Fig. 3.2 that each pair of 'sacrificial electrodes' is internally connected with each other, and are not inter connections with the outer electrodes. Such an arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections (Pretorius et al., 1991).

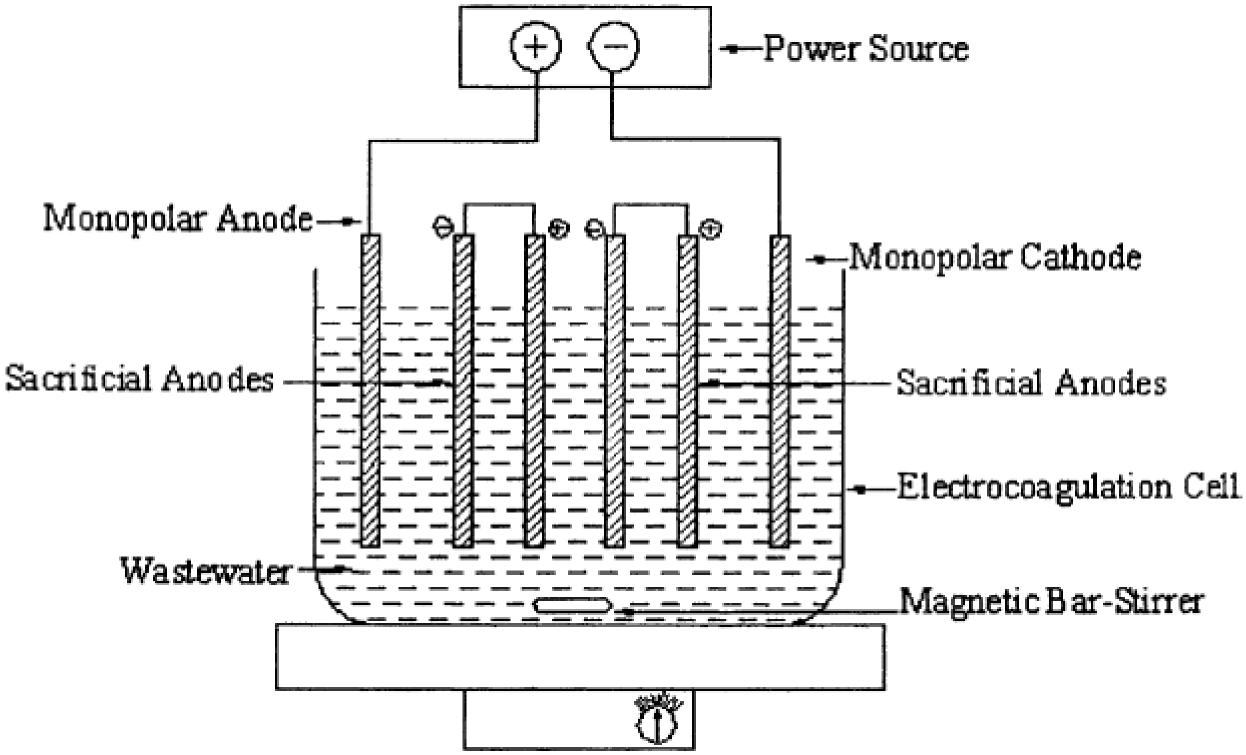

Fig. 3.2: Bench-scale Electrocoagulation reactor with mono polar electrodes in series connection

Since the cells connected in series have higher resistance, a higher potential difference is required for a given current to flow. The same current would, however, flow through all the electrodes. In parallel arrangement, the electric current is divided between all the electrodes in relation to the resistance of the individual cells.

(iii) Bipolar electrodes in parallel connection

Fig. 3.3 shows an arrangement of an EC cell with bipolar electrodes in parallel. The sacrificial electrodes do not have any electrical connection and are placed between the two parallel electrodes. Only the two mono polar electrodes are connected to the electric power source. Such a cell arrangement provides a simple set-up, which facilitates easy maintenance during use. 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 as compared to the parallel side beside it. In this case the sacrificial electrodes are also known as bipolar electrodes (Pouet et al., 1995; Mameri et al., 1998).

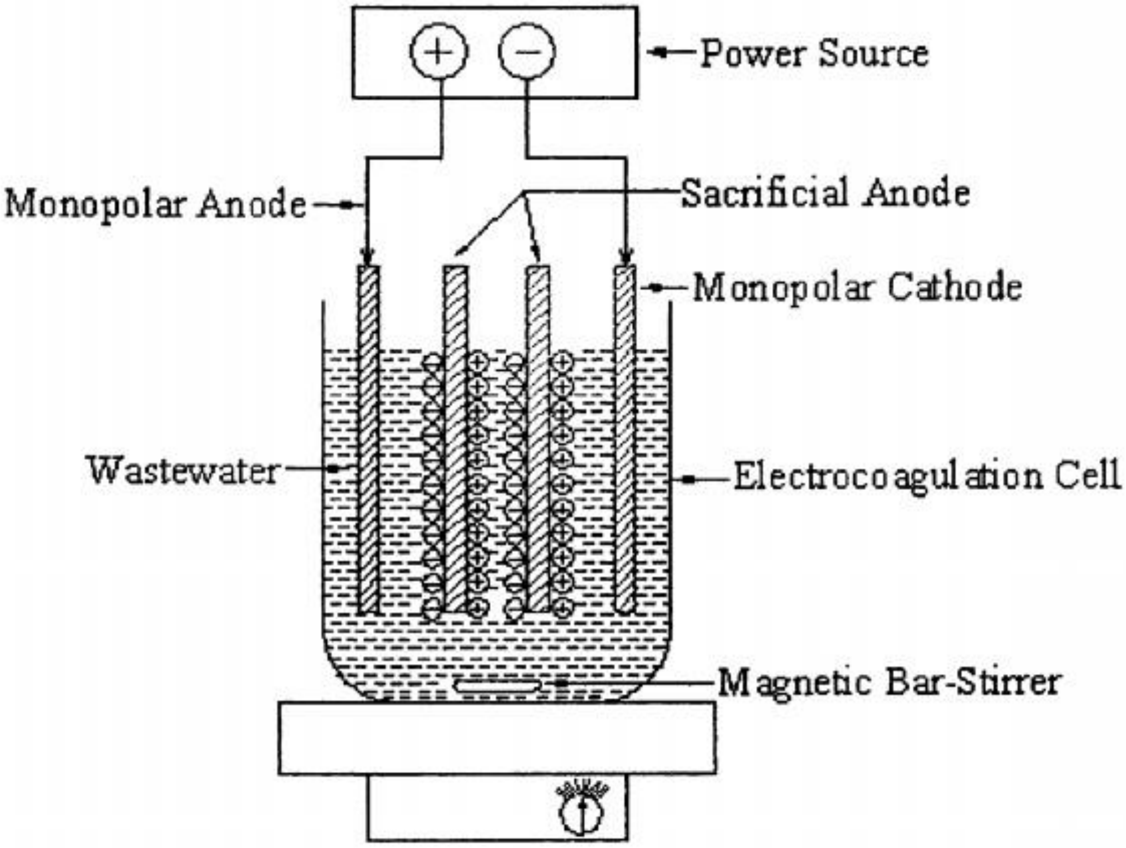

Fig. 3.3: Bench-scale Electrocoagulation reactor with bipolar electrodes in parallel connection

3.4 Advantages

- EC requires simple equipment and is easy to operate.
- Low initial investment is required with low operating cost.
- The electrolytic processes in the EC cell are controlled electrically and with no moving parts which induce wear and tear. Thus requiring less maintenance.
- As no chemicals are required in EC, there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances.
- EC is composed of mainly metallic oxides/hydroxides. Sludge formed by EC tends to settle readily and are easy to de-water, so low sludge generation can be done.
- EC flock can be separated faster by filtration as it tends to be much larger, consists of less bound water, acid-resistant and more stable.

- Effluents produced in EC have less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
- The EC process has the capability of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
- The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
- EC produces palatable, clear, colourless, odourless water with zero discharge.
- EC can handle large variation in the waste streams with multiple contaminants.
- The EC technique can be easily used in rural areas where electricity is not available, since a solar panel can produce sufficient power to carry out the process. Dosing the incoming sewage waste water with sodium hypochlorite helps tremendously in reduction of biochemical oxygen demand (BOD) and consequent chemical oxygen demand (COD). Sodium hypochlorite can be generated using electrochlorinators.
- Due to the excellent EC removal of suspended solids and the simplicity of the EC operation, tests conducted for the U.S. Office of Naval Research concluded that the most promising application of EC in a membrane system was found to be as pre-treatment to a multi-membrane system of UF/RO or microfiltration/reverse osmosis (MF/RO). In this function the EC provides excellent protection of the low-pressure membrane that is more general than that provided by chemical coagulation and more effective. EC is more effective at removing many species that chemical coagulation and other alternatives.

3.5 Disadvantages (Chaturvedi 2013).

- Efficiency of electrocoagulation cell reduces in some systems due to formation of an impermeable layer of oxides film at the cathode.
- High conductivity of the waste water suspension is required.
- Gelatinous hydroxide might become soluble in some cases.
- Due to oxidation, the sacrificial anode is dissolved in the waste water. Hence it needs to be regularly replaced.
- Electricity may be expensive to use in some cases.

CHAPTER-4

MATERIAL AND METHOD

4.1 General

This chapter reports explanation of materials and experimental methods adopted during the electrochemical treatment of dairy waste water using aluminium (Al) electrode. The experimental details includes set-up, chemicals and electrode used and various studies performed during the dairy waste water treatment by electrochemical treatment method have been explained in details

4.2 Wastewater and Instrumentation

Dairy industry wastewater was collected from Verka Milk Plant, Patiala, Punjab, India. Since, dairy wastewater is highly perishable; therefore, to prevent deterioration, collected dairy industry wastewater was preserved at ≈ 2 °C.

The collected dairy wastewater was characterised for COD, BOD, total nitrogen (TN), total solids and Turbidity (Table 4.1).

Table 4.1 Dairy industry wastewater Characteristics

Parameter	**Values**	
	Untreated	**EC Treated**
COD (mg/l)	2800	806
BOD (mg/l)	2285	630
TN (mg/l)	15.12	3.92
Total solids (mg/l)	22000	2000
Turbidity (NTU)	844.9	1.3

All the chemicals used in this study were of Analytical reagent (AR) grade. To measure the COD a digestion unit (Spectra lab, 2015D, India) and double beam UV-visible spectrophotometer (HACH, DR 5000, USA) were used. BOD was measured using Digital BOD-measurement system (WTW

Oxitop IS 6, Germany), and turbidity meter supplied by Spectra lab India (NT 2000) was used to measure the turbidity. Total nitrogen (TN) was determined using the standard Kjeldahl met**.**

4.3 Reactor and Experimental Procedure

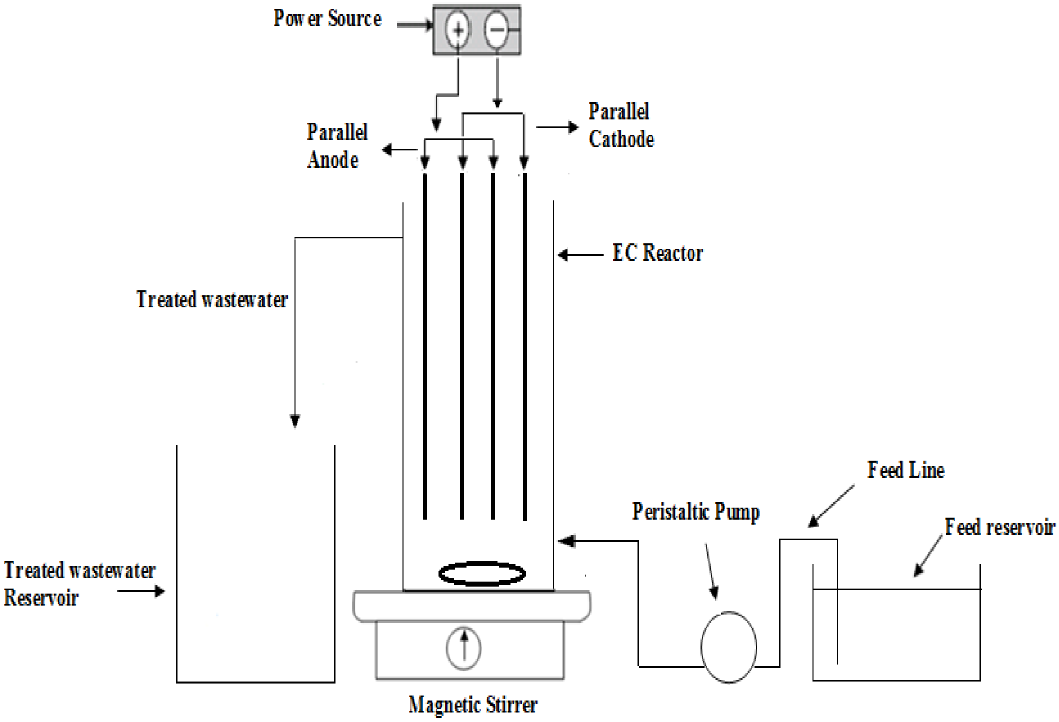

Fig 4.1. Schematic view of continuous electrochemical reactor

Experiments were conducted in a continuous EC reactor made of Perspex having net working volume of 1.3 liter (8.5 cm×8.5 cm×25.5 cm) (Fig 4.1). Two pairs of Al plates each having 1 mm thickness with face area of 21 cm x 5 cm were used as electrodes with inter-electrode spacing of 1 cm. The dairy wastewater was pumped from feed reservoir to the EC reactor with the help of peristaltic pump (MICLINS PP- 30-EX). Current was supplied by means of a constant current/voltage digital direct current power supply (0-20 V, 0-5 A; Make Crown Electronics Delhi, India). A magnetic stirrer was used to agitate the content in the EC reactor.

NaCl at the rate of 2 g/l was added to the dairy wastewater to increase the conductivity. Then after, as per the experimental condition required, dairy wastewater was adjusted to desired pH level using NaOH/H_2SO_4. To conduct the experiment, the reactor was first instantaneously filled with dairy wastewater, and the feeding of dairy wastewater to the EC reactor was made continuous with the desired flow rate (residence time, τ). The elapsed time (t) was measured when the power supply was switched on, and current was kept constant during the experiment. After the desired time intervals samples were collected at the outlet of the reactor and %COD removal (Y_1) and specific energy consumed (kWh per kg of COD removed, Y_2) were calculated.

4.4 Experimental Design, Modeling and Optimization

Three variables, namely Initial pH (pH_i): 4.5-9, residence time (τ): 30-150 min and elapsed time (t): 30-150 min were selected as the process variables, whereas, %COD removal (Y_1) and specific energy consumed (kWh per kg of COD removed, Y_2) were considered as responses of the system. Dependency of Y_1 on pH_i was evaluated by classical method. For this, experiments were conducted at various pHi: 4.5-9 keeping current (i)= 3.7 A, τ = 45 min and t=150 min constant, and Y_1 was measured.

Five level full factorial central composite design (CCD) of response surface methodology (RSM) was applied to design experiments, modeling and optimization of independent variables (τ = 30-150 min and t =30-150 min) and responses [%COD removal (Y_1), and specific energy consumed (kWh per kg of COD removed, Y_2)].

For this purpose, the independent variables were coded at five levels between -2 to +2, and total of 14 experiments were suggested by RSM (Table 4.2). Experiments suggested by the RSM were conducted at optimized value of pH_i and i= 3.7 A.

The data obtained from the conducted experiments (Table 4.2), were processed for Eq. (5) with RSM through ANOVA to obtain the interaction between the process variables and the responses.

$$Y = c_o + \sum_{i=1}^{4} c_i X_i + \sum_{i=1}^{4} c_{ii} X_i^2 + \sum_{i=j}^{3} \sum_{i=j+1}^{4} c_{ij} X_{ij} \qquad \textbf{(5)}$$

Where, Y is response; c_o, c_i, c_{ii}, c_{ij} are constant coefficients and X_i the independent process variables. The fit quality of quadratic model was evaluated by the coefficient of determination, R^2 and adjusted R^2.

In this study there are two responses. Therefore, multi-response process optimization of RSM with desirability function was used to optimize the EC treatment of dairy wastewater

(Kushwaha et al., 2011b; Jeong and Kim, 2009). In this process, the overall desirability (D) is explained by following equation:

$$D = (d_1 \times d_2 \times d_3 ....)^{\frac{1}{\eta}} \qquad \textbf{(6)}$$

Where, $0 \leq D \leq 1$ and η is number of responses, and d individual desirability.

Table 4.2 Suggested experiments with process variables values and responses for EC treatment of dairy wastewater

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

Predicted*: predicted by RSM

CHAPTER-5

RESULT AND DISCUSSION

5.1 General

This chapter report electrochemical treatment of actual dairy waste water in Continuous mode using Aluminium (Al) electrode. Result obtained during the treatment of actual dairy waste water and their interpretations have been discussed in detail.

The optimization of process for removal of COD and energy consumed has been mentioned using central composite design based on response surface methodology (RSM). For optimization of the EC treatment of dairy wastewater, multi-response process optimization utilizing desirability function of RSM was used.

5.2 Effects of pH_i on %COD Removal, Y_1

To explore the effect of pH_i on Y_1, experiments for EC treatment of dairy wastewater were conducted at varying pH_i: 4.5-9 at i=3.7, τ = 45 min, and Y_1 was measured by collecting the samples at the outlet of the reactor at various time intervals (Fig 4.1).

During EC treatment Al^{3+} ions and OH^- ions are added to the solution due to oxidation of anode and reduction of cathode, respectively, and in subsequent process variety of monomeric and polymeric aluminium hydrolyzed species are produced. The quantity and the type of hydrolyzed species produced depend on generated Al^{3+} ions concentration and solution pH, respectively. In acidic pH range Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ etc. are formed, while in highly basic pH $Al(OH)_4^-$ ions are formed (Duan et al., 2003; kushwaha et al., 2011). Detailed literature about various reaction during EC treatment is available in literature (Kushwaha et al., 2010; Kushwaha et al., 2011; Korbahti et al., 2003; Chen 2004). In addition to this, due to presence of NaCl which was added to increase the conductivity of dairy wastewater, chlorine gas is discharged at anode. Further, due to hydrolysis and ionization reaction various chlorine species (HOCl and ClO^-) are formed depending on medium pH (Kushwaha et al., 2010; Korbahti et al., 2003; Lin et al., 1998; Deborde et al., 2008). ClO^- ions are produced in good quantity at highly basic pH, and reported to be a strong oxidant (Deborde et al., 2008).

Fig 5.1 illustrates effect of pH_i on Y_1 at various elapsed times (t). Maximum Y_1 value of 60.36 was found at pH^{-}_{i}= 4.5 and t= 150 min. On increasing the pH_i upto 7.0, Y_1 value continuously decreased to 32.0 at t= 150 min. Further for all values of $pH_i > 7.0$ Y_1 value was found to increase, and it is nearly constant to ≈39.0. As discussed in our previous research paper (Kushwaha et al., 2010; Kushwaha et al., 2011), due to dairy wastewater isoelectric point (pH_{iec}) being 4.2 (Selmer-Olsen et al., 1996), at $pH_i > pH_{iec}$ colloids and proteins present in the dairy wastewater are negatively charged and are destabilized by Al^{3+} produced and various hydrolyzed species; Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$ etc. during the EC reaction. This may be the cause of higher Y_1 value at high acidic pH (pH_i =4.5) EC treatment. Increase in pH_i to 7.0, decreases the concentration of Al^{3+} and its hydrolysed products (Duan et al., 2003; kushwaha et al., 2011). Consequently Y_1 value was observed to be decreased.

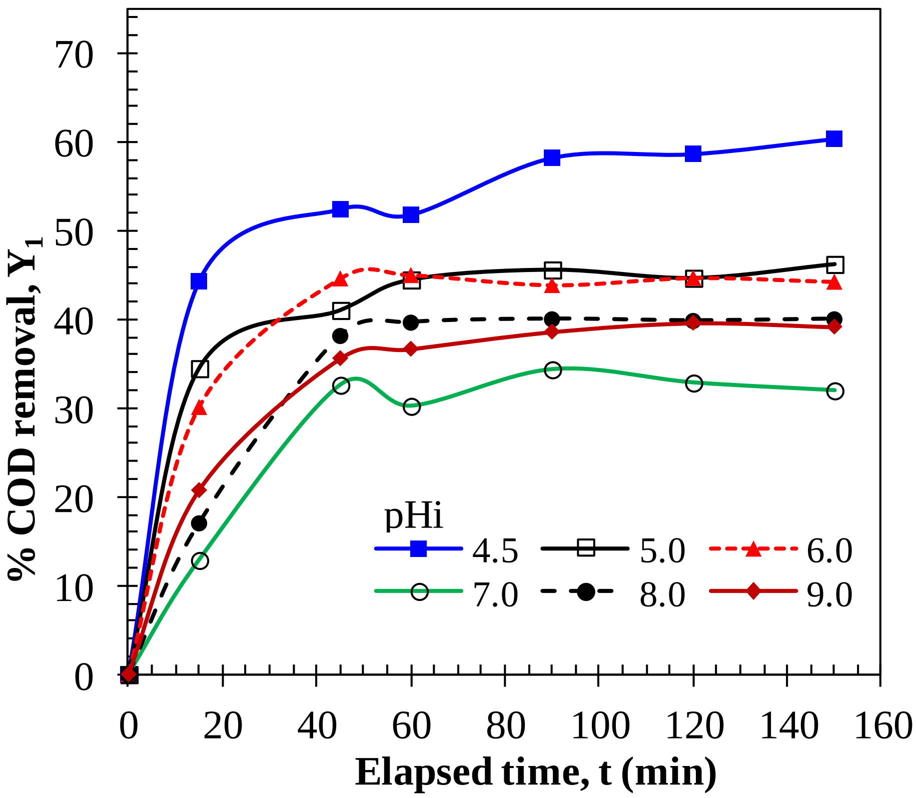

Fig. 5.1 Effect of pH_i on %COD removal by EC treatment of dairy wastewater (Current, i= 3.7 A, residence time, τ = 45 min)

Moreover, for $pH_i > 7.0$ $Al(OH)_4^-$ ions are formed which is incapable of removing COD. But it can be seen in the Fig 5.1 Y_1 value was found to increase beyond $pH_i = 7.0$. This increase in Y_1 value may be attributed to indirect oxidation of pollutants by ClO^- ions. Since, maximum Y_1 value of 60.36 was found at $pH_i = 4.5$, therefore, further study was conducted at $pH_i = 4.5$.

5.3 Effects of Residence Time (τ) and Elapsed Time, t on Y_1 and Y_2

To see the effect of residence time (τ) and elapsed time (t), on Y_1 value, the experiments were conducted at $pH_i = 4.5$ and current, i= 3.7 A as per suggested by the CCD under RSM (Table 4.1), and the COD concentrations and hence Y_1 value were monitored at the outlet of the reactor at various time intervals for 30, 60, 90, 120 and 150 min of τ (Table 4.1). The experimental results were then fitted to quadratic model and it was evaluated by RSM using ANOVA. ANOVA showed significant quadratic model fitting showing model F-value, R_2 and adjusted R_2 of 10.03, 0.862 and 0.776, respectively (Table 5.1). Fig. 5.2, shows predicted Y_1 value plotted against actual experimental values, and it can be seen that the actual data are in good agreement with predicted. This reflects a good fitting of observed to the predicted values by RSM. Values of "Prob>F" greater than 0.1 indicate that model terms are not significant. In the present study, τ, t and τ_2 are significant terms (Table 5.1). Quadratic equation in terms of coded variable for %COD removal is given below:

$$Y_1 = 65.46 + 4.16A + 2.34B - 1.12A^2 - 0.69B^2 - 0.052AB \quad (7)$$

Table 5.1 ANOVA for COD and specific energy consumption

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

A: residence time, τ

B: Elapsed time, *t*

$^{\#}$ R^2: 0.862; Adjusted R^2: 0.776

$^{\$}$ R^2: 0.98; Adjusted R^2: 0.96

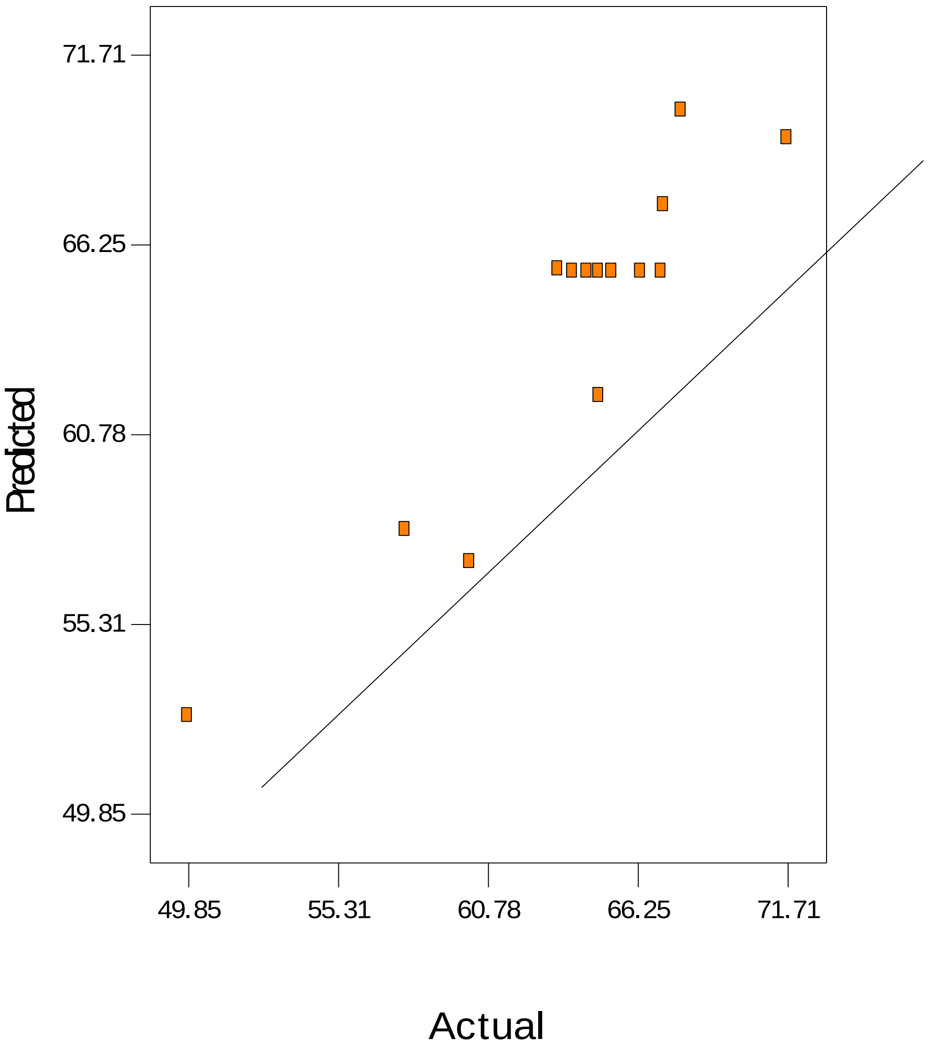

Fig. 5.2 Predicted verses actual plot for %COD removal, Y_1

The classical 2-D and response surface 3-D plots for dependency of Y_1 on τ and t are shown in Fig. 5.3 and 5.4. It may be observed in Fig. 5.3 and 5.4 that, for all values of τ, increasing t value improves the Y_1 value. After 150 min of t, Y_1 values were found to be 56.07, 62.23, 64.86, 67.86 and 72.3 at 30, 60, 90, 120 and 150 min of τ (Fig 5.3). With increase in τ value, it can also be observed that steady state is achieved in EC reactor at earlier t value. For τ = 30 min, steady state was achieved at t= 120 min, while for all τ > 30 min, steady state was achieved nearly at t= 90 min. This may be due to fact that, at higher τ value, higher amount of Al^{3+} and $Al(OH)^{2+}$, $Al(OH)_2^+$ etc. are generated (Kushwaha et al., 2010; Kushwaha et al., 2011; Thakur et al., 2009; Kumar et al., 2009), and hence, maximum possible removable COD is removed at lower t value.

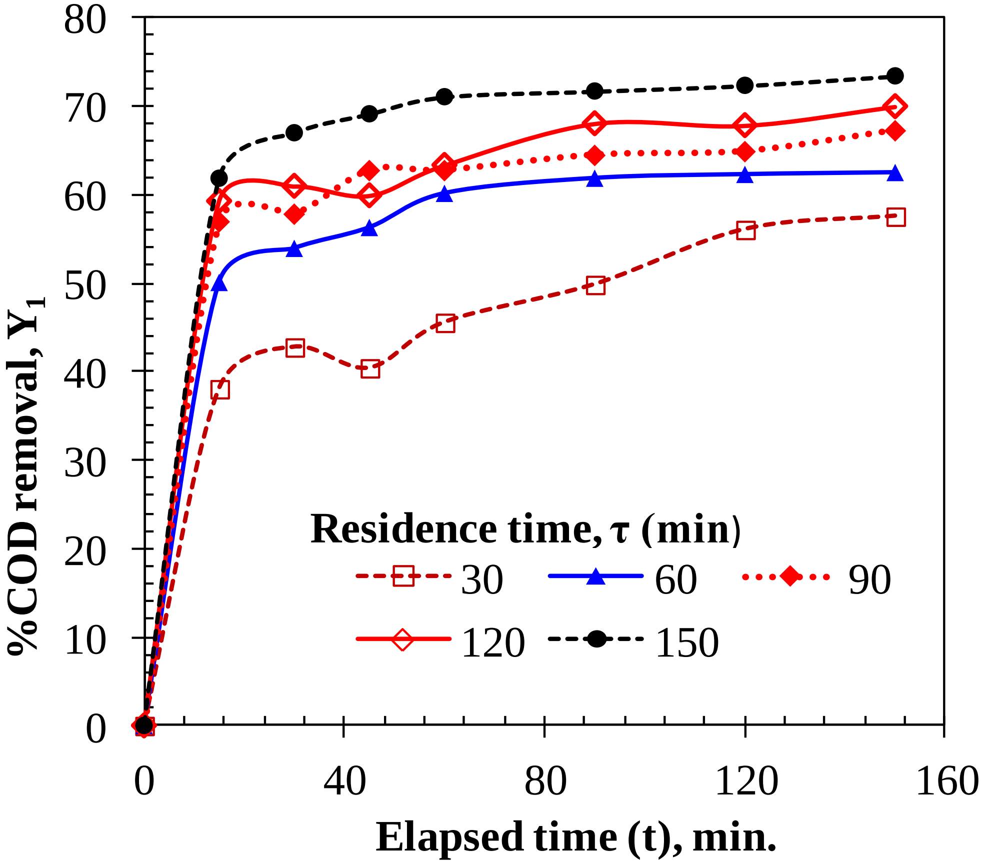

Fig. 5.3 Effect of residence time on %COD removal, Y_1 by EC treatment of dairy wastewater (Current, i= 3.7 A, pH_i = 4.5)

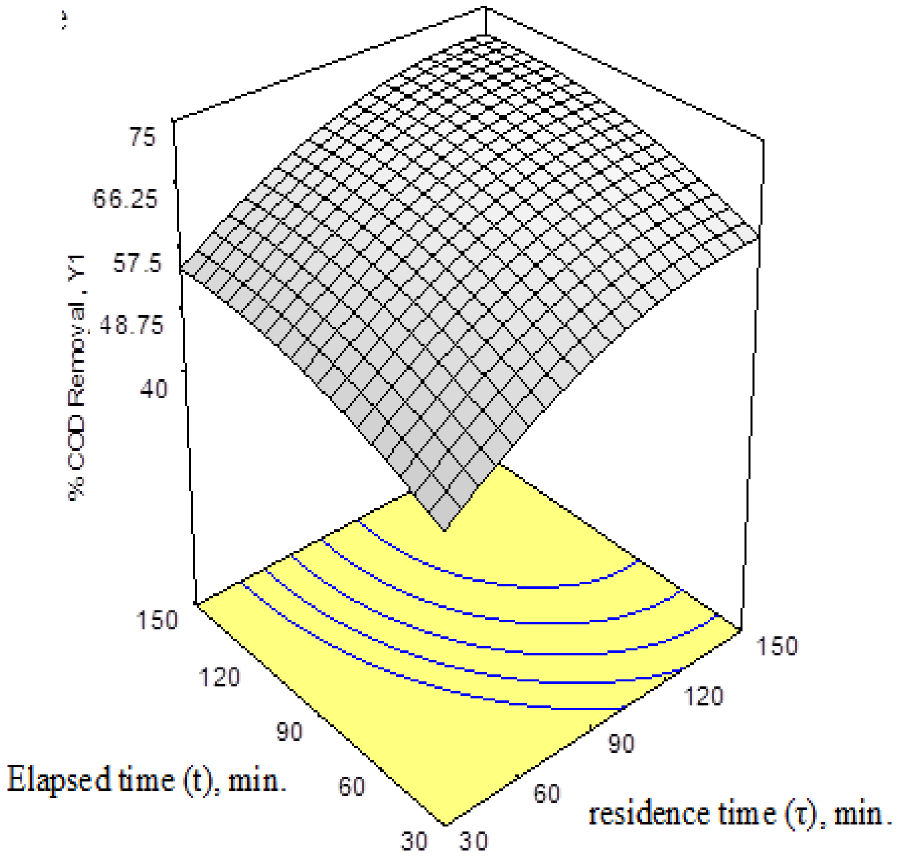

Fig. 5.4 3-D response surface graph for %COD removal, Y_1 versus *t* and τ for the EC treatment of dairy wastewater at pH_i=4.5 and *i* =3.7 A

To investigate the effect of τ and t on Y_2 value, experiments were conducted and results are shown in Table 4.1. Actual Y_1 values from experiments were plotted against RSM predicted values (Fig. 5.5). This shows that the actual data are in good agreement with predicted values. Table 5.1 shows ANOVA for the quadratic model fitted for response Y_2. Model F-value, R_2 and adjusted R_2 of 68.09, 0.98 and 0.96, respectively, implies quadratic model satisfactorily explain the response Y_2. Also, τ, t and τ_2 were found noteworthy terms for response Y_2. The approximating quadratic equation Y_2 is given below:

$$Y_2 = 8.33 - 1.0A + 2.59B + 0.39A^2 - 0.13B^2 - 0.12AB \qquad (7)$$

3-D response surface plot for dependency of Y_2 on τ and t are shown is shown in Fig 5.6. It can be observed in Fig. 5.6 that Y_2 value is comparatively high at lower τ value, and decreased on increasing τ up to τ ≈100 min. Beyond τ =100 min, change in Y_2 was observed marginal. This trend of variation in Y_2 value was observed at all t value. At lower τ, low COD removal and higher steady state time (t) is responsible for increasing the Y_2 value. At any τ, Y_2 value was always found to increase with increase in t value.

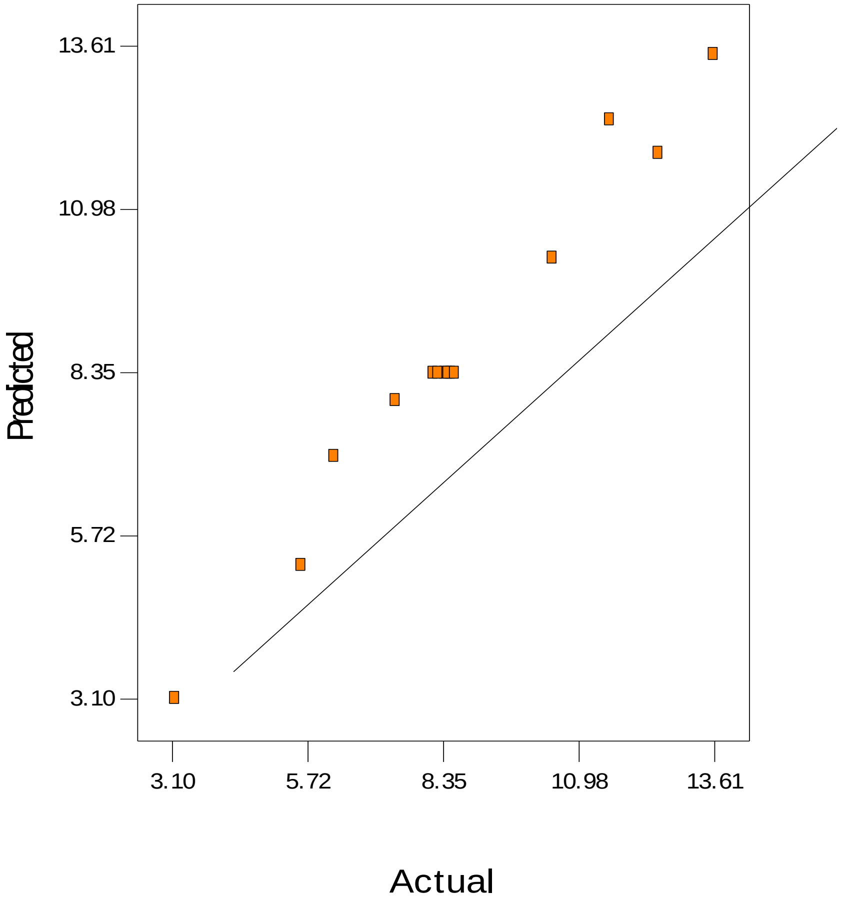

Fig. 5.5 Predicted verses actual plot for Specific energy consumed, Y_2

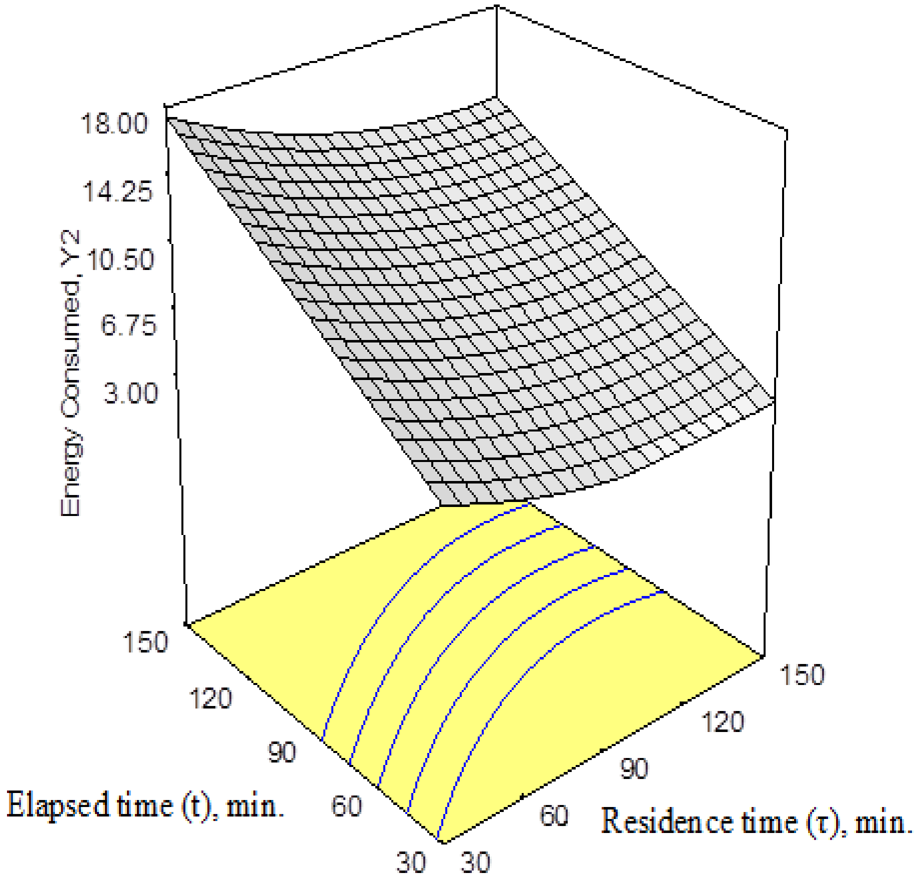

Fig. 5.6 3-D response surface graph for specific energy consumed, Y_2 versus *t* and τ for the EC treatment of dairy wastewater at pH_i=4.5 and *i* =3.7 A

5.4 Optimization

For optimization of EC treatment of dairy wastewater in view of cost, residence time (τ) and Y_2 was set to be minimized within elapsed time, t = 30-150 min, whereas Y_1 was maximized. The constraints used for optimization is shown in Table 5.2. Suggested optimized values of τ, t, Y_1 and Y_2 by RSM were found to be 141 min, 52 min, 67% and 4.62 kWh/kg of COD removed, respectively, with desirability value of 0.464. At these optimized values of EC process variables three authentication runs were performed. The average values of Y_1 and Y_2 were found to be 71.21% and 4.32 kWh/kg of COD removed, respectively. Other wastewater characteristics at optimized parameters are shown in Table 4.1. Marginal error of 5.9% and 6.4% in Y_1 and Y_2, respectively, showed good agreement between experimental and predicted values.

Table 5.2 Constraints used for the optimization of continuous EC treatment of dairy wastewater

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

CHAPTER 6

CONCLUSIONS

Continuous EC treatment process variables, namely pH_i, residence time (τ) and elapsed time (t) were studied to elucidate their effect on the %COD removal (Y_1) and specific energy consumed (kWh per kg of COD removed, Y_2). On the basis of the results and discussions for the treatment of dairy industry waste water samples by continuous electrochemical treatment following major conclusions were found.

- In highly acidic pH values, Al^{3+} and various hydrolyzed species; $Al(OH)^{2+}$, $Al(OH)_2^{+}$ etc. were found responsible for COD removal. While, at highly basic pH, ClO^{-} ions indirectly oxidized the COD.
- ANOVA showed significant quadratic model fitting showing R^2 and adjusted R^2 of 0.862 and 0.776, respectively, for response Y_1, while respective values for Y_2 were found to be 0.98 and 0.96, respectively.
- Optimized values of τ, t, Y_1 and Y_2 by RSM were found to be 141 min, 52 min, 67% and 4.62 kWh/kg of COD removed, respectively, with desirability value of 0.464.
- At optimized set of parameters actual experiment showed Y_1 and Y_2 values being 71.21% and 4.32 kWh/kg of COD removed, respectively.

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