TREATMENT OF DISTILLERY EFFLUENT USING ELECTROCOAGULATION

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"TREATMENT OF DISTILLERY EFFLUENT USING ELECTROCOAGULATION"**, in the partial fulfilment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand (India), is an authentic record of my own work carried out during the period from June 2007 to June 2008 under supervision of **Dr. I. D. Mall**, Professor, and **Dr. V. C. Srivastava,** Lecturer, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee,

I have not submitted the matter, embodied in this dissertation for the award of any other degree or diploma.

Date: June 2008

Place: Roorkee

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

Most of the distilleries in India and the world over employ bio-methanation of molasses spent wash in a bio-digester plant followed by two-stage aerobic treatment as a treatment strategy. The bio-digester effluent (BDE) generated after this treatment strategy still has a high chemical oxidation demand (COD) and dark brown color which can not be directly discharged into a water body.

In the present study, electrocoagulation (EC) has been employed for the COD and color removal of a BDE in a batch EC reactor using stainless steel (SS) electrode. A central composite (CC) experimental design has been employed to evaluate the individual and interactive effects of four independent parameters namely initial pH (pH : 3.5-9.5), current density (j : 39.06-195.31 A/m^2), inter-electrode distance (g : 1-2 cm) and electrolysis time (t : 30-150 min) on the COD and color removal efficiency. Pareto analysis of variance (ANOVA) showed a high coefficient of determination value (R^2 =0.9144) for COD and (R^2=0.7650) for Color between the experimental values and the predicted values by a second-order regression model. Maximum COD removal of 61.58% and color removal of 99.17 % was observed at optimum conditions. Detailed physico-chemical analysis of electrode and residues (scum and sludge) of the EC process has also been carried out. A strategy for the disposal of EC residues has been proposed in the present thesis.

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NOMENCLATURE

ABBREVIATIONS

BDE	Bio-digester Effluent
CC	Central Composite
CD	Current Density, A/m^2, mA/cm^2
COD	Chemical oxygen demand, mg/l
DTA	Derivative thermal analysis
DTGA	Differential thermogravimetric analysis
EC	Electrocoagulation
ECR	Electrochemical reactor
ECT	Electrochemical treatment
EDX	Energy Dispersive X-ray analysis
F	Faraday's constant, 96500 C/mol
IED	Inter-electrode Distance
NTU	Nephelo turbidity unit
PCU	Platinum cobalt unit
pH_{PZC}	Point of zero charge
SEM	Scanning electron microscope
SS	Stainless Steel
TA	Thermal analysis
TDS	Total dissolved solids, mg dm^{-3}
TGA	Thermogravimetric analysis
TS	Total solids, mg dm^{-3}

NOTATIONS

pH_0	Initial value of pH
j	Current Density A/m^2
g	Electrode Gap cm

Chapter 1

INTRODUCTION

1.1 General

India has been known as original home of sugar and sugarcane. Sugar industry is second largest agro-industry in India. There are more than 571 sugar industries which produce around 20.1 million tonne of sugar. The water pollution becomes more serious in most of the sugar industries because of the very high contain of chemical oxygen demand (COD), biological oxygen demand (BOD), color and inorganic matter. During the process of sugar manufacturing about 0.4-0.45 tonne of molasses per tonne of sugar is generated as by product which is used as a feed stock for distilleries. Molasses consist of water (17-25%), sucrose (30-40), glucose (4-9), fructose (5-12), polysaccharides (2-5) and inorganic matter. About 90% of molasses goes into production of alcohol and the rest 10% is used for cattle feed, foundries and manufacturing of citric acid.

Alcohol distilleries are regarded as one of the most polluting industries by the Government of India. Alcohol is separated by distillation and the residual liquor is discharged as effluent. This effluent, called as spentwash, is highly acidic, dark coloured and contains high percentage of organic and inorganic matter both in suspended and dissolved forms (Subramanian et al., 2005). For every liter of alcohol production, about 12-14 l of wastewater is discharged which affect the soil and groundwater resources of the region. Distillery spent wash is considered as a very high strength wastewater having very high COD and BOD with low pH and dark brown color (Goel et al., 2003). The high organic content of molasses spent wash makes anaerobic treatment attractive in comparison to direct aerobic treatment. Therefore, bio-methanation is employed as a primary treatment step. It is often followed by two-stage aerobic treatment before discharge into a water body or on land for irrigation (Nandy et al., 2002). Though biological treatment results in significant COD removal, still the effluent retains high amount of COD and color (Inanc et al, 1999). The melanoidins are barely affected by conventional biological treatment such as methane fermentation and the activated sludge process, and they cause COD and color in the final effluent (Migo et al., 1993).

The regulatory agencies in India require the distillery units to meet the effluent discharge quality standards for release of the wastewater into surface waters (COD < 0.1 kg m^{-3}, biological oxidation demand (BOD) < 0.03 kg/m^3) and sewers (COD < 0.3 kg/m^3, BOD < 0.1 kg/m^3) (CPCB, 2006).

1.2 Profile of Indian Distillery

The technique for fermentation and distillation is believed to be have been available in India since Vedic times, with references to somras (alcohol) being available in ancient literature. The first known Indian distillery was established in 1805 at Janjmow, Kanpur in Uttar Pradesh for the production of rum for the army. The industry received a major boost during the Second World War when distilleries were encouraged to produce anhydrous ethanol for mixing with petrol, which was in short supply. As a result, many distilleries came up in the major cane growing areas of Uttar Pradesh and Maharashtra. However, the shortage of petrol vanished after World War II and thereafter alcohol production was mainly for potable purposes.

When India became independent in 1947, the production capacity of alcohol was 60 million liter. From 1960 to 1993, nearly 50% of alcohol produced was utilized for industrial purposes. However, decontrol of molasses in 1993, which resulted in its price increase, caused a setback to this sector. However, the potable liquor sector continues to post a steady 8% growth (year).

At present there are about 325 distilleries in the country with a total installed capacity of 3.5 billion liter per annum.

1.3 Distillery Industry

1.3.1 Process Technology

Distillery is unit plant used for the production of ethyl alcohol by the use of molasses. This process contains four procedures, dilution of molasses, fermentation, rectification or distillation, packing. Molasses is raw material for distillery, this raw come from sugar industries. During this process some waste material comes out, one of them is spent wash. This spent wash come from rectification unit of distillery. This spent wash contain many valuable compound which can be used further by some other industries generally fertilizer industries. The overview of manufacturing process of alcohol is shown in Fig. 1.1.

Feed Preparation: Molasses is diluted with water to obtain a feed containing 15% - 16% sugar. The pH is adjusted, if required, by addition of sulphuric acid. More recently, sugarcane juice has also been used directly as a starting material for alcohol production.

Fermentation: The diluted molasses solution is transferred to the fermentation tank where it is inoculated with typically 10% by volume yeast (Saccharomyces cerevisiae). The mixture is then allowed to ferment anaerobically under controlled conditions of temperature and pH. The process involves –

1. Conversion of sucrose to glucose and fructose

   $$C_{12}H_{22}O_{11} + H_2O \textbf{ Invertase} \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

2. Fermentation of glucose to alcohol releasing carbon dioxide and heat.

   $$C_{12}H_{12}O_6 + H_2O \textbf{ Zymase} \rightarrow 2C_2H_5OH + 2CO_2 + 23.5\ Kcal$$

Since the reaction is exothermic, the fermenter is cooled to maintain a reaction temperature to 25-32 °C. Fermentation typically takes 48 to 80 h for completion and the resulting broth contains 6-8% alcohol. Once fermentation is complete, yeast is separated by settling and the cell-free broth is taken for distillation.

Distillation: The cell-free fermented broth is pre-heated to about 90 °C and is sent to the de-gasifying section of the analyzer column. The bubble cap fractionating column removes any trapped gases (CO_2' etc.) from the liquor which is then steam heated and fractionated to give 40% alcohol. The bottom discharge from the analyzer column is the effluent (spent wash). The alcohol vapors from the analyzer column are further taken to the rectifying column where by reflux action, 95-99% rectified alcohol is trapped, cooled and collected.

Stillage Processing: The spent wash at approximate 12.6% w/w concentration from distillation is concentrated in a multi effect evaporator to approximate 55% w/w. This concentrated spent wash will then be burnt in the boiler to produce high pressure steam. The steam is then sent to turbine to generate electric power for its captive use in the industry. The exhaust steam from turbine will be utilized in evaporation and distillery plants.

Packing: Rectified spirit (96% ethanol by volume) is marketed directly for the manufacture of chemicals such as acetic acid, acetone, oxalic acid and absolute alcohol. Denatured ethanol for industrial and laboratory use typically contains 60-95% ethanol as well as between 1% to 5% each of methanol, isopropanol, methyl isobutyl ketone (MIBK), ethyl acetate, etc.

1.3.2 Environmental Pollution from Distillery

In India, most of the distillery industries use molasses obtained from sugar industries as raw material. During the manufacturing process of alcohol large amount of wastewater like, distillery effluent and spent wash come out. Characteristic of distillery effluent and spentwash is shown in Table 1.1 and 1.2. This spent wash come from rectification unit of distillery. This spent wash contain many valuable compound which can be used further by some other industries generally fertilizer industries.

Sources of Wastewater: For every liter of alcohol produced molasses-based distilleries generate 8-15 L of wastewater characterized by high BOD (45-60 000 mg/l), high COD (80-160 000 mg/l) and dark color. The most significant sources of wastewater in a distillery plant among the various process stages are fermenter, condenser, bottling, and distillation operations. Wastewater generated from different operation and its characterization is shown in Table 1.3 and 1.4.

Permissible Effluent Quality: Permissible concentration of the discharge effluent from various industries is directly linked to the different legislation and water pollution policies. In India, the Environment (Protection) Act, 1986 and rules and regulation are made by government to protect the environment from the waste discharge by industries. The Ministry of Environment and forest (MOEF), Govt. of India and Central Pollution Control Board (CPCB) has mentioned Minimal National Standard (MINAS) for the discharge of pollutants from industries. The discharge standard mention by CPCB and ISI standard (IS: 506-1980) for distillery effluent are tabulated in Table 1.5 and 1.6.

Table 1.1 Characteristics of Distillery Effluent

S.No.	Parameter	Range*
1.	pH	4.3-5.3
2.	Total Suspended Solids	12,000-14,000
3.	Total Dissolved Solids	45,000-75,000
4.	BOD_5, 20 °C	40,000-50,000
5.	COD	80,000-1,00,000

Table 1.2 Characteristic of Spent Wash of Molasses

Characteristic	From literature	Data from 15 factories
pH	4.5 to 5.0	3.0 to 4.0
Total solid	50,000 to 90,000	1,500 to 1,04,000
Volatile Solid	53,000 to 60,000	1,100 to 75,000
Ash	26,000 to 30,000	200 to 22,00
Calcium as (CaO)	2,600 to 4,000	-
Potash as (K_2O)	6,000 to 15,000	300 to 7,200
Sodium salt as (Na_2O)	1,500 to 2,000	-
Iron etc. hydroxide	100 to 300	-
Acid insoluble	1,000to 1,500	-
BOD_5, 20 °C	30,000 to 70,000	10,000 to 73,000
Phosphorus	-	1,000 to 10,000
Nitrogen (N)	-	100 to15,000

Table1.3 Wastewater Generated in Different Operations (S. Majumdar, personal communication)

Distillery operations	Average wastewater generation (kl/d)	Specific wastewater generation (kl wastewater/kl alcohol)
Spent wash (from distillation)	511.4	11.9
Fermenter cleaning	108.2	2.5
Fermenter cooling	307.7	7.2
Condenser cooling	34.2	0.8
Floor wash	47.6	1.1
Bottling plant	126.9	3.0

Table 1.4 Typical Characteristics of Various Wastewaters Streams (S. Majumdar, personal communication)

Parameter	Spent wash	Fermenter cooling	Fermenter cleaning	Condenser cooling	Fermenter wash	Bottling plant
Color	Dark brown	Colorless	Colorless	Colorless	Faint	Colorless
pH	4-4.5	6.26	5.0-5.5	6.8-7.8	6	7.45
Alkalinity (mg/l)	3500	300	Nil	-	40	80
Total solids (mg/l)	100000	1000-1300	1000-1500	700-900	550	400
Suspended solids (mg/l)	10000	220	400-600	180-200	300	100
BOD (mg/l)	45000-60000	100-110	500-600	70-80	15	5
COD (mg/l)	80000-120000	500-1000	1200-1600	200-300	25	15

Table 1.5 Standard of Distillery Effluent (CPCB, 2006)

Characteristics	Maximum discharge limit
pH	5.5-9.0
BOD_3 at 27 °C	30 mg/l for disposal into inland surface water
	100 mg/l for disposal on land for irrigation
Color and Odor	All effort should be made to remove color and unpleasant odor as far as practicable

Table 1.6 ISI Standards (IS: 506-1980) for Composition of Distillery Effluent

Characteristics	For discharge into water course	For discharge into public sewers	For discharge on land
pH	5.5-9.0	5.5-9.0	5.5-9.0
BOD_5 (mg/l)	100	500	500
Total suspended solids (mg/l)	100	600	-
Oil and grease (mg/l)	10	100	6-10
Temperature (°C)	Shall not exceed 40°C in any section of the stream within 15 meters from effluent outlet		

well as between 1% to 5% each of methanol, isopropanol, methyl isobutyl ketone (MIBK), ethyl acetate, etc.

1.3.2 Environmental Pollution from Distillery

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Sources of Wastewater: For every liter of alcohol produced molasses-based distilleries generate 8-15 L of wastewater characterized by high BOD (45-60 000 mg/l), high COD (80-160 000 mg/l) and dark color. The most significant sources of wastewater in a distillery plant among the various process stages are fermenter, condenser, bottling, and distillation operations. Wastewater generated from different operation and its characterization is shown in Table 1.3 and 1.4.

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1.4 Wastewater Treatment Methods

The treatment of the effluents by the normal methods depends upon the quantum, concentration, toxicity and presence of non-biodegradable organics (Mall, 2005). Several treatment methods are suggested for the wastewater from distillery industry, e.g., biological treatment (Basak and Gökay, 1999; Clemente et al., 2004;) adsorption (Shawwa et al., 2001); wet oxidation (Verenich et al., 2000; Fox and Noike 2004); evaporation of water, concentration of the DWW followed by incineration, anaerobic treatment (bio-methanation) followed by secondary and tertiary treatments, but many of these methods are using more quantity of water, less efficient and more expensive than simple discharge (Garad et al., 2006). Hence, these methods become obsolete and new methods need to be sought.

Electrocoagulation (EC) is an enigmatic technology. This technology lies at the intersection of three or more fundamental technologies - electrochemistry, coagulation and flotation. EC is a complex process with a multitude of mechanisms operating synergistically to remove pollutants. This process is used to remove suspended (fine) solids and dissolved molecules. EC enhances the rate of removal of turbidity to the order of 99% in the distillery effluent

1.5 Environmental Impact

Environmental impact due to in plant and off plant activity in distillery industries is shown in Fig. 1.2.

- Pollution of water, air and soil due to accidents with transport and storage of (by) products.
- Air pollution due to bagasse burning.
- Air pollution and inconvenience due to cane and cane residue burning.

- Human health effects, for both workers and local population, due to agrochemicals.
- Contamination of groundwater by agrochemicals, fertilizer and deposition of liquid and solid residues on the soil.

1.6 Aims and Objectives

In the present work, we aim to treat BDE using EC technology. Only few studies are reported for the EC treatment of distillery spent wash. However, no study is reported for the treatment of BDE using EC method. EC process generates some amount of residue (scum and sludge). Disposal of these residues is very important from environmental point of view. No literature is available in the open literature where residue disposal has been investigated. Based on literature review, the main objectives of the present study are as follows:

1. To characterize the BDE for its various characteristics.
2. To optimize the COD and color removal of BDE by EC using stainless steel (SS) electrodes in a batch EC reactor.
3. To study the effects of four operational parameters namely initial pH, current density, inter-electrode distance and electrolysis time on the COD and color removal utilizing full factorial central composite design based on response surface methodology.
4. To carry out detailed physico-chemical analysis of electrode and residues (scum and sludge) to understand the EC mechanism.
5. To devise a strategy for the disposal of EC residues based on thermo-degradation analysis.

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Alkalinity (mg/l)	3500	300	Nil	-	40	80
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Suspended solids (mg/l)	10000	220	400-600	180-200	300	100
BOD (mg/l)	45000-60000	100-110	500-600	70-80	15	5
COD (mg/l)	80000-120000	500-1000	1200-1600	200-300	25	15

Table 1.5 Standard of Distillery Effluent (CPCB, 2006)

Characteristics	Maximum discharge limit
pH	5.5-9.0
BOD_3 at 27 °C	30 mg/l for disposal into inland surface water
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Table 1.6 ISI Standards (IS: 506-1980) for Composition of Distillery Effluent

Characteristics	For discharge into water course	For discharge into public sewers	For discharge on land
pH	5.5-9.0	5.5-9.0	5.5-9.0
BOD_5 (mg/l)	100	500	500
Total suspended solids (mg/l)	100	600	-
Oil and grease (mg/l)	10	100	6-10
Temperature (°C)	Shall not exceed 40°C in any section of the stream within 15 meters from effluent outlet		

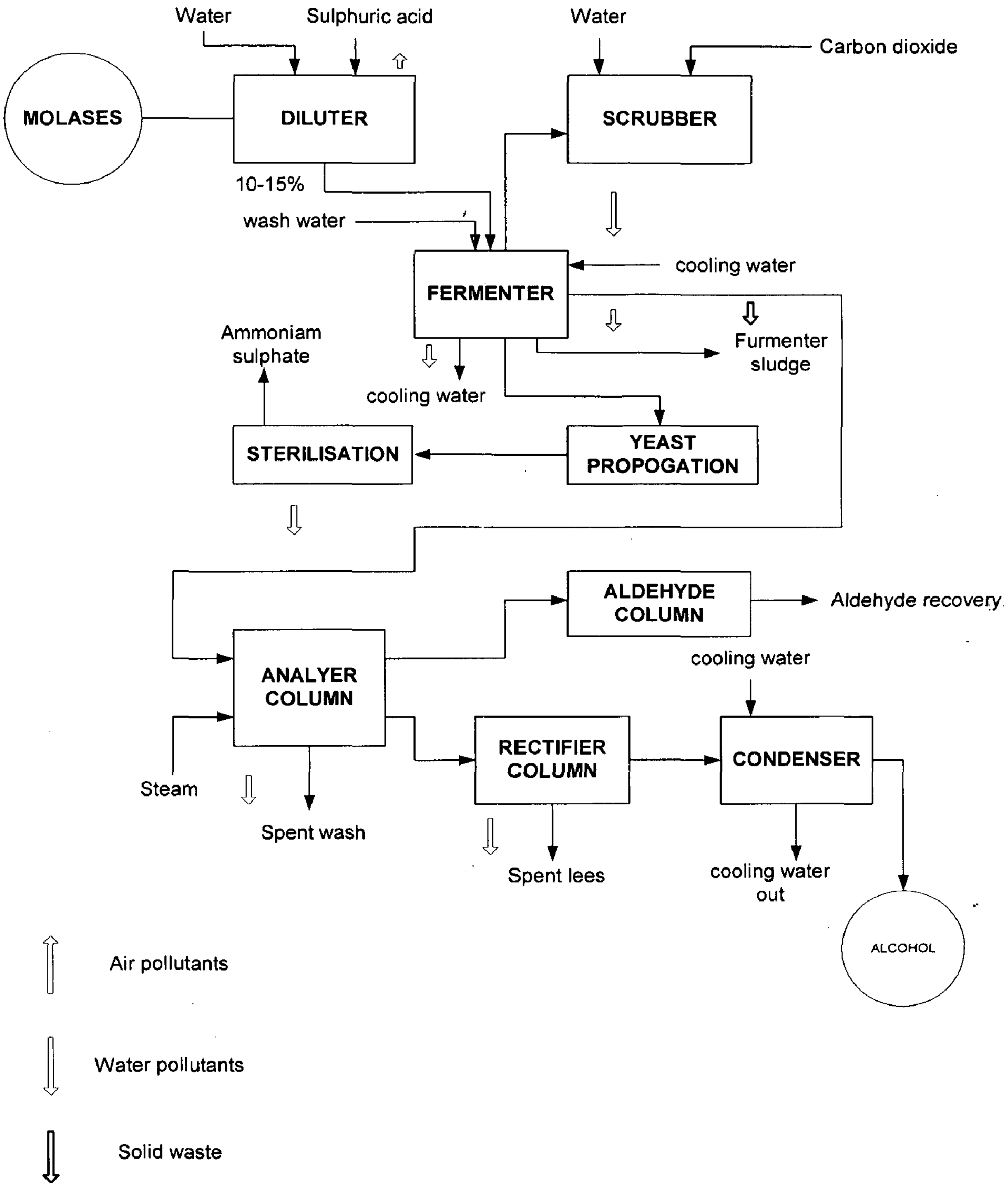

Fig 1.1 Process Manufacturing of Alcohal

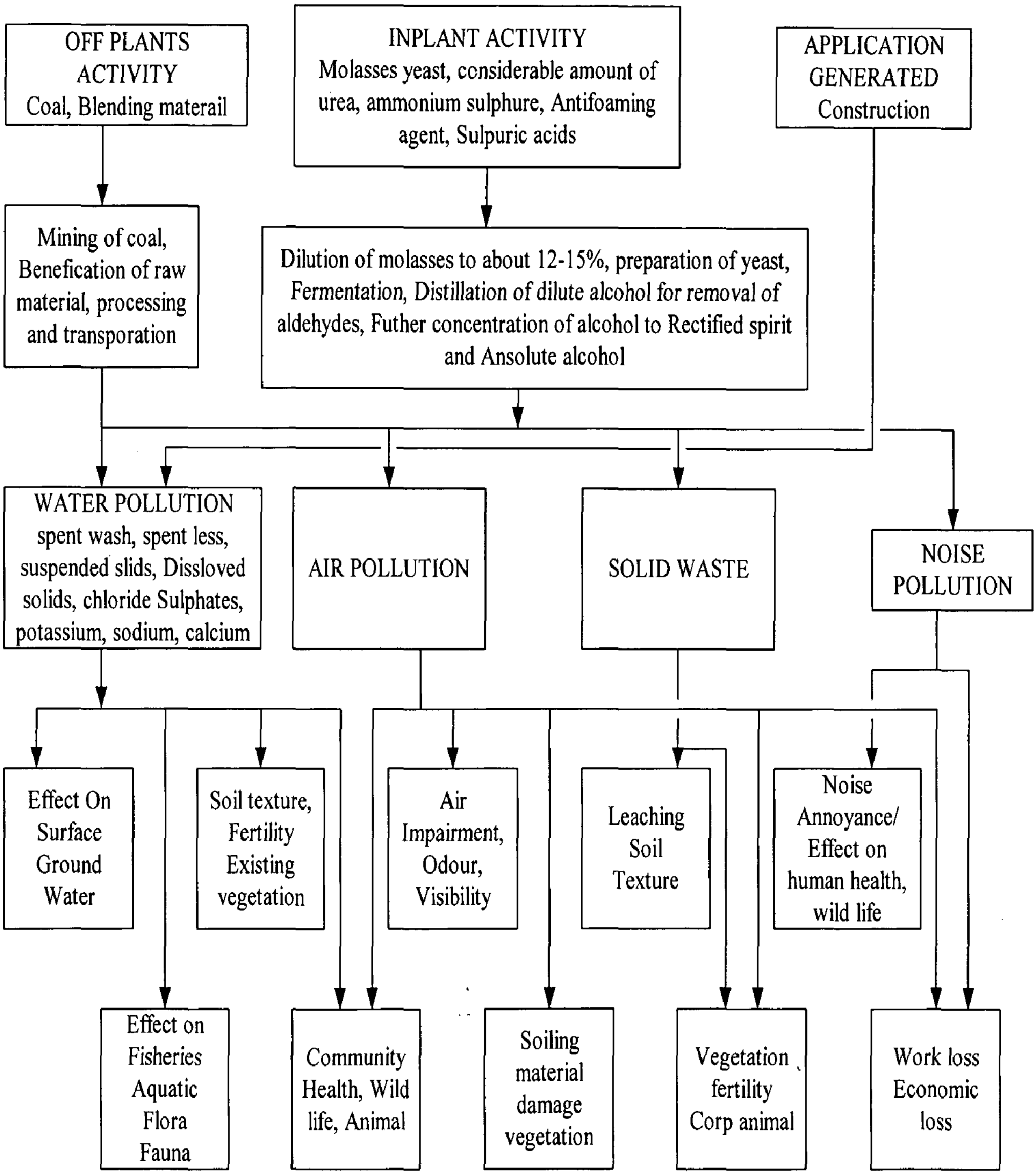

Fig. 1.2 Net Impact: Adverse/Beneficial

CHAPTER 2

LITERATURE REVIEW

2.1 General Scope

This chapter presents a critical and concise review of the existing open literature electrochemical coagulation for the treatment of distillery wastewater. Electrochemical treatment (ECT) although has been used for treating polluted wastewaters. The following sections focus on the fundamentals of this treatment technology, which among others includes the process and design parameters of ECR used in water/wastewater treatment. The research works have been discussed with a view to gauge the efficacy of the treatment and the requirements of the regulatory and statutory authorities on the discharge of effluents in the open sewers, on the land and in the surface waters. Physico-chemical and engineering aspects of the sludge generated in the ECR are also dealt with.

2.2 Treatment Methods of Distillery Effluent

Alcohol is manufacture from molasses, generates large volumes of wastewater that is of serious environmental concern. The effluent is characterized by extremely high chemical oxygen demand (COD) 80,000-100,000 mg/l and biochemical oxygen demand (BOD) 40,000-50,000 mg/l, low pH, strong odor and dark brown color (Central Pollution Control Board (CPCB) 1994, 2003). India is the second largest producer of alcohol with a projected annual production of about 2300 million liter in 2006-07 (Subramanian et al., 2005), alcohol distilleries are rated as one of the 17 most polluting industries. Apart from high organic content, distillery wastewater also contains nutrients in the form of nitrogen

1660-4200 mg/l, phosphorus 225-3038 mg/l and potassium 9600-17,475 mg/l (Mahimairaja and Bolan, 2004) that can lead to eutrophication of water bodies. In an earlier review on this subject, (Sheehan and Greenfield, 1980) discussed treatment options practiced in the 1970s. More recently, (Wilkie et al., 2000) have examined characteristics and anaerobic treatment of effluent obtained from different feedstock used for alcohol manufacture. This review focuses on the advances in molasses-based distillery wastewater treatment in the last two decades and the emerging technologies in this field.

2.2.1 Biological Treatment

Presently anaerobic biological treatment systems like bi- (or di-) phasic and UASB processes and their variants are more popular. In bi-phasic system, the first stage of the anaerobic treatment is the acid formation (or acidogenic) stage, where the carbonaceous matter gets hydrolyzed and converted into volatile acids by facultative anaerobic microorganisms (acidogens). In the second stage, anaerobic methanogens degrade these acids into methane and carbon dioxide

The effluent from the anaerobic biodigester (UASB or its variants) which is referred to as the biodigester effluent (or BDE) still has high COD (30-40 kg/m^3) and BOD (5-10 kg/m^3). Therefore, it has to be treated in the secondary treatment unit. In secondary treatment, the BDE is treated aerobically requiring high efficiency of oxygenation through either surface aerators or submerged high pressure bubblers. It is able to reduce the COD upto 8-15 kg/m^3 and residual BOD in the range of 3-7 kg/m^3. Besides this, the open lagoon treatment system (aerobic treatment system) causes odor and ground water pollution problems. The effluent coming out from aerobic treatment system contains substantial amount of nutrients like nitrogen, potassium and phosphorus, therefore after suitable dilution, it may be used for irrigation and as a source of fertilizer (ferti-irrigation).

A number of research workers have suggested suitable application rates for this effluent under different conditions for ferti-irrigation in order to avoid the possibility of removalin crop yields because of inorganic toxicity. The color of the effluent may cause to removalin the oxygen diffusion and sunlight penetration, which is essential for crops and aquatic life. High salt load, mainly potassium and sulphur, into soil system may hamper the sustained crop yields due to continued long term applications of effluents in agriculture. A progressive and large alcohol based organic chemicals unit uses ferti-irrigation technique with the treated effluent having a BOD of < 500 mg/dm^3.

2.2.2 Physico-chemical Treatment

Adsorption: Activated carbon is a widely used adsorbent for the removal of organic pollutants from wastewater but the relatively high cost restricts its usage. Significant decolorization was observed in packed bed studies on anaerobically treated spentwash using commercial activated charcoal with a surface area of 1400m^2/g (Chandra and Pandey, 2000). Almost complete decolorization (49.9%) was obtained with 70% of the diluted sample, which also displayed over 90% BOD and COD removal. Mall and Kumar (1997) compared the color removal using commercial activated carbon and bagasse flyash. 58% color removal was reported with 30 g/l of bagasse fly ash and 80.7% with 20 g/l of commercial activated carbon. Since the bagasse fly ash has high carbon content and the adsorbed organic material further increases its heating value, the spent adsorbent can be used for making fire briquettes. Yet another adsorbent that has been examined is the natural carbohydrate polymer chitosan derived from the exoskeleton of crustaceans. (Lalov et al., 2000) studied the treatment of distillery wastewater using chitosan as an anion exchanger. At an optimum dosage of 10 g/l and 30 min contact time, 98% color and 99% COD removal was observed.

Coagulation and Flocculation: Almost complete color removal 98% of biologically treated distillery effluent has been reported with conventional coagulants such as ferrous sulfate, ferric sulfate and alum under alkaline conditions (Pandey et al., 2003). The best results were obtained using Percol 47, a commercial organic anionic polyelectrolyte, in combination with ferrous sulfate and lime. The combination resulted in 99% removalin color and 87 and 92% removalin COD and BOD, respectively. Similar findings have also been reported by (Mandal et al., 2003). Coagulation studies on spentwash after anaerobic-aerobic treatment have also been conducted using bleaching powder followed by aluminum sulfate (Chandra and Singh, 1999). The optimum dosage was 5 g/l bleaching powder followed by 3 g/l of aluminum sulfate that resulted in 96% removal in color, accompanied by up to 97% removalin BOD and COD. Non-conventional coagulants namely wastewater from an iron pickling industry which is rich in iron and chloride ions and titanium ore processing industry containing significant amounts of iron and sulfate ions have also been examined (Pandey et al., 2003). The iron pickling wastewater gave better results with 92% COD removal, combined with over 98% color removal. Though the titanium processing wastewater exhibited similar color removal levels, the COD and BOD reductions were perceptibly lower.

Wet Oxidation Process: The wet oxidation at high pressure and temperature has not been applied due to large volume of BDE. (Dhale et al., 2000) have reported on the wet oxidation of pretreated BDE. They first heated the effluent in absence of air at 150 °C, cooled and then flocculated it with synthetic iron based polymer followed by wet oxidation of BDE having initial COD in the range of 600-800 mg/dm^3.

This process is the liquid phase oxidation of organics and oxidizable inorganic components at high temperature 125-320 °C and pressure 5-200 bar using oxidants air, O_2, H_2O_2, ozone, etc. with or without a catalyst. At these conditions the solubility of oxygen gets enhanced, providing increased driving forces for oxidation. The organic compounds get oxidized and converted into CO_2 and other innocuous end products. Carbon is oxidized to CO_2, nitrogen is converted into NH_3, NO_3, or elemental nitrogen; halogen and sulfur are converted to inorganic halides and sulfates.

As the temperature is increased, the oxidation gets enhanced and the treated effluent contains mainly low molecular weight oxygenated compounds, predominantly carboxylic acids. The extent of oxidation depends mainly on the temperature, oxygen partial pressure, residence time and the ability of the pollutants to oxidize.

Ion Exchange (IX): In this process undesirable ions in the feed water are exchanged for desirable ions as the water passes through granular chemicals, called ion-exchange resins. For example, cation exchange resins are typically used in homes and municipal water treatment plants to remove calcium and magnesium ions in "hard" water and by industries in the production of ultra-pure water. The higher the concentration of dissolved solids in the feed water, the more often the resins will need to be replaced or regenerated. With rising costs for resins and for disposing of regeneration solutions, IX is now competitive with RO and ED only in treating relatively dilute solutions containing a few hundred ppm of dissolved solids. Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal waste. But this method is not economical as far as the cost is concerned (Slokar and Le Marechal, 1998).

Membrane Treatment/Reverse Osmosis: This process may be applied to reduce the COD and the dissolved metals of the distillery effluent. Membrane technology has had wide application in wastewater treatment and desalination through reverse osmosis. In this process, a pressure difference across a membrane is used to overcome the osmotic pressure gradient. Cellulose acetate membranes are the most common, used in either wound, hollow fiber, tubular or plate and frame configuration. The micro porous hollow fiber membranes are used to separate the solute concentration in the range of 10 to 10000 mg/dm^3 (Kentish and Stevens, 2001). The fouling of membranes has been a major obstacle in the use of reverse osmosis. This liquid membrane emulsion was brought in contact of DWW in a batch mode by stirring at 110 rpm. The process has been found to reduce 87 % COD and 97.3 % BOD at optimum operating conditions (Kumaresan et al., 2003).

Microfiltration: Microfiltration is an important separation process, as the permeate flux is higher than that of any other membrane processes and the permeate quality is much better than that of the conventional separation processes such as sedimentation, centrifugation, filtration, flotation, etc. Most of the pollutants produced in the water have particle sizes ranging from 0.05 - 10 μm and can be removed by MF as they fall within the range of microfiltration process.

Ultrafiltration: Ultrafiltration (UF) membranes allow the passage of water and retain high molecular weight solutes and colloidal particles. UF pore sizes usually ranges from 5 - 20 *nm* and retain fine colloids, macromolecules, and micro-organisms. Partial retention of some ions may occur due to the charge interaction.

Nanofiltration: The nanofiltration membranes (NF) are believed to have pores (2 - 5 *nm*) and partially retain ions, through small and mono-valent ions, and low molecular weight organics tend to pass. NF membranes usually have significantly higher water permeability than that of RO membranes and also operate at lower pressure (typically 7 - 30 *bars*).

Concentration-Incineration Process: Due to very large volume and very high BOD and COD of DWW, and also the requirement of very low BOD and COD for the treated DWW for discharge into the surface waters and on land, several distilleries concentrate DWW through multi-effect evaporators followed by incineration of the concentrate to recover the maximum energy in the form of steam, and minerals and inorganic salts which serve as plant nutrients in the form of ash. During evaporation, in multi-effect evaporators, the stillage is concentrated (more than 50-80%) to give a syrup with a co-production of evaporator condensate which is very low in organics (COD < 10 g/dm^3). The condensate is of a quality that can be used for both the boiler feed and as the cooling make-up water.

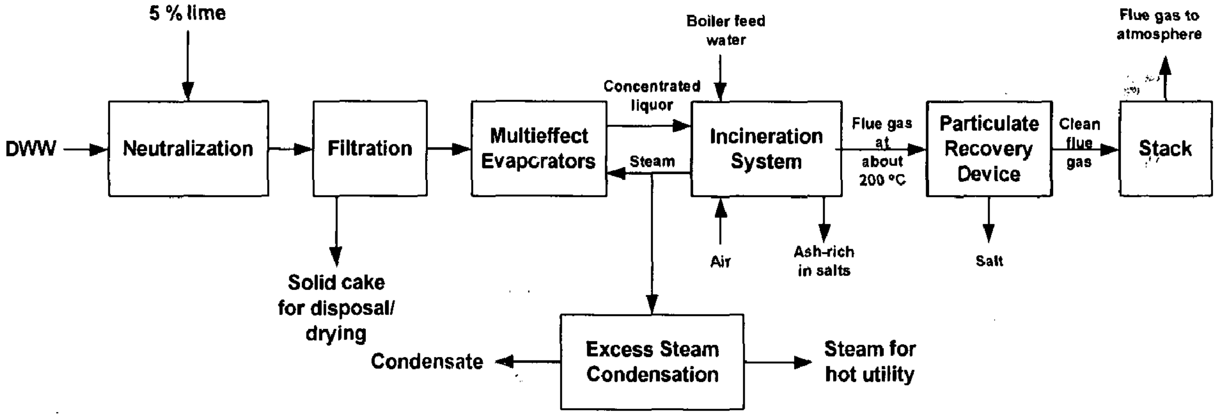

Fig. 2.1 DWW Concentration and Incineration Process.

The general unit operations involved in the evaporator concentration - incineration system is shown in Fig. 2.1

The DWW having a pH in the range of 4.0 - 4.5 is neutralised using lime solution (~ 5 %). The neutralization is carried out in three tanks. The first tank receives the wash, the permeability than that of RO membranes and also operate at lower pressure (typically 7 - 30 *bars*).

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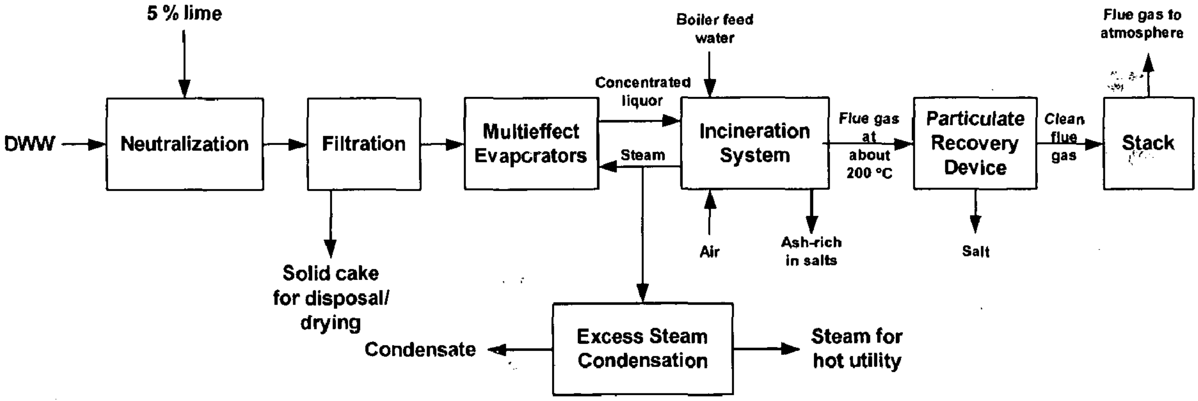

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The DWW having a pH in the range of 4.0 - 4.5 is neutralised using lime solution (~ 5 %). The neutralization is carried out in three tanks. The first tank receives the wash, the second is used for neutralizing and settling and the third pumps the neutralized wash to the filter press, where suspended impurities are removed. The filtrate is sent to multiple effect evaporators. The vacuum in the last effect is maintained at about 0.01 MPa by a two stage steam ejector or a vacuum pump. The concentrated liquor obtained from the evaporators is fed to the incineration system.

Biomethanation using Ecomet XT: Anaerobic biomethanation system uses a specially designed Mixed Tank Biodigester; called Ecomet XT^R, to convert organic matter into useful energy in the form of Biogas. The biological process of conversion takes place at Mesophilic temperature in a controlled atmosphere ensuring maximum conversion efficiency and production of Biogas. Ecomet XT is specially designed to handle highly toxic distillery waste taking into account the suspended solids, toxic compounds and high COD and BOD in spent wash, shock loads arising out of distillery operation and variations in feed characteristics, variation in temperature conditions.

Bio-composting Process: Composting is process of converting organic matter into manure, rich in humus and plant nutrients. This alternative of utilizing digested/raw spent wash in combination with press mud/filter cake from sugar mill has been widely accepted and implemented. The wastewater from the distillery in raw or concentrated form or from the Biogas plant can be further treated in the Composting system. Like biomethanation, biocomposting is also a biological process and needs a system, which will provide food, air, and moisture in appropriate quantity to the organisms. Hence the design of mixing and aeration system, the cycle of operation are of paramount importance for optimum results. To avoid ground pollution, spent wash is sprayed in a controlled manner on the windrows, which are formed on the fields by composting machine driven by tractor. A proper leachate management system in and around the compost plot to take care of flooding in rainy season is important. Ground surface has to be made suitable to facilitate vehicular movement. A well-designed Bio-composting process can ensure zero pollution when enough Press Mud as filler material is available and process norms are strictly adhered to. It is the most cost-effective solution available when weather conditions are favorable.

Table 2.1 Principle of different Wastewater Treatment Technique

Technique	Principle	Reference
Adsorption	Surface adherence. Decolorization is a result of two mechanisms: adsorption and ion exchange and is influenced by many physio-chemical factors, such as, dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time	Mall et al. (2005), Chakraborty et al. (2005), Kasgoz et al. (2005), Mall et al. (2006), Orfio et al. (2006), Chu and Chen (2002), Liversidge et al. (1997), Gupta and Shukla (1992), Mckay et al. (1980) etc
Biological Processes	Self purification, use of biological organisms	Daneshvar et al.(2006), Chen et al.(2005), Gill et al.(2002),etc
Electrocoagulation	Electrocoagulation involves the generation of coagulants in situ by dissolving electrically metal ions from metal electrodes. The metal ions generation takes place	Do and Chen (1994), Kim et al. (2002), Can et al. (2003), Alinsafi et al. (2004), Mollah et al. (2004), Pathak et al. (2004), Kobya et al. (2005), Golder et al. (2005),

	at the anode and hydrogen gas is released from the cathode. The hydrogen gas would also help to float the flocculated particles out of the water.	Ghalwa et al. (2005), Daneshvar et al. (2002, 2004, 2006), S. Mahesh et al. (2006), Aleboyeh et al. (2007) etc
Membrane Processes	Selective permeability, filteration	Qin et al. (2007), Allegre et al. (2006), Mozia et al. (2005), Machenbach (1998) etc
Composting	Converting organic matter into manure, rich in humus and plant nutrients.	Marhuenda et al. (2007), Bustamante et al. (2008), Satisha et al. (2006), Suthar et al. (2008) etc

2.3 Selection of Methodology

There are various method and techniques exit for the treatment of wastewater. Physical process which include sedimentation, adsorption, membrane filtration, ion exchange, Irradiation, or Chemical processes are used for the removal of floating and settleable solids and also degradation of volatile organic compounds present at low concentrations in contaminated media. Biological process in which bacteria break down the organic parts of wastewaters; usually accomplished by bringing the wastewater and bacteria together in trickling filters, aerobic, anaerobic or in the activated sludge process.

Distillery effluent is acidic having low pH (4-5) and high COD, organic and inorganic matter contain which are difficult to decompose biologically, conventional physico-chemical and biological treatment processes, Moreover all these processes are costly and cannot be used by small industries.

EC technology removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species. These species neutralize the electrostatic charges on suspended solids resultant separation from the aqueous phase. EC can remove 75-99% of metals and 90-99% of suspended solids while reducing BOD and COD by 50-75%. EC eliminates the need of adding expensive chemicals as coagulants to the wastewater and, therefore generates less solid waste, thus saving on disposal costs. EC process provides a simple, reliable and cost-effective method for the treatment of wastewater without any need for additional chemicals, and thus the secondary pollution

2.4 Literature Review

This section of these chapter deals with the review of EC and treatment of Distillery Effluent. There has been lots of treatment process has been studied like adsorption process for treatment of dye (Mall et al., 2005) on reactive red (kasgoz et al., 2005) similarly for chemical process (Lucas et al., 2007) and for biological process (Dansehvar et al., 2006)

Electrocoagulation is an effective alternate technique for wastewater treatment. Recently a lot of work has been done on the treatment of wastewater from various industries using this method.

Table 2.2 Literature Review

Author	Literature
Yousuf and Mollah 2004	Electrocoagulation is an evolving technology that is being effectively applies today for the wastewater treatment, the paucity of scientific understanding of the complex chemical and physical process involved is limiting future design and hindering progress. The objective of this review through a survey of the literature is to bring the chemistry and physical processes involved into perspective and to focus attention on those areas critically needing researches
Manisankar and Viswanathan 2004	Electrochemical treatment processes for the treatment of distillery effluent to provide valuable contributions to the protection of the environment. Electrolysis of distillery effluent was carried out in a static electrochemical reactor. Two different types of anodes, planar graphite (Gr) and titanium substrate insoluble anodes (TSIA) were chosen for the treatment of distillery effluent. Lead dioxide coated on titanium (PbO_2-Ti) and ruthenium oxide coated on titanium (RuO_2-Ti) electrodes were used as TSIA. Current density (C.D.) was varied from 1.5 to 5.5 A/dm^2. Complete decolorisation was obtained in both cases. A maximum of 92% of chemical oxygen demand (COD) reduction, 98.1% of biological oxygen demand (BOD) removaland 99.5% of absorbance removalwere obtained in the set up in which RuO2-Ti as anode and stainless steel as cathode were used.
Holt and	Coagulation and flocculation are traditional methods for the treatment

Barton 2002	of polluted water. Electrocoagulation presents a robust novel and innovative alternative in which a sacrificial metal anode doses water electrochemically. This has the major advantage of providing active cations required for coagulation, without increasing the salinity of the water. Electrocoagulation is a complex process with a multitude of mechanisms operating synergistically to remove pollutants from the water. A wide variety of opinions exist in the literature for key mechanisms and reactor configurations. A lack of a systematic approach has resulted in a myriad of designs for electrocoagulation reactors without due consideration of the complexity of the system. A systematic, holistic approach is required to understand electrocoagulation and its controlling parameters. This will enable *a priori* prediction of the treatment of various pollutant types.
Aleboyeh et al., 2007	The decolorization of C.I. Acid Red 14 (AR14) azo dye by EC process in a batch reactor. Response surface methodology (RSM) was applied to evaluate the simple and combined effects of the three main independent parameters, current density, time of electrolysis and initial pH of the dye solution on the color removal efficiency and optimising the operating conditions of the treatment process. Analysis of variance (ANOVA) showed a high coefficient of determination value (R^2 = 0.928) and satisfactory prediction second-order regression model was derived. Maximum color removal efficiency was predicted and experimentally validated. The optimum current density, time of

Table 2.3 (Contd.)

Type of wastewater	Removal path	Reactor shape, mode of operation and volume	Electrode material, size		Env. parameters monitored	Removal (%)	Current/CD and voltage, pH, ET	Reference
			Anode/cathode/no.	Size, effective surface area				
Textiles	ECO	circular, batch, Lab scale pilot	Ti/Pt, SS: 304	Ti/Pt 18 cm long and 1 cm dia, SS:5 cm dia, 02	COD, BOD, chlorides	COD: 86% BOD: 71% COD/BOD: 1.52	20 V, 50A	Vlyssides et al., 1999
Petrochemicals	EF+EC	cuboidal, batch, 0.5 l	Graphite and SS mesh for EF/02, Fe andAl for EC/16	9 cm x 10 cm, 35 cm^2	COD, turbidity, phenol, grease, pH	Turbidity: 83 and 88% for EC and EF	14 mA/m^2	Dimoglo et al., 2004
Tannery	ECO	Circular, batch, 1 l	Ti/PbO_2/ SS/02	100 cm^2,	COD, Cr_{total} TOC, TKN	COD: 35% TOC: 84% Cr_{total}: 93%	400 A/m^2	Szpyrkowicz et al., 2005
Chemical-mechanical planarization	EC+EF	cylindrical, batch, 7.5 cm dia, 25.4 cm height reactor, 0.8 l	Wrought iron, SS cylinder/02	-	TOC, turbidity	TOC: 81%	pH:5-8, 10 min ET	Kin et al., 2006

Barton 2002	of polluted water. Electrocoagulation presents a robust novel and innovative alternative in which a sacrificial metal anode doses water electrochemically. This has the major advantage of providing active cations required for coagulation, without increasing the salinity of the water. Electrocoagulation is a complex process with a multitude of mechanisms operating synergistically to remove pollutants from the water. A wide variety of opinions exist in the literature for key mechanisms and reactor configurations. A lack of a systematic approach has resulted in a myriad of designs for electrocoagulation reactors without due consideration of the complexity of the system. A systematic, holistic approach is required to understand electrocoagulation and its controlling parameters. This will enable *a priori* prediction of the treatment of various pollutant types.
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	electrolysis and initial pH of the dye solution were found to be 102A/m^2, 4.47 min and 7.27, respectively. Under optimal value of process parameters, high removal (>91%) was obtained for Acid Red 14. Graphical response surface and contour plots were used to locate the optimum point.
Holt et al. 2002	Electrocoagulation is a complex process with a multitude of mechanisms operating synergistically to remove pollutants from the water. A wide variety of opinions exist in the literature for key mechanisms and reactor configurations. A lack of a systematic approach has resulted in a myriad of designs for electrocoagulation reactors without due consideration of the complexity of the system. A systematic, holistic approach is required to understand electrocoagulation and its controlling parameters. This will enable *a priori* prediction of the treatment of various pollutant types.
Mahesh et al. 2006a	Electrochemical degradation of agri-based paper mill wastewater (black liquor) was investigated in a 2 dm^3 electrolytic batch reactor using iron plate electrodes. Of the four-, six-, and eight-plate configurations, a current density of 55.56 A/m^2 at neutral pH with a six-plate arrangement was found to be optimal, achieving a maximum chemical oxygen demand (COD) and color removal of 80% and 90% (175 platinum-cobalt units (PCU)), respectively. The chemical dissolution of iron was strongly influenced by pH$_0$. Electrochemical treatment at higher pH$_0$ (pH$_0$ g 9) increases the dissolution of iron electrodes by an

	order of magnitude. At the optimal current density, the iron electrode consumed is 31.27 g/m2âh, achieving maximum COD removal. An increase in salinity reduces the treatment time significantly, and the sludge settling characteristics also improve. The addition of polyacrylamide (10 mg/dm^3) to the electrochemical reactor enhances the COD removal rate with a very short treatment time with excellent sludge settleability. Coagulation using alum (360 mg/dm^3) along with 20 mg/dm^3 polyacrylamide (PAA) further reduced COD values to <180 mg/dm^3 and a near 100% (<5 PCU) color removal. An overall COD removal of 91% and color removal of near 100% could be achieved by electrochemical treatment followed by coagulation/flocculation.
Diaz et al. 2006	The removal of organic pollutants from a highly complex industrial wastewater by aluminium electrocoagulation process coupled with biosorption was evaluated. Under optimal conditions of pH 8 and 45.45A/m^2 current density, the electrochemical method yields a very effective removalof all organic pollutants, this removalwas enhanced when the biosorption treatment was applied as a polishing step. Treatment reduced chemical oxygen demand (COD) by 84%, biochemical oxygen demand (BOD_5) by 78%, color by 97%, turbidity by 98% and fecal coliforms by 99%. The chemical species formed in aqueous solution were determined. The initial and final pollutant levels in the wastewater were monitored using UV-vis spectrometry and cyclic voltammetry. Finally, the morphology and elemental

	current densities), whereas EC with Al electrodes was more beneficial for COD removal in terms of electrical energy consumption (5 kWh/m3 wastewater for EC with Al electrodes instead of 9 kWh/m3 wastewater for EC with SS electrodes).
Daneshvar et al, 2006	Decolorization of C.I. Acid Red 14 (AR14) azo dye by electrocoagulation (EC) process was studied in a batch reactor. Response surface methodology (RSM) was applied to evaluate the simple and combined effects of the three main independent parameters, current density, time of electrolysis and initial pH of the dye solution on the color removal efficiency and optimising the operating conditions of the treatment process. A 23 full factorial central composite face centred (CCF) experimental design was employed. Analysis of variance (ANOVA) showed a high coefficient of determination value (*R*2 = 0.928) and satisfactory prediction second-order regression model was derived. Maximum color removal efficiency was predicted and experimentally validated. The optimum current density, time of electrolysis and initial pH of the dye solution were found to be 102Am−2, 4.47 min and 7.27, respectively. Under optimal value of process parameters, high removal (>91%) was obtained for Acid Red 14. This study clearly showed that response surface methodology was one of the suitable methods to optimize the operating conditions and maximize the dye removal. Graphical response surface and contour plots were used to locate the optimum point.

2.5 ECT of Waters

Electrochemical technology has been used in the treatment of a wide variety of raw water and wastewaters. The types of water and wastewaters are given below:

Waters: Removal of fluoride, arsenic, iron, selenium etc. from ground/surface waters for drinking purpose and disinfection of waters, etc.

Synthetic wastewaters: CMP planarization, dye wastewaters, chromium containing effluent, cyanide wastewaters, etc.

Real wastewaters: Wastewaters or treated wastewaters from dairies, tanneries, food processing, textiles, poultry slaughter houses, oil mills, beer brewery, restaurant, pulp and paper mills, distilleries, potato chips manufacturing, petrochemicals, etc.

As seen from the review systems using a variety of anode and cathode geometries exist. Table 2.3 briefly describes a select patented information/knowledge which is relevant to ECT of water/wastewaters.

Table 2.3 Brief Summary of Parameter of Recent Work on Electrocoagulation of Wastewater

Type of wastewater	Removal path	Reactor shape, mode of operation and volume	Electrode material, size		Env. parameters monitored	Removal (%)	Current/CD and voltage, pH, ET	Reference
			Anode/cathode/no.	Size, effective surface area				
Distilleries	ECT	nm	Planar graphite and Ti substrate insoluble anodes	nm	pH: 6.9-7.2 color: Dark brown BOD: 7000 COD: 2000	COD: 80.6% BOD: 90% Color: 100%	1.5 - 5.5 A/dm^2 (opt)	Manishankar et al., 2003
Distilleries (Bewerage alcohol)	ECO	cylindrical, batch, 0.9 l	Graphite particles and Ti sponge, Ti/RuO_2	-	COD, color	COD: 89.62% Color: 92.44% TS: 67.77%	0.0045 A/m^2, pH opt. 1.0	Piya-areetham et al., 2006
Electro-plating	ECP	cuboidal, continuous, 6 l	Monopolar,SS and SS/06	10 x 30 cm	Cr^{6+} conductivity	SVI:60-80	> 3.2 pH opt.	Kongsricharoern and Polprasert 1995
Egg processing	EC	Cuboidal 1.0 l	Al/Fe/SS 02	30 cm^2	COD, Turbidity	COD: 92-97% Turbidity: 99%	$pH_{adjusted}$: 4.5	Xu et al., 2002

	order of magnitude. At the optimal current density, the iron electrode consumed is 31.27 g/m2âh, achieving maximum COD removal. An increase in salinity reduces the treatment time significantly, and the sludge settling characteristics also improve. The addition of polyacrylamide (10 mg/dm^3) to the electrochemical reactor enhances the COD removal rate with a very short treatment time with excellent sludge settleability. Coagulation using alum (360 mg/dm^3) along with 20 mg/dm^3 polyacrylamide (PAA) further reduced COD values to <180 mg/dm^3 and a near 100% (<5 PCU) color removal. An overall COD removal of 91% and color removal of near 100% could be achieved by electrochemical treatment followed by coagulation/flocculation.
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	composition of the biosorbent was characterized with scanning electron microscopy (SEM) and energy dispersion spectra (EDS).
Yusuf Yavuz 2006	Electrochemical treatment of alcohol distillery wastewater using iron electrode with and without the presence of H_2O_2 was investigated. The effects of sodium sulfate concentration as supporting electrolyte, current density, pH and H_2O_2 concentration on the removal efficiency were investigated. As a result of the electrofenton (EF) study, COD removal efficiency of 92.6% for an initial COD of 4985 mg/l and TOC removal efficiency of 88.7% for an initial TOC of 1507 mg/l were achieved for the pre-treated alcohol distillery wastewater (PTDW) with the additions of 0.3MNaSO4 and 60000 mg/l H_2O_2 at pH 4. In the same study, specific energy consumption of 0.53 kWh/g COD removed was reached at the current density of 60 mA/cm^2. On the other hand, electrocoagulation (EC) alone was found ineffective in all experimental conditions studied. According to the results obtained, by contrast with EC, EF process is very efficient for the treatment of alcohol distillery wastewater which has high concentration of refractory organic matters.
Chaudhari et al. 2005	Removal of molasses-derived color and chemical oxygen demand from the biodigester effluent of a molasses-based alcohol distillery effluent treatment plant was observed using inorganic coagulants—FeCl3, AlCl3 and polyaluminium chloride (PAC). The coagulation/flocculation yield about 55, 60 and 72% COD reductions and about 83, 86 and 92% color reductions, with the use of 60 mM/l

	AlCl3, 60 mM/l FeCl3 and 30 ml/l of polyaluminium chloride, respectively, at their optimum initial pH. The critical pH of the effluent-coagulant mixture plays a very significant role in the coagulation/flocculation process, with pH0 5.5 being the optimum for PAC. The solid residue, obtained by filtration and drying from the use of PAC has specific energy of 13.4 MJ/kg and can be used as a medium energy fuel material. The filtration characteristics of the flocculated effluent are poor. High COD removalof the waste water by flocculation with PAC may be a better alternative to the conventional aerobic treatment process of the biodigester effluent.
Idil et al., 2007	The treatment of real reactive dyebath effluent comprising of an exhausted reactive dyebath and its sequential rinses with electrocoagulation (EC) using aluminum (Al) and stainless steel (SS) electrodes. The experimental study focused on the effect of applied current density (22-87 mA/cm2; at an initial, optimum pH of 5.5) on decolorization and COD removal rates using Al and SS as electrode materials. Results have indicated that the treatment efficiency was enhanced appreciably by increasing the applied current density when Al electrodes were used for EC, whereas no clear correlation existed between current density and removal rates for EC with SS electrodes the treatment efficiency could only be improved when the applied current density was in the range of 33-65 mA/cm2. It was established that EC with SS electrodes was superior in terms of decolorization kinetics (99-100% color removal after 10-15 min EC at all studied

	current densities), whereas EC with Al electrodes was more beneficial for COD removal in terms of electrical energy consumption (5 kWh/m3 wastewater for EC with Al electrodes instead of 9 kWh/m3 wastewater for EC with SS electrodes).
Daneshvar et al, 2006	Decolorization of C.I. Acid Red 14 (AR14) azo dye by electrocoagulation (EC) process was studied in a batch reactor. Response surface methodology (RSM) was applied to evaluate the simple and combined effects of the three main independent parameters, current density, time of electrolysis and initial pH of the dye solution on the color removal efficiency and optimising the operating conditions of the treatment process. A 23 full factorial central composite face centred (CCF) experimental design was employed. Analysis of variance (ANOVA) showed a high coefficient of determination value (*R*2 = 0.928) and satisfactory prediction second-order regression model was derived. Maximum color removal efficiency was predicted and experimentally validated. The optimum current density, time of electrolysis and initial pH of the dye solution were found to be 102Am−2, 4.47 min and 7.27, respectively. Under optimal value of process parameters, high removal (>91%) was obtained for Acid Red 14. This study clearly showed that response surface methodology was one of the suitable methods to optimize the operating conditions and maximize the dye removal. Graphical response surface and contour plots were used to locate the optimum point.

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As seen from the review systems using a variety of anode and cathode geometries exist. Table 2.3 briefly describes a select patented information/knowledge which is relevant to ECT of water/wastewaters.

Table 2.3 Brief Summary of Parameter of Recent Work on Electrocoagulation of Wastewater

Type of wastewater	Removal path	Reactor shape, mode of operation and volume	Electrode material, size		Env. parameters monitored	Removal (%)	Current/CD and voltage, pH, ET	Reference
			Anode/cathode/no.	Size, effective surface area				
Distilleries	ECT	nm	Planar graphite and Ti substrate insoluble anodes	nm	pH: 6.9-7.2 color: Dark brown BOD: 7000 COD: 2000	COD: 80.6% BOD: 90% Color: 100%	1.5 - 5.5 A/dm^2 (opt)	Manishankar et al., 2003
Distilleries (Bewerage alcohol)	ECO	cylindrical, batch, 0.9 l	Graphite particles and Ti sponge, Ti/RuO$_2$	-	COD, color	COD: 89.62% Color: 92.44% TS: 67.77%	0.0045 A/m^2, pH opt. 1.0	Piya-areetham et al., 2006
Electro-plating	ECP	cuboidal, continuous, 6 l	Monopolar,SS and SS/06	10 x 30 cm	Cr^{6+} conductivity	SVI:60-80	> 3.2 pH opt.	Kongsricharoern and Polprasert 1995
Egg processing	EC	Cuboidal 1.0 l	Al/Fe/SS 02	30 cm^2	COD, Turbidity	COD: 92-97% Turbidity: 99%	pH$_{adjusted}$: 4.5	Xu et al., 2002

Table 2.3 (Contd.)

Type of wastewater	**Removal path**	**Reactor shape, mode of operation and volume**	**Electrode material, size**		**Env. parameters monitored**	**Removal (%)**	**Current/CD and voltage, pH, ET**	**Reference**
			Anode/cathode/no.	**Size, effective surface area**				
Olive mill	EC	cuboidal, batch, 0.5 l	Al/Fe/16	35 cm^2	COD, color	COD: 42% Color: 90-97%	CD: mA/cm^2 pH: 6.2 ET= 30 min	Inan et al., 2004
Industrial wastewater	EC	batch, 4 l	Fe	0.066 m^2	COD, color	COD: 84% Color: 97%	CD: 45.45 A/m^2 , pH: 8	Ivonne et al, 2006
Azo dye-Acid Red 14	EC	batch ,0.5 l	Fe (ST 37-2) Steel (grade 304)	-	color	Color: 93%	CD: 80 A/m^2 ET: 4 min pH: 6-9	Daneshvar et al. 2004
Dyebath	EC	batch, 2 l	Al, SS (grade 304)	-	Color, COD	Color: 95% COD: 60%	CD: 43 mA/cm^2 ET: 50 min	Idil et al, 2007
Metal cutting fluid	EC	batch	Fe, Al	143 cm^2	COD, TOC	COD: 92% TOC: 80%	CD: 60 A/m^2 pH: 7 ET: 25 min	Koby et al, 2007
Distillery	ECT	batch, 1 l	Fe	100 cm^2	COD, TOC	COD: 92.6% TOC: 88.7%	CD:60 mA/cm^2 pH: 4	Yusuf, 2006

Table 2.3 (Contd.)

Type of wastewater	Removal path	Reactor shape, mode of operation and volume	Electrode material, size		Env. parameters monitored	Removal (%)	Current/CD and voltage, pH, ET	Reference
			Anode/cathode/no.	Size, effective surface area				
Textiles	ECO	circular, batch, Lab scale pilot	Ti/Pt, SS: 304	Ti/Pt 18 cm long and 1 cm dia, SS:5 cm dia, 02	COD, BOD, chlorides	COD: 86% BOD: 71% COD/BOD: 1.52	20 V, 50A	Vlyssides et al., 1999
Petrochemicals	EF+EC	cuboidal, batch, 0.5 l	Graphite and SS mesh for EF/02, Fe andAl for EC/16	9 cm x 10 cm, 35 cm^2	COD, turbidity, phenol, grease, pH	Turbidity: 83 and 88% for EC and EF	14 mA/m^2	Dimoglo et al., 2004
Tannery	ECO	Circular, batch, 1 l	Ti/PbO_2/ SS/02	100 cm^2,	COD, Cr_{total} TOC, TKN	COD: 35% TOC: 84% Cr_{total}: 93%	400 A/m^2	Szpyrkowicz et al., 2005
Chemical-mechanical planarization	EC+EF	cylindrical, batch, 7.5 cm dia, 25.4 cm height reactor, 0.8 l	Wrought iron, SS cylinder/02	-	TOC, turbidity	TOC: 81%	pH:5-8, 10 min ET	Kin et al., 2006

Table 2.3 (Contd.)

Type of wastewater	**Removal path**	**Reactor shape, mode of operation and volume**	**Electrode material, size**		**Env. parameters monitored**	**Removal (%)**	**Current/CD and voltage, pH, ET**	**Reference**
			Anode/cathode/no.	**Size, effective surface area**				
Kraft Pulp and paper mill	EC + C	cuboidal, batch, 2.0 l	Monopolar,Fe and Fe/06	9 cm x 10 cm, 900 cm^2	COD, color	COD: 80% BOD: 77% Color: ~90%	55.56 A/m^2 opt., 1 cm spacing opt., pH ~7, 60 min	Mahesh et al., 2006 - Part - I
Textiles	ECT	cuboidal, batch, 1 l and continuous (0.75 lpm)	CI/CI/08	324 cm^2	COD, color (turbidity)	92.5 A/m^2 COD: 51%	50 min	Lin and Peng 1994
Tannery waste liquors	EC	cylindrical, batch, 0.8 l	Axial Ti/Pt anode, peripheral SS 304 cathode	20 cm dia, 25.4 cm height reactor	Detoxification	COD: 83% BOD: 66% TSS: 26% Phenol: 99%	15 V, 100A, 3h ET	Vlyssides etal., 1997

2.6 Conclusions from Literature Review

1. There are many processes for the treatment of wastewater such as adsorption, biodegradation, membrane, RO, chemical coagulation and electrocoagulation.
2. Physical and chemical methods are effective only if the effluent volume is small. This limits the use of physio-chemical methods, such as membrane filtration to small-scale in situ removal.
3. A limiting factor of removal methods is cost. This is true even in lab-scale studies, and methods, therefore, are unable to be used by large-scale industry.
4. Electrocoagulation is an electrochemical wastewater treatment technology that is currently experiencing both increased popularity and considerable technical improvements. Electrocoagulation has already proven very effective in the removal of contaminants from water
5. EC process would eliminate adding expensive chemicals to the wastewater and would subsequently generate less solid waste, thus saving on disposal costs.
6. The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
7. EC process provides a simple, reliable and cost-effective method for the treatment of wastewater without any need for additional chemicals, and thus the secondary pollution.

Chapter 3

ELECTORCOAGULATION FUNDAMENTALS

3.1 General

The basic concept of Electrocoagulation (EC) consists in applying direct current from an external source between the sacrificial anode and the cathode (not necessarily of inert material) to enhance contact between the dispersed particles in the solution and promote *in-situ* coagulation. Addition of metal salts electrochemically at concentrations greater than the solubility limit of the metal hydroxide will result in the formation of hydroxide precipitate.

The EC process takes advantage of the combined effect of charge neutralization/surface complexation/adsorption onto the in-situ formed metal hydroxides produced from the oxidation of corrodible anode materials (Fe, Al) and the combined effect of flotation/concentration/collection of the metal hydroxide scum plus adsorbed pollutants by the hydrogen gas bubbles formed at the cathode To fully exploit electrocoagulation potential, a quantitative understanding of the interactions occurring between the fundamental process mechanisms is required.

3.2 Mechanism of EC

The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity. The mechanisms of removal of ions by EC will be explained with the help of reaction equation.

It is generally accepted that the EC process involves three successive stages:

(a) Formation of coagulants by electrolytic oxidation of the 'sacrificial electrode';

(b) Destabilization of the contaminants, particulate suspension, and breaking of emulsions;

(c) Aggregation of the destabilization phases to form scum. The destabilization mechanism of the contaminants, particulate suspension, an breaking of emulsions has been described in board steps and may be summarized as follows (Mollah et al., 2001)

1. Compression of the diffuse double-layer around the charged species, which is achieved by the interactions of ions generated by dissolution of the sacrificial electrode, due to passage of current through the solution
2. Charge neutralization of the ionic species present in wastewater, which is caused by the counter ions, produced by the electrochemical dissolution of the sacrificial electrode. These counter ions reduce the electrostatic inter-particle repulsion sufficiently so that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
3. Flock formation, and the Flock formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles that have not been complexed. Details of these steps are lacking and require further study.

An electrocoagulation reactor is an electrochemical cell, where a sacrificial metal anode (aluminium, iron, stainless steel) is used to dose polluted water with a coagulating agent (Vik *et al.*, 1984; Holt *et al.*, 1999; Barkley *et al.*, 1993; Pouet and Grasmick, 1995). Electrocoagulation introduces metal cations *in situ*, rather than via external dosing. Simultaneously, electrolytic gases are generated (typically hydrogen at the cathode). Electrocoagulation has the capability to remove a wide range of pollutants including suspended solids, heavy metals, dyes, organic material (such as sewage), FOG's (*i.e.* fats, oils and greases), ions and radionuclides.

pH of the solution is of vital importance in the performance EC process. Various reactions take place in the EC reactor with iron as electrode material.

At iron anode, in situ generation of coagulants takes place by dissolving iron ions from SS electrodes (Thella et al., 2008)

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad (3.1)$$

Also, in acidic pH, the electrode is attacked by H^+ and enhances its dissolution by following reaction:

$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2 \qquad (3.2)$$

The oxygen evolution reaction may also take place at anode and is represented as:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad (3.3)$$

Ferrous ions are oxidized to ferric ions by oxygen in the aqueous phase

$$Fe^{2+} + 1/4O_2 + 1/2H_2O \longrightarrow Fe^{3+} + OH^- \qquad (3.4)$$

Other reactions taking place in the vicinity of the anode are:

Under alkaline condition

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \qquad (3.5)$$

Under acidic condition

$$Fe^{2+} + 1/4O_2 + 5/2H_2O \longrightarrow Fe(OH)_3 + 2H^+ \qquad (3.6)$$

At cathode, H_2 production occurs via following removalreaction:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad (3.7)$$

Typically, at the cathode the solution becomes alkaline with time. The applied current forces OH^- ion migration to the anode, so that the pH near the anode is higher than that in the bulk solution, thus favoring ferric hydroxide formation.

Precipitation and adsorption are the two major interaction mechanism considered during EC process. Each of the mechanism is applicable at different pH ranges. At low pH values, metal species like Fe^{2+} generated at the anode bind to the anionic colloidal particles present in the BDE, thus neutralizing their charge and reducing their solubility. This process of removal is termed precipitation. The adsorption mechanism operates at higher pH range (> 6) and involves adsorption of organic substances on amorphous metal hydroxide precipitates (Gregory and Duan, 2001; Gurses et al., 2002; Duan and Gregory, 2003; Can et al., 2003). In the present case, for pH < 6, the primary mechanism is charge neutralization by monomeric cationic iron species, while for higher pH; sweep coagulation with amorphous iron hydroxide explains the results (Canizares et al., 2007).

3.3 Type of Electrocoagulation

EC can be performing in batch and continuous type. . Following text gives a brief detail of both types of process.

3.3.1 Batch Electrocoagulation Process

This process is carried out in a reactor with a magnetic stirrer to agitate the solution. Batch experiments were conducted for four stainless steel electrode configurations at varying current intensities by using digital power supply. To optimize various parameters for high reactor efficiency, the experimental runs were taken at varying current density, pH, as a function of electrolysis time. Samples were drawn at regular intervals and at the end of the electrochemical process. The samples were filtered and analyzed for pH, COD and color by using pH meter and UV/VIS spectrophotometer. In the batch process we can treat a fixed wastewater volume per treatment cycle.

3.3.2 Continuous Electrocoagulation Process

The feed tank and the ECR were stirred continuously to maintain uniform concentration of the feed and to ensure good mixing in the reactor. A magnetic stirrer was used for continuous stirring at the bottom of the ECR. The flow rate of the feed to the reactor was maintained through a peristaltic pump (Miclins-20 PP, India). The voltage across the cell was measured using a digital multimeter (Kiethley make, Germany). Samples were collected at regular time intervals at the ECR outlet, filtered and analyzed for pH, color, COD by using pH meter and UV/VIS spectrophotometer. Continuous process is capable for treating large volume of waste water. The key advantage of such reactor systems is that their coagulant requirement is usually fixed, major advantages in terms of design and operation.

3.4 Factor Affecting Electrocoagulation

1. pH
2. Electrolysis time
3. Current density
4. Inter electrode gap
5. Electrode material and shape

3.4.1 pH

The initial pH (pH_0) of the wastewater will have a significant impact on the efficiency of the ECR. The performance efficiency of the ECT depends on the nature of the contaminants with the highest removal efficiencies obtained at near neutral pH. The pH effect gets reduced when the wastewater has high electrical conductivity. The effluent pH after ECT would increase for acidic influent but would decrease for alkaline influent.

The incremental increase in pH with an incremental increase in the amount of current applied tends to decrease at higher current (Nielson and Smith, 2005, Mahesh et al., 2006 a). The general cause of the pH increase can be explained from the following equation.

$2\,H_2O + 2e^- = H_{2\,(g)} + 2OH^-$ (cathode) (3.8)

This reaction shows that the cathode generates hydrogen gas, (which attaches to the flocculated agglomerates, resulting in flocks floating to the surface of the water-akin to a dissolved air flotation unit) 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 electroflocculation system (Donini et al., 1994; Koren and Syversen, 1995; Mahesh et al., 2006b).

The following reaction, which would also impact pH, is theoretically possible:

$2\,H_2O = O_{2\,(g)} + 4H^+ + 4\,e^-$ (3.9)

This reaction occurs at the anode but has a minor impact than the cathodic reaction in Eq. 3.9. These two reactions tend to neutralize pH (i.e., the neutralizing reaction dominates during the appropriate acidic or alkaline condition to push pH levels towards the second equation).

3.4.2 Electrolysis Time

The COD and color removal efficiency directly depends on concentration of ions produced as time increases ion concentration increases thereby hydroxide forms flocks increase, thus percentage removal increases with time

3.4.3 Current Density

Current density (CD) is the ratio of the current across the electrodes divided by the active area of the electrode (A/m^2 or mA/m^2). In all EC processes current is most important parameter for controlling the reaction rate within the reactor When the current increases the efficiency of the ion production on the anode any the cathode increases therefore there is an increase in the flock production in the solution and hence an improvement in the efficiency of color or COD removal .Moreover, bubble generation rate increases, this increases the separation effect and the bubble size decreases with increasing current , which are both beneficial for high pollutant removal efficiency by H_2 floatation.

3.4.4 Inter Electrode Gap

Usually Percent removal decreases with increase in the electrode gap. With increasing distance between electrodes less interaction of ions with hydroxide polymer expected .In the other words, decreasing of local concentration and electrostatic attraction are the reasons for decreasing of removal of pollutants.

The ohmic potential drop is proportional to the inter-electrode spacing, reducing this spacing is of great importance for reducing the electrolysis energy consumption (Chen et al., 2000). Narrower gaps enhance mass transfer characteristics and increase ohmic loss. Decrease in gap results increased in electrolyte resistance. The planned electrode gap, however, depends on the practicality and field conditions. A minimum electrode spacing of 3 mm and 8 mm is possible when handling synthetic wastewaters and real wastewaters, respectively. Narrow spacing of less than 10 mm is accompanied with low energy consumption. At increased inter electrode spacing, an increase in cell voltage occurs (Yu et al., 2005) causing an increase in the power consumption. When planning for high SA/V reactors, the inter electrode gap should be just sufficient enough to provide sufficient turbulence in-between the electrodes which initiate mass transfer within the ECR. Spacing less than 10 mm reduces the swirling velocity of the liquid medium between the electrodes thus affecting the pollutant removal efficiency (Mahesh et al., 2006 a).

3.4.5 Electrode Material and Shape

Efficiency of any ECT process depends on the type of electrode used in the ECR. The treatment efficiency depends on the affinity of the pollutant towards the ions generated by electrode material such as iron, which is the most suitable electrode for the removal of as from water, (Kumar et al., 2004). Usually electrodes are rectangular or square in shape and are arranged in bi-polar form, a alternative design with cylindrical electrodes is suggested when electrode passivation is a problem (Chen, 2004).

3.5 Advantage and Limitation of EC

Advantages:

1. Simple to use, portable, on-site treatment that does not increase the salinity of water
2. Environmental compatibility-electrons as clean reagents and no need to add extra reagents.
3. Destroys/inactivates and removes bacteria, virus and cysts and adds no harmful chemicals to water.
4. Can effectively destabilize even the smallest colloidal particle.
5. Simple equipment which could be designed to virtually any size with an easy start-up (unlike in biological treatment) and as a stand-alone system.

6. Electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring low maintenance.
7. Cost effectiveness- the required equipment and operations are very simple and, if properly designed and operated, are also inexpensive.
8. EC treated wastewater gives colorless and odorless, palatable and more or less clear water.
9. The gas bubbles produced during electrolysis can enhance flotation atop the ECR which can be later on skimmed off for settling.
10. Produces less TDS in the treated wastewater in comparison to chemical coagulation methods.
11. A low volume sludge producing technique; sludge formed has quick settling characteristics with easy dewater ability.
12. Requires low current, can run using green processes such as solar, wind mills and fuel cells and convenient in remote areas.
13. Electrochemical waste destruction processes run at very high electrochemical efficiency and operate essentially under the same conditions for a wide variety of wastewaters.

Limitations

1. There are relatively few “showcases” for this treatment technology.
2. Periodic replacement of sacrificial electrodes on its complete/partial dissolution.
3. The use of electricity in many places may be expensive.
4. Minimum conductivity of the wastewater suspension may be required depending on the reactor design configuration.

5. Chemical reactions, corrosion, adsorption, etc., at the electrode surface may cause complications when not in use.
6. An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit.

3.6 Factors Affecting Selection of ECR

Reactors used for energy conversion and electrochemical synthesis are different from those used in the destruction of contaminants/pollutants present in water or wastewaters. Therefore, it is important to select (or design) an ECR for a specific use. Fig. 3.2 show the classification of operating modes and types of ECR. The form of the reactants/pollutants/contaminants and products and the mode of operation (batch and continuous) are also important design factors. The desirable factors in the reactor design and their implications include the following (Walsh and Reade, 1994).

1. Moderate costs (low- cost components, a low cell voltage and a small pressure drop across the reactor)
2. Convenience and reliability in operation (designed for facile installation, maintenance, and monitoring)
3. Appropriate reaction engineering (uniform and appropriate values of current density, electrode potential, mass transport and flow)
4. Simplicity and versatility (in an elegant design, which is attractive to the end users).

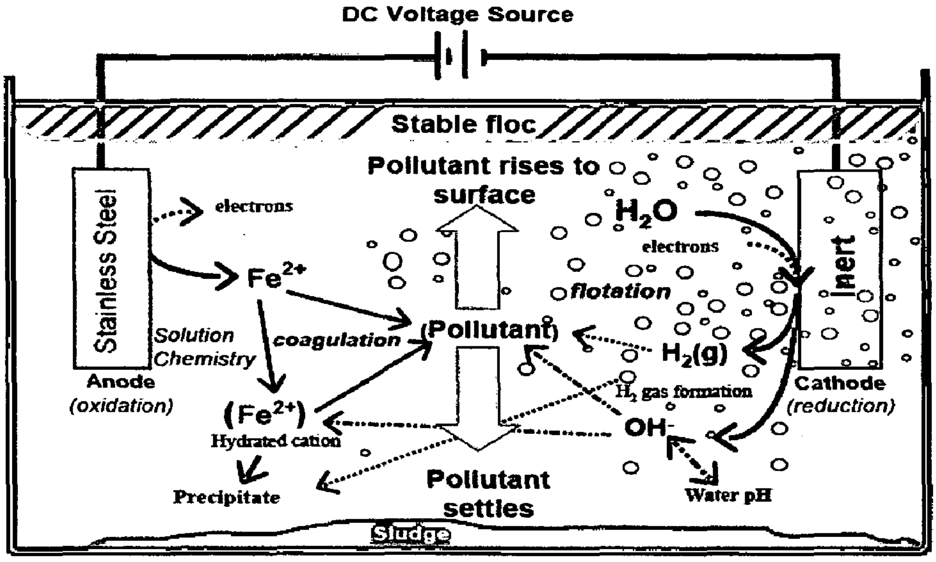


Fig. 3.1 Mechanism of Electrocoagulation

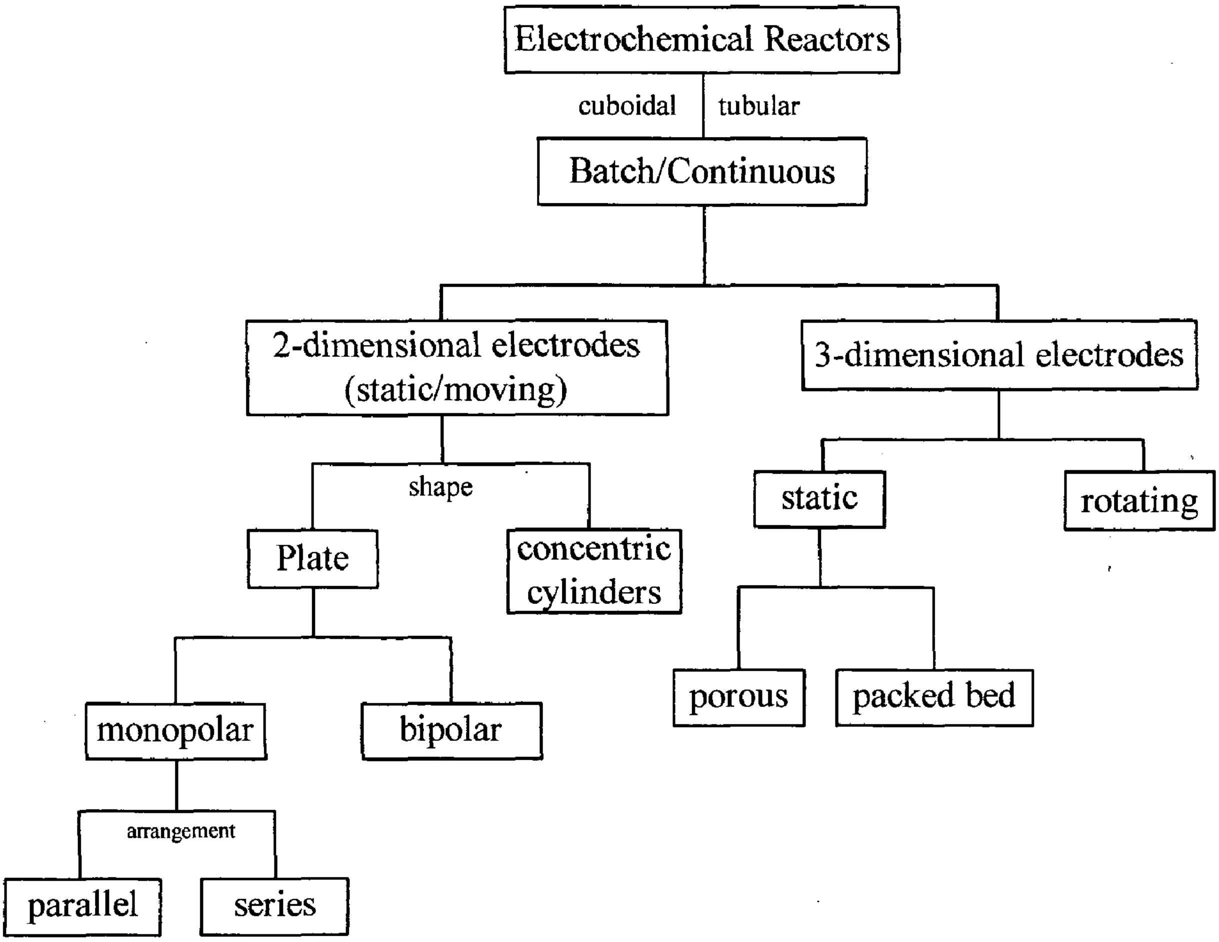


Figure 3.2 Classification of Electrochemical Reactors - Type of Reactors and

Chapter 4

MATERIAL AND METHODS

4.1 General

This chapter deals with the treatment of bio-digester effluent (BDE) by electrocoagulation (EC) method using stainless steel (SS) as an electrode. The experimental details include characterization of BDE, residue, electrode and the materials and methods used for the treatment and characterization processes, details about the experimental program and details about the analytical methods used.

4.2 Characterization of Bio-digester Effluent (BDE)

Anaerobic treated distillery wastewater was procured from Doon Valley distilleries near Dehradun. The BDE obtained from nearby distillery was characterized for various parameters namely COD, total solids, total dissolved solids, sulphate, chloride, etc. as per standard method of analysis (Cleceri et al., 1998).

4.3 Material and Methods

4.3.1 Reactor

The experimental setup used for the treatment of (BDE) is shown in Fig. 1. Experiments were carried out using lab-scale rectangular batch reactor made of Perspex glass having 1.5 l (108 mm × 108 mm × 130 mm) reactor volume. Stainless steel (SS) plates having thickness 3 mm, and 100 mm × 80 mm dimensions were used as electrodes. Area of electrodes dipped into the solution was 80 mm × 80 mm, thus the total effective surface area of each electrode was 112 cm^2. Two pairs of such electrodes were used in the present study. Characteristic of EC cell is shown in Table 4.1. The spacing between two electrodes in EC cell was varied in the range of 1-2 cm. A gap (g) of 5 cm was maintained between the bottom of the electrodes and the bottom of the cell to allowed easy stirring. Magnetic stirrer was used to agitate the solution. The current density (j) was maintained constant by means of a precision digital direct current power supply (0-20 V, 0-5 A).

Cleaning of the electrodes before and after the experiments was done by ordinary detergent and 15% HCl solution followed by washing with water for perfect cleaning. To maintain a fixed inter-electrode distance non conducting wire was used as the electrode separator. Electrodes were arranged in parallel as the series arrangement will have higher resistance.

4.3.2 Experimental Design

A total of 28 experiments have been employed in this work to evaluate the individual and interactive effects of the four main independent parameters on the COD and color removal efficiency. Percentage COD and color removal has been taken as a response (Y) of the system, while four process parameters, namely, pH_0: 3.5-9.5; Current Density (j): 39.06-196.31 A/m^2; Electrode Spacing (g): 1-2 cm; and Time (t): 30-150 min have been taken as input parameters. For statistical calculations, the levels for the four main variables X_i (X_1 (pH_0), X_2 (j), X_3 (g), X_4 (t)) were coded as x_i according to the following relationship

$$x_i = (\mathrm{X_i} - X_0)/\delta X \tag{4.1}$$

Where, X_0 is value of X_i at the centre point and δX presents the step change. The variables and levels of the design model are given in Table 4.2. Independent parameters for different experiments runs are given in Table 4.3. From experimental observations, it was assumed that the higher order interactions were small relative to the low order.

4.3.3 Experimental Procedure

Each experimental run was performed as per the conditions specified in the design matrix Table 4.2. The pH of the solutions was measured and adjusted by adding 0.1 N NaOH or 0.1 N H_2SO_4 solutions. The electrode spacing was set appropriately as per design condition, and 1.5 l effluent of known initial COD (COD_0) was fed into the reactor at the beginning of a run. Power supply was switched on at $t=0$. Current density was maintained constant during the run. Samples were drawn from supernatant liquid, and its final COD was measured.

The percentage COD removal was calculated using the following relationship:

$$\text{Percentage COD removal } (Y) = 100(COD_0 - COD_t)/COD_0 \tag{4.2}$$

where, COD_0 is the initial COD (mg/l) and COD_t is the COD after t (min) of electrolysis time (mg/l)

4.4 Analysis of BDE Sludge and SS electrodes

The analysis following the experiments includes the SEM (scanning electron microscope), DTA (Differential Thermal Analysis) - TGA (Thermogravimetric Analysis) and SEM of the electrodes.

4.4.1 Scanning Electron Micrograph (SEM)

To understand the morphology of the electrode before and after the EC of BDE, and to study the distribution of the elements in the electrode and residues (scum and sludge), a scanning electron microscope (SEM) QUANTA, Model 200 FEG, USA was employed. Samples were first gold coated using Sputter Coater, Edwards S150 to provide conductivity to the samples, and then the SEM.

4.4.2 Energy Dispersive X-ray spectrometer (EDX)

The elemental composition of the top scum and settled sludge samples were determined using an Energy Dispersive X-ray (EDX) analyzer/Spectrometer (model ECON-149-10, country). The scanning energy for EDX analysis ranged from 0-20 KeV with an elapsed time of 100 s. The particle size in the treated BL slurry was analyzed using a particle analyzer-CIS 100 (Ankersmid Ltd., Israel) using WCIS-Software.

4.4.3 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) of the residues was carried out using Perkin Elemer (Pyris Diamond) Thermogravimetric Analyser. Thermogravimetric (TG), differential thermogravimetric (DTG) and the derivative thermal (DTA) analyses were carried out from the data and plots obtained from the instrument.

Differential Thermal Analysis (DTA) measures the difference in temperature between a sample and a thermally inert reference as the temperature is raised. The plot of this differential provides information on exothermic and endothermic reactions taking place in the sample. Temperatures for phase transitions, melting points, crystallization can all be determined using the computer controlled graphics package. Maximum temperature for this instrument is 1350 °C; variable atmospheres. Typical heating rates are 1020°C per minute. Optimum sampie size is 50-100 mg; ideally, the sample should be ground to 100 mesh.

Thermogravimetric Analysis (TGA) measures changes in weight of a sample with increasing temperature. Moisture content and presence of volatile species can be determined with this technique. Computer controlled graphics can calculate weight percent losses. Maximum temperatures are 1250 °C for the TGA-7 and 1000 °C for the TGA 2050; variable atmospheres. Typical heating rate is 10° per minute. Optimum sample size is 50 - 100 mg.

Table 4.1 Characteristic of EC cell

Electrode	
Material (anode & cathode)	Stainless Steel
Shape	Rectangular plate
Size	8cm-8cm
Thickness	3 mm
Plate arrangement	Parallel
Effective surface area	64 cm^2
Reactor	
Material	Perspex
Type	Batch mode
Dimensions	10.8 cm-10.8 cm-13.0 cm
Volume	1.5 l
Electrode gap	1-2 cm
Stirring mechanism	Magnetic bar
Power supply	Direct current (DC)
Voltage range (V)	0-20
Current range (A)	0-5

Table 4.2. Process Parameters and their levels for EC Treatment of Bio-digester Effluent using Stainless-Steel Electrode

Variable, unit	**Factors**			**Level**		
	X	-2	−1	0	1	2
Initial pH, pH_0 (-)	X1	3.5	5	6.5	8	9.5
Current density, j (A/m^2)	X2	39.06	78.13	117.19	156.25	195.31
Inter electrode distance, g (cm)	X3	1	1	1.5	2	2
Time of electrolysis, t (min)	X4	30	60	90	120	150

Table 4.3 Coded and Uncoded values of Experimental Runs

		CODED VALUES				UNCODED VALUES			
Std Order	Run Order	pH	Current Density(A/m^2)	IED (cm)	Time (min)	pH	Current Density(A/m^2)	IED (cm)	Time (min)
18	1	2	0	0	0	9.5	117.19	1.5	90
28	2	0	0	0	0	6.5	117.19	1.5	90
2	3	1	-1	-1	-1	8	78.13	1	60
31	4	0	0	0	0	6.5	117.19	1.5	90
8	5	1	1	1	-1	8	156.25	2	60
14	6	1	-1	1	1	8	78.13	2	120
13	7	-1	-1	1	1	5	78.13	2	120
19	8	0	-2	0	0	6.5	39.06	1.5	90
24	9	0	0	0	2	6.5	117.19	1.5	150
10	10	1	-1	-1	1	8	78.13	1	120
5	11	-1	-1	1	-1	5	78.13	2	60
20	12	0	2	0	0	6.5	195.31	1.5	90
23	13	0	0	0	-2	6.5	117.19	1.5	30
17	14	-2	0	0	0	3.5	117.19	1.5	90
7	15	-1	1	1	-1	5	156.25	2	60
15	16	-1	1	1	1	5	117.19	1.5	90
3	17	-1	1	-1	-1	5	156.25	1	60
16	18	1	1	1	1	8	156.25	2	120
4	19	1	1	-1	-1	8	156.25	1	60
12	20	1	1	-1	1	8	156.25	1	120
6	21	1	-1	1	-1	8	78.13	2	60
1	22	-1	-1	-1	-1	5	78.13	1	60
11	23	-1	1	-1	1	5	156.25	1	120
9	24	-1	-1	-1	1	5	78.13	1	120

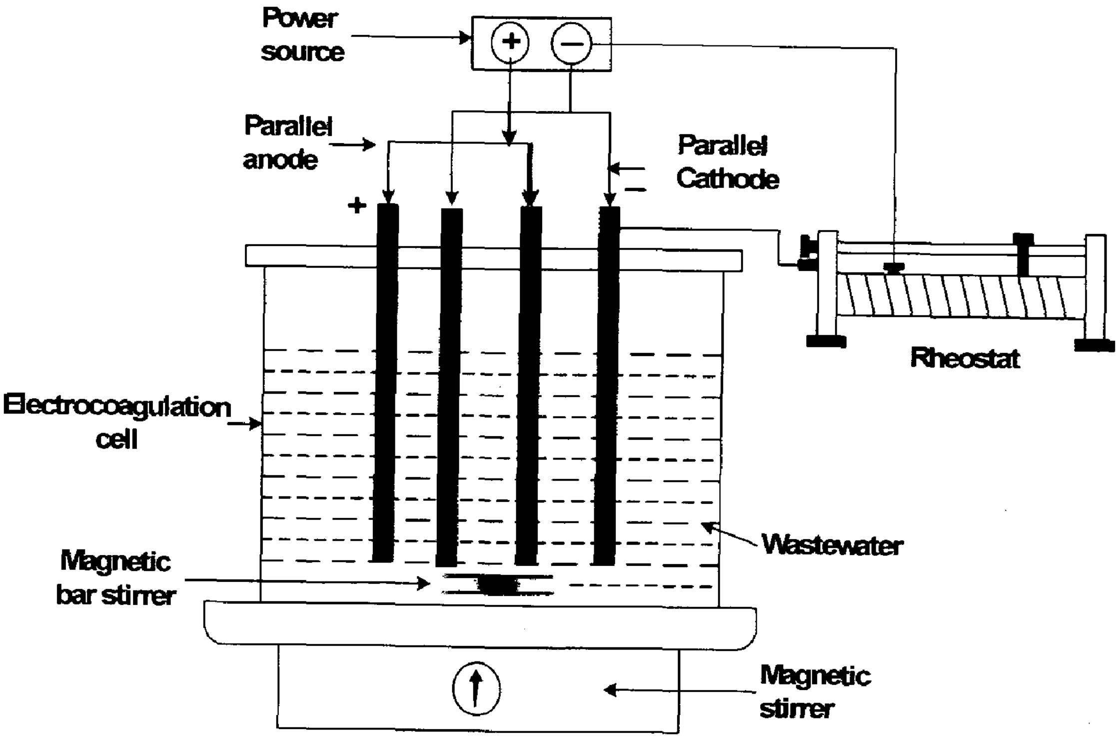


Fig. 4.1 Experimental setup of Electrocoagulation

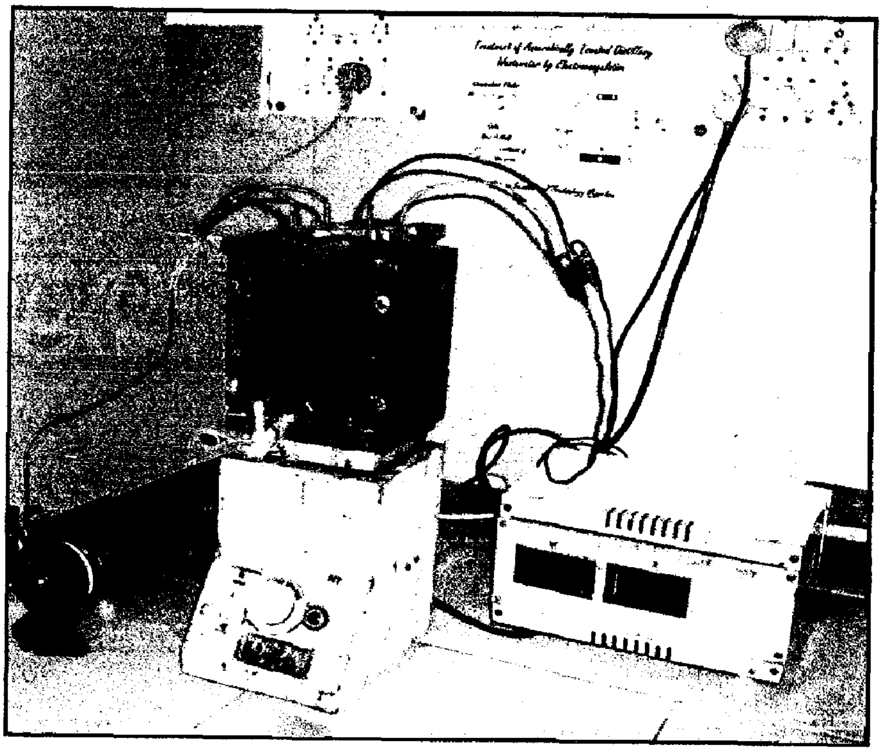


Fig. 4.2 Actual Setup of Experiment

Chapter 5

RESULT AND DISCUSSION

5.1 General

This chapter presents the results and discussions of the electrocoagulation (EC) in batch and characterization of bio-digester effluent (BDE) as wastewater. The optimization of the process for the removal of COD and color has be mention by using full factorial central composite (CC) design based on response surface methodology (RSM). Pareto analysis of variance (ANOVA) is also mention. Finally, the EC generated solid residues, their physico-chemical and thermal characterizations are presented.

5.2 Characterization of Bio-digester Effluent (BDE)

The BDE obtained from nearby distillery was characterized for various parameters namely COD, total solids, total dissolved solids, sulphate, chloride, etc. as per standard method of analysis (Cleceri et al., 1998). The main characteristics of the effluent used for the present study are given in Table 5.1.

5.3 Fitting of Second-Order Polynomial Equation and Statistical Analysis

Experiments were performed to study the affect of pH, *j*, *g*, and *t* on the COD and color removal efficiency of the EC process. The results of the *Y* (response) of COD and color removal by EC were measured according to design matrix and the measured responses are listed in Table 5.2

Linear, interactive, quadratic and cubic models were fitted to the experimental data to obtain the regression equations. A system with several variables is affected primarily by some of the main effects and lower order interactions, and higher order interactions are usually small as compared to the lower order interactions. Therefore, in the present work only two-way interactions were considered. Two different tests namely sequential model sum of squares and model summary statistics were employed to decide about the adequacy of various models to represent COD and color removal by EC. Results of these tests are given in Table 5.3 and 5.4, respectively. Cubic model was found to be aliased. For quadratic and linear models, p value was lower than 0.02, and both of these could be used for further study as per sequential model sum of squares test. As per model summary statistics, the quadratic model was found to have maximum "Adjusted R-Squared" and the "Predicted R-Squared" values excluding cubic model which was aliased. Therefore, quadratic model was chosen for further analysis.

To analyze a process or system including a response Y, where Y depends on the input factors , ,...,.. , 1 2 k x x x the relationship between the response and the input process parameters are described as (Montgomery, 1991)

$$Y = f(x_1, x_2, \ldots\ldots\ldots\ldots, x_k) + \varepsilon \qquad (5.1)$$

Where, f is the real response function its format being unknown, and ε is the residual error which describes the differentiation that can be included by the function f.

Considering all the linear, square and linear by linear interaction terms, the quadratic response model can be described as

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_{ii}^2 + \sum \beta_{ij} x_i x_j + \varepsilon \qquad (5.2)$$

Where, β_o is the offset term, β_i is the linear effect of the input factor x_i, β_{ii} is the quadratic effect of input factor x_i and β_{ij} is the linear by linear interaction effect between the input factor x_i and x_j (Benyounis et al., 2005).

A manual regression method was used to fit the second order polynomial given by Eq. (5.3) and (5.4), respectively to the experimental data and to identify the relevant model terms. The final equation obtained in terms of coded factors is given below:

% COD removal

$$\begin{aligned} Y &= 48.90 - 3.91X1 + 6.95X2 + 2.71X3 + 6.56X4 - 2.82X1^2 - 2.24X2^2 + 3.48X3^2 - 1.99X4^2 \\ &+ 1.93X1.X2 - 0.52X1.X3 + 2.04X1.X4 - 0.56X2.X3 - 1.83X2.X4 - 3.06X3.X4 \quad (5.3) \end{aligned}$$

% Color removal

$$\begin{aligned} Y &= 95.40 - 4.22X1 + 3.41X2 + 0.037X3 + 5.53X4 - 4.91X1^2 - 2.06X2^2 + 9.41X3^2 - 5.25X4^2 \\ &+ 1.39X1.X2 - 0.18X1.X3 + 0.23X1.X4 - 1.18X2.X3 - 0.53X2.X4 - 0.33X3.X4 \quad (5.4) \end{aligned}$$

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using ANOVA (Huiping et al., 2007). The ANOVA for the second-order equation is presented in Table 5.5 and 5.6, respectively. According to ANOVA (Table 5.5 and 5.6), the Fisher F values for all regressions were higher. The large value of F indicate that most of the variation in the response can be explained by the regression equation. The associated p value is used to estimate whether F is large enough to indicate statistical significance, p value lower than 0.05 indicates that the model is statistically significant (Segurola et al., 1999). The ANOVA indicated that the equation adequately represented the relationship between the response (the percentage COD and color removal and the significant variables. The model gave coefficient of determination (R^2) value of 0.9144 and 0.765 and an adjusted-R^2 value of 0.8222 and 0.5119 for COD and color, respectively, which are high and advocate a high correlation between the observed and the predicted values. The ANOVA result for the COD and color removal by EC with SS electrodes system shows F- value of 9.92 and 3.0227, respectively. This implies that the terms in the model have a significant effect on the response. The probability p is less than 0.05. This indicates that the model terms are significant at 95% of probability level. Any factor or interaction of factors with $p < 0.05$ is significant. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. For the present study, signal to noise ratio was found to be 11.83, which indicates adequate signal. Therefore, quadratic model can be used to navigate the design space.

The ANOVA results show that j, t and pH_0 are the significant factors that affect the COD and color removal by EC. The constant, which does not depend on any factors and interaction of factors, shows that the average COD is 48.9% and color is 95.4% removal of BDE by EC process using SS electrodes, and that this average removal is independent of the factors set in the experiment. The ANOVA analysis shows that the form of the model chosen to explain the relationship between the factors and the response is correct (Kim et al., 2003).

Data were also analyzed to check the normality of the residuals. A normal probability plot or a dot diagram of these residuals is shown in Fig. 5.2. The data points on this plot lie reasonably close to a straight line, lending support that the results of ANOVA analysis are correct. Fig. 5.3 shows the relationship between the actual and predicted values of Y. It is seen in Fig. 5.3 that the developed model is adequate because the residuals for the prediction of each response are minimum, and the data points lie close to the diagonal line.

5.4 Effect of Various Parameters on Maximum COD and Color Removal Efficiency

The inferences obtained from the response surfaces to estimate maximum COD and color removal with respect to each variable; and each variable's effect on COD and color removal efficiency are discussed below.

Effect of Current Density and pH: Experiments were carried out by varying j from 39.06 to 195.31 A/m^2 and under different pH_0 from 3.5 to 9.5. The results are plotted in Fig. 5.4. The COD and color removal efficiency was found to increase with an increase in j values at any value of pH_0. According to Faraday's law given below, the theoretical amount of ion produced per unit surface area (m) is directly proportional to the j passed for time t.

$$m = \frac{Mjt}{ZF} \tag{5.5}$$

Where, Z is the number of electrons involved in the oxidation-reduction reaction; for Fe, Z=2. M is the atomic weight of anode material, for SS, M=55.85 g/mol and F is the Faraday's constant (96486 C/mol). COD and color removal by EC is governed by the formation of metal-hydrous ferric oxide complexes. It can be inferred from Fig. 4 that higher COD and color removal efficiency is achieved at higher j value. This is due to the higher dissolution of electrode material with higher rate of formation of iron hydroxides resulting in higher COD and color removal efficiency due to co-precipitation (Golder et al., 2007). Also, increased amount of sludge produced from the electrodes at higher j value enhances the COD and color removal efficiency via sweep coagulation (Guo et al., 2006).

In an attempt to investigate the influence of pH_0 on the EC process, pH_0 of the effluent was varied in the range of 3.5 to 9.5. The results illustrated in Fig. 5.4 demonstrate the COD and color removal efficiency at different pH_0. The results reveal that at pH_0~6.75, the COD and color removal efficiency was maximum. For $pH_0 < 6$, the protons in the solution get reduced to H_2, and thus, the proportion of hydroxide ion produced is less and consequently there is less COD and color removal efficiency (Modirshahla et al., 2007).

Effect of Inter Electrode Gap and Time: The COD and color removal efficiency depends directly on the concentration of ions produced by the electrodes which in-turn depends upon t. The effect of g and t on COD and color removal by EC under varying g (from 1 to 2 cm) and t (from 30 to 150 min) is plotted in Fig. 5.5. When the value of t increases, an increase occurs in concentration of iron ions and their hydroxide Flocks. Consequently, an increase in the t increases the COD and color removal efficiency Fig. 5.5.

The electrical conductivity is directly proportional to the distance between the two electrodes. As the distance between the anode and the cathode (g) increases, resistance (R) offered by the cell increases. From Faraday's law, the amount of iron oxidized decreases as g increases, and thus, the COD and color removal efficiency generally decreases. Fig. 5.5 shows the effect of g on the COD and color removal efficiency during EC process. It can be seen that the COD and color removal efficiency generally remained constant with an increase in g. It seems that other factors namely j, pH_0 and t have over-riding effect on COD and color removal efficiency as compared to g. Therefore, the effect of g of COD and color removal efficiency gets marginalized in the present study.

5.5 Selection of Optimal Levels and Estimation of Optimum Response Characteristics

Optimal level of various parameters obtained after examining the response curves and contour plots (not shown here) are summarized in Table 8. Maximum COD and color removal of 61.6% was obtained at pH_0= 6.75, j=146.75 A/m^2, g= 1 cm and t= 130 min. Three confirmation experiments were conducted at selected optimal levels of the process parameters and 63.1% average COD removal and 99.75% average color removal was observed at optimal conditions.. The removal percentages obtained through confirmation experiments are within 95% confidence interval of the predicted values

5.6 Physico-chemical Analysis of Electrodes and Residues

5.6.1 SEM Analysis of Electrode and Residue

SEM images of fresh SS electrodes; and used electrode before and after cleaning are shown in Fig. 5.6. The surface of the original SS plate surface prior to its use in EC experiments is rough, and this roughness is uniformly distributed throughout the surface with no dents on the surface. Fig. 5.6 also shows the SEM of the same electrode after several cycles of its use in EC experiments. The SEM of one such electrode before its cleaning in one such EC cycle is also shown at different magnifications. The electrode surface is now found to contain a number of dents having widths in the range of 50-500 μm. These dents are formed around the nucleus of the active sites where the electrode dissolution took place producing iron hydroxide. Amorphous organics are seen adhered to the surface of the uncleaned electrode. The cleaned electrode shows same types of dents with some micro-Flocks and sludge particles entrapped in it.

Fig. 5.7 shows SEM images of dried scum and sludge obtained during the EC process. Both scum and sludge are crystalline in nature with 50-200 μm width. The average size of crystalline sludge particles is bigger than that of the scum particles.

5.6.2 TGA Analysis of Residue

The sludge generated during the EC process poses disposal and management problem. EC sludge can be dried and thermally degraded. The bottom ash obtained after its combustion can be blended with the cementitious mixtures. To study the degradation kinetics of scum and sludge, TGA was carried out. In the present study, the operating pressure was kept slightly positive, the air flow rate was maintained at 200 ml/min and the heating rate was maintained at 100 °C/min. The TGA, differential thermal analysis (DTA) and differential thermal gravimetery (DTG) curves of the EC scum and sludge in oxidizing atmosphere is shown in Fig. 5.8 and 5.9, respectively. The TGA trace of the scum Fig. 5.8 in oxidizing atmosphere shows the loss of moisture and the evolution of some light weight molecules including water (2.4% weight loss) from 25 to 100 °C. Higher temperature drying (from 100 to 250 °C) occurs due to loss of the surface bound water. The rate of weight loss was found to increase between ~250 to ~700 °C (~38% weight loss). This weight loss is generally associated with the evolution of CO_2 and CO. In the last temperature range between ~700 to 1000 °C, residues oxidize and lose their weight gradually; and there is ~4.5% weight loss. Maximum degradation rate of 2.84 mg/min was observed at 300 °C. The strong exothermic peak centered between 250-700 °C is due to the oxidative degradation of the sample. This broad peak as that observed from the first derivative loss curve may be due to the combustion of carbon species. Thermal degradation characteristics of sludge Fig. 5.9 shows removal of moisture (about 2.5%) up to temperature of 100 °C followed by an active degradation zone between 100 and 400 °C. Total degradation during this zone is about 27%. Beyond 400 °C, the residues oxidize and lose their weight gradually; and there is ~6% weight loss. Residue left at 1000 °C is the weight of the ash. It is 63.4% of the total sludge. Thus, the amount of ash in sludge is higher than that of scum which showed 41.4% ash. Therefore, it is expected that the amount of organics is low in sludge as compared to that in scum. Hence, the calorific value of sludge is expected to be lower than that of scum.

5.6.3 EDX Analysis of Residue

EDX of scum and sludge is shown in Fig. 5.10, and the results are given in Table 5.8. Scum and sludge obtained after EC experiments were found to contain 12.28% and 24.52% iron; 29.35% and 15.26% carbon; 25.03% and 24.01% oxygen, respectively. Thus, scum contains lesser amount of iron and higher amount of carbon and oxygen as compared to sludge. This was as expected from the TGA analysis.

Heating value of scum and sludge as determined from bomb calorimeter were found to be 7.8 and 3.3 MJ/kg, respectively. Higher heating value of scum is due to the higher percentage of carbon content present in the scum

Scum and sludge can be utilized for making blended fuel briquettes with other organic fuels. This could be used as a fuel in the furnaces. The bottom ash obtained after its combustion can be blended with the cementitious mixtures which is to be further used in construction purposes. Setting and leaching tests on the cementitious mixtures have shown that the bottom ash can be incorporated into the cementitious matrices to a great extent (75 wt.% of total solid) without the risks of an unacceptable delay of cement setting and an excessive heavy metals leachability from solidified products (Mangialardi, 2003; Srivastava et al., 2006). This method of EC residue disposal recovers energy from the residues as well it chemically fixes the iron and other toxic metals present in EC sludge.

Table 5.1 Characteristics of Bio-digester Effluent

Characteristics	Value
COD (mg/l)	9310
BOD (mg/l)	3724
Cl^- (g/l)	2.0
Total solid (g/l)	17
Total dissolved solids (g/l)	15.6
pH	8.5
TOC (mg/l)	5750
Conductivity (milli mhos)	5.37
Turbidity (NTU)	1400
Color	Dark black

Table 5.2 Full Factorial Design used for the EC Treatment of Bio-digester Effluent

Std. order	Run order	pH_0 (x1)	j (x2)	g (x3)	t (x4)	% COD reduction		% Color reduction	
						$Y_{\exp}$ (%)	Y_{pre} (%)	$Y_{\exp}$ (%)	Y_{pre} (%)
1	9	5	78.125	1	60	27.39	31.02	87.1	87.22083
2	23	8	78.125	1	60	21.24	16.31	82.25	75.91208
3	20	5	156.25	1	60	45.27	45.85	94.2	94.68375
4	15	8	156.25	1	60	42.4	38.84	94.53	88.9175
5	17	5	78.125	2	60	48.33	44.74	95.8	90.66833
6	5	8	78.125	2	60	26.69	27.94	83.29	78.65708
7	19	5	156.25	2	60	63.96	57.31	89.8	93.40875
8	28	8	156.25	2	60	43.51	48.22	92.13	86.94
9	18	5	78.125	1	120	54.92	49.84	95.5	99.53875
10	14	8	78.125	1	120	36.27	43.29	91.6	89.1425
11	3	5	156.25	1	120	58.24	57.36	99.1	104.8842
12	22	8	156.25	1	120	55.29	58.51	96.05	100.0304
13	21	5	78.125	2	120	47.38	51.31	94.9	101.6638
14	24	8	78.125	2	120	43.61	42.66	92.2	90.565
15	12	5	156.25	2	120	52.01	56.57	97.1	102.2867
16	2	8	156.25	2	120	58.9	55.64	95.7	96.73042
17	10	3.5	117.1875	1.5	90	43.71	45.46	94.6	84.1725
18	11	9.5	117.1875	1.5	90	31.56	29.81	56.88	67.3075
19	13	6.5	39.0625	1.5	90	26.68	26.04	75.7	80.33583
20	8	6.5	195.3125	1.5	90	53.2	53.84	98.6	93.96417
21	6	6.5	117.1875	1.5	30	23.55	27.83	52	63.34583
22	4	6.5	117.1875	1.5	150	58.35	54.07	96.8	85.45417
23	26	6.5	117.1875	1.5	90	48.9	48.9	95.4	95.4
24	27	6.5	117.1875	1.5	90	48.9	48.9	95.4	95.4
25	25	6.5	117.1875	1.5	90	48.9	48.9	95.4	95.4
26	7	6.5	117.1875	1.5	90	48.9	48.9	95.4	95.4
27	16	6.5	117.1875	1.5	90	48.9	48.9	95.4	95.4
28	1	6.5	117.1875	1.5	90	48.9	48.9	95.4	95.4

Table 5.3 Adequacy of the Models Tested for COD

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	**Remark**
Sequential Model Sum of Squares						
Mean	56328.01	1	56328.01			
Linear	2676.66	4	669.16	16.50	< 0.0001	Suggested
2FI	338.90	6	56.48	1.616	0.2029	
Quadratic	284.97	4	71.24	2.99	0.0588	Suggested
Cubic	308.32	7	44.046	485.88	< 0.0001	Aliased
Residual	0.54	6	0.09			
Total	59937.42	28	2140.62			
Source	**Std. Dev.**	**Predicted R^2**	**Adjusted R^2**	**R^2**	**PRESS**	**Remark**
Model Summary Statistics						
Linear	6.36	0.59	0.69	0.74	1469.27	Suggested
2FI	5.91	0.41	0.73	0.83	2128.41	
Quadratic	4.87	0.36	0.82	0.91	2278.72	Suggested
Cubic	0.30		0.99	0.99		Aliased

Table 5.4 Adequacy of the Models Tested for Color

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	**Remark**
Sequential Model Sum of Squares						
Mean	228300	1	228300			
Linear	1438.43	4	359.61	3.99	0.01	Suggested
2FI	60.58	6	10.1	0.085	0.99	
Quadratic	1188.55	4	297.14	4.68	0.01	Suggested
Cubic	820.31	7	117.19	132.63	< 0.0001	Aliased
Residual	5.3	6	0.88			
Total	231800	28	8278.46			
Source	**Std. Dev.**	**Predicted R^2**	**Adjusted R^2**	**R^2**	**PRESS**	**Remark**
Model Summary Statistics						
Linear	9.5	0.08	0.30	0.40	3222.12	Suggested
2FI	10.88	-0.39	0.08	0.42	4896.67	
Quadratic	7.97	-0.949	0.51	0.76	6849.3	Suggested
Cubic	0.94		0.99	0.99		Aliased

Table 5.5 ANOVA of the Second-order Polynomial Equation for COD

Source	Coefficient Estimate	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Model		3300.54	14	235.75	9.92	< 0.0001	Highly significant
intercept	48.9						
X1	-3.91	367.31	1	367.31	15.46	0.0017	Significant
X2	6.95	1159.12	1	1159.12	48.79	< 0.0001	Highly significant
X3	2.71	117.56	1	117.56	4.95	0.0445	Low significant
X4	6.56	1032.68	1	1032.68	43.46	< 0.0001	Highly significant
$X1^2$	-2.82	190.35	1	190.35	8.01	0.0142	Low significant
$X2^2$	-2.24	120.42	1	120.42	5.07	0.0423	Low significant
$X3^2$	3.48	72.74	1	72.74	3.06	0.1037	
$X4^2$	-1.99	94.8	1	94.8	3.99	0.0671	Low significant
X1xX2	1.93	59.41	1	59.41	2.5	0.1378	
X1xX3	-0.52	4.36	1	4.36	0.18	0.6755	
X1xX4	2.04	66.54	1	66.54	2.8	0.1181	
X2xX3	-0.56	5.07	1	5.07	0.21	0.6516	
X2xX4	-1.83	53.4	1	53.4	2.25	0.1577	
X3xX4	-3.06	150.12	1	150.12	6.32	0.0259	Low significant
Residual		308.87	13	23.76			
Lack of Fit		308.87	8	38.61			
Pure Error		0	5	0			
Cor Total		3609.41	27				

Table 5.6 ANOVA of the Second-order Polynomial Equation for Color

Source	**Coefficient Estimate**	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	**Remark**
Model		2687.55	14	191.96	3.02	0.02	Significant
intercept	95.4						
X1	-4.21	426.62	1	426.62	6.71	0.02	
X2	3.40	278.55	1	278.5	4.38	0.05	
X3	0.03	0.0216	1	0.0216	0.00	0.98	
X4	5.52	733.15	1	733.15	11.54	0.00	Significant
$X1^2$	-4.91	579.77	1	579.77	9.12	0.01	Significant
$X2^2$	-2.06	102.09	1	102.09	1.60	0.22	
$X3^2$	9.40	530.79	1	530.79	8.35	0.01	Significant
$X4^2$	-5.25	661.5	1	661.5	10.41	0.00	Significant
X1xX2	1.38	30.71	1	30.719	0.48	0.49	
X1xX3	-0.17	0.49	1	0.49	0.00	0.93	
X1xX4	0.22	0.83	1	0.83	0.01	0.91	
X2xX3	-1.18	22.30	1	22.30	0.35	0.56	
X2xX4	-0.52	4.48	1	4.48	0.07	0.79	
X3xX4	-0.33	1.74	1	1.749	0.02	0.87	
Residual		825.61	13	63.50			
Lack of Fit		825.61	8	103.20			
Pure Error		0	5	0			
Cor Total		3513.17	27				

Table 5.7 Optimum and Confirmative values of Process Parameters for Maximum COD and color Removal Efficiency

Optimal levels of process parameters	Predicted optimal value with 95% Confidence intervals (%)	Average of Confirmation experiments (%)
$pH_0 = 6.75$	(COD) $54.14 < 61.58 < 69.02$	63.09
j =146.75 A/m	(Color) $92.26 < 99.17 < 116.57$	99.75
g = 1 cm		
t = 130 min		

Table 5.8 EDX Properties of Scum and Sludge

Element	Wt%	
	Scum	**Sludge**
Fe	12.28	24.52
C	29.35	15.26
O	25.03	24.01
Ni	02.02	03.49
Cr	07.13	06.97
Ca	00.34	00.33
Pd	00.71	00.35
Gd	01.23	01.74
Pr	00.63	01.09
Mn	00.38	00.74
Au	12.23	13.79
Rb	00.49	00.73
Nb	03.90	04.46
Mo	04.27	02.51

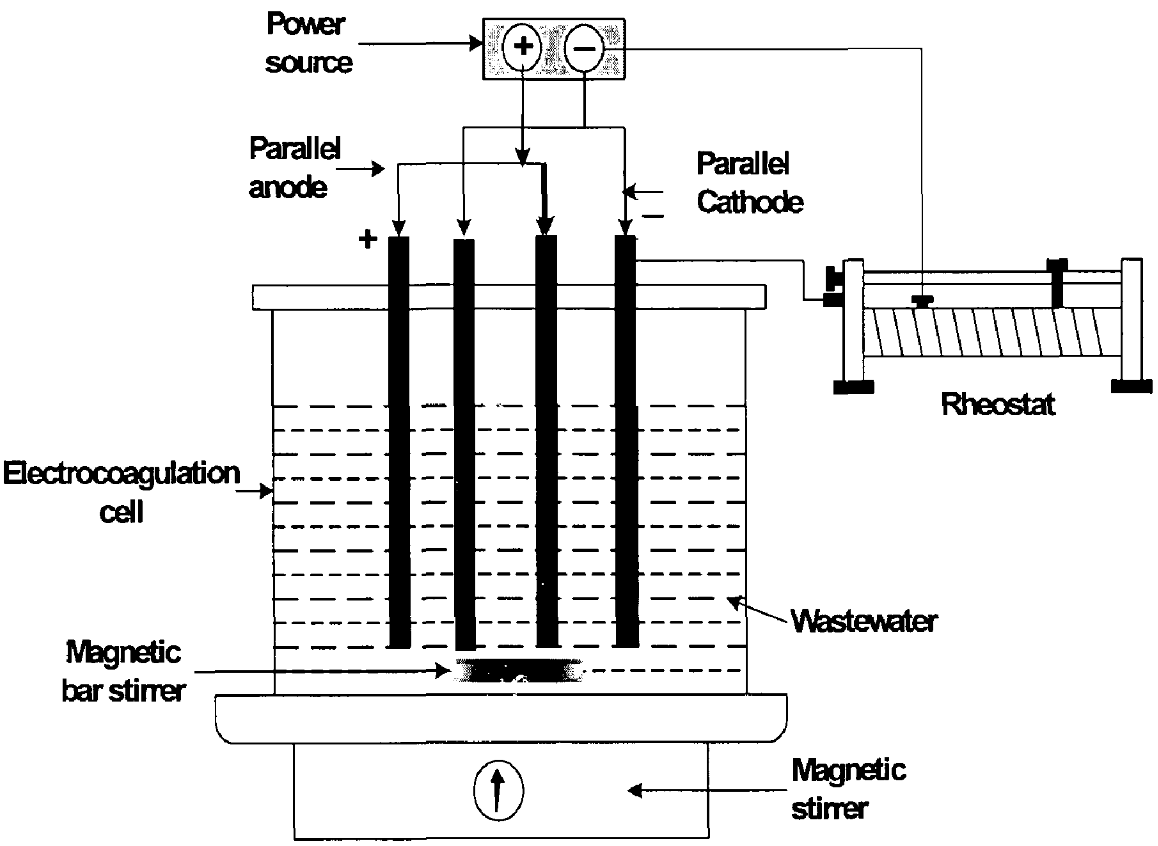
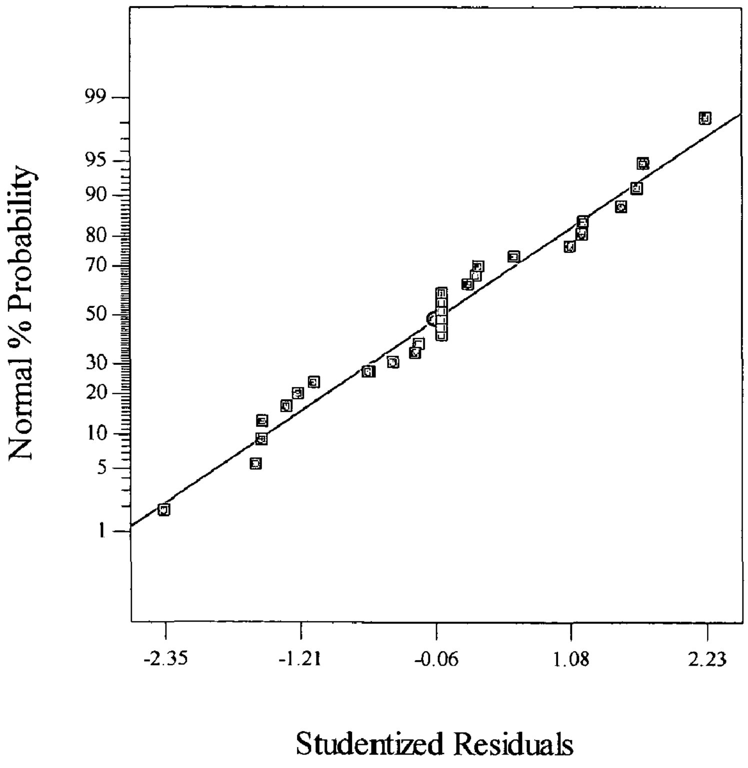
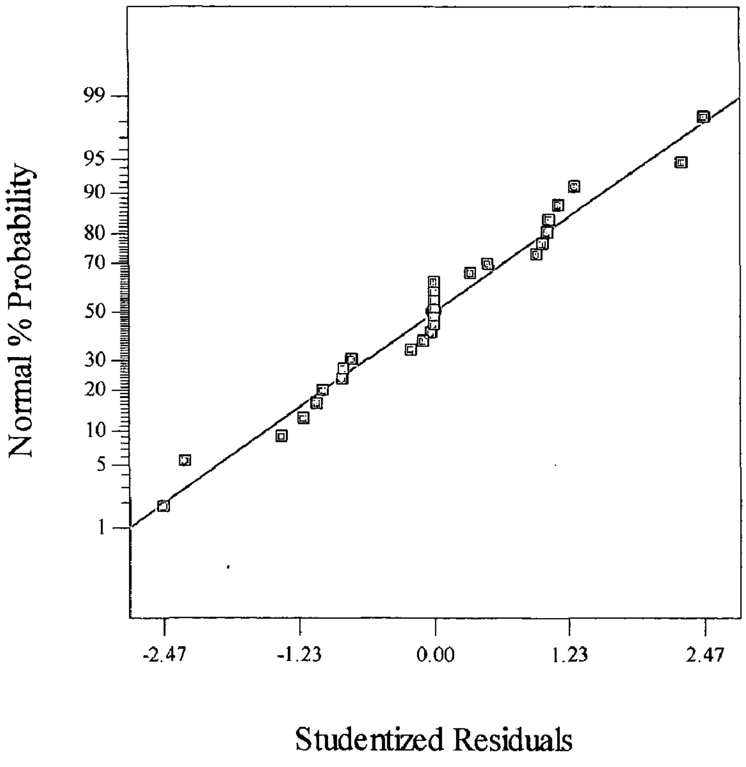


Fig. 5.1. Schematic Diagram of the Experimental Setup used for the Electrocoagulation study

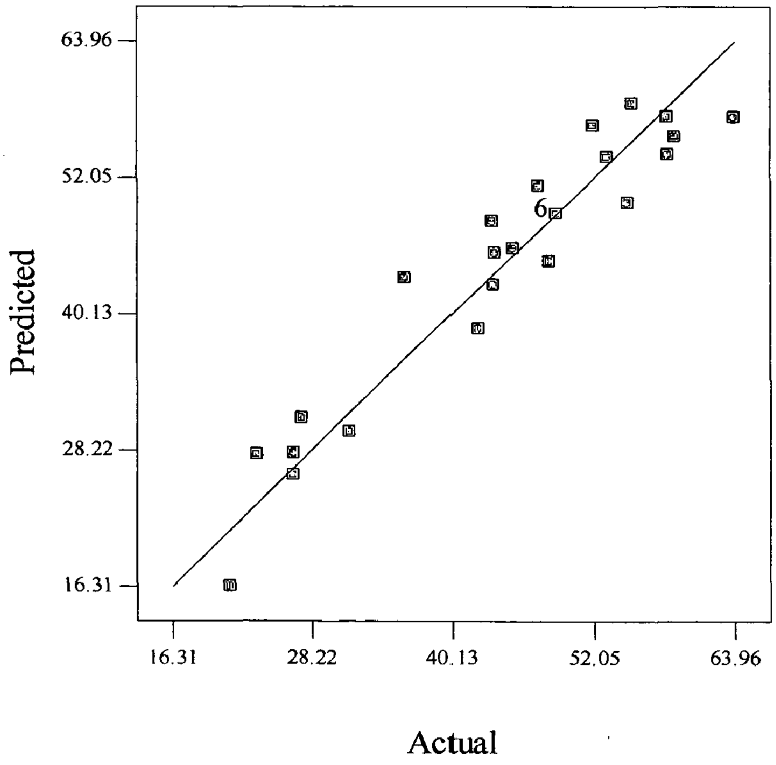


(A)

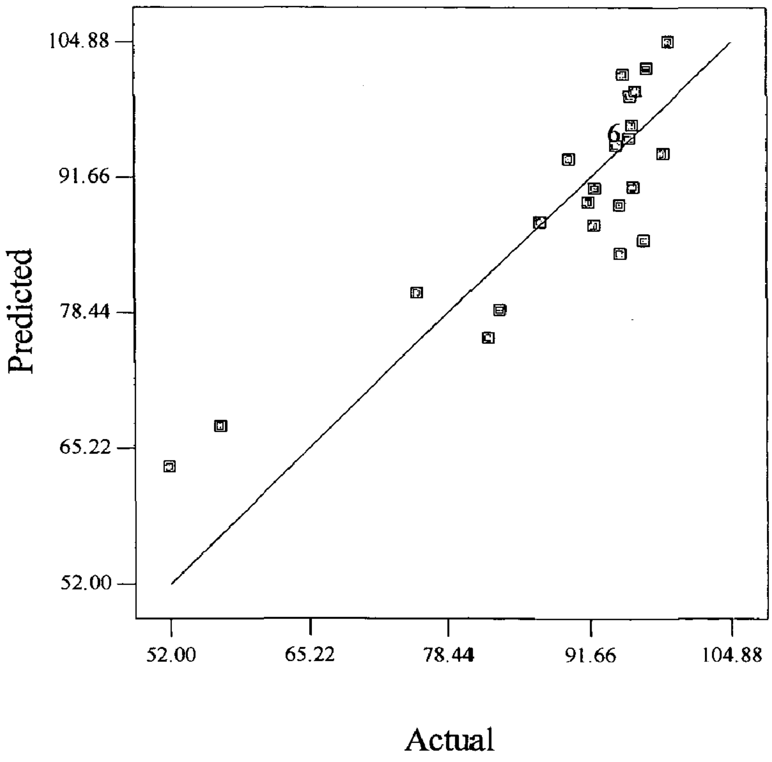


(B)

Fig. 5.2 Normal % Probability versus Residual Error, (A) COD removal and (B) Color removal

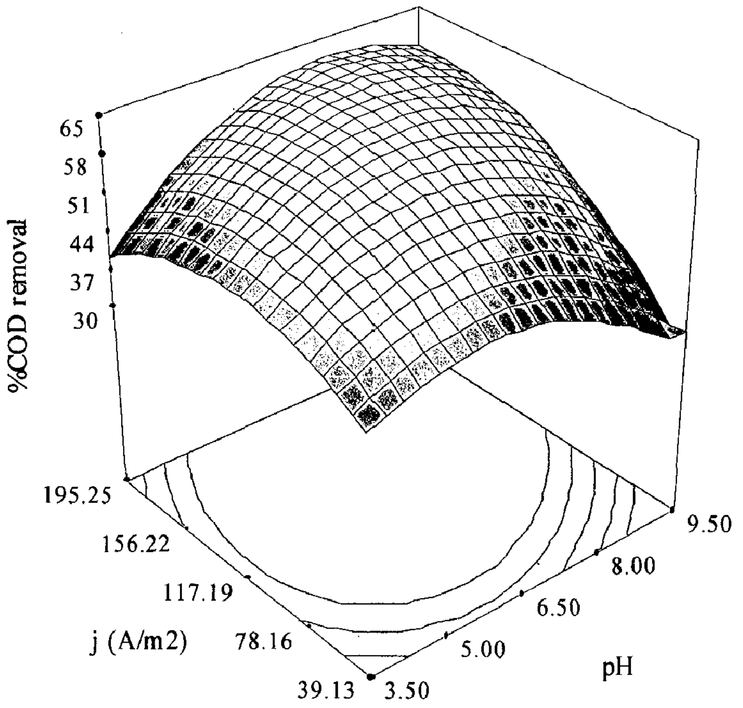


(A)

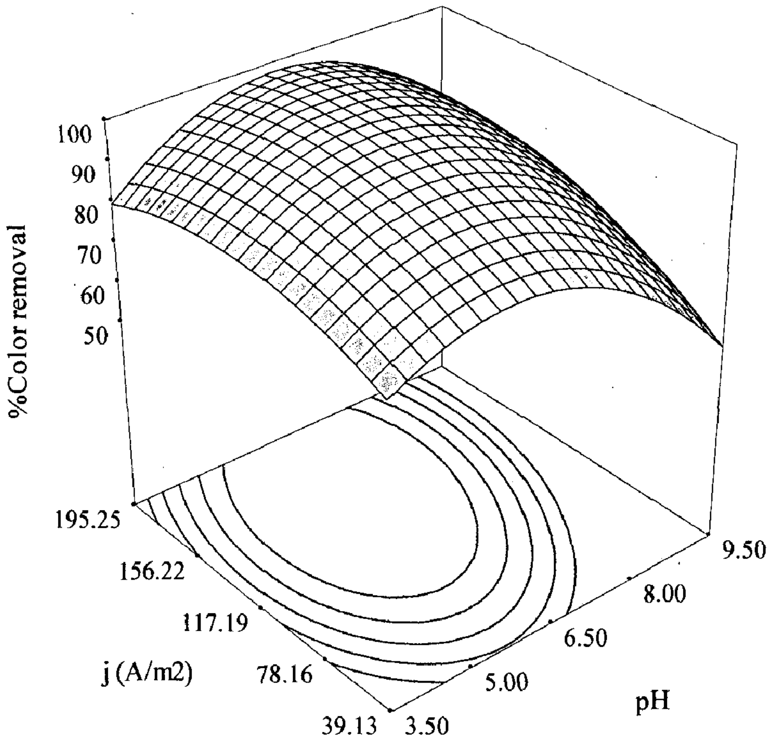


(B)

Fig. 5.3. Scatter Diagram of Predicted Response versus Actual Response for the EC Treatment of Bio-digester Effluent, (A) COD removal and (B) Color removal

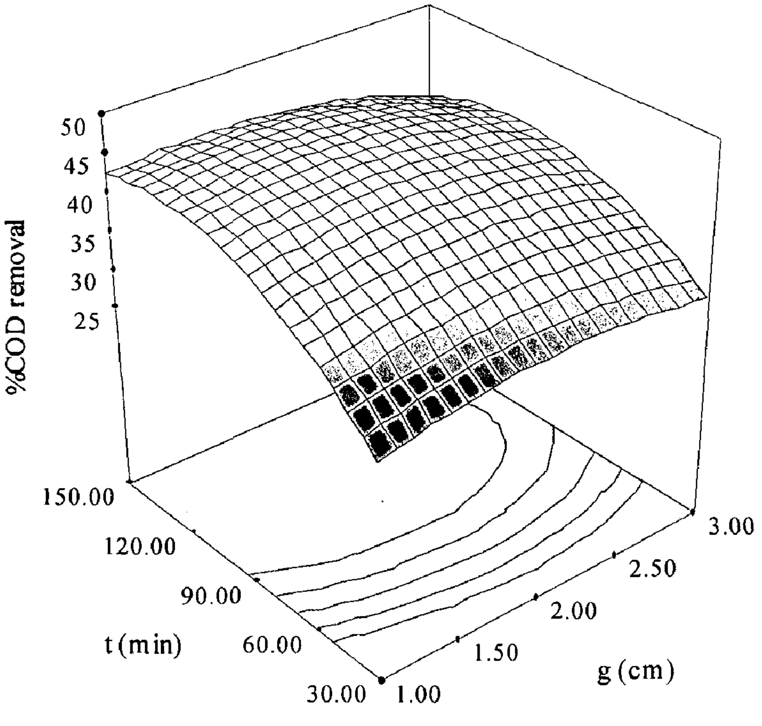


(A)

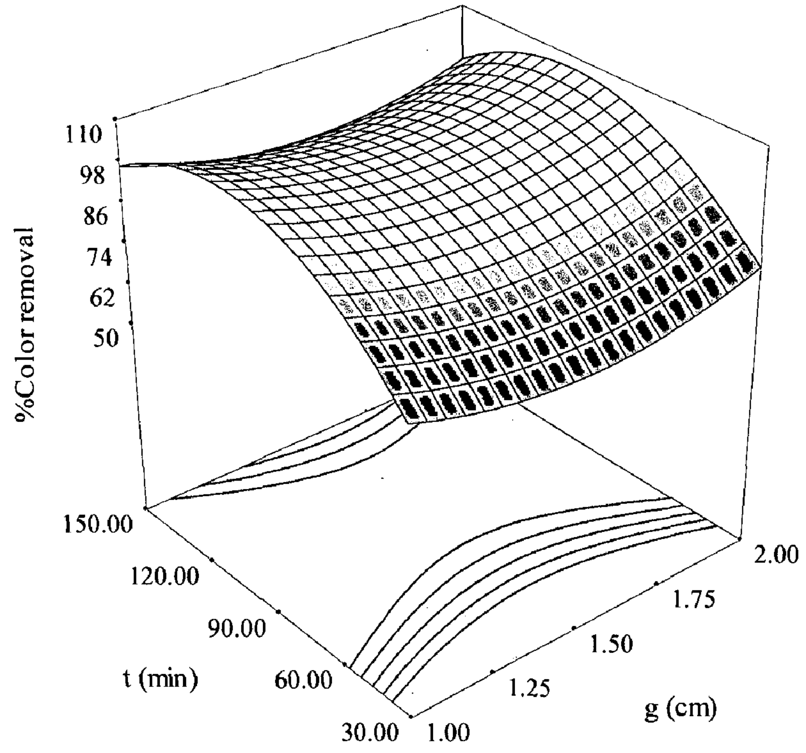


(B)

Fig. 5.4. 3D Response Surface Graph for COD and Color Removal versus Current Density and pH for the EC Treatment of Bio-digester Effluent, (A) COD removal and (B) Color removal

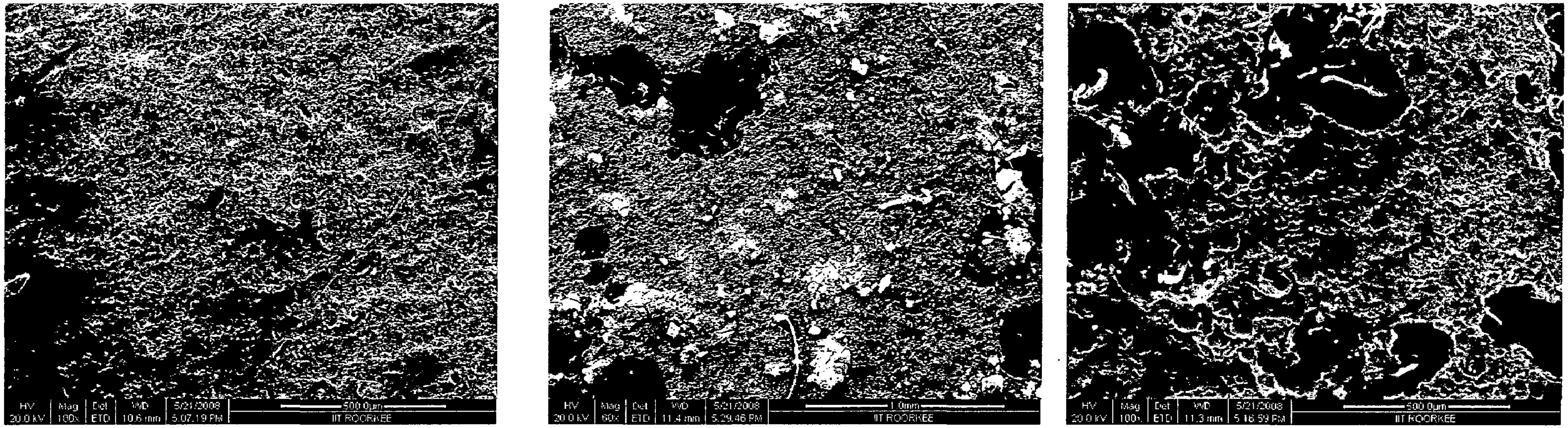


(A)

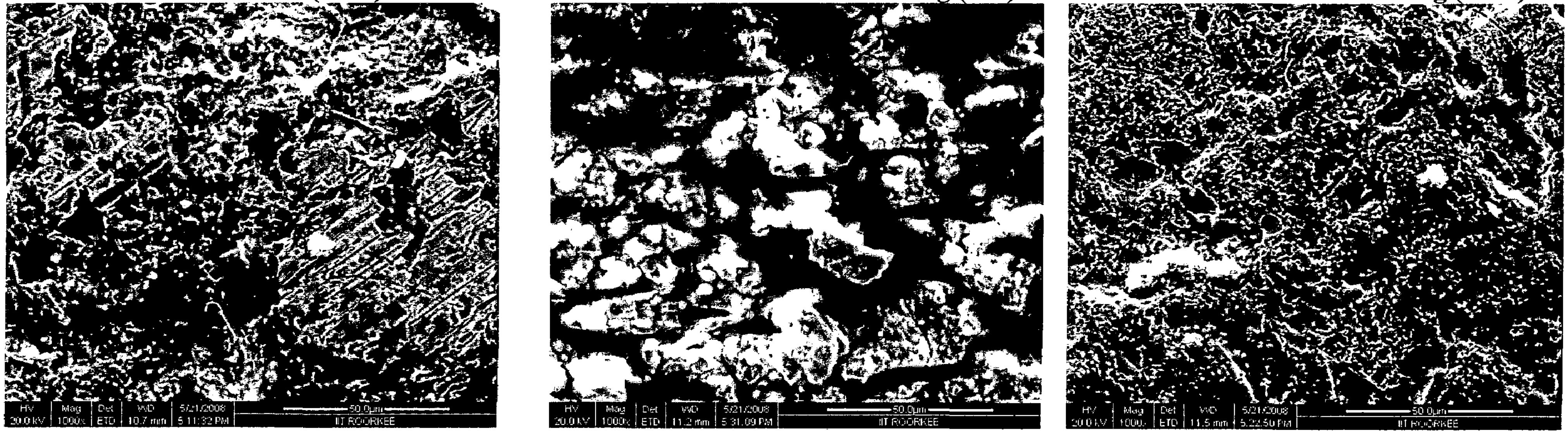


(B)

Fig. 5.5. 3D Response Surface Graph for COD and Color Removal versus Electrode Gap and Time for the EC Treatment of Bio-digester Effluent, (A) COD removal and (B) Color removal

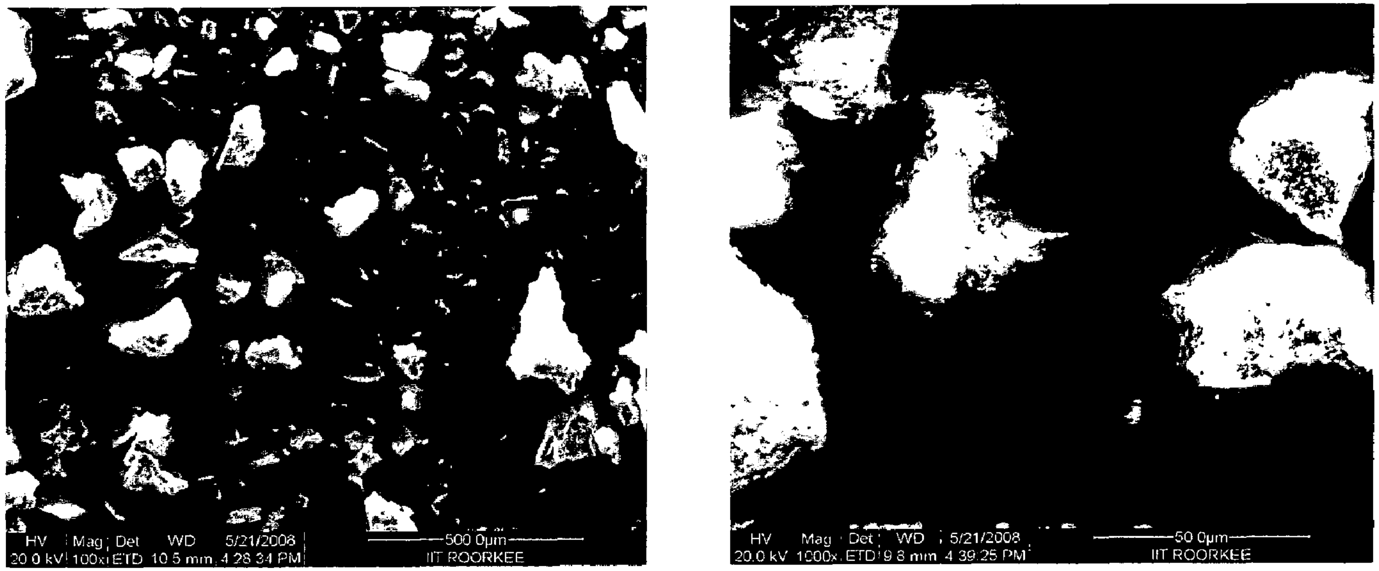


Fresh electrode (100x) Used electrode without cleaning (60x) Used electrode after cleaning (100x)



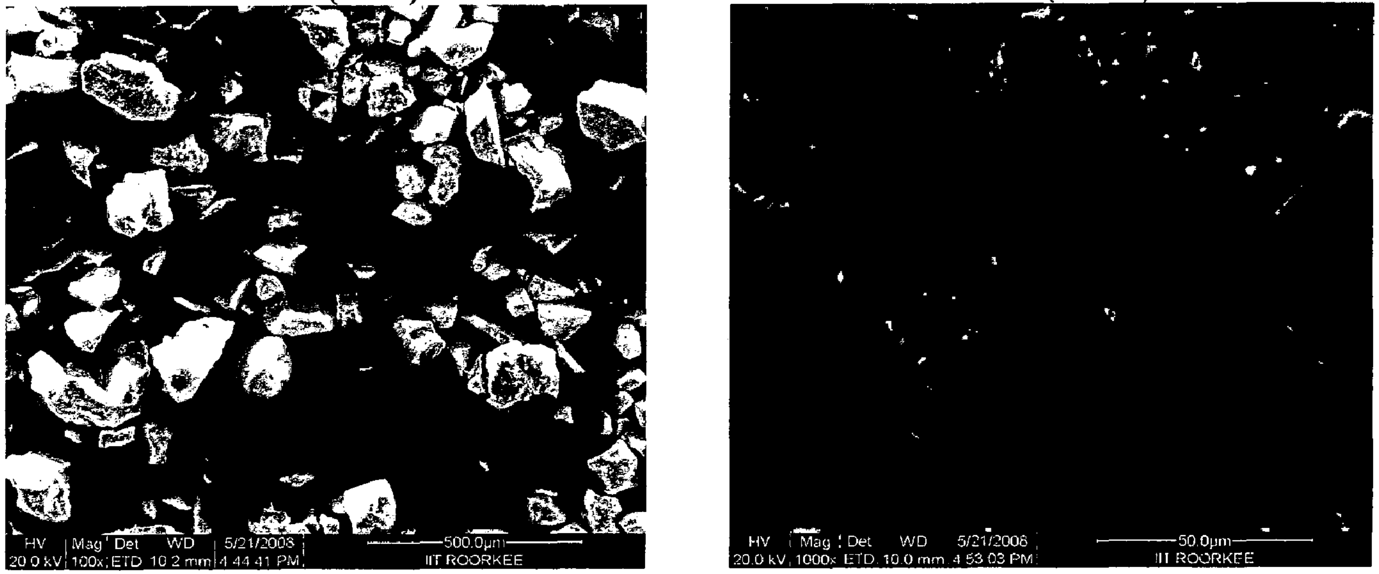
Fresh electrode (1000x) Used electrode without cleaning (1000x) Used electrode after cleaning (1000x)

Fig. 5. 6. SEM Images of Stainless Steel Electrode Prior to its use; Un-cleaned and Cleaned Electrodes after its use in EC Experiments



Scum (100x)

Scum (1000x)



Sludge (100x)

Sludge (1000x)

Fig. 5.7. SEM Images of the Scum and the Sludge at various Magnifications.

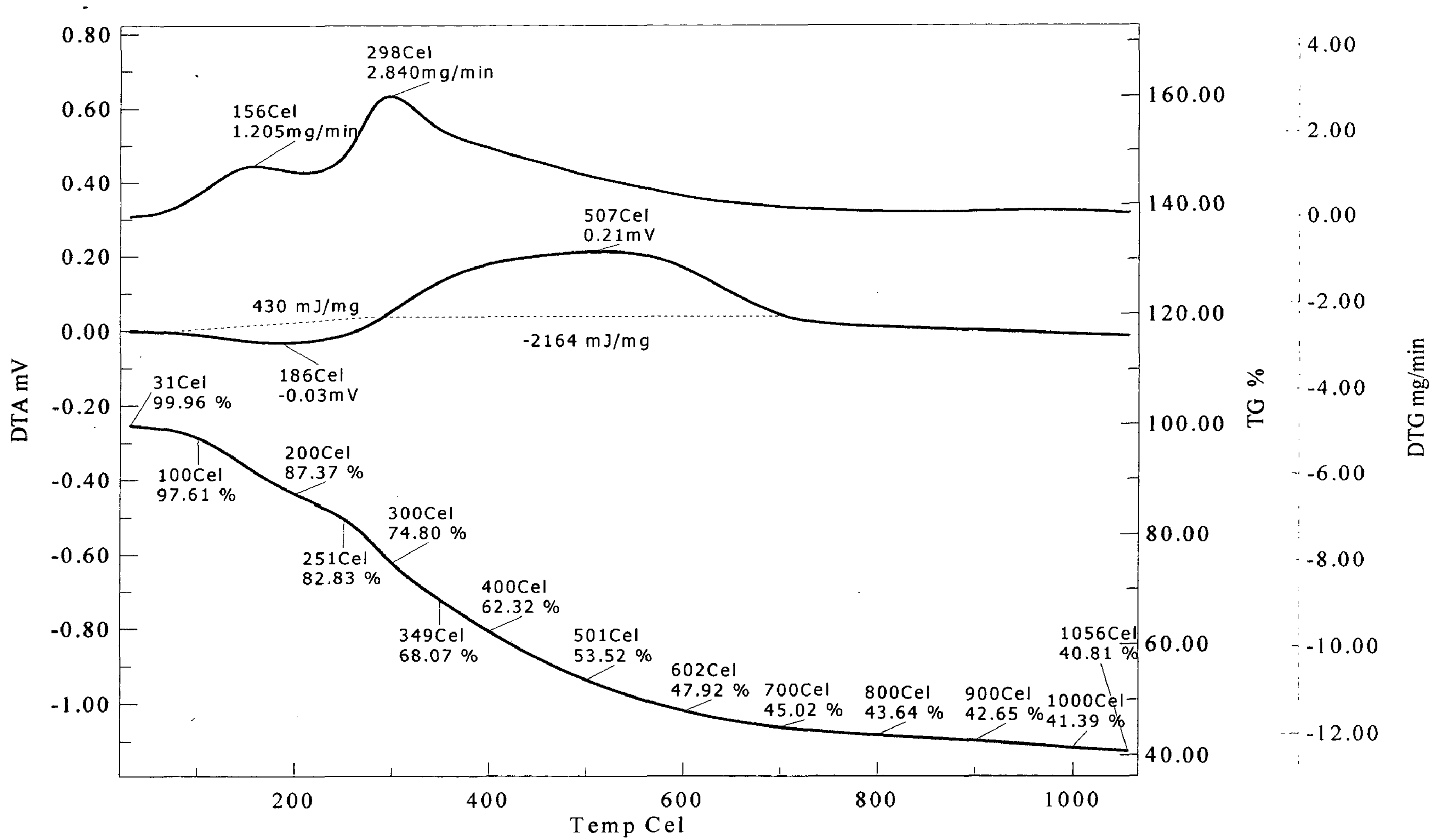


Fig. 5.8. Thermogravimetric Analysis of Scum under Air Atmosphere

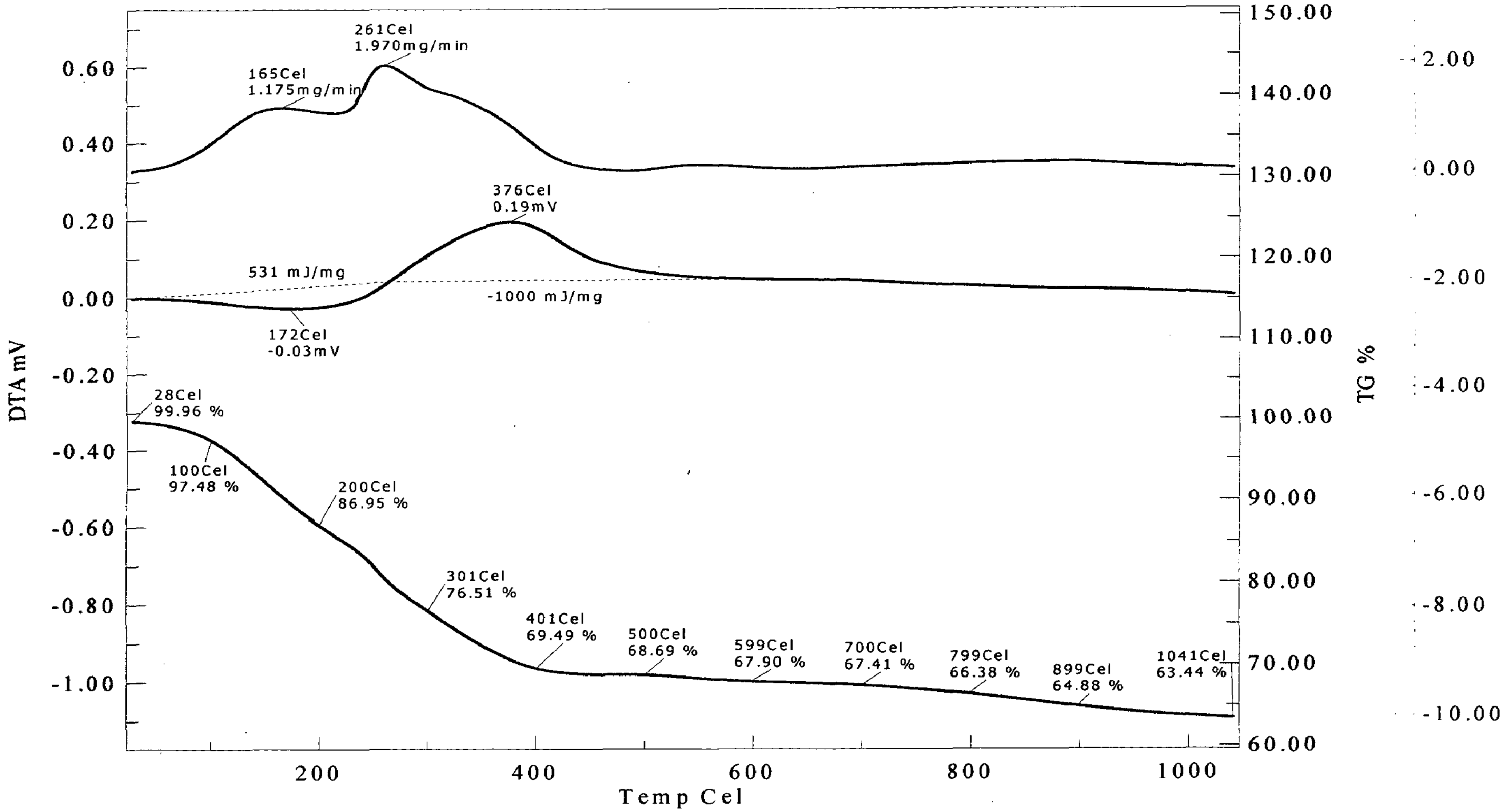
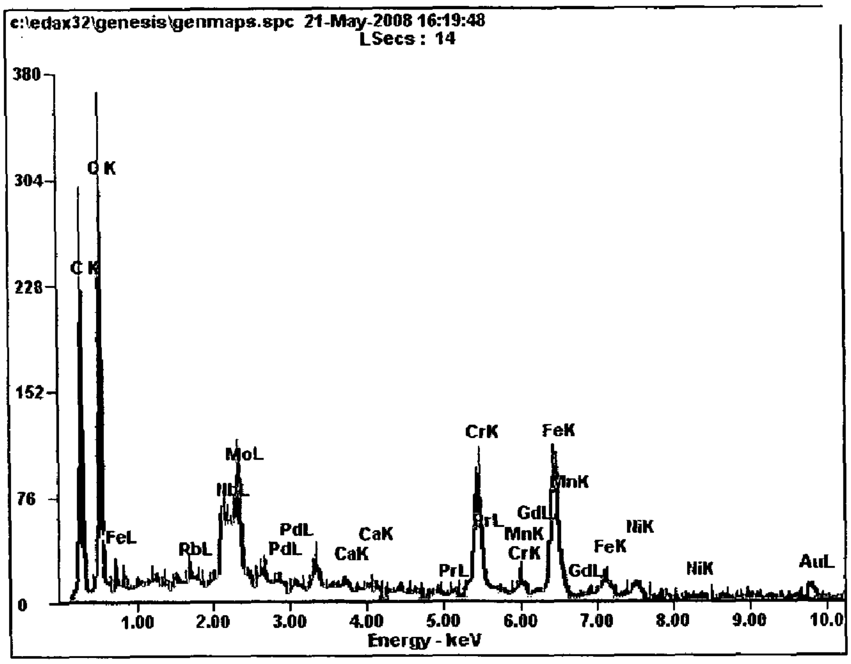
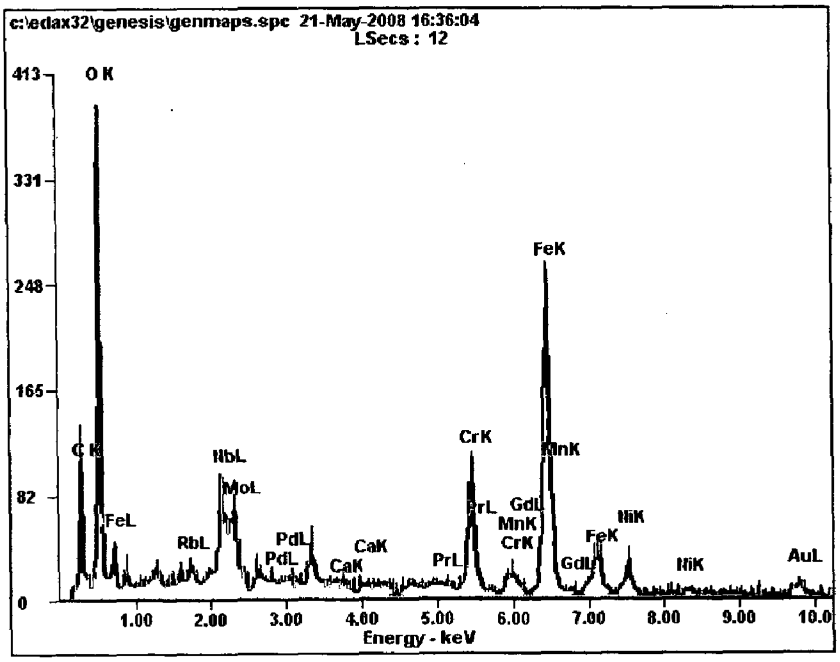


Fig. 5.9. Thermogravimetric Analysis Sludge under Air Atmosphere



Scum



Sludge

Fig. 5.10. EDX of Scum and Sludge

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The major conclusions drawn from the present work are given below:

1. Electrocoagulation (EC) can be employed as a treatment method for chemical oxygen demand (COD) and color removal of bio-digester effluent (BDE).
2. A central composite (CC) design was successfully employed for experimental design, analysis of results and optimization of the operating conditions for maximizing the COD and color removal.
3. COD removal and color efficiency was maximum at pH_0~6.75. For $pH < 6$, charge neutralization by monomeric cationic iron species was the primary mechanism for COD and color removal, while for higher pH, sweep coagulation with amorphous iron hydroxide explained the results.
4. COD and color removal was found to increase with an increase in current density (j) and time (t).
5. Maximum COD and color removal efficiency of 61.58% and 99.75% respectively was observed at optimum pH_0, j, g and t values of 6.75, 146.75 A/m^2, 1 cm and 130 min, respectively.
6. A second-order regression model was fitted to the experimental data. Analysis of variance showed a high coefficient of determination value for COD ($R^2 = 0.9144$) and color ($R^2 = 0.765$) removal, thus, showing a satisfactory fit of the second-order regression model.
7. SEM analysis of the used electrode surface showed the presence of a number of dents with width in the range of 50-500 μm.

8. Scum obtained after the EC process was found to have greater heating value as compared to the sludge. This was attributed to the higher percentage of carbon content present in the scum as shown by EDX analysis.
9. Residues of the EC process (scum and sludge) can be utilized for making blended fuel briquettes with other organic fuels, which can be further used as a fuel in the furnaces. The bottom ash obtained after its combustion can be blended with the cementitious mixture. This mixture can be used in construction purposes, thus, recovering energy from the residues as well as chemically fixing the iron and other toxic metals present in the EC sludge.
10. Results show that EC can be used as a potentially viable and inexpensive tool for the treatment of BDE.

6.2 Recommendations

This study has brought forth a number of considerations which may be of interest to pursue further research in the area of EC of BDE and other wastewaters generated in distillery and various other industries. Based on the experiences gained during the present work, the following recommendations are being made for future research:

1. EC of the BDE should be studied by other electrodes so as to improve the COD removal efficiency.
2. Batch and continuous EC may be carried out for the treatment of distillery effluents and other industrial wastewaters.
3. Since the EC is not able to remove the COD completely, it is essential to further treat the wastewater by other post-treatment options, like coagulation and/or adsorption to meet the stipulated regulatory discharge standards of the effluents.

REFERENCES

Barkley, N.P., Farrell, C.W., Gardner-Clayson, T.W., 1993. "Alternating current electrocoagulation for superfund site remediation". *Air Waste* 43, pp. 784–789.

Benyounis, K.Y., Olabi, A.G., Hashmi, M.S.J., 2005. "Effect of laser welding parameters on the heat input and weld-bead profile". J. Mater. Process. Technol. 164–165, 978-985.

Can, O.T., Bayramoglu, M., Kobya, M., 2003. "Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes". Ind. Eng. Chem. Res. 42, 3391-3396.

Canizares, P., Jimenez, C., Martınez, F., Saez, C., Rodrigo, M.A., 2007. "Study of the electrocoagulation process using aluminum and iron electrodes". Ind. Eng. Chem. Res. 46, 6189-6195.

Central Pollution Control Board (CPCB), 2003. "Environmental management in selected industrial sectors status and needs". PROBES/97/ 2002–03, CPCB, Ministry of Environment and Forest, New Delhi.

Chandra, R., Pandey, P.K., 2000. "Decolorization of anaerobically treated distillery effluent by activated charcoal adsorption method". *Indian J. Environ. Prot.* 21 (2), pp. 134–137.

Chandra, R., Singh, H., 1999. "Chemical decolorization of anaerobically treated distillery effluent". *Indian J. Environ. Prot.* 19 (11), pp. 833–837.

Chaudhari, P.K., Mishra, I.M., Chand, S. 2005. "Catalytic thermal pretreatment (catalytic thermolysis) of biodigester effluent of an alcohol distillery plant". Ind. Eng. Chem. Res. 44, 2518-2524.

Chen, X., Chen, G., Po, L.Y., 2000. "Separation of pollutants from restaurant wastewater by electrocoagulation". Sep. Purif. Technol. 19, 65–76. 16

Cleceri, L.S., Greenberg, A.E., Eaton, A.D., 1998. "Standard methods for the examination of water and wastewater": 20th edition, American Public Health Association, Washington DC.

CPCB, 2006. "Pollution control acts, rules and notifications issued there under". Central Pollution Control Board, Delhi, India.

Dhale, A.D., Mahajani, V.V., 2000. "Treatment of distillery waste after bio-gas generation: wet oxidation". *Indian J. Chem. Technol.* 7 (2000), pp. 11–18.

Duan, J., Gregory, J., 2003. "Coagulation by hydrolysing metal salts". Adv. Colloid. Inter. Sci. 100 –102, 475–502.

Fox, M., Noike, T., 2004. " Wet oxidation pretreatment for the increase in anaerobic biodegradability of newspaper waste". Bioresource Technology 91 273–281.

Garad, N.M., 2006. " Bio mass energy utilization". National conference on emerging tech and appl. Computer science department, Saurashta University, Rajkot 1-2 Oct.

Goel, P.K., Chandra, R., 2003. "Distillery effluent treatment by methane production". In advance in industrial wastewater treatment ABD publisher. Jaipur, India , pp, 164-179.

Golder, A.K., Samanta, A.N., Ray, S., 2007. "Removal of trivalent chromium by electrocoagulation". Sep. Purif. Technol. 53, 33–41.

Gregory, J., Duan, J., 2001. "Hydrolyzing metal salts as coagulants: Pure Appl". Chem. 73, 2017.

Guo, Z.R., Zhang, G., Fang, J., Dou, X., 2006. "Enhanced chromium recovery from tanning wastewater". J. Cleaner Prod. 14(1), 75–79.

Gurses, A., Yalcüin, M., Dogar, C., 2002. "Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables". Waste Manage. 22, 491.

Hernández, I.L., Díaz, C.B., Morales, G.R., Bilyeu, B., Núñez, F.U., 2006. "A combined electrocoagulation–sorption process applied to mixed industrial wastewater". Journal of Hazardous Materials Volume 144, Issues 1-2, 1 June 2007, Pages 240-248.

Holt, P.K., Barton, G. W. and Mitchell, C. A. 1999. "Electrocoagulation as a wastewater treatment". EERE Organising Team, Castlemaine, Victoria, pp.

Holt, P.K., Barton, G.W., Wark, M., Mitchell, C.A., 2002. "A quantitative comparison between chemical dosing and electrocoagulation". Colloid Surface A: Physico Chem. Eng. Aspects 211, 233–248.

Huiping, L., Guoqun, Z., Shanting, N., Yiguo, L., 2007. "Technologic parameter optimization of gas quenching process using response surface method". Comput. Mater. Sci. 38(3), 561- 570.

Idil, A.A., Isık K.lı., Deniz H., Elif K., 2007. "Electrocoagulation of a real reactive dyebath effluent using aluminum and stainless steel electrodes". Journal of Hazardous Materials xxx (2007) xxx–xxx.

Inanc, B., Ciner, F., Ozturk, I., 1999. "Color removal from fermentation industry effluents". Water Sci. Technol. 40(1), 331–338.

Inanc, B., Ciner, F., Ozturk, I., 1999. "Colour removal from fermentation industry effluents". *Water Sci. Technol.* 40 (1), pp. 331–338.

Ivonne L.H. , Carlos B.D., Gabriela R.M., Bryan B. , Fernando U.N., 2006. "A combined electrocoagulation–sorption process applied to mixed industrial wastewater".

Jiang, J.Q., Graham, N., Andre, C., Geoff, H.K., Brandon, N., 2002. "Laboratory study of electrocoagulation- floatation for water treatment". Water Res. 36, 4064–4078. 17.

Kim, H.M., Kim, J.G., Cho, J.D., Hong, J.W., 2003. "Optimization and characterization of UVcurable adhesives for optical communication by response surface methodology". Polym. Test. 22, 899-906.

Kobya, M., Ciftci, C., Bayramoglu, M., Sensoy, M.T., 2007. "Study on the treatment of waste metal cutting fluids using electrocoagulation". Separation and Purification Technology xxx (2007) xxx–xxx.

Lalov, I.G., Guerginov, I.I., Krysteva, A., Fartsov, K., 2000. "Treatment of wastewater from distilleries with chitosan". *Water Res.* 34 (5), pp. 1503–1506.

Mahesh, S., Prasad, B., Mall, I.D., Mishra, I.M., 2006a. "Electrochemical degradation of pulp and paper mill wastewater". Part 1. COD and color removal". Ind. Eng. Chem. Res. 45 2830- 2839.

Mahesh, S., Prasad, B., Mall, I.D., Mishra, I.M., 2006b. "Electrochemical degradation of pulp and paper mill wastewater part II. Characterization and analysis of sludge". Ind. Eng. Chem. Res. 45, 5766-5774.

Mahimairaja, S., Bolan, N.S., 2004. "Problems and prospects of agricultural use of distillery spentwash in India". In: Third Australian and New Zealand Soil Science Societies Joint Conference, Sydney, Australia, 5–9 December 2004.

Mall, I.D., Kumar, V., 1997. "Removal of organic mater from distillery effluents using low cost adsorbent". *Chem. Eng. World* XXXII (7), pp. 89–96.

Mangialardi, T., 2003. "Disposal of MSWI fly ash through a combined washing immobilization process". J. Hazard. Mater. B98, 225–240.

Manisankar, P., Rani, C., Viswanathan, S., 2004. "Effect of halides in the electrochemical treatment of distillery effluent". Chemosphere 57 961– 966.

Marhuenda-Egea, F.C., Mart´ınez-Sabater, E., Jord, J., Moral, R., Bustamante, M.A., Paredes, C., P´erez-Murcia, M.D., 2007. "Evaluation of the aerobic composting process of winery and distillery residues by thermal methods". Thermochimica Acta 454 (2007) 135–143

Matteson, M.J., Dobson, R.L,. Glenn, R.W.J., Kukunoor, N.S., Waits, W.H.I., Clayfield, E.J., 1995. "Electrocoagulation and separation of aqueous suspensions of ultrafine particles". *Colloids Surf., A* 104, pp. 101–109.

Migo, V.P., Matsumara, M., Rosario, E.J.D., Kataoka, H., 1993. "Decolorization of molasses wastewater using an inorganic flocculant". J. Fermentation Bioeng. 75(6), 438–442.

Modirshahla, N., Behnajady, M.A., Kooshaiian, S., 2007. "Investigation of the effect of different electrode connections on the removal efficiency of tartrazine from aqueous solutions by electrocoagulation". Dyes Pigment 74(2), 249-257.

Montgomery, D.C., 1991. "Design and Analysis of Experiments": Third ed., Wiley, New York.

Nandy, T., Shastry, S., Kaul, S.N., 2002. "Wastewater management in a cane molasses distillery involving bioresource recovery". J. Environ. Manag. 65, 25–38.

Pandey, R.A., Malhotra, S., Tankhiwale, A., Pande, S., Pathe, P.P., Kaul, S.N., 2003. "Treatment of biologically treated distillery effluent—a case study". *Int. J. Environ. Stud.* 60 (3), pp. 263–275.

Pouet, M.T., Grasmick, A., 1995. "Urban wastewater treatment by electrocoagulation and flotation". Water Sci. Technol. 31, 275–283. 18.

Satisha, G.C., Devarajan, L., 2006. "Effect of amendments on windrow composting of sugar industry Pressmud". Waste Management 27 1083–1091.

Satyawali, Y. , Balakrishnan ,M., 2006. "Wastewater treatment in molasses-based alcohol distilleries for COD and color removal": A review.

Segurola, J., Allen, N.S., Edge, M., Mahon, A.M., 1999. "Design of eutectic photo initiator blends for UV/curable acrylated printing inks and coatings". Prog. Org. Coat. 37, 23-37.

Sheehan, G.J., Greenfield, P.F., 1980. "Utilization, treatment and disposal of distillery wastewater". Water Research 14 (3), 257–277.

Srivastava, V.C., Mall, I.D., Mishra, I.M., 2006. "Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash". Chem. Eng. J. 117(1), 79-91.

Subramanian, K.A., Singal, S.K., Saxena, M., Singhal, S., 2005. "Utilization of liquid biofuels in automotive diesel engines: An Indian perspective". Biomass Bioenerg. 29(1), 65–72.

Suthar, S., Singh, S., 2008. "Feasibility of vermin-composting in bio-stabilization of sludge from a distillery industry". Science of the Total Environment 394 (2008) 237–243.

Thella, K., Verma, B., Srivastava, V.C., Srivastava, K.K., 2008. "Electrocoagulation study for the removal of arsenic and chromium from aqueous solution". J. Environ. Sci. Health Part A 43, 554–562.

Tir, M., Moulai-Mostefa, N., 2008. "Optimization of oil removal from oily wastewater by electrocoagulation using response surface method". J. Hazard. Mater. In Press, doi:10.1016/j.jhazmat.2008.01.051.

Vik, E.A., Carlson, D.A., Eikum, A.S., Gjessing, E.T., 1984. "Electrocoagulation of potable water". Water Res. 18, 1355–1360.

Vlyssides, A.G., Israilides, C.J., Loizidou, M., Karvouni, G., Mourafeti, V., 1997. "Electrochemical treatment of vinasses from beet molasses". Water Sci. Technol. 36(2/3),271–278.

Wilkie, A.C., Riedesel, K.J., Owens, J.M., 2000. "Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks". *Biomass Bioenergy* 19 (2), pp. 63–102.

Yusuf, Y., 2006. "EC and EF processes for the treatment of alcohol distillery wastewater". Separation and Purification Technology 53 135–140.

http://www.praj.net/v2/index.php?option=com_content&task=view&id=247&Itemid=94.

http://www.cpcb.nic.in/Environmental%20Standards/Effluent/standard27.html

http://www.praj.net/wastewatersystems.htm