ELECTROCHEMICAL TREATMENT OF BIODIGESTER DISTILLERY EFFLUENT WITH AND WITHOUT AERATION

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
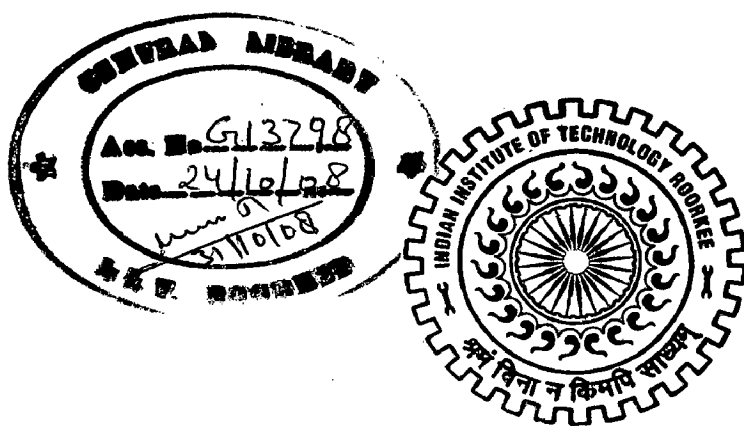*of*

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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JUNE, 2008

I hereby declare that the work which is being presented in the dissertation report entitled **"ELECTROCHEMICAL TREATMENT OF BIODIGESTER DISTILLERY EFFLUENT WITH AND WITHOUT AERATION"** in partial fulfilment of the requirements for the award of the degree **Master of Technology** with specialization in **Industrial Pollution Abatement,** to the **Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee** is an authentic record of my own work carried out during a period from July 2007 to June 2008 under the supervision of **Dr. I.M. Mishra,** Professor, Chemical Engineering Department, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(MANDAPAKA PAVAN KUMAR)

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

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ACKNOWLEDGEMENT

ABSTRACT

Distillery wastewaters are considered as one of the serious pollution problems of the countries producing alcohol from the fermentation and subsequent distillation of sugar cane molasses. Over half a million liter of bio-digester effluent gets generated on a daily basis from a typical distillery producing ethanol from cane molasses. This effluent is difficult to treat by conventional biological treatment processes like activated sludge or anaerobic lagoons. Electrochemical treatment is one of the emerging technologies in secondary and tertiary treatment. It was employed for the removal of color and COD from the bio-digester distillery effluent. The applied voltage was kept above 12 V while the current density used was varied from 50 to 90 A m^{-2} for the present study. The overall treatment time employed for the treatment process was 4 h. Six number of electrodes with an inter electrode distance of 10 mm were used in the present study. The electrochemical treatment yielded a maximum COD and color removal of ~80 and ~90%, respectively. Aeration was also employed along with the electrochemical treatment to see its effect on the removal efficiencies. Removal efficiencies ~75% COD and ~ 80% color) were found to be lower in case of aeration as compared to that without aeration.

CONTENTS

NOMENCLATURE

N	Number of electrodes
pH_0	Initial pH
pH_f	Final pH
A	Ampere
APHA	American Public Health Association
BOD	Biological Oxygen Demand
CD	Current Density
CF	Coagulation Filtration
CMF	Coagulation Microfiltration
CPCB	Central Pollution Control Board
COD	Chemical Oxygen Demand
DC	Direct Current
DTA	Differential Thermal Analysis
DTG	Differential Thermal Gravimetric
DWW	Distillery Wastewater
EC	Electrocoagulation/ Electrochemical
ECT	Electrochemical Treatment
ECR	Electrochemical Reactor
EDS	Energy Dispersive Spectrometer
EDTA	Ethylene Diamine Tetraacetic Acid
EF	Electro-Floatation
EPA	Environmental Protection Agency
ET	Time required for Treatment
FTIR	Fourier Transform Infrared Spectroscopy
I	Current
NF	Nanofiltration
PCU	Platinum Cobalt Units
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
TA	Thermal Analysis
TEM	Transmission Electron Microscopy
V	Voltage
WHO	World Health Organization
WWW	Winery Wastewater
XRD	X-Ray Diffration

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Over half a million liter of spentwash effluent is generated from a typical distillery producing ethanol from cane molasses as raw material on a daily basis. Apart from being highly colored, the spentwash effluent is difficult to treat by conventional biological treatment processes like activated sludge or anaerobic lagoons. Usually it has an extremely high chemical oxygen demand (COD) (Ghosh et al., 2002). The spentwash is treated on a primary basis by anaerobic digestion for generation of methane while reducing its COD and color and there by the organic loading, and then it is treated aerobically using trickling filter or by activated sludge systems. However, spentwash disposal even after conventional treatment is hazardous and has a high pollution potential due to the accumulation of non-biodegradable compounds, which are mostly coloured and has a high COD value. The dark brown colour of the treated spentwash is mainly due to melanoidins that remain in the effluent undegraded even after conventional treatment. Therefore, a complementary treatment process is also required to remove the color and the residual COD.

1.1 TREATMENT METHOD FOR DSW

High biological oxygen demand (BOD) and COD values of the effluent indicate that energy of the carbonaceous wastes must be recovered, or must be made to sustainable values, so that they can be discharged. Various methods based on energy recovery include: evaporation of water, concentration of the distillery waste water (DWW) followed by incineration; wet oxidation, catalytic thermolysis at moderate to low temperatures and at autogenous pressure, anaerobic treatment (bio-methanation) followed by secondary and tertiary treatments.

These treatment technologies are adsorption, catalytic wet air oxidation, catalytic thermolysis. Various studies have been made using various adsorbents for the removal of COD from distillery waste water (Satyawali and Balakrishnan, 2007, 2008). Also distillery wet air oxidation under high pressure has been employed for the treatment of distillery waste (Chaudhari, 2005).

Under this secondary and tertiary treatment methods, one of emerging treatment technology is electrochemical (EC) treatment. EC Technology has been employed for the treatment of various textile waste water like pulp and paper, distillery removal of heavy metals, removal of arsenic, and dyes etc. It is one of the emerging technologies and has been employed for the treatment of various wastewater generated by various industries. (Mollah et al., 2004) suggested that the future of treatment of waste water is dependent on the electro chemical technology. As a treatment technology it is one of the simple methodologies as there are not many complexities involved.

Electrochemical treatment has been used extensively for treating polluted wastewaters. It has proved to be an efficient technique in a wide variety of polluted wastewaters. Electrochemical treatment can remove 75-99% of metals and 90-99% of suspended solids while reducing BOD and COD by 50-75%. Sometimes the process is also marketed as having the ability to reduce the amount of inorganic salts in the water being treated. Electrochemical treatment eliminates the need of adding expensive chemicals as coagulants to the wastewater and, therefore generates less solid waste, thus saving on disposal costs. On the basis of the above described and the comparison given by EPA, electrochemical treatment technique was chosen for the treatment of the Biodigester effluent. In the following section basic fundamentals about the ECT is being discussed.
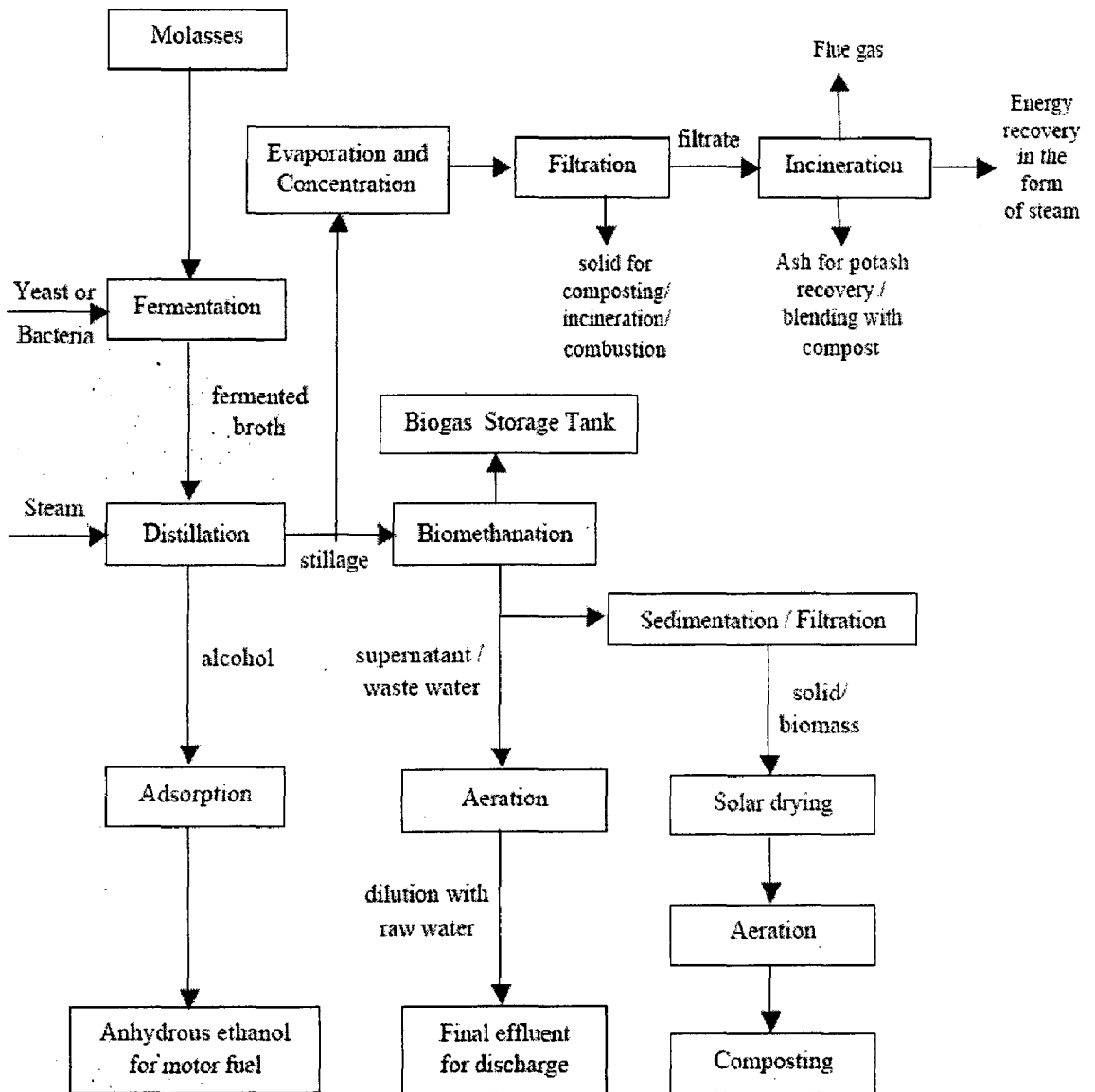
Fig. 1.1 Flow sheet for technique used for alcohol production from molasses (Chaudhari, 2005)

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1.2 BASIC FUNDAMENTALS OF ECT

ECT technology lies in the intersection of three fundamental technologies – electrochemistry, coagulation and filtration. A conceptual framework of the ECT technology is as shown in the Fig.1.2. The figure shows the different processes involved in ECT, the vertical arrows show the removal path which can be adjusted by the operating parameters like current density, voltage etc. The intersection of all the three technologies results in the ECT process. The characteristics of these technologies and their combination are shown within the three circles and their intersection. The parameter which influences the ECT process are the characteristics of the water/ wastewaters to be treated, type of electrode material used, shape and size of electrode and its arrangement, reactor design, applied current density, temperature, pH of the untreated liquid etc. The effects of these parameters are described briefly.

1.2.1 Current Density (CD)

The amount if ion generation during the ECT depends upon the applied current, a larger current supply means a smaller ECR required for treatment. However, large current supply results in lower current efficiency of the process. If an ECT process is to be operated for long time without maintenance, a CD value of 20-25 A/m^2 is required (Chen, 2004).

1.2.2 Water/wastewater characteristics

The efficiency of any ECT process depends on the characteristics of water/wastewater used. Large amount of salts and ions facilitates the ECT by increasing its conductivity, but increases the sludge generation. Presence of any oxidizing agent enhances the removal efficiency of the ECT process (Hansen, 2006).
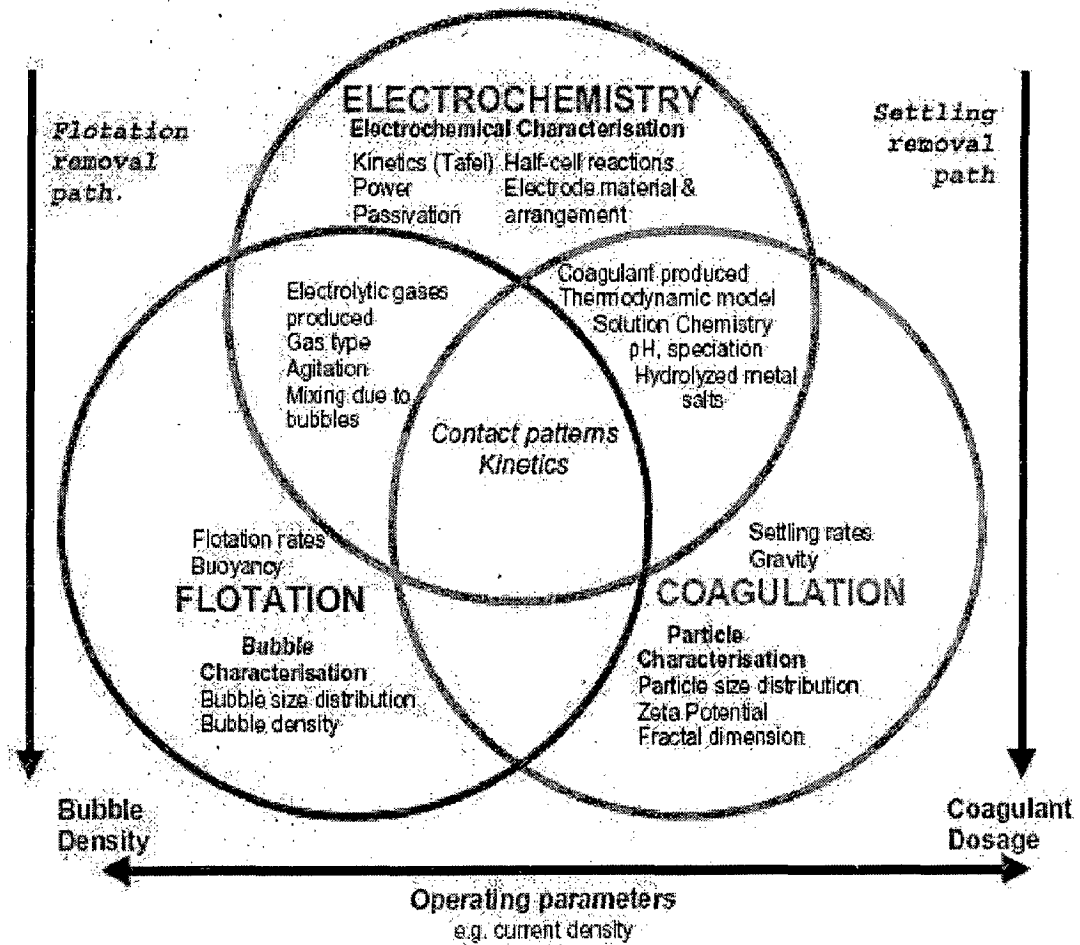
Fig. 1 2. Conceptual framework of ECT (Holt et al., 2005)

1.2.3 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).

1.2.4 ECR design

To keep the design of ECT process simple the electrodes are generally arranged in bipolar form and the flow is between the electrodes. When the passivation of electrode surface takes place flowrate is increased to minimize the affects (Chen, 2004). Use of horizontal flow and vertical flow ECR are also proposed. A horizontal flow ECR with sedimentation basin is used by Hansen et al. (2006).

1.2.5 Temperature

The effect of temperature on the ECT technology is not very much researched. Qiu et al. (1988) reported an increase in the current efficiency of aluminum electrodes up to 60°C which decreased on further increasing the temperature.

1.2.6 pH

The pH of the water/wastewater effect can be seen in the current efficiency and the solubility of hydroxides in the ECR. Power consumption is high in the neutral pH range due to fluctuations in the conductivity of the reactor content (Chen, 2004).

1.3 OBJECTIVES OF THE PRESENT STUDY

A technology is required for the treatment which is not only cost effective but can also meet the standards of the treatment technology. Based on testing and comparison of various treatment technologies and also the results of these treatment technologies, ECT was chosen as the treatment method to be employed for the treatment.

1. To check the efficiency of the ECT for the removal of COD and color from biodigester distillery wastewater

2. To see the effect of operating parameters like current density, time, etc.

3. To characterize the electrodes, sludge and scum by various techniques to understand EC mechanism.

LITERATURE SURVEY

This chapter gives the overview of various treatment methodologies for the treatment of distillery wastewater, and also presents the application of electrochemical method for the treatment of various types of wastewasters.

2.1 TREATMENT OF DISTILLERY WASTEWATERS

Kannan et al. (2006) have compared the treatment potential of ECT in the treatment of Distillery waste with and without the presence of activated *Areca catechu* nut carbon where they have reported 99% removal of the turbity along with removal of essential parameters.

Satyawali and balakrishnan (2007) reviewed the existing status and advances in biological and physico-chemical methods applied to the treatment of molasses-based distillery wastewater considering both laboratory and pilot/industrial studies. The limitations in the existing processes were also summarized and potential areas for further investigations were discussed.

Satyawali and balakrishnan (2007) examined 19 carbon samples prepared by acid and thermal activation of various agro-residues viz. bagasse, bagasse flyash, sawdust, wood ash and rice husk ash for color removal from biomethanated distillery effluent. the authors reported that Phosphoric acid carbonized bagasse B (PH) showed the maximum color removal (50%) and commercial activated carbons AC (ME) and AC (LB) showed better performance of over 80% color removal. The authors also stated that apart from color removal, activated carbon treatment also showed reduction in chemical oxygen

demand (COD), total organic carbon (TOC), phenol and total Kjeldahl nitrogen (TKN). The performance was related to the characteristics of the investigated samples.

Ghosh et al. (2002) studied the application of two bacterial strains, *Pseudomonas putida* U and *Aeromonas* strain Ema, in a two-stage column bioreactor to reduce COD and the colour of the anaerobically treated spentwash under aerobic conditions. The authors reported that in the first stage, *P. putida* reduced the COD and colour by 44.4 and 60% and in the second stage, the *Aeromonas* strain Ema, reduced the COD by about 44.4%. Algal bioassay was used to evaluate the quality of spentwash before and after treatment by the two bacterial strains. The authors stated that the spentwash was eutrophic before experimental treatment, but, after treatment, distillery spentwash showed poor growth of the test alga even at higher spentwash concentrations.

Chaudari et al. (2007) studied the removal of molasses-derived colour and chemical oxygen demand from the biodigester effluent of a molasses-based alcohol distillery effluent treatment plant by using inorganic coagulants—$FeCl_3$, $AlCl_3$ and polyaluminium chloride (PAC). The coagulation/flocculation yielded about 55, 60 and 72% COD reductions and about 83, 86 and 92% colour reductions, with the use of 60 mM-l^{-1} $AlCl_3$, 60 mM l^{-1} $FeCl_3$ and 30 ml/l of polyaluminium chloride, at their optimum initial pH. The critical pH of the effluent–coagulant mixture plays a very significant role in the coagulation/flocculation process, with pH_0 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^{-1} and can be used as a medium energy fuel material. The filtration characteristics of the flocculated effluent are poor.

Chaudari et al. (2007) treated the sugarcane molasses-fed distillery wastewater (DWW) which has very high biochemical and chemical oxygen demand (BOD and COD) by the catalytic thermal pretreatment (or catalytic thermolysis, CT) process to recover the majority of its energy content with consequent COD and BOD removal using CuO catalyst. Experiments were conducted in a 1 dm^3 stainless steel pressure reactor in a batch mode in the temperature range of 100–140 °C and corresponding autogenous pressure with CuO mass loading in the range of 2–5 kg m^{-3}. The initial pH (pH_0) was found to have profound impact on the efficiency of thermolysis in COD removal with the optimum pH_0 2. At 140 °C with 3 kg m^{-3} catalyst loading and pH_0 2, a maximum of 60% COD was reduced. The authors reported that the CT process follows a two step mechanism: with each step obeying the first order reaction kinetics with respect to COD and a fractional order 0.37 and 0.29 with respect to catalyst mass loading for the first and second steps. Also they reported that the CT process results in the formation of settleable solid residue and the slurry obtained after the thermolysis had good filtration characteristics. At 140 °C and pH_0 2, the solid residue had a C:H atomic ratio of 1:1.08 with a heating value of 21.77 MJ kg^{-1}.

2.2 ELECTROCHEMICAL TREATMENT OF WASTEAWATERS

Krishna Prasad et al. (2007) have optimized the parameters of electro-coagulation (EC) of a distillery spent wash by Box–Behnken design of surface response analysis in terms of color removal. They employed the design to derive a statistical model for the effect of parameters studied on removal of color using iron anodes. The current density (31 mA cm^{-2}), dilution (17.5%) and time of electrolysis (4 h) was found to be the

optimum conditions for maximum 95% color removal. The authors found that the actual color removal at optimized conditions to be 93.5% which confirms close to the predicted response using response surface methodology.

Kusakabe et al. (2004) treated copper ions and chelating agents in water simultaneously by using a packed-bed electrode cell. The cathode packings were graphite particles or graphite felt and the anode packings used by them were platinum-plated titanium pellets, β-PbO_2 particles or oxidized lead spheres. The catbolyte as reported by authors had ethylene diamine tetra acetic acid (EDTA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA) or glycine chelate of copper, while the anolyte contained the corresponding chelating agents. The initial concentration of chelating agents as used by them was 0.01 M for each experiment. The electrowinning of copper and the removal of chemical oxygen demand (COD) were achieved in the cathodic and the anodic chamber, respectively, under galvanostatic conditions. The graphite felt gave better results than the graphite particles because of the large surface area of the felt. Of the anodic packings, the platinum-plated titanium pellets and the β-PbO_2 particles showed equal suitability for COD removal. In the case of the platinum-plated titanium pellets, the current efficiency for COD removal of EDTA, NTA and IDA was 1.4, 0.7 and 0.32, respectively, in the range 0-12 kC. The removal of COD for EDTA, NTA and IDA under the same conditions was 41, 36 and 25%, respectively. The electro-oxidation of EDTA proceeded more efficiently in the lower pH range.

Pak et al. (2000) designed and operated an electrochemical reactor to treat the solution containing copper ions. They investigated the design parameters for the electrochemical reactor using the porous cathode and RuO_2/ IrO_2/Ti anode. The porous

cathode was prepared by the electroless nickel deposition on polyurethane. They also selected apparent current, the gap between cathode and anode, and hydraulic retention time (HRT) as design parameters. They reported that the copper removal rate increased with an increase in apparent current and was not affected by the gap between the cathode and the anode. They also reported that a reduction in hydraulic retention time stimulated the mass transfer toward the electrode and increased the cathodic current efficiency. Dimensional analysis was conducted to obtain the design equation for scale-up of the electrochemical reactor.

As described by Moreno-Casillas et al (2007) who have reviewed the COD removal by ECT technology, stated the actual situation of the ECT or the challenge faced by the ECT and the results obtained in laboratories under controlled conditions cannot always be extended to industrial environments. Although EC finds its application over a century, it has always had an adverse effect on the treatment when it comes to industrial scale. This is due to many reasons as in the industrial scale, all the controlled cannot be maintained all the time, which has made ECT as an enigmatic Treatment. They have thoroughly given the information regarding the advantages and disadvantages of ECT as a treatment technology. They have done work on removal of COD by electrocoagulation technique and have presented a detailed report and explanations along with the results they have conducted on various compounds and electrodes. In their paper they have also presented the in detail description about the process, the parameters contributing to the COD and also have presented the different cases of COD removal.

Kirzhner et al. (2008) examined the potential of electrocoagulation (EC), to treat different winery wastewaters (WWW), which were characterized by heavy loads of

organic pollutants. EC of WWW was conducted at 2A, and applied voltage up to 10V. the authors carried out laboratory tests of raw WWW treatment in different application periods (from 10 to 40 min), and the removal efficiency was studied. The potential of EC to improve the water quality of raw WWW, prior to further processing, was demonstrated and found that enhanced removal of the WWW pollutants was found at longer treatment periods. A 10 min batch treatment of WWW produced 16.4–27.9% reduction of the biochemical oxygen demand (BOD), 28.2–41.9% of the chemical oxygen demand (COD), and 89.2% the total phosphorus. At 1:1, W:F dilution, 97.5 and 95.6% of the BOD were removed, after 23 days of treatment, with the floating *Hydrocotyle umbellate* and *Eichhornia crassipes* plants and aeration, respectively, as compared to 28.5% in the control. Emergent plants (salt marshes with rushes) proved to be exceptionally effective in removing 99.2% of the BOD and 98.2% of the COD. These plants performed well at the high organic loads of the WWW. A scheme for a two-stage treatment of raw WWW was described, wherein the first stage WWW is treated by EC and its effluent with reduced organic load and then purified in the second stage, comprising aquatic plants.

Koyba et al. (2003) have treated the textile waste waters by ECT by using the iron and the aluminium electrodes. The effects of relevant wastewater characteristics such as conductivity and pH, and important process variables such as current density and operating time on the chemical oxygen demand (COD) and turbidity removal efficiencies were explored. The electrode and energy consumptions for each electrode were calculated and the results show that iron is superior to aluminum as sacrificial electrode material, from COD removal efficiency and energy consumption points.

Mollah et al. (2001) have given a review on the application and science aspects of Electro Coagulation EC for treatment of the waste water by covering the various aspects that like the advantages and disadvantages and the areas where further research is required along with the literature. Although electrocoagulation is an evolving technology that is being effectively applied today for wastewater treatment, the paucity of scientific understanding of the complex chemical and physical processes 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 research.

Ofir et al. (2007) made a comparison between two technologies: electro flocculation (EF) and chemical flocculation (CF), which could be used as pretreatment in wastewater treatment. Natural water reservoir or wastewater intended for reuse, that contains high concentrations of iron particulates, often requires particle destabilization and removal. These particles could be removed by flocculation process applying ferric chloride (CF) or by Fe_{3+} ion (EF) that change to Fe_{2+} in a short time. EF, a fairly new environmentally-friendly process has been developed with the aim of reducing, or even avoiding altogether, the amount of chemicals required during pretreatment. The behavior of iron oxide and hydroxide colloid in EF aims at solving the problem of contaminated water or industrial wastewater. In this paper EF with iron electrodes and chemical dosing with ferric chlorides were investigated for several types and different concentrations of iron suspension. The results show a gradual rise in absolute ζ-potential and an increase in particle size with flocculation time. The results of both processes were compared through the efficiency of solid/liquid separations performed by sludge sedimentation and

filtration. Preliminary testing identified the process conditions, pH of the water treated, dosage of the coagulant, mixing conditions, conductivity, and current density.

Mollah et al. (2004) Electrocoagulation is an electrochemical wastewater treatment technology that is currently experiencing both increased popularity and considerable technical improvements. There has been relatively little effort to better understand the fundamental mechanisms of the processes, particularly those that could provide design parameters to optimize the performances of this relatively simple and inexpensive technique. In a research programme to delineate the mechanisms of the fundamental processes involved in, the authors have realized that the technology has been insufficiently reviewed with emphasis on the fundamentals and their relationship to the performance of this technology. This paper presents an in-depth discussion and consideration of the factors that need to be addressed for optimum performance of this technology. Recent improvements of this technique and the theoretical model studies are also reviewed.

Vik et al. (1984) studied the Coagulation caused by electrolytically produced ions (electrocoagnlation) followed by filtration as a possible alternative to the conventional coagulation process. They have presented results showing the correlation between the current density and the aluminum dosing and also provided results showing the necessary overpotential. The process was efficient with regard to removal of aquatic humus. They also compared this method with conventional coagulation which showed that the aquatic humus was removed equally well with both methods. They also reported that the conventionally coagulated water (using alum) contained higher concentrations of sulphate and thus had a higher specific conductivity than the electrochemically treated

water where the electrochemically treated water contains higher residual aluminum concentrations than the conventionally treated water due to the higher pH values.

Chen (2006) has reviewed the design and applications of electrochemical technologies in water and wastewater treatment. The author made focus mainly on to electrodeposition, electrocoagulation (EC), electroflotation (EF) and electrooxidation. Through revision was made by citing large number of publications. The author stated that Electrodeposition is effective in recover heavy metals from wastewater streams, which can be considered as an established technology with possible further development in the improvement of space-time yield. The author also stated that EC has been in use for water production or wastewater treatment, while finding more applications using either aluminum, iron or the hybrid Al/Fe electrodes. The separation of the flocculated sludge from the treated water can be accomplished by using EF. The author also stated that the EF technology is effective in removing colloidal particles, oil&grease, as well as organic pollutants. It was proven to perform better than dissolved air flotation, sedimentation, impeller flotation (IF). He also stated that the newly developed stable and active electrodes for oxygen evolution would definitely boost the adoption of this technology. Electrooxidation is finding its application in wastewater treatment in combination with other technologies. It is effective in degrading the refractory pollutants on the surface of a few electrodes. Titanium-based boron-doped diamond film electrodes (Ti/BDD) show high activity and give reasonable stability. Its industrial application calls for the production of Ti/BDD anode in large size at reasonable cost and durability.

Mahesh et al. (2006 a) was investigated The electrochemical degradation of agri-based paper mill wastewater (black liquor) in a 2 dm^3 electrolytic batch reactor using iron

plate electrodes of 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 authors reported that at the optimal current density, the iron electrode consumed is 31.27 g m^{-2} h^{-1}, achieving maximum COD removal. The authors also reported that the addition of polyacrylamide (10 mg dm^{-3}) to the electrochemical reactor enhanced the COD removal rate with a very short treatment time with excellent sludge settleability with the specific energy consumption (SEC) reduced from 6.64 to 5.73 kWh kg^{-1} of COD removed with the addition of NaCl (625 mg dm^{-3}). The post treatment of electrochemically treated wastewater by chemical 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% was achieved by the authors by electrochemical treatment followed by coagulation/flocculation.

Mahesh et al. (2006 b) reported the characteristics and the management of the sludge generated by the batch electrochemical (EC) treatment of the black liquor (BL) of a small paper mill based on agricultural waste as raw material. This study showed that the sludges obtained from the EC treatment of the BL at its natural pH without any additive and with 625 mg dm^{-3} sodium chloride (NaCl) or 10 mg dm^{-3} polyacrylamide (PAA) during the EC process had very good settling characteristics. They reported that addition of PAA hastened the EC process, and the sludge settling rate improves considerably. The results of the gravity filtration of the treated BL showed that the addition of NaCl (625 mg dm^{-3}) improved the filtration characteristics and reduced the values of the specific

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cake resistance (R). They also studied and reported that prolonged use of iron anodes produces a large number of dents on their surface which was because of the anode dissolution during the EC process. They showed the dents formed by SEM images of the electrodes. The authors also made thermal analysis which gave good combustion characteristics and complete oxidation of the EC process sludge at about 400 °C, with a heating value of 11.33 MJ kg^{-1}. They also suggested that the sludge obtained during the treatment process could be dewatered, dried, and used in the furnace/incinerators for its heat recovery, and the ash could either be blended with organic manure for use in agriculture/horticulture or may be blended with clay/coal fly ash to make bricks/ceramic tiles for the building industry.

EXPERIMENTAL MATERIALS AND METHODS

3.1 GENERAL

This chapter deals with the materials and experimental methods description adopted during the treatment of distillery wastewaters using the electrochemical treatment (ECT) technology.

3.2 MATERIALS

3.2.1 Wastewater: The distillery wastewater, bio-digester effluent waste used in the present study was collected from a nearby distillery (The Bajaj Hindustan Ltd., Gaugnauli, Saharanpur (UP)).

3.2.2 Electrodes: The iron sheets were used as electrode material. These sheets were procured from the local suppliers.

3.2.2.1 Electrode Preparation

The iron electrode plates as procured from the local suppliers were cut in to the required shape, degreased manually and were treated with 15% H_2SO_4 for cleaning followed by washing with distilled water and oven drying at temperature slightly geater than the ambient temperature prior to their use in the EC experiments. The two-dimensional schematic view of the plate electrode is shown in Fig. 3.1. The three-dimensional schematic arrangement of the iron plate electrodes in parallel is shown in Fig. 3.2.

Each electrode plate having dimensions 90 mm x 100 mm x 1.5 mm (thick) was used in this study.
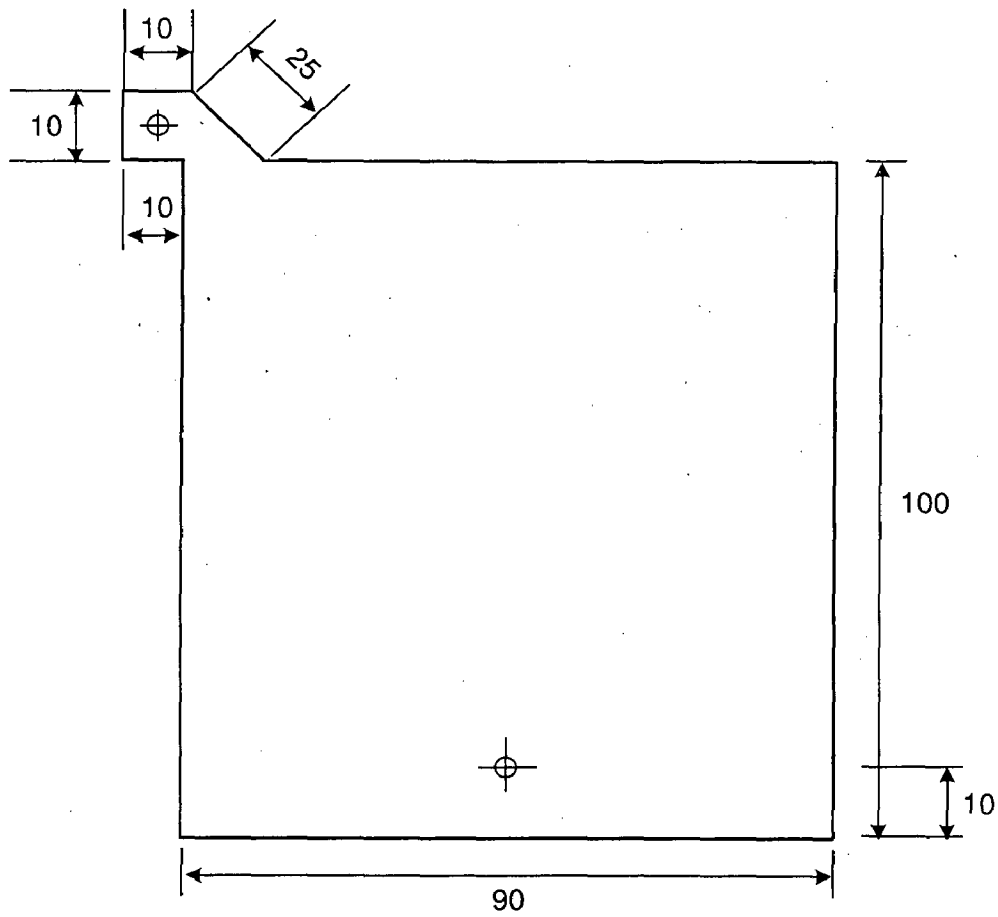

Fig. 3.1 Two-dimensional schematic view of the plate electrode
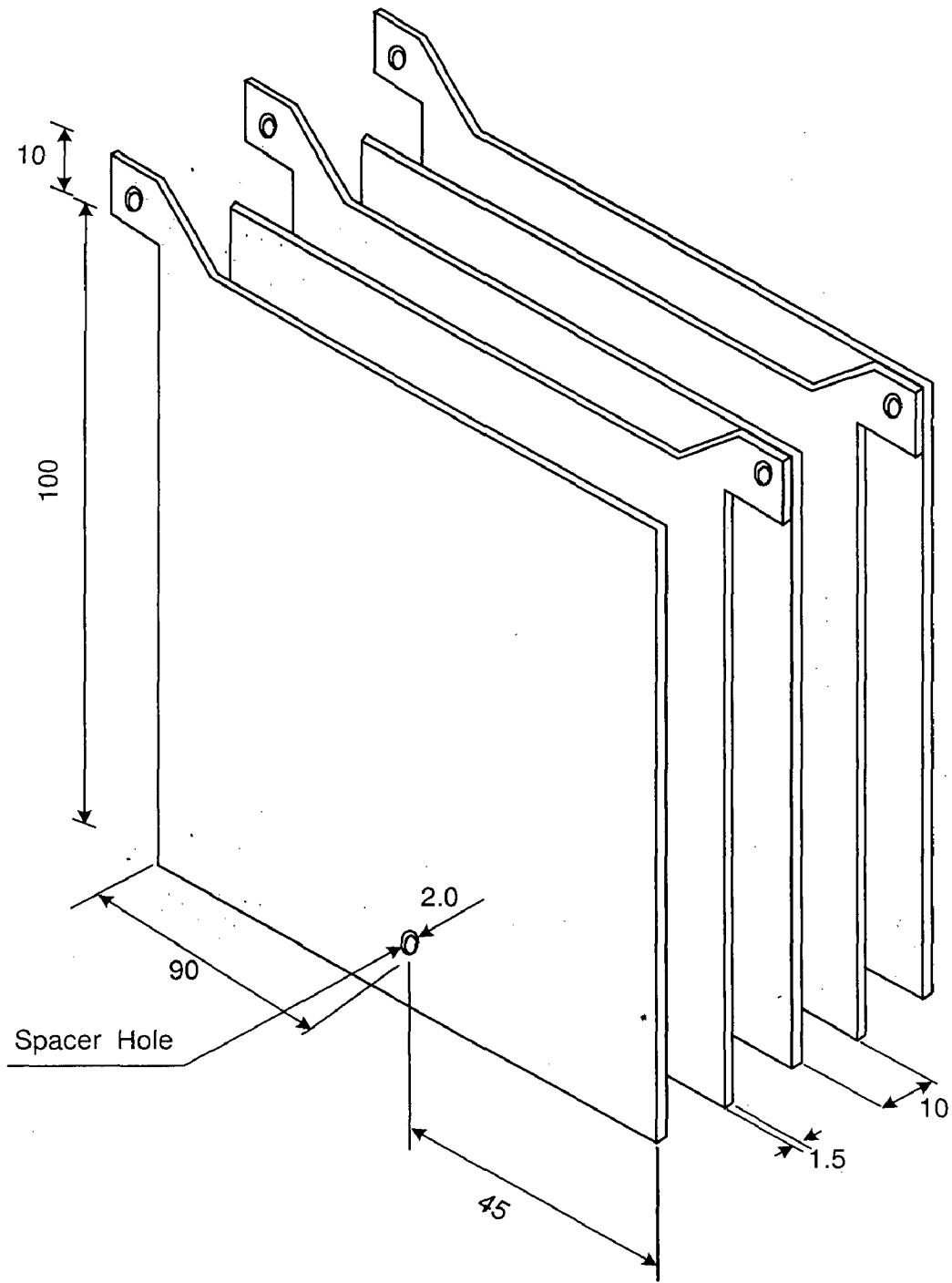
(All dimensions are in mm)

Fig. 3.2 Three-dimensional schematic arrangement of the plate electrodes

(All dimensions are in mm)

3.2.3 Electrochemical Reactor (ECR)

The ECR used in the experiments was made of plexiglass sheets, and was cubical in shape. Space was provided for magnetic stirring, and aeration arrangement was also made inside the reactor. The dimensional characteristics of the reactor and the configuration details are as shown in Table 3.1. A magnetic stirrer was used for continuous stirring at the bottom of the ECR.

Table 3.1 Characteristics of the EC-cell

Reactor characteristics	
Make	plexiglass
Reactor type	Batch, which may be converted in to a continuous reactor
Dimensions (mm)	116 x 117 x 166 (length x width x height)
Volume (dm^3)	2.0
Electrode gap (mm)	10
Type	Up flow
Mode	Batch / Continuous
Stirring mechanism	Magnetic bar
Electrodes	
Material (Anode and Cathode)	Iron
Shape	Rectangular plate
Size of each plate (mm)	90 x 100
Thickness (mm)	1.5
Plate arrangement	Parallel
Each plate electrode surface area (dm^2)	0.90
Submergence	Full

3.3 CHARACTERIZATION OF DWW USED FOR ECT

3.3.1 pH

The pH of the water used was determined using the standard digital pH meter (Naina Solaris, Delhi).

3.3.2 Color

The color of the water sample was measured using the standard Platinum Cobalt Method. The results are reported in platinum cobalt units (PCU).

3.3.3 COD

COD of the DWW was measured analytically by using the COD Meter. The procedure employed for the measurement was as follows:

Initially the $K_2Cr_2O_7$ sample was prepared (for 250 ml flask) by dissolving 2.554 g of $K_2Cr_2O_7$ and by adding considerable amount of distilled water. Then 8.325 g of HgSO4 was weighed and dissolved in 41.75 ml of conc. H2SO4. The remaining volume was made to the mark by adding distilled water. Then the silver sulphate sample was made by weighing 1.1 g of silver sulphate and dissolving it in 250 ml of conc. H_2SO_4. 1.5 ml of $K_2Cr_2O_7$ sampled prepared and 3.5 ml of the silver sulphate sample along with the 3 ml of the sample for which COD had to be measured was kept in digester for 2 hrs and 150 °C. Then they were cooled at room temperature and then were measured by using COD meter.

3.3.4 Analysis of the sludge and iron electrodes

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

3.3.4.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope (LEO 435VP, England) is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

SEM images of iron plates before and after electrochemical treatment were obtained using the microscope operating with SEM detector.

3.3.4.2 TG-DTA-TGA

Thermal analysis was conducted using the thermal analysis instrument (Perkin-Elmer Pyris Diamond). 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.

Thermogravimetric Analysis (TGA) measures changes in weight of a sample with increasing temperature.

3.3.4.3 X-ray diffraction (XRD)

X-ray scattering (XRD) techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an x-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. This analysis was conducted using the X-ray diffractometer (Bruxer AXS D8 advance) instrument.

3.4   Experimental Set-up and Program

The schematic diagram of the laboratory scale experimental set-up used in the electrochemical degradation studies is shown in Fig. 3.3.and Fig. 3.4 shows the laboratory scale set up without and with aeration.

The experimental proceedings started by acquisition of the cold rolled iron sheet, from Roorkee Steels, Roorkee; from which the electrodes were fabricated; sheet thickness was 1.5 mm. Rectangular electrodes of size 9 cm x 10 cm x 0.15 cm were fabricated in the department.. The plates, if connected in series, have higher resistance. In a parallel arrangement, the electric current is divided between all the electrodes in relation to the resistance of the individual cell. Therefore, the electrode plates were arranged in parallel. The electrode plates were cleaned manually by abrasion with

sandpaper, and they were treated with 15% H_2SO_4 for cleaning followed by washing with distilled water prior to their use. The electrodes were spaced 10 mm apart (because <10 mm spacing between electrodes prevented movement of liquid adsorbate in the interstitial spaces of the electrodes thus, hindering/affecting removal efficiency). The anode and the cathode leads were connected to the respective terminals of the direct current (DC) rectifier through a resistance box. Electric power was supplied by a stabilized power source through the DC rectifier fitted with an ammeter and voltmeter. In each run, 2 dm^3 of wastewater was fed into the electrochemical reactor. Experiments were conducted with six plate configurations at varying current intensities(2, 3, 4, 5, and 6 A) and voltage between 0 and 15 V. To maintain a fixed inter-electrode distance non conducting wire was used as the electrode separator. All the experiments were conducted at room temperature with a sample of known initial COD and color. The magnetic stirring was provided by a magnetic stirrer. Samples were drawn at regular intervals and at the end of the electrochemical process, filtered, and analyzed for pH, COD, and color. Most of the EC test runs lasted for 240 min.
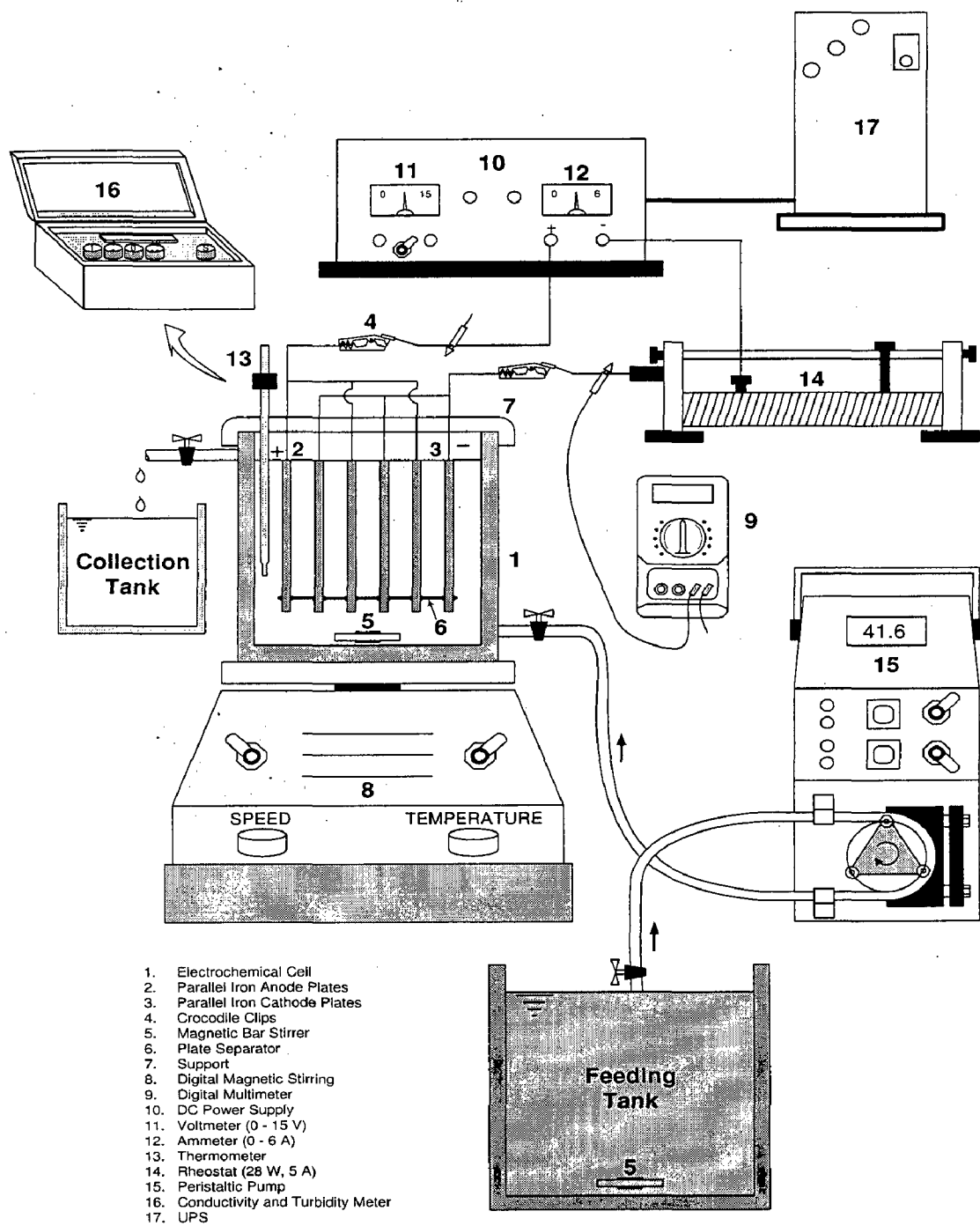
Fig. 3.3 Laboratory scale experimental setup for EC treatment.

1. Electrochemical Cell
2. Parallel Iron Anode Plates
3. Parallel Iron Cathode Plates
4. Crocodile Clips
5. Magnetic Bar Stirrer
6. Plate Separator
7. Support
8. Digital Magnetic Stirring
9. Digital Multimeter
10. DC Power Supply
11. Voltmeter (0 - 15 V)
12. Ammeter (0 - 6 A)
13. Thermometer
14. Rheostat (28 W, 5 A)
15. Peristaltic Pump
16. Conductivity and Turbidity Meter
17. UPS

Fig. 3.4 Image showing the reactor set up at laboratory without and with aeration

RESULTS AND DISCUSSION

4.1 GENERAL

This chapter gives the results of the experiments conducted in the present study and the discussions there on. The results and discussions include electrochemical (EC) treatment of distillery wastewater in a batch reactor with aeration and without aeration, mechanism of electrochemical treatment and discussion on the sludge characteristics.

4.2 ELECTROCHEMICAL TREATMENT OF DISTILLERY WASTE WATER IN A BATCH REACTOR WITHOUT AREATION

Based upon the earlier EC studies on the treatment of pulp and paper wastewater, (Mahesh 2007), number of electrodes employed in the present study were six and the inter-electrode distance was kept constant at 10 mm.

The experiments were initially done without any dilution of distillery wastewater (DWW). Current density was kept in the range of 50-90 A m^{-2} and the treatment time was kept constant at 4 h (Krishna Prasad et al., 2007). Initial experiments with original DWW showed insignificant COD and color removal, therefore, original DWW was diluted 10 times and all further experiments were done with the diluted DWW.

The color and COD of the diluted DWW was 20,000 PCU and 3660 mg l^{-1}, respectively. These values calculated were taken as the initial values for all the further experiments.

Fig. 4.1 shows the variation of the COD removal as a function of current density. For 50 A m^{-2} current density, the COD removal was ~50%. Further increase in current density up to 70 A m^{-2} showed exponential increase in COD removal. COD removal showed steady behavior in the range of 70-90 A m^{-2}. For current density of 90 A m^{-2}, 80% COD removal was observed.

The pH of the solution varied from 9.46 during the starting stage to as high as 12.53 during the finishing time of 240 min being employed as the treatment time of operation.

Fig. 4.2 shows the variation of the color removal as a function of current density. 80% color removal of the diluted DWW was observed at 50 A m^{-2} current density. The variations in the current density in steps of 10 yielded the variations in the Color removal percentage with a slight dip in value during the change of current density from 60-70 Am^{-2}. Then there on, a steady behavior was observed in the removal percentage. The removal percentage increased to ~90% at 90 Am^{-2}. The treatment of DWW at various current densities showed the color and COD removal of more than 80% at 90 Am^{-2} current density. This shows that the dilution percentage and the treatment time used in the treatment process were appropriate.

4.3 ELECTROCHEMICAL TREATMENT OF DISTILLERY WASTE WATER IN A BATCH REACTOR WITH AERATION

In order to compare and know the effect of aeration for the treatment of the DWW by electrochemical treatment, the aeration of the DWW was employed in the EC reactor.

The aeration was done using a normal aqua pump with such intensity so that the whole reactor is aerated with no dead volumes or dead space being present in the EC reactor.

Fig. 4.3 describes the variation of the COD as a function of current density. The COD removal of the diluted DWW was 50% at 50 A m^{-2} current density. A steady behavior was observed in the removal percentage. The removal percentage increased to ~ 75% at 90 Am^{-2}. The pH of the solution increased from an initial value of 9.56 to as high as 12.21 during 4 h treatment time of operation.

The variations of the color as a function of current density are shown in the Fig 4.4. 60% color removal of the diluted DWW was observed at 50 A m^{-2}. A steady behavior was observed in the removal percentage with further increase in current density and the removal percentage increased to 80% at 90 Am^{-2}.

4.4 COMPARISON OF THE TREATMENT PROCESS WITH AND WITHOUT AERATION

A lot of variation in terms of the removal percentage was observed during the course of treatment with and without aeration. During aeration, an important observation made was that the removal percentages were less as compared to the normal process of EC without aeration. During aeration as described earlier, the removal percentage was very less during the early stages and then there was a steady increase in the percentage removal with the variations in the current densities from 50 to 90 A m^{-2}. COD removal was at least 5% higher as compared to EC with aeration at all current densities.

Similarly all the color removal percentages observed without aeration were 80%, where as it was around 75% with aeration Also there was a slight steady behavior in the

color removal percentage irrespective of the variations in the current density values with the EC experiments were done with aeration.

4.5 EFFECT OF APPLIED VOLTAGE ON THE REMOVAL EFFICIENCY:

During the course of the experiments it was observed that the applied voltage has an impact on the removal efficiency. For better removal efficiency a voltage greater than 12 was taken for all the experiments. This was confirmed during the course of the experiment. An experimental run where the current density was 90 A m^{-2} and the applied voltage was 10 V, the color removal efficiency reduced to 0.60 and the COD had fallen to ~ 0.45. Where as in a experimental run where the applied voltage was 13.5 V and the current density was 70 A m^{-2} the removal percentage obtained was ~72% for COD and 84% for Color. Hence, from this experimental analysis it can be stated that the applied voltage also has an effect on the removal efficiency and the applied voltage must be greater 12 V for better results.

4.6 TIME VERSES REMOVAL EFFICIENCY:

Fig. 4.6 (A,B,C,D) showing the hourly variations of the sample collected during the treatment process. From the figure, it is evident that the maximum removal is obtained after the 2 h of treatment. The removal efficiency increases with an increase in the treatment time, however, the maximum color and COD removal was observed during the 3rd h of operation. The removal efficiency progresses at a steady rate during the last hour of operation.
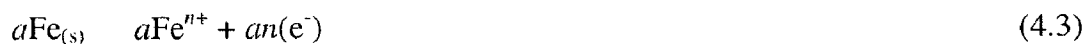
4.7 MECHANISM OF ELECTROCHEMICAL TREATMENT

The electrochemical processes offer significant potential for removing soluble organic and inorganic species from solution. EC operating conditions are highly dependent on the chemistry of the aqueous medium, especially conductivity and pH. Other important characteristics such as type of electrodes, and retention time between plates, plate spacing and chemical constituent concentrations rule over the operating parameters of the process. The sacrificial or the consumable anode continuously produces metal ions that are essentially required for the process. These cations neutralize the negative charge of the particles carried toward the anodes and facilitate coagulation. In the following study the sacrificial anodes are of iron.

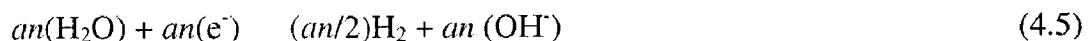The anode - cathode reactions involved are as follows:

With iron as the electrode material:-

$$Fe_{(s)} \quad Fe^{2+} + 2e^- \qquad (4.1)$$

$$Fe^{2+} \quad Fe^{3+} + e^- \qquad (4.2)$$

Anode:

$$a Fe_{(s)} \quad a Fe^{n+} + an(e^-) \qquad (4.3)$$

$$2H_2O \quad O_2 + 4H^+ + 4e^- \qquad (4.4)$$

Cathode:

$$an(H_2O) + an(e^-) \quad (an/2)H_2 + an\ (OH^-) \qquad (4.5)$$

$$4H^+ + 4e^- \quad 2H_2 \qquad (4.6)$$

where, constant a is a stoichiometric coefficient and n is number of electrons (Parga et al., 2005)

4.8 SCANNING ELECTRON MICROSCOPY (SEM)

SEM images of the iron electrodes before and after EC treatment were obtained to compare their surface texture. Sludge SEM images were also obtained. The surface of the anode prior to its use, in the EC experiments was uniform bearing nano-sized crystals. Fig. 4.8 shows the SEM image of the same anode plate after several cycles of its use in ECT experiments for a total duration of ~4 h. The anode plate surface was found to be rough, with a large number of small sized three dimensional dents of ~100-200 μm in width and depth. These dents are formed around the nucleus of the active sites where the anode dissolution occurs producing iron hydroxides. The edges of the electrodes (anode) and the plate surfaces wear off giving iron hydroxide for scum formation with the increase in the number of cycles of experiments. The formation of large number of dents may be attributed to the consumption of the anode material at active sites due to the generation of dioxide at its surface. These dents end up as deep holes which tend to entrap byproducts such as micro-scum and sludge particles. Similar observations were drawn by (Mahesh et al., 2006b). Thus the SEM images give the information for the expected life of electrodes.

Fig. 4.9 shows the images of ECT generated sludge at 100X magnification. Obtained image shows the non uniform structure of the sludge.

4.9 ENERGY DISPERSIVE X-RAY ANALYSIS

EDAX analysis of the sludge and scum obtained during the course of treatment and the electrode before and after EC was performed to estimate the composition of various elements present in the sludge, scum and electrodes respectively. The analysis

shows the amount of variation of the Fe present in the anode, cathode, sludge and the scum. It can be seen that the Fe has high amount in the electrodes, sludge and scum. As the electrodes are made up of iron the amount of iron present in the analysis of the respective parts are also high. The EDAX of the scum, sludge and the electrodes are given in Fig. 4.10 and 4.11.

4.10 CALORIFIC VALUE

The calorific value of the sludge and the scum were analyzed by using the bomb calorimeter. The calorific value of the scum was obtained as 6.429 MJ kg^{-1} and that of the sludge was 4.619 MJ kg^{-1}. The sludge and scum have a good heating value and could be used as a fuel.

4.11 THERMAL ANALYSIS (DTA-DTG-TG)

The thermal degradation (gasification) characteristics of EC generated sludge was studied using the thermo-gravimetric (TGA) and differential Thermal (DTA) analysis techniques. The thermal degradation of the residue was carried out non-isothermally. The principal experimental variables which could affect the thermal degradation characteristics in air flow in a TGA are the pressure, the air (purge gas) flow rate, the heating rate, the weight of sample and the sample size fraction. In the present study, the operating pressure was kept slightly positive, the purge gas (air) flow rate was maintained at 200 ml min^{-1} and the heating rate was maintained at 10 K min^{-1}.

The thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and differential thermal gravimetric (DTG) curves of the EC generated sludge is shown in Fig.4.12. The TG traces for the EC generated sludge shows that the rate of weight loss. In

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this temperature range the sludge oxidizes and loses its weight gradually. The sludge gets oxidized at very early stage i.e. in the temperature range of 25 to 450°C.

The strong exothermic peak centered between 25-450°C is due to the oxidative degradation of the sample. This broad peak as that observed from the first derivative loss curve (dTG), may be due to the combustion of carbon species. At higher temperatures (450-992°C) the sample presents a very less weight loss up to 992°C. The weight becomes almost constant after 500°C. The maximum rate of weight loss was obtained as 162.1 μg min^{-1} at peak temperature of 81°C. At about 500°C, the organics of the residue got oxidized, leaving the ash fraction in sludge. It may be noted that the ash content is very high in the sludge. The nature of the TG curve gives a clear indication that the two step degradation takes place for the EC generated sludge. The oxidation of the adsorbents shows exothermicity. This table also shows the temperature span of the exothermicity. The exothermicity occur in the temperature span of 150-450 °C with the energy of -2638 mJ mg^{-1}.
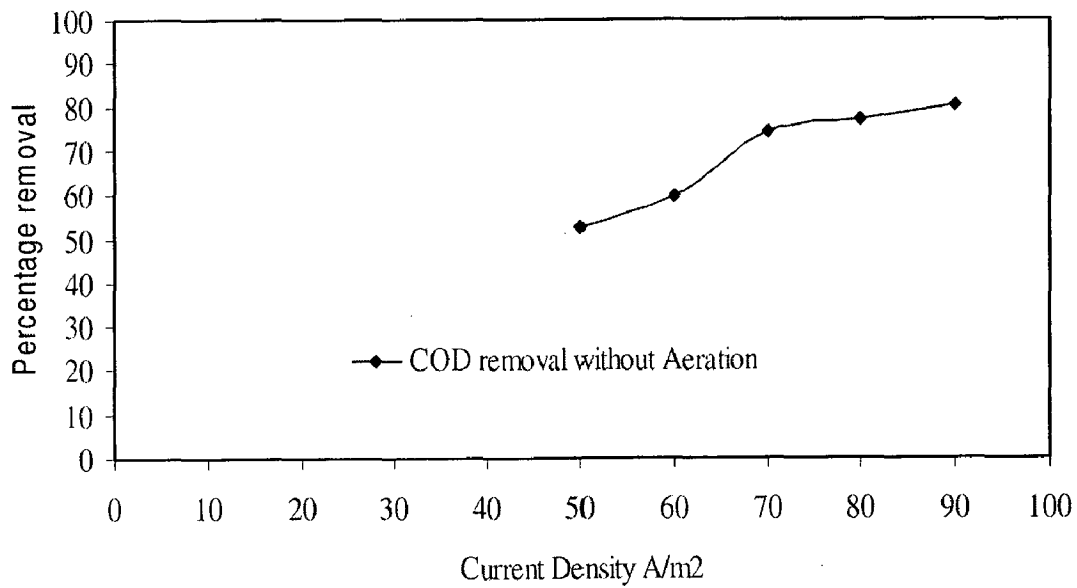
Fig. 4.1 COD removal without aerationfrom DWW in batch ECR:

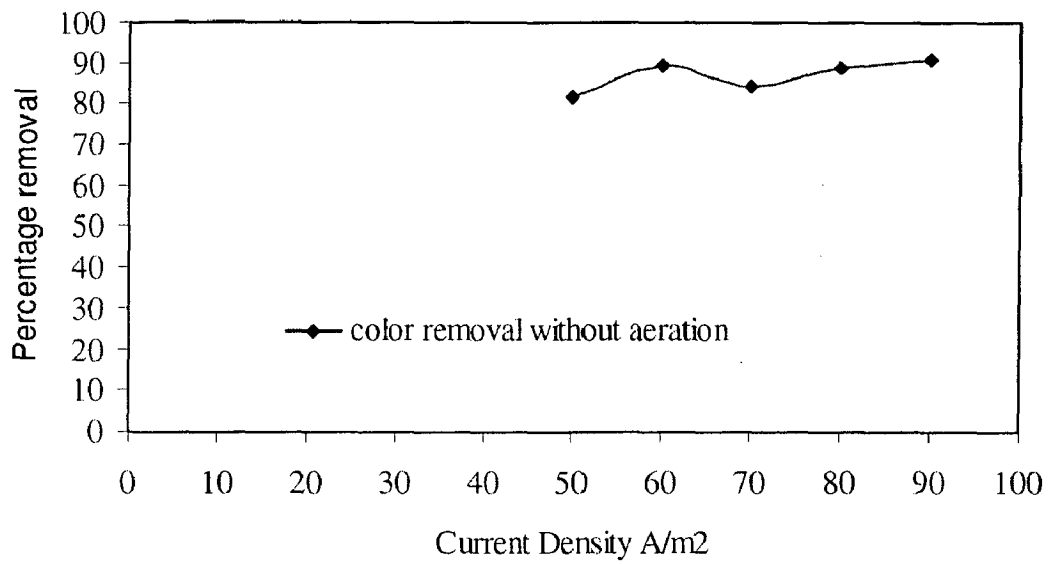$N = 6$, $pH_0 = 9.46\text{-}9.68$, $pH_f = 11.78 - 12.53$, $ET = 240$ min

Fig. 4.2 Color removal without aeration from DWW in batch ECR:
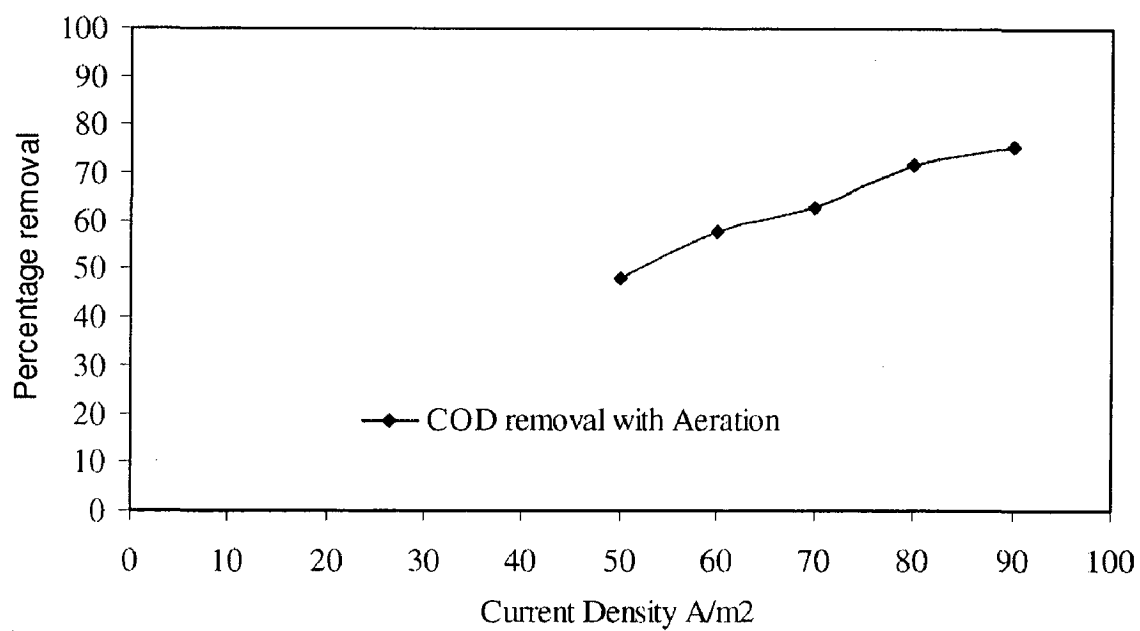
$N = 6$, $pH_0 = 9.46$-9.68, $pH_f = 11.78$ - 12.53, $ET = 240$ min

Fig. 4.3 COD removal with Aeration from DWW in batch ECR:

$N = 6$, $pH_0 = 9.56\text{-}9.76$, $pH_f = 11.28 \text{ - } 12.21$, $ET = 240$ min
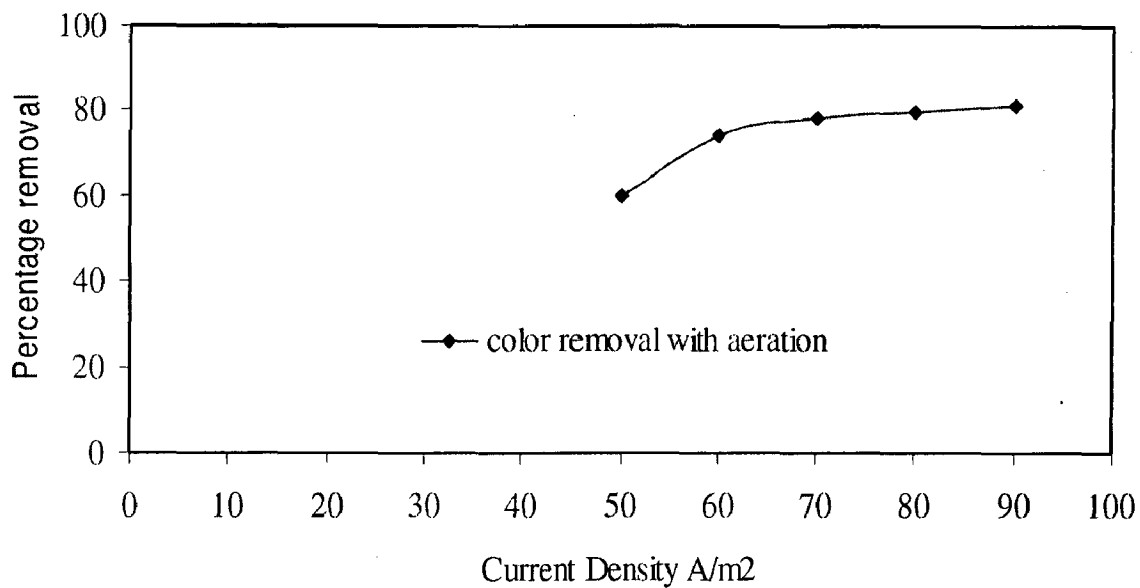
Fig. 4.4 Color removal with Aeration from DWW in batch ECR:

N = 6, pH$_0$ = 9.56-9.76, pH$_f$ = 11.28 - 12.21, ET = 240 min
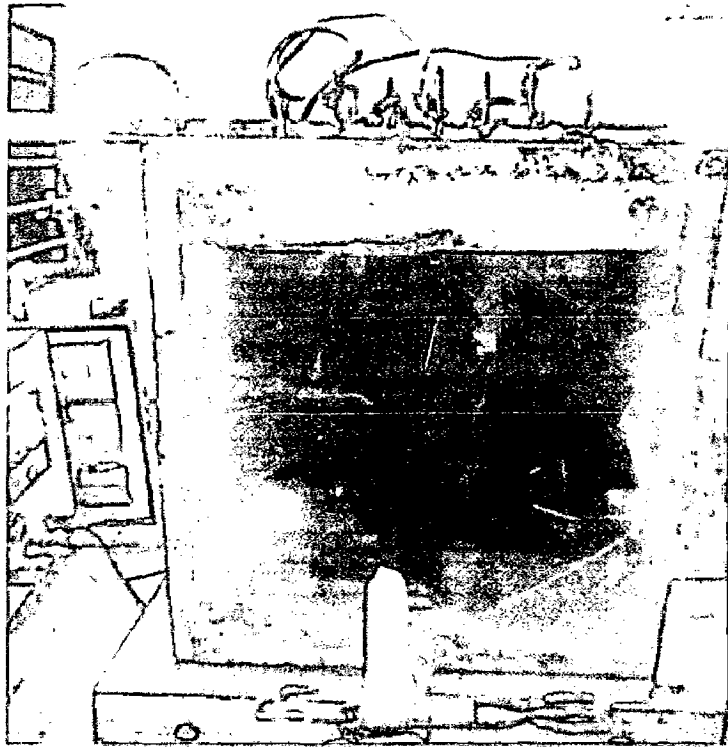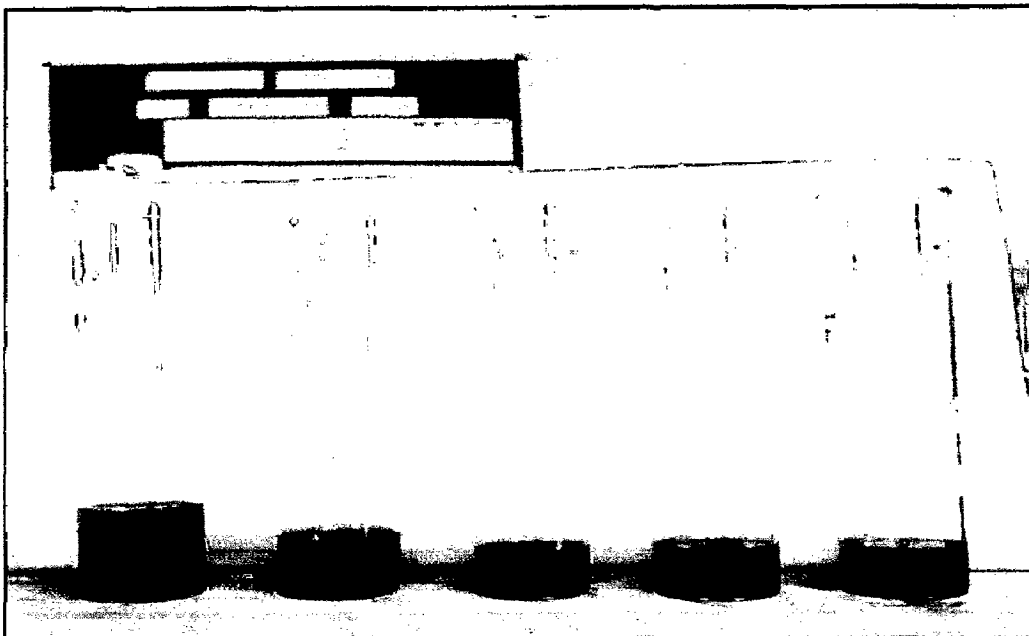
Scum formation during EC treatment

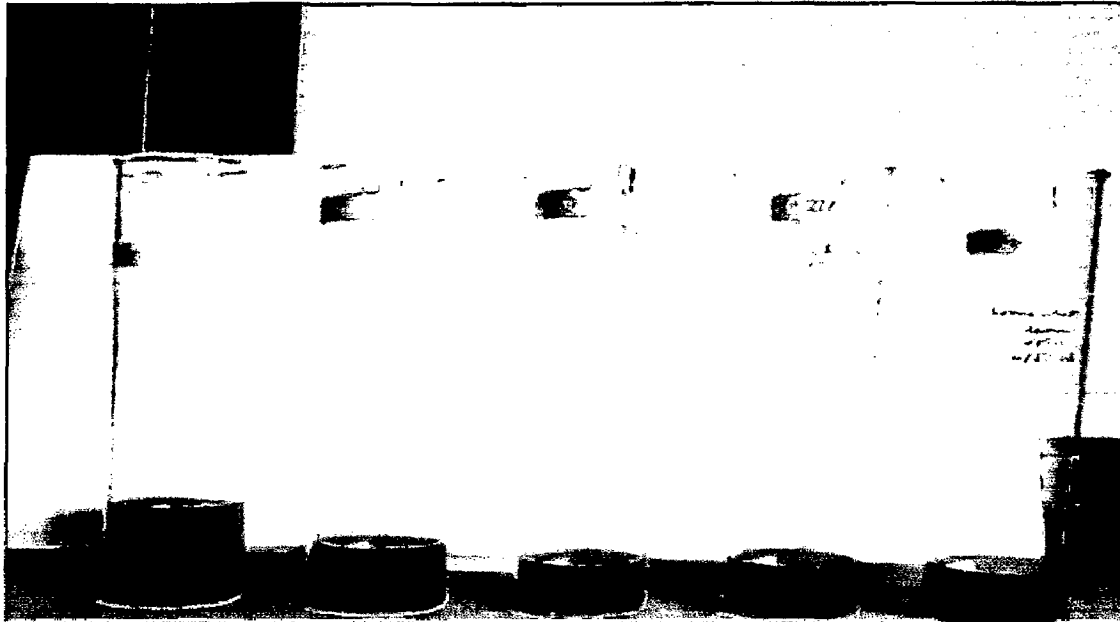Scum formation atop the EC reactor

Fig. 4.5 Images showing scum formation
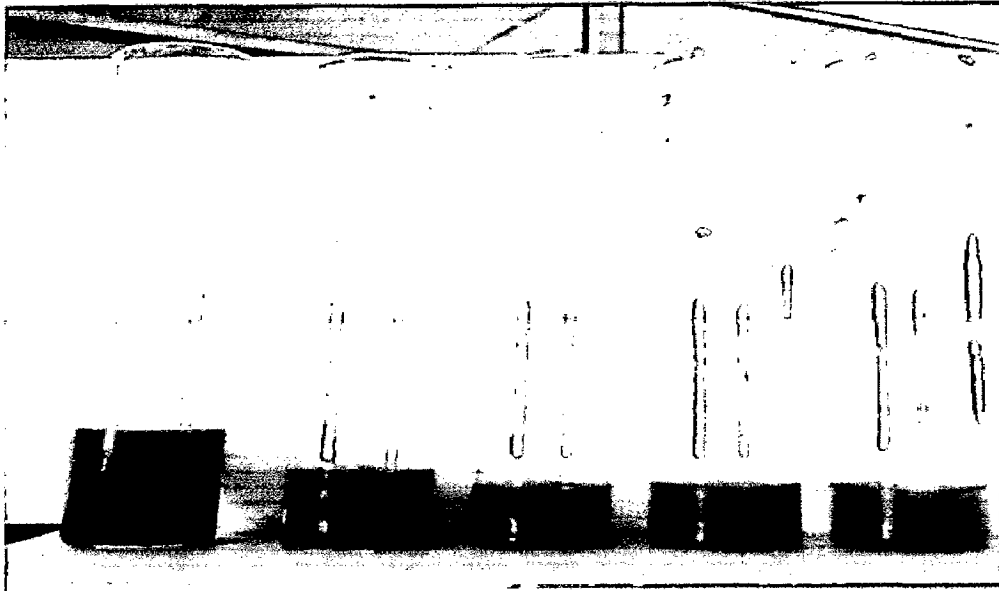
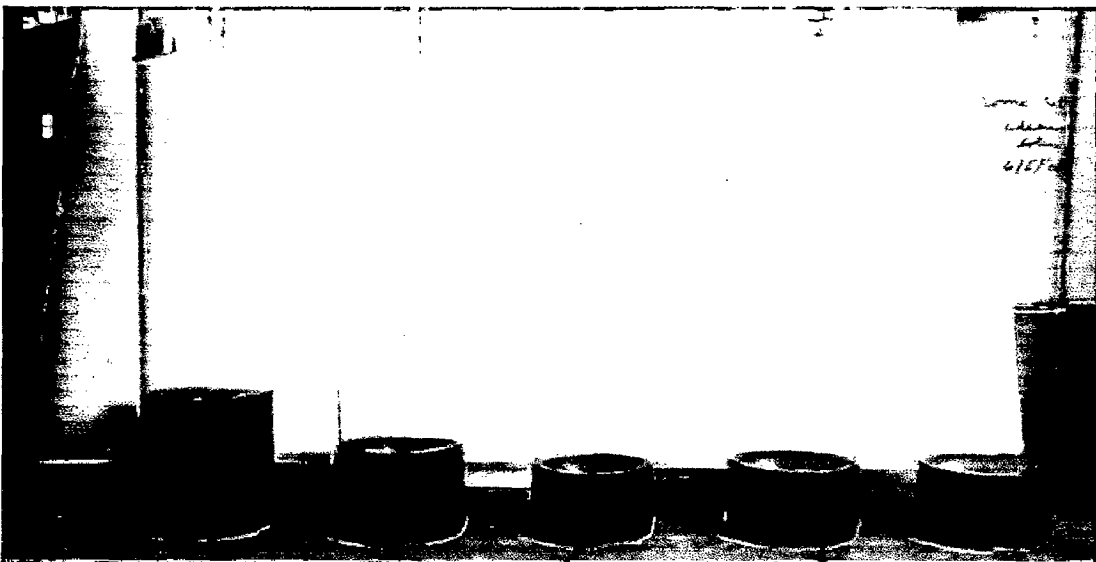A.Current density = 60 Am $^{-2}$ (a) Initial DWW (b) t=1 h (c) t=2 h (d) t=3h (e) t=4 h

B. Current density = 70 Am $^{-2}$ (a) Initial DWW (b) t=1 h (c) t=2 h (d) t=3h (e) t=4 h

Fig. 4.6 (A-B) Images showing color removal at various current densities.

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a   b   c   d   e

C. Current density = 60 Am $^{-2}$ (a) Initial DWW (b) t=1 h (c) t=2 h (d) t=3h (e) t=4 h

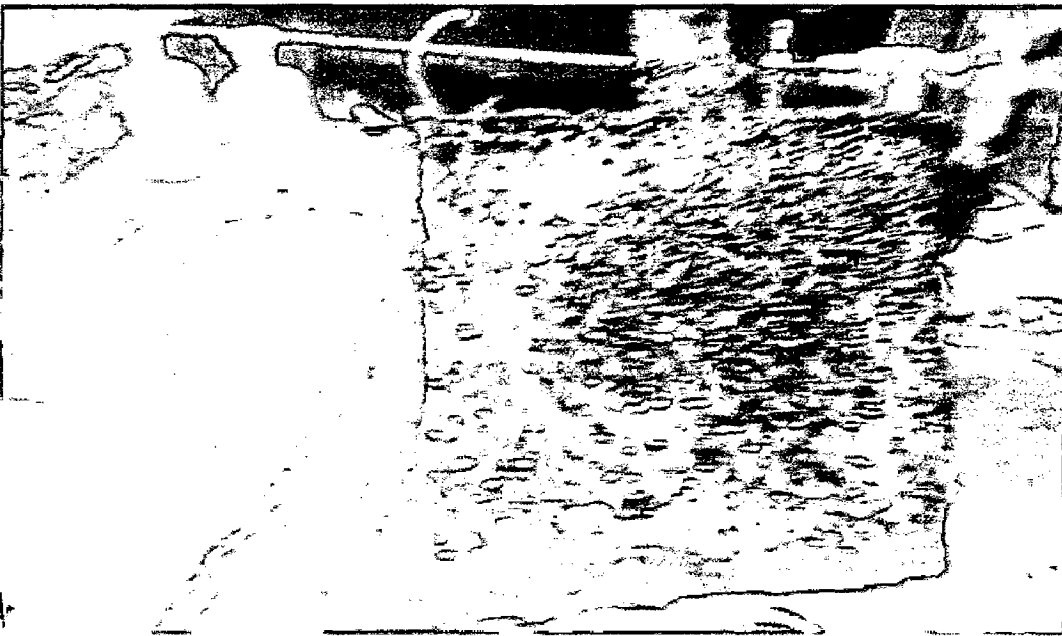a   b   c   d   e

D. Current density = 60 Am $^{-2}$ (a) Initial DWW (b) t=1 h (c) t=2 h (d) t=3h (e) t=4 h

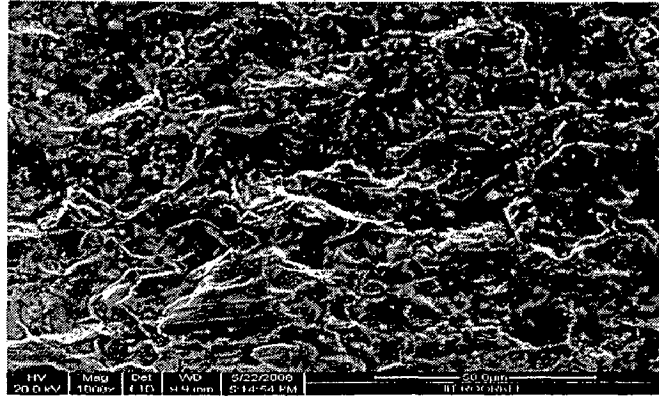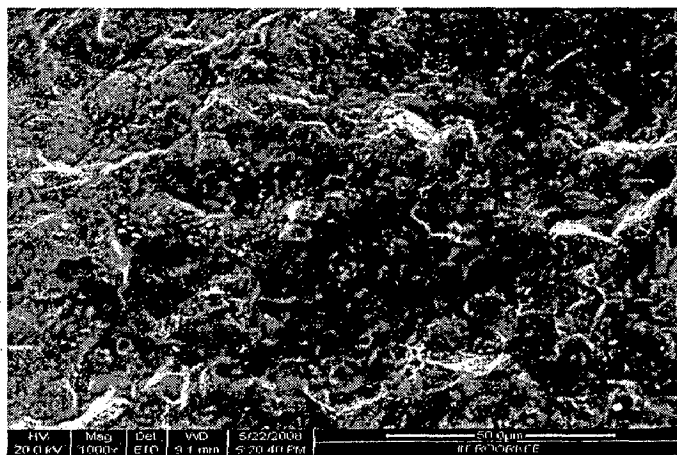Fig. 4.6 (C-D) Images showing color removal at various current densities.

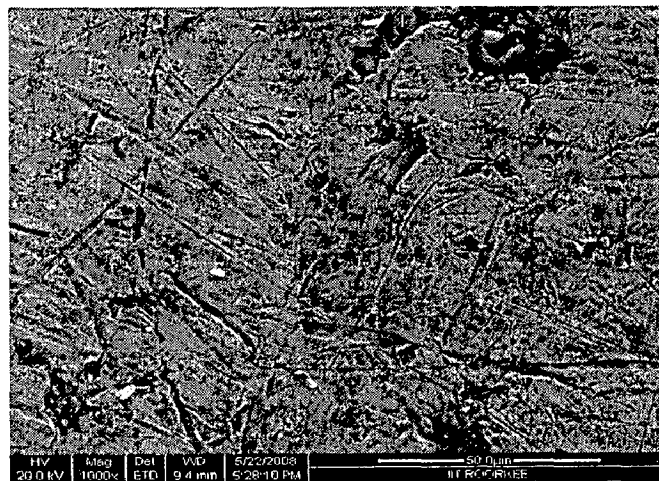a. Anode after ECT

b. Cathode after ECT

Fig. 4.7 Image of anode and cathode after the ECT
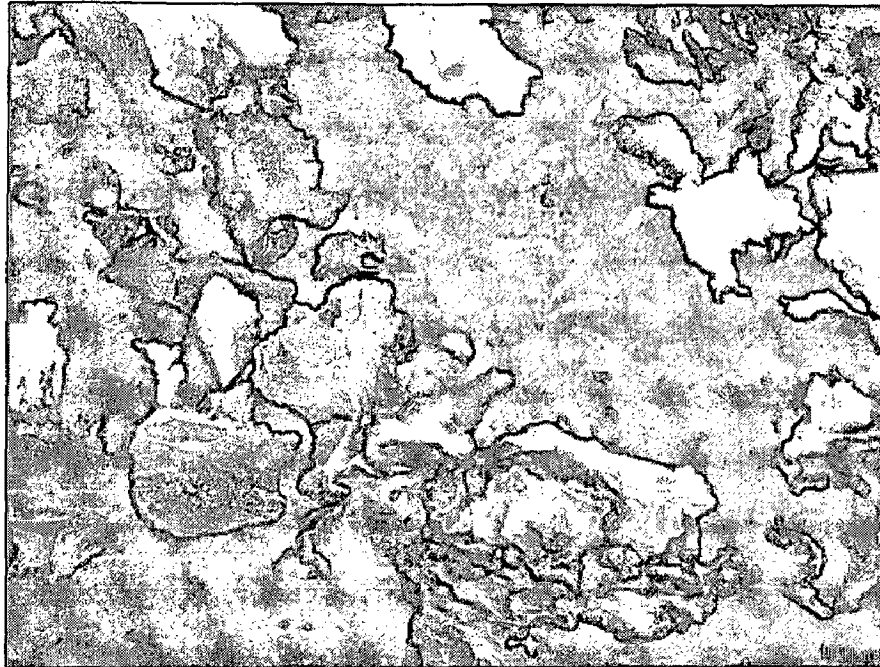
(a).Anode after ECT

(b). Cathode after ECT

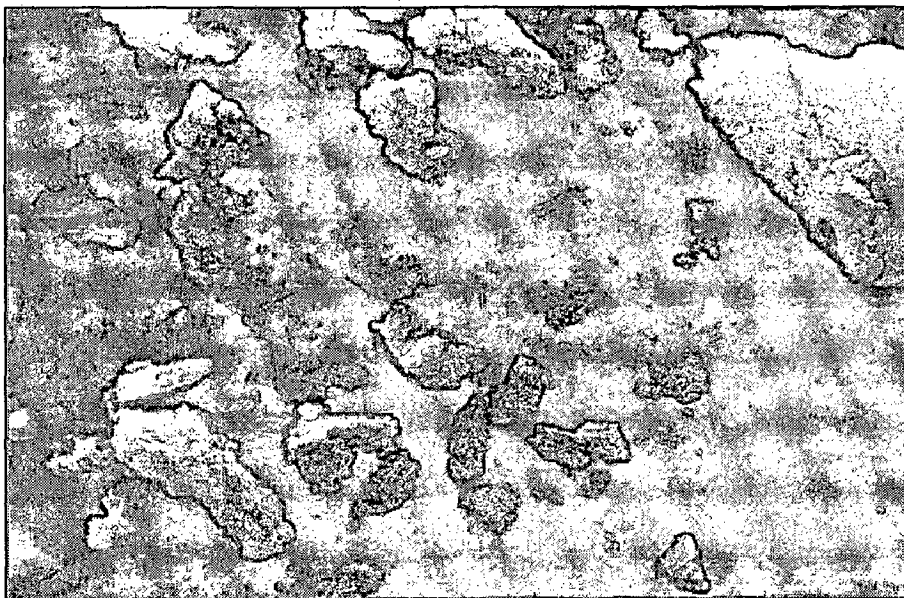

(c). Normal Electrode before ECT

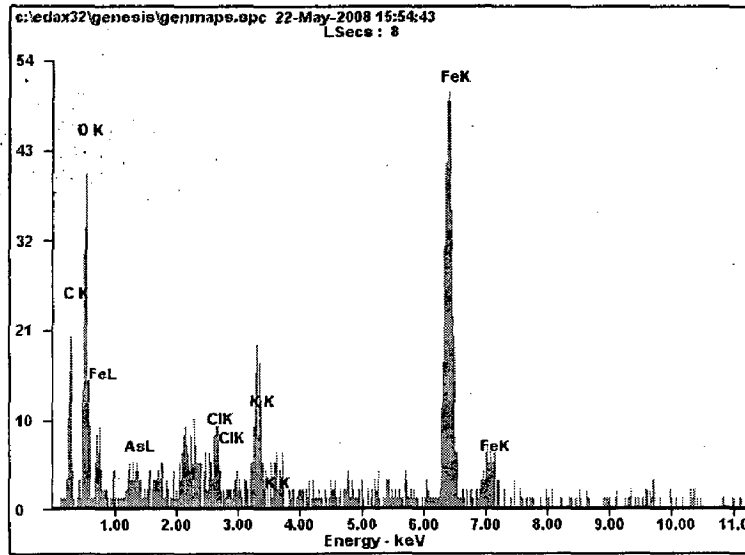**Fig.4.8 SEM images of various electrodes at 1000X magnification**

(a) Scum

(b) Sludge

Fig. 4.9 SEM images of Sludge and Scum obtained after treatment at 200X

magnification

a) Scum
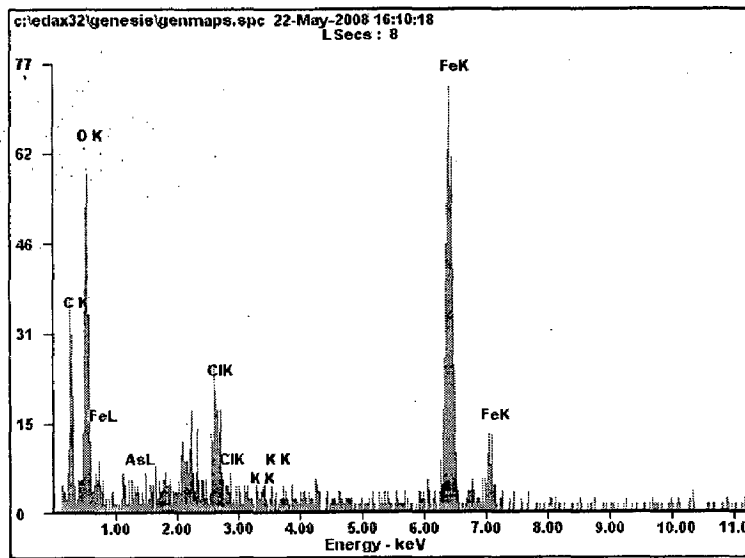
b) sludge

Fig. 4.10 EDAX of scum and sludge formed during the course of treatment
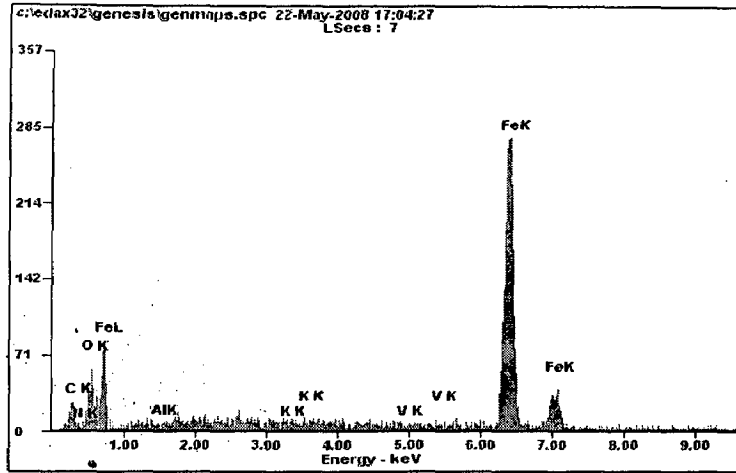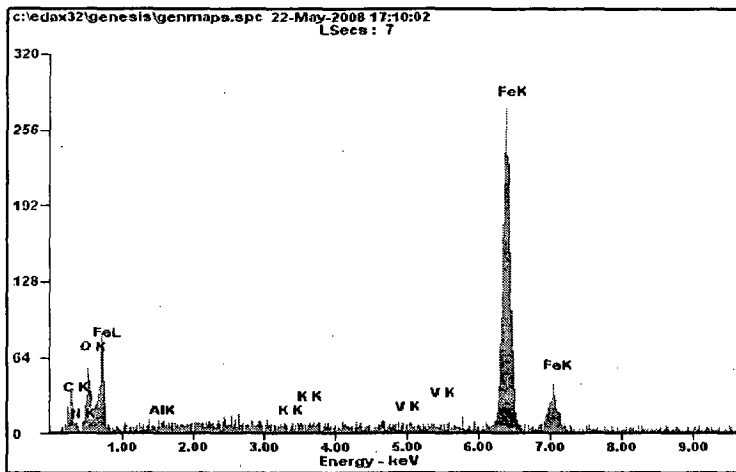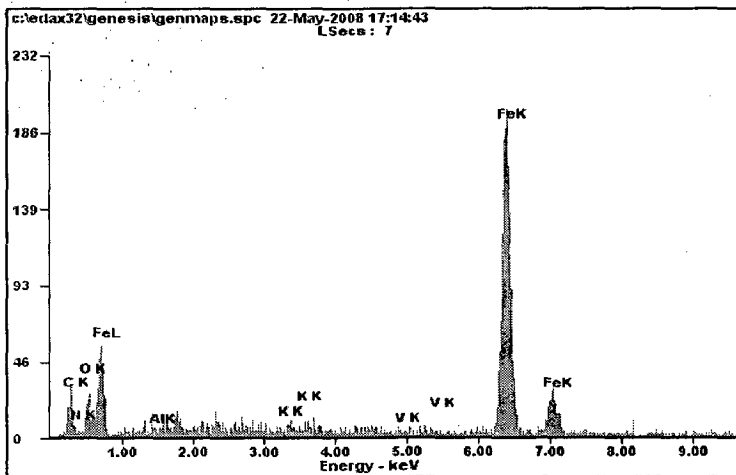
Fig. 4.11 EDAX of Electrodes A. Anode, B. Cathode and C. normal electrode

TG %

DTG ug/min

DTA uV

81Cel
162.1ug/min

213Cel
157.6ug/min

266Cel
142.9ug/min

379Cel
87.3ug/min

600Cel
136.2ug/min

261Cel
24.2 uV

377Cel
7.4 uV

636Cel
-20 uV

-11.9 mJ/mg

193 mJ/mg

80Cel
-5 uV

-2638 mJ/mg

25Cel
100.00 %

101Cel
91.39 %

199Cel
82.43 %

300Cel
69.95 %

399Cel
61.22 %

500Cel
58.53 %

600Cel
57.11 %

701Cel
55.17 %

800Cel
54.53 %

900Cel
53.96 %

1003Cel
53.61 %

Temp Cel

Fig. 4.12 Thermal Analysis (DTA-DTG-TG) of Sludge using Air atmosphere

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CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

The following conclusions can be drawn from the present work:

1. COD and color removal of the bio-digester distillery effluent was found to be significantly affected by the variation in current density during the EC process.

2. Optimum value of current density and electrolysis time were found to be 90 A m^{-2} and 4 h, respectively.

3. For a solution having initial COD of 3660 mg l^{-1} and color of 20,000 PCU, COD and color removal efficiency were found to be 80 and 90% respectively.

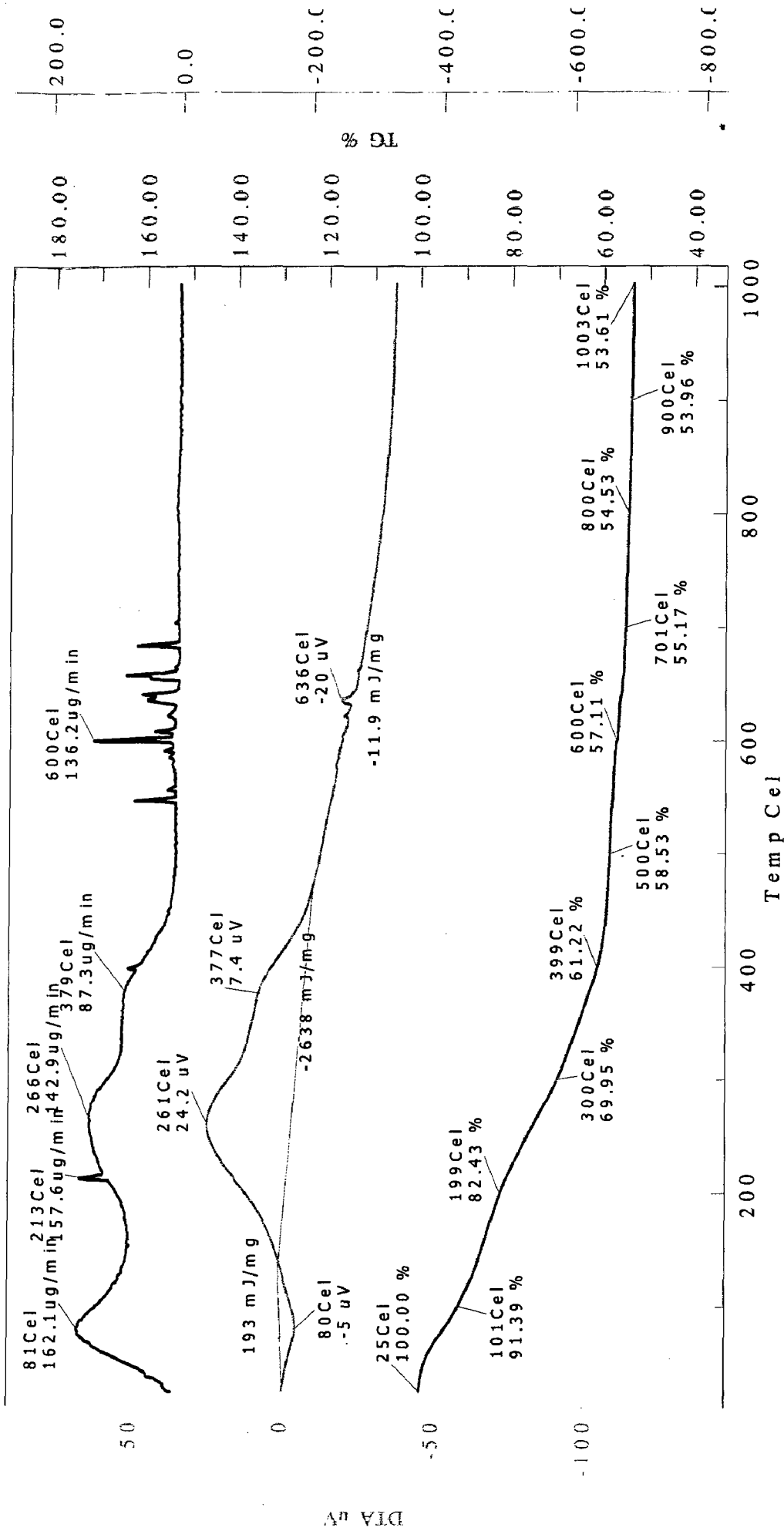4. Activation during the EC process was found to have negative effect on COD and color removal efficiency.

5. EDX showed the presence of Iron in sludge and scum.

6. Thermo gravimetric study and calorific value of the sludge showed that the sludge could be utilized as a fuel.

7. Overall, EC can be applied for the treatment of bio-digester distillery effluent.

5.2 RECOMMENDATION

1. In future, the ECT process can be used for the treatment of various other highly contaminated wastewaters like textile, pulp and paper, tanning, etc.

2. A combination ECT process and any other process like adsorption, fenton oxidation can be employed for getting achieving higher removal efficiencies.

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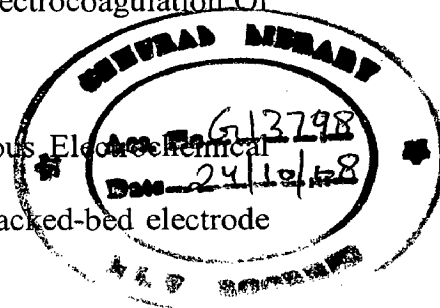
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APPENDIX

Table 4.1 Batch ECT experiments on Diluted DWW without aeration

No. of Electrodes	Voltage (V)	Current Density (A m⁻²)	Initial pH	Final pH	Initial COD (mg l⁻¹)	Final COD (mg l⁻¹)	Percentage removal (%)	Initial Color (PCU)	Final Color (PCU)	Percentage removal (%)
	12.0	50	9.46	11.78	3660	1740	52.5641	20,000	3700	81.5
	13.5	60	9.53	11.91	3660	1480	59.6153	20,000	2100	89.5
6	14.5	70	9.62	12.06	3660	950	74.0384	20,000	3100	84.5
	15	80	9.58	12.28	3660	850	76.9230	20,000	2200	89
	13.5	90	9.68	12.53	3660	730	80.1282	20,000	1800	91

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Table 4.2 Batch ECT experiments on Diluted DWW with aeration

No. of Electrodes	Voltage (V)	Current Density (A m⁻²)	Initial pH	Final pH	Initial COD (mg l⁻¹)	Final COD (mg l⁻¹)	Percentage removal (%)	Initial Color (PCU)	Final Color (PCU)	Percentage removal (%)
	12.0	50	9.56	11.21	3660	1900	48.0769	20,000	8000	60
	13.5	60	9.558	11.56	3660	1550	57.6923	20,000	5200	74
6	14.5	70	9.68	11.76	3660	1360	62.8205	20,000	4400	78
	15	80	9.62	11.91	3660	1030	71.7948	20,000	4100	79.5
	13.5	90	9.76	12.21	3660	890	75.6410	20,000	3800	81