Electro-chemical Treatment of Wastewater

A
DISSERTATION

Submitted in partial fulfillment of the requirements
for the Award of the Degree of

Masters of Technology
(Environment Science & Technology)

Under the Guidance of
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Candidate's Declaration

I, hereby declare that the work presented in the dissertation entitled **"Electrochemical treatment of wastewater"** in partial fulfillment of the requirement for the award of the degree of Masters of Technology, Department of Biotechnology and Environmental Sciences, Thapar University, Patiala, is an authentic record of my own work during the period of ten months from August 2007 to May 2008, under the supervision of Dr. A.S. Reddy, Department of Biotechnology & Environmental Sciences, Thapar University. The report has not been submitted for the award of any other degree or certificate in this or any other university.

Place: Patiala

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

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Certificate

This is to certify that the thesis entitled "**Electro-chemical treatment of wastewater**" submitted by Ankit Mohta in partial fulfillment of the requirements for the award of Degree of Masters of Technology in Environment Science and Technology to Thapar University, Patiala, is a record of student's own work carried out by his under my supervision and guidance. The report has not been submitted for the award of any other degree or certificate in this or any other University or Institute.

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ACKNOWLEDGEMENT

The key elements concentration, dedication, hard work and application are not the only essential factors for achieving the desired goals but also guidance, assistance and co-operation of people is necessary.

I would like to express my deep and sincere gratitude to my supervisor **Dr. A.S. Reddy** Associate Professor. His wide knowledge and logical way of thinking have been of great value for me. His understanding and personal guidance have provided a good basis for the present thesis. Especially the strict and extensive comments and many discussions and the interactions with Dr. Reddy had a direct impact on the final form and quality of this thesis.

I owe my sincere thanks to **Dr. N. Das**, Head of Department of Biotechnology and Environmental Science for support and to Science & Technology Entrepreneur's Park for providing facilities.

I wish to express my sincere thanks to **Dr. Anita Rajor** Department of Biotechnology and Environmental Sciences who has been constant source of inspiration throughout this thesis work.

I wish to express my sincere thanks for the possible help extended especially by **Mr. M. S. Bhatti, Mr. Sidharth Sharma, Mr. Amit Polestya** and **Mr. Anuj Tripathi.** Without their guidance and suggestion, this work would indeed have been very difficult for me to tackle.

I also thank to all the faculty and staff members of DBTES and Science & Technology Entrepreneur's Park, Thapar University, Patiala, for their co-operation and support throughout the course work.

I would like to make special acknowledge to some of my colleagues, who have been always there for me, listening to me, rejoicing, complaining and pondering my way throughout my M.Tech. Study

ABSTRACT

This study aims to investigate the treatment of wastewater from rubber reclaiming industry and first extraction stage effluent from a pulp and paper mill using electro-coagulation and electro-flocculation. Removal of color, turbidity, chemical oxygen demand (COD), oil and grease and total solids from the effluents was investigated at different pHs and different electrolyte doses by using two types of electrodes Aluminum (Al) and Stainless Steel respectively at various electrolysis times (5.0 to 35 minutes at 5 minutes interval). In case of rubber sample, among Stainless steel and Aluminum electrodes, maximum removal efficiency was found with Stainless steel electrodes. it was observed that the experiments carried out at pH 7, voltage 4 V, an electrolysis time of 15 minutes and electrolyte dose (NaCl) of 0.8 g/l were sufficient for the maximum removal of these pollutants with Stainless steel electrodes. The maximum removal efficiency of various parameters by Stainless steel electrodes found were: COD 70%, total solids 60% and oil and grease 80%. In case of bleach effluent, maximum removal efficiencies were found with Aluminum electrodes in comparison to Stainless steel electrodes. It was observed that the experiments carried out at 5V, an electrolysis time of 15 minutes and at pH 2 were sufficient for maximum removal of these pollutants with Aluminum electrodes. The maximum removal efficiency of color, turbidity and COD by Aluminum electrodes were 98%, 76% and 86% respectively. In both the cases, It was found that 15 minutes of electrolysis time was sufficient for maximum removal of pollutants and further increase in residence time for electro-chemical treatment imposes no further positive effect on the pollutants removal.

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CHAPTER-1

Introduction/Background information

Wastewater treatment (to comply with applicable effluent standards) is a real challenge for many of the industries. Treatment provided to the wastewater should be feasible, cost effective and should ensure consistence compliance with prescribed effluent standards. Very often feasible treatment technologies may not be available for some of the wastewaters. These wastewaters are often known as difficult wastewaters. Treatment of these wastewaters may require segregation of the culprit wastewater streams at source and pretreatment prior to addition to other wastewaters for treatment and disposal. Here, objective of the pre-treatment is to make the wastewater compatible for mixing with other wastewaters and to improve the treatability of the overall wastewater of the industrial unit. This pre-treatment approach, for the segregated wastewater streams, makes the otherwise costly wastewater treatment technologies feasible. Low volumes and high strength of the segregated wastewater streams are responsible for this.

Electrochemical treatment technology is one such costly technology, which may prove suitable for the pretreatment/treatment of some of the difficult industrial wastewaters. Electrochemical technology is not new and is known since 1890s (Ferreira., et al). But it has never been used as main stream technology for wastewater treatment. This is mainly because of perceived high cost. At the same time it is believed that this technology can prove appropriate especially for difficult wastewaters (bleach effluent, rubber wastewater, spent wash, textile dye effluent, heavy metal contaminated wastewater, lactose mother liquor etc.).

In this report, results are obtained from the attempts of using electrochemical treatment technology for the laboratory scale pre-treatment of a high strength difficult wastewater generated by a reclaimed rubber unit and first extraction stage effluent from a large integrated pulp and paper mill.

Objective of this study was to develop a pretreatment system for the reclaimed rubber wastewater stream and bleach effluent and to optimize the electrochemical treatment process for the wastewater.

1.1: Scope of work

1. Literature has been obtained from **Mr. M.S.Bhatti** lecturer in Guru Nanak Dev University, Amritsar. Some of the literature searched from sciencedirect.com and googlesearch.com.
2. To work on electro-chemical treatment of industrial wastewater
    - Wastewater from rubber reclaiming industry
    - First extraction stage effluent from a pulp and paper mill
3. We did not emphasized on electro-chemistry but mainly emphasized on electro-chemical treatment of wastewater.

1.2: importance of work

1. We did work on two types of wastewaters: (1) bleach effluent of pulp and paper industry and wastewater from rubber reclaiming industry, so this report is of immense use for us to know about the treatability studies of these wastewaters and if any person want to do work then this report will be immense use as starting material.
2. Some of the papers were not read and we go through from the abstracts only because these papers were not completely linked to our topic.

1.3: Overview of Contents of the Seminar

This seminar report includes four chapters and references:

Chapter-1 is introduction and it highlights the background information tells about scope, importance and limitation and provides overview of contents of the seminar.

Chapter-2 deals with the Fundamentals of electrochemical treatment. It provides us the information on basic theory, mechanism and processes, basic components, advantages and disadvantages of electrochemical treatment.

Chapter-3 is the Applications of electrochemical treatment technology for wastewater treatment. This chapter compiles the types of wastewater treated, different types of electrodes used in the process, efficiency for different type of wastewaters and cost effectiveness of this technology in comparison to other technology.

Chapter-4 is Materials and Methods. This chapter gives the information about the characteristics of wastewaters used in study, experimental setup and treatability studies done on the wastewaters.

Chapter-5 is Result and Discussions. This chapter compiles data obtained for the treatment of selected wastewaters.

Chapter-6 is conclusion. Here summary of the report is presented and it is also highlighted the need of technology for treatment of different wastewaters

CHAPTER-2

Fundamentals of electro-chemical Treatment

2.1: Electrochemical treatment

Electrochemical treatment is a technique in which the wastewater is treated by applying electric current through electrodes in a reactor. The electrodes generate the positive and negative ions which combine to form metal hydroxides flocs. These metal hydroxide flocs combine with pollutant particles and settled down. Application of electric current also generates oxidizing groups like HOCl which destroy or oxidize the organic pollutants (dyes etc.). Along with ions generation, gas bubbles are also generated from the cathode in the form of hydrogen gas. These gas bubbles stick to the pollutant particles and float them to surface of the water. This technology is used for removal of metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species.

2.2: Electrochemical treatment system

It includes a reactor where the wastewater is subjected for actual electrochemical treatment. This reactor may be preceded by a pretreatment unit for making the wastewater compatible for electrochemical treatment. The reactor may be followed by a post treatment unit where in the pollutants after the electrochemical treatment/ conversion are removed. Electrochemical treatment system demands a regulated supply of DC power to the reactor so a power system is provided for transforming AC power to DC. Please see figure -1 for the schematic diagram of electrochemical treatment system.

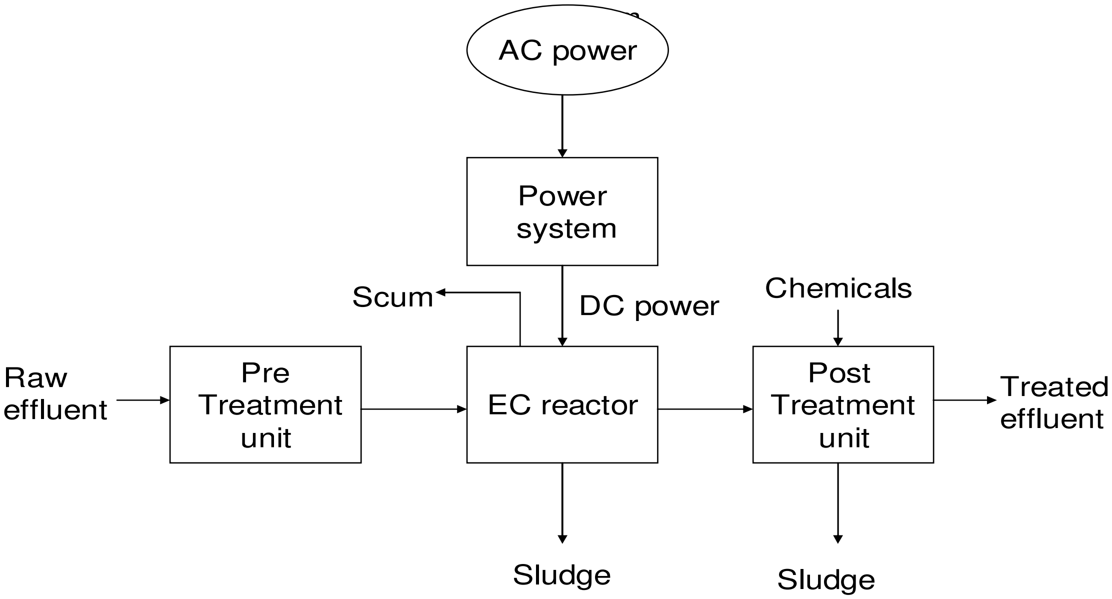


Fig. 1 Schematic diagram of a typical electrochemical treatment

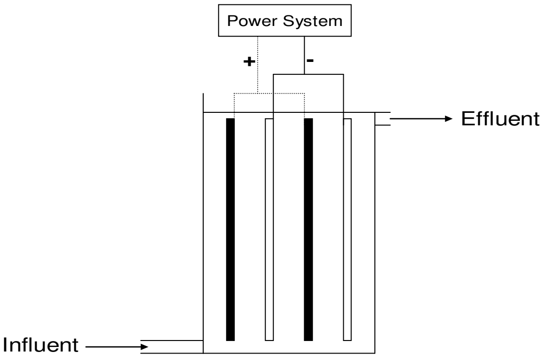


Fig. 2 Electro-chemical reactor

2.2.1: Pre-treatment unit:

In this unit the wastewater is pre-treated to make it compatible for electro-chemical treatment. The pretreatment units includes any process: it may be addition of electrolyte (NaCl, sodium sulphate) to maintain the conductivity, a tank for the settling of suspended solids, a screen for the removal of coarse particles, or may be tank for addition of chemicals like HCl and NaOH for pH adjustment.

2.2.2: The reactor:

Reactor allows electro-oxidation, electro-coagulation and electro-flocculation of the loaded wastewater. The reactor includes electrodes (cathodes and anodes) which may be sacrificial or non-sacrificial. Iron and Aluminum are the sacrificial electrodes while stainless steel is generally a non sacrificial electrode. Electrode used (anode and cathode) may depend on electrochemical reactions desired in the reactor. For electro-coagulation and electro-flocculation to occur sacrificial electrodes (iron and Aluminum) are favored.

Non sacrificial electrodes (graphite, stainless steel, titanium coated with oxides) are favored when the treatment desired is mainly electro-chemical oxidation. The reactor can be considered to include three components: body of the reactor, inlet section and outlet section. Outlet section may also include provisions for foam breaking and skimming etc. Pumping and other provisions for the passage of wastewater through the reactor and for recycling of treated effluent, if needed, can also be considered as part the inlet section. Body of the reactor houses electrodes and actual electrochemical reaction occur here.

2.2.3: Post treatment unit:

In this unit the pollutants after the electro-chemical treatment/conversion are removed. The pollutants are removed by the use of chemicals like polyelectrolyte, by filtration of treated effluent or by simple sedimentation in the sedimentation tank.

2.2.4: Power system:

For supplying the needed DC power at desired voltage and amperage, the power system is needed. System converts the input alternating current into Direct current (DC) of desired voltage. A power system has many provisions to get the desired voltage and current. Power system has the facility of polarity change at desired regular intervals. Polarity reversal do not dramatically fluctuate the voltage of the delivered power. Regulation of voltage of the output DC power should be possible and it should remain constant throughout the experiment. Provisions should be there for the measurement of the power measurement of the power consumption and for the indication and knowing of the voltage and amperage of the DC power supplied.

2.3: Mechanism of treatment and role of electrodes

Electro-chemical treatment is actually a combination of many processes like; 1) electro-oxidation 2) electro-coagulation and 3) electro-flocculation. Floatation and precipitation also occurs during electrochemical treatment. Electro-oxidation deals with the generation of the ions from the electrodes by the process of oxidation. Electro-coagulation is the process in which neutralization of charges occurs by electrochemical treatment. Electro-flocculation is the process where metal ions released from the metal electrodes combine with hydroxide to form insoluble precipitate along with which the pollutant particles are co-precipitated. In electro-floatation process, the gas bubbles (because of the generation of the hydrogen gas) are produced on the electrodes in the electrochemical reactor. The EC technology offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions.

Electrochemical treatment is also associated with one or more of the following: (1) dissolution of the metal electrodes. (2) electro-oxidation, electro-coagulation and electro-flocculation of the waste water. (3) Heating of the waste water. (4) Gas production and subsequent flotation (5) settling of the flocculated solids and (6) deposition of the solids on the electrode surfaces.

2.3.1: Electro-oxidation:

Electro-oxidation is a process in which the pollutants are destroyed or oxidized and converted into simpler forms like carbon-di-oxide and water. This oxidation process can be either direct oxidation or indirect oxidation. Direct oxidation is an anodic oxidation process. Here the pollutants are first adsorbed on the anode surface and then destroyed by anodic electron transfer reaction. In the indirect oxidation process, strong oxidants like hypochlorite, chlorine, ozone, hydrogen per-oxide, hydroxyl ions (OH^-) are electrochemically generated at the anode. According to (**Gotsi et al.**, **2005**) generation of the hypochlorite / chlorine can be shown by the following reactions:-

$$H_2O + S \longrightarrow S[OH^{\cdot}] + H^+ + e^- \qquad (1)$$

$$R + S[OH^{\cdot}] \longrightarrow S + RO + H^+ + e^- \qquad (2)$$

Where "S" is anode surface and R is the organic matter

In the presence of chloride, chloro-hydroxyl radicals are also formed on the anodes surface and these oxidize the organic matter:

$$H_2O + S + Cl^- \longrightarrow S[ClOH^{\cdot}] + H^+ + 2e^- \qquad (3)$$

$$R + S[ClOH^{\cdot}] \longrightarrow S + RO + H^+ + Cl^- \qquad (4)$$

Reaction between water and radicals near the anode yield strong oxidizing agents like molecular oxygen, free chlorine and hydrogen peroxide:

$$H_2O + S[OH^{\cdot}] \longrightarrow S + O_2 + 3H^+ + 3e^- \qquad (5)$$

$$H_2O + S[ClOH^{\cdot}] + Cl^- \longrightarrow S + O_2 + Cl_2 + 3H^+ + 4e- \qquad (6)$$

$$H_2O + S[OH^{\cdot}] \longrightarrow S + H_2O_2 + H^+ + e^- \qquad (7)$$

Further more free chlorine and oxygen can react on the anode yielding secondary oxidants such as chlorine di oxide and ozone, respectively.

$$H_2O + S[ClOH^{\cdot}] + Cl_2 \longrightarrow S + ClO_2 + 3H^+ + 2Cl^- + e^- \qquad (8)$$

$$O_2 + S[OH^{\cdot}] \longrightarrow S + O_3 + H^+ + e^- \qquad (9)$$

2.3.2: Electro-coagulation and electro-flocculation

Application of electric current to sacrificial electrodes, usually Aluminum or iron generates aluminum and ferrous ions. These ions act as coagulating agents. They neutralize the electrostatic charges on colloidal particles and facilitate coagulation and then separation from the solution. This treatment also prompts precipitation of some of the metals and salts.

According to (Mollah ***et al., 2001)*** electro-coagulation process involves three successive stages:

1. Formation of coagulants by electrolytic oxidation of the sacrificial electrode
2. Destabilization of colloidal contaminants and breaking of emulsions
3. Aggregation of destabilized particles to form flocs

The destabilization mechanism of the contaminants, particulate suspension, and breaking of emulsions can be summarized as follows:

1. Compression of the diffuse double-layer around the charged species.
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-Walls attraction predominates, thus causing coagulation.
3. Floc formation, and the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles that have not been complexed.

There are varieties of ways in which the pollutant species can interact in solution:

1. Migration to oppositely charged electrode (electrophoresis) and aggregation due to charge neutralization.
2. Cations or hydroxyl ions (OH^-) form precipitates with the pollutant.

3. The metallic cations interact with OH^- ions to form metal hydroxides, on which adsorption of pollutants takes place. (Bridge coagulation).
4. Metal hydroxides form larger lattice-like structures that sweep through the water (Sweep coagulation).
5. Oxidation of the pollutants.

The reactions that take place on the electrode surfaces during electro-coagulation and electro-flocculation are as follows:-

(Ferrreira., et al) Reactions at the aluminum electrode are:

At Anode:

$Al(s) \longrightarrow Al\ (aq)^{3+} + 3e$ (1)

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

At Cathode:

$2\ H\ (aq.)^+ + 2\ e^- \longrightarrow H^2\ (g)$ (3)

$2\ H_2O\ (l) + 2\ e^- \longrightarrow H_2\ (g) + 2\ OH^-\ (aq)$ (4)

$Al^{3+} + H_2O \longrightarrow Al\ (OH)^{2+} + H^+$ (5)

$AlOH^{2+} + H_2O \longrightarrow Al\ (OH)_2^+ + H^+$ (6)

$Al\ (OH)_2^+ + H_2O \longrightarrow Al\ (OH)_3 + H^+$ (7)

$Al\ (OH)_3^0 + H_2O \longrightarrow Al\ (OH)_4^- + H^+$ (8)

$2\ H_2O \longrightarrow 4\ H^+ + 4\ e^- + O_2\ (g)$ (9)

Reaction at the electrodes:

(Daneshwar ***et al.,*** **2004)** proposed two mechanisms for production of hydroxides and iron:

Mechanism 1

At Anode:

$4\ Fe(s) \longrightarrow 4\ Fe^{2+}\ (aq) + 8e^-$ (10)

$2H_2O\ (l) \longrightarrow O_2\ (g) + 4H^+ + 4e^-$ (11)

The generated ion and oxygen dissolved react to form $Fe\ (OH)_3$

$4\ Fe^{2+} + 10\ H_2O\ (l) + O_2\ (g) \longrightarrow 4\ Fe\ (OH)_3\ (s) + 8\ H^+$ (12)

At Cathode

$8\ H^+ + 8\ e^- \longrightarrow 4\ H_2\ (g)$ (13)

$2\ H_2O\ (l) + 2\ e^- \longrightarrow H_2\ (g) + 2\ OH^-$ (14)

Mechanism 2

At Anode:

$Fe(s) \longrightarrow Fe^{2+}\ (aq) + 2\ e^-$ (15)

$Fe^{+2}(aq) + 2OH^-(aq) \longrightarrow Fe\ (OH)_2\ (s)$ (16)

$2H_2O\ (l) \longrightarrow O_2\ (g) + 4H\ (aq) + + 4e^-$ (17)

Cathode:

$2\ H_2O\ (l) + 2\ e- \longrightarrow H_2\ (g) + 2\ OH^-(aq)$ (18)

The Fe^{3+} ions may suffer hydration and depending on the solution pH, $Fe\ (OH)_2+$, and $Fe\ (OH)_3$ may be present in acid conditions.

The reactions involved are:

$Fe^{3+}\ (aq) + H_2O\ (l) \longrightarrow Fe\ (OH)_2+\ (aq) + 2H^+\ (aq)$ (19)

$Fe^{3+}\ (aq) + 2H_2O\ (l) \longrightarrow Fe\ (OH)^{+2}\ (aq) + 2H^+\ (aq)$ (20)

$Fe^{3+}\ (aq) + 3\ H_2O\ (l) \longrightarrow Fe\ (OH)_3\ (aq) + 3H^+\ (aq)$ (21)

Under basic conditions $Fe\ (OH)_6^-$ and $Fe\ (OH)_4^-$ may be present

2.3.3: Electro-flotation:-

Electro-flotation is a continuous process. In these process uniform size small bubbles of Hydrogen gas is generated at the cathode surface during the electrolysis of water. These gas bubbles stick to the pollutant particles and float them to surface of the water (**Koren** *et al.***, 1995)**. This process mainly consists of four steps: (1) gas bubble generation (2) contact between gas bubble and oil drop (3) gas bubble adsorption on the surface of the particle (4) gas bubble and oil drops rising on to the surface. In electrochemical process, it is easy to adjust the gas bubble flux, by varying the current across the electrodes. Distributions of gas bubbles are also (initially) because the bubbles are produced at whole of the surface of the electrode. At the top surface foam comprising of gas bubbles as well as floating particles are formed and these are removed by the skimming. The rate of flotation depend on many factors like: (1) surface tension of solution, (2) gas bubble diameter, (3) size of the particle, (4) water residence time in the electrolytic cell, (5) particle and gas bubble zeta potential, (6) temperature, (7) pH and (8) pollutant particle concentration.

The size of the bubble depends on many conditions:

1. Gas bubble charge.
2. Cathode surface morphology.
3. Polarization potential
4. Current density. (**Khosla** *et al.,* 1991) have reported that gas bubble size decreases with increasing current density)
5. Temperature (It is found that gas bubble size increases with increase in temperature)
6. pH Smallest gas bubble found at neutral pH i.e. at 7)
7. Bubble contact angle.

2.3.3.1: Gas bubble formation:

Gas bubble formation generated at the electrodes (hydrogen bubble at cathode and O_2 bubbles at anode) involves three basic steps in their development: (1) nucleation (2) growth and (3) detachment. Nucleation occurs in energy favorable spaces like pits and scratches. These places have higher voltage than the other cathode surface. According to (***Khosla*** *et al.,* **1991)** by pulse electrolysis the energy favorable places are less important as nucleation sites, and nucleation is more uniform over the cathode surface.

Growth of gas bubbles is driven by high internal pressure and transport of dissolved gas through the gas / liquid interface because of the super-saturation of the gas in the liquid. Another mechanism of growth of gas bubble is coalescence. This occurs when two gas bubbles collide and become a single gas bubble. The mechanism of gas bubble collision is that the gas bubbles rolls around the cathode surface and then collide with other gas bubbles which come into path.

Detachment of gas bubble is dependent on the bubble contact angle and the size of bubble. Pulsating electrolysis gives the shock to bubbles which result into the early detachment of bubble from the surface of the electrode. The presence of surface-active substances in the liquid also helps in decreasing the bubble size as they reduce the surface tension between the solution and surface of the electrodes and the bubbles.

2.4: Operating parameters of electrochemical treatment process

The design of the electro-coagulation unit greatly affects the operation and its efficiency. The main issues generally considered are (1) geometry of unit (2) electrode material (3) pH (4) conductivity (5) TDS (6) voltage (7) current density and (8) temperature.

(1) **Geometry:** geometry of the reactor affects the operational parameters including bubble path, flotation effectiveness, floc formation, mixing and settling characteristics.

(2) **Electrode material**: In any electrochemical process, the electrode material has significant effect on effluent treatment. For drinking water treatment, the electrode material should be nontoxic for human health. Iron and Aluminum are usually preferred because of their low cost and easy availability. However, iron electrode has a disadvantage as it turns the effluent color into green or hard yellow. This coloration comes from the Fe^{2+} ions (green) and Fe3+ ions (yellow) generated during electrolytic treatment. With the Aluminum electrode, the effluent becomes clear and stable, with no change in color. Plate types of Electrodes are generally used for the treatment. Either bipolar type or mono polar type electrodes are generally used by keeping one side of electrodes insulated by applying some coating.

(3) **pH**: pH plays a very important role in treatment process. It is found that low pH is generally favorable for maximum pollutants removal. The basic reason behind this is, in low pH metal electrode become more unstable and more reactive, so they release more ions in the solution and hence enhance

dissolution of metals in the solution. But very less pH is not favorable because at very low pH the flocs will not aggregate or they become dissolve in the solution and hence the settling will not be proper. As the pH increases the efficiency for color removal, COD and turbidity decreases. For electro-oxidation pH is generally maintained around 2-3, and for Electro-flocculation pH is generally maintained in between 4-6.

(4) **Conductivity:** Conductivity also plays a significant role as usually higher the conductivity higher will be the removal efficiency. It also determines the voltage and energy consumptions. Increasing conductivity increases power consumption. The optimum value of conductivity was found to be in betwwn 300-500 micro Simons/cm.

(5) **TDS:** TDS are indirectly related to the conductivity of the solution.

(6) **Voltage**: - voltage influences the electro-flocculation process very much. Voltage can be related to current density, effluent's conductivity, electrodes spacing and its surface state (Chen et al., 2002) by the following equation:

$$U=\delta * d/k$$

Where

U = applied tension, V
δ = current density, A/m2
d = distance between electrodes, m
k = electrolyte conductivity, S/m.

(7) **Current density**: current density (*I*) is the current delivered to the electrode divided by the active surface area of the electrode. It determines both the rate of electrochemical metal dosing and electrolytic bubble production. Different current densities may be desirable under different situations. High current densities are desirable for separation processes involving flotation tanks or large settling tanks, while small current densities are appropriate for electro-coagulators that are integrated with conventional sand and coal filters.

(8) **Temperature**: According to (**Daneshwar** *et al*., 2004) increase in temperature of solution provides an increment of removal efficiency because of the increase in the ion movements that facilitate collision of ions with coagulated material. However if the temperature is >300K, the removal efficiency decreases because breakage of flocs from the increased movement of the ions. Also very high temperature increases the solubility of precipitates.

(9) **Consuming of electrodes:**

First Faraday's law is directly linked to electro-flocculation, the consumed mass of electrodes is directly linked to the electric current applied and is mathematically defined by the following equation:

$$M_{el} = i.t.M / F.z$$

Where:

M_{el} = maximum amount of electrodes mass consumed (grams)
i = electrical current (Ampere)
t = total time of current application (s)
M = molar mass of the main electrode element (g/mol)
z = number of electrons involved in oxidation reaction of anode's element
F = Faraday constant, 96500C/mol

Considering this is a theoretical calculated value usually is near the result experimentally determined, however mistakes can be detected if the electrode's set geometry is not properly determined and if the reactor is not operating in optimal conditions.

(10) **Distance between Electrodes**

It's an important variable when an operational costs optimization of a treatment unit is needed, so according to when the effluent conductivity is relatively high, a bigger spacing should be used between electrodes. In situations with an average value of conductivity, the spacing between electrodes should be reduced because it will decrease the energy consumption without a change in current.

2.5: Advantages and disadvantages of electro-chemical treatment

2.5.1: Advantages

1. It requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running.
2. Wastewater treated by electrochemical treatment gives palatable, clear, colorless and odorless water.
3. Sludge formed by electro-chemical treatment tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low sludge producing technique.
4. Flocs formed by this process are similar to chemical floc, except that the flocs tend to be much larger, contain less bound water, are acid-resistant and more stable, and therefore, can be separated faster by filtration.
5. This process produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
6. The electro-chemical treatment 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. This process avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used.
8. The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
9. The electrolytic processes in the electro-chemical cell are controlled electrically with no moving parts, thus requiring less maintenance.

10. The electrochemical technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

2.5.2: Disadvantages

1. The ‘sacrificial electrodes’ are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.
2. The use of electricity may be expensive in many places.
3. An impermeable oxide film may be formed on the cathode leading to loss of efficiency of this unit.
4. High conductivity of the wastewater suspension is required.
5. Gelatinous hydroxide may tend to solubilize in some cases.

CHAPTER-3

Application Of electrochemical treatment technology for wastewater treatment

3.1: Introduction:

The present work has the objective of giving a general idea about the main aspects over the electro-flocculation, including the main reason for the application’s stagnation since 1990s. Electro - flocculation is a technique used to treat wastewater since 19th century. This was originally developed in 1870s for the treatment of sewage and industrial wastewater. In 1890s, large scale wastewater treatment plants were commissioned in London (Matteson et al., 1995), while electrolytic sludge treatment plants were operating as early as 1911 in various parts of USA (Holt et al., 2005). In Brazil (1909), the electrolytic process was appeared when a sanitation engineer used this technology for the treatment of irrigation wastewater for the reutilization of Nitrogen (N_2), Phosphorus (P) and Potassium (K) (Ferreira et al). By the year 1930 however, all such plants had been abandoned due to higher operating cost. Since then, lot of work has been done on this technology, but, as it was not cost effective, it has never been taken as ‘main stream water treatment technology’.

Later in 1978, the electrolytic treatment study was restarted in Brazil with CESAN's engineer who started to test electro-flocculation in deep water well containing high iron concentration, and in August 15th, 1985 they develop the 1st wastewater treatment facility using the electro-flocculation process. (Ferreira et al).

Basic reasons behind the failure of this technology were lack of systematic approach to electro-coagulation reactor design and operation, and the issue of the electrodes replacements. The need for the replacement of electrodes together with high consumption of electrical energy made both the initial cost as well as operating cost higher in comparison to the other treatment technologies. This resulted in the loss of potential benefits of this technology.

In recent times, there has been some interest is renewed in water treatment plants based on electro-chemical treatment technology for treatment of some difficult wastewaters like spent wash, removal of heavy metals, bleach effluent of pulp and paper industries and rubber wastewaters etc. for which the alternative technologies are not feasible.

In this chapter, review of literature on the electrochemical treatment technology for wastewater treatment is presented. The review is presented under the following heads:

3.2: Heavy metal removal by electro-chemical treatment

Gao *et al.* **(2005)** carried out work on the removal of hexavalent chromium from the wastewater generated by a fertilizer industry. He used 'iron electrodes', and reported conversion of hexavalent form of chromium to trivalent form, which is less toxic. The Cr^{+3} ions are further converted into the $Cr(OH)_{3,}$ which later on precipitated and settled down by using alum and a surfactant. pH range of 5-8 was reported as optimum for the treatment. He used an electrolyte (NaCl 0.1 M) for increasing conductivity of the wastewater to the desired level. Power consumption in the treatment was less than 1kWh/m3 at the optimum conductivity of 1.5mS/cm. and optimum charge loading of 2.5 Faradays/m^3. The treated effluent had <3mg/l of suspended solids and <0.5 mg/l of total chromium**.**

Mukhopadhyay *et al.* **(*2007)*** worked out some experiments on removal of hexavalent chromium to trivalent chromium. Iron electrodes were used in the process. Cr (VI) is first reduced to Cr (III) in acidic pH by a reducing agent which is followed by precipitation of trivalent chromium along with metal hydroxide in alkaline pH.

Adhoum *et al.* (2004) did the experiments for the treatment of electroplating wastewater containing $Cu^{2+,}$ Zn^{2+} and Cr (VI). He used aluminum as sacrificial anode for the treatment. The Results demonstrated that maximum removal efficiency was achieved when the pH range was 4 – 8. The optimum current density was found to be in range of 10 – 50 A/M^2. Time required for maximum removal was found to be in range of 20 – 25 min. The removal rates of copper and zinc were found to be five times quicker than chromium because of difference in removal mechanisms. The electrode and electricity consumption were found to be 1g/l and 32 Ah/l respectively. **Kim** ***et al.*** (**2004)** observed the Influence of anodic treatment on heavy metal Cr (VI), Cu (II), and Ni (II) ion removal by activated carbon fibers (ACFs). For this Phosphoric acid (A-ACFs) and ammonia (B-ACFs) were used as acidic and basic electrolytes, respectively. The basic concept was that the heavy metal become adsorb on the carbon filters. By electrochemical treatment the activated carbon became oxidized and developed some functional groups (phenolic groups, carboxylic, lactonic, and oxygen containing groups) which made the carbon surfaces hydrophilic and increased their adsorption capacities. The results showed that adsorption capacity of the electrochemically oxidized ACFs was improved in the order B-ACFs>A-ACFs>untreated-ACFs.

Hunsom *et al.* (2005) carried out the experiments on electrochemical treatment of heavy metals (Cu^{2+}, Cr$^{6+,}$ Ni$^{2+)}$ from industrial effluent. He used stainless steel as cathode and titanium coated with ruthenium oxide as anode respectively. Brightener was also added in the solution in order to increase the removal efficiency. pH was kept constant at 1. Applied current densities were 10 to 90 A/m2. It was found that the reactor was capable of treating plating wastewater with low energy consumption (42.30 kwh/kg metal) and low operating cost (5.43 US\$/m^3). More than 99% of metal reduction was achieved and the final concentrations of all the metals were below the permissible limits. Brightener was found to be no significant effect on the copper reduction. **Ratna** ***et al.*** (2004*)* worked on the removal of arsenic from wastewater. He studied the removal of arsenic (III) and arsenic (V) by three types of electrodes, iron, aluminum and titanium. The current density applied was from 6.5A/m^2 to 15.3A/m^2, and the voltage range was 0-15Volts. The results demonstrated that iron had the maximum removal efficiency (99%) for As (III) than the other electrodes. He that electro – flocculation is the dominant removal mechanism for As (III) whereas the removal of As (V) by both the processes (EC and chemical coagulation) was nearly same. Current density was found to be directly proportional to removal efficiency and pH has not significant effect in the range from 6-8. The optimum electrolysis time was found to be 30 minutes for maximum removal.

Hansen *et al.* **(2006*)*** did the experiments on removal of arsenic by electro coagulation. He used electrodes made up of iron plates. The current density range was from 80 A/ m^2 to 120A / m^2. Electrolysis time was around 9 minutes and the DC current was reversed in each two minutes. Iron hydroxides were formed in the solution which later on precipitates out along with heavy metals. **Parga** *et al.* ***(*2005)** also worked on Arsenic removal via electro-coagulation from heavy metal contaminated groundwater. He used carbon electrodes and an air injection system in reactor. The conductivity of wastewater was maintained at 0.95 micro Simons by adding Nacl. It was suggested that during the process, magnetic particles of magnetite and amorphous iron oxy - hydroxides were produced which react with arsenic and remove both arsenic (III) and arsenic (V) with more than 99% efficiency from sample.

Casqueria *et al.* (2006) worked on the removal of zinc from liquid streams. The pollutants mainly were removed by electro-flotation. Two types of electrodes were used, platinum as anode and stainless steel as cathode. The results showed that 96% removal can be possible by electro flotation by using sodium dodecyl sulfate as a collector in 3:1 stoichiometric ratio with metal concentration. Optimum current density was found to be 80A/m^2, optimum pH was neutral and range for electrolysis time was found to be 15 – 20 minutes for maximum removal efficiency.

Bazrafshan *et al.* (2006) worked on the removal of cadmium from industrial effluents by electro - coagulation process using iron electrodes. The process of cadmium ion removal was studied at pH 3, 7 and 10 and at electric potential of 20, 30 and 40 volts. The results showed that initial concentration of cadmium affects the removal efficiency as higher electric potential and more reaction time was needed. Maximum 99% removal was obtained at voltage 40V and electrolysis time 20 minutes.

Meunier *et al*. **(2006*)*** studied the comparison between electro coagulation and chemical precipitation for metal removal (Cd, Cr, Cu, Ni, Pb and Zn) from acidic soil leachate (ASL). Chemical precipitation was evaluated by using calcium hydroxide, whereas electro-coagulation was evaluated in an electrolytic cell by using steel electrodes. During experiment the current was maintained at 3.0A, retention time of 90 min. and pH was neutral. Chemical precipitation was as effective as electro-coagulation in removing all the metals from ASL having low contamination levels up to 30 mg/l. Both the treatment processes reduced the residual concentrations of Cr, Cu, Pb and Zn below the acceptable level from the initial concentration of 100mg/l, but Ni and Cd were more effectively removed by electrochemical treatment. Electro-coagulation process was found to be more effective when ASL was specifically enriched with high concentration of Pb and More than 99.5% of Pb was removed <u>regardless of the initial Pb concentration</u> imposed in ASL. The cost of electro coagulation process ranged from US$ 8.83 to 13.95 tds^{-1}, which was up to five times lower than the cost of chemical precipitation.

Khelifa *et al***. (2005)** did work on treatment of metal finishing effluents containing Cu and Ni. They used the electrodes made up titanium coated with ruthenium oxide as an anode and the stainless steel as a cathode. <u>Sodium sulfate</u> was also added in the solution as a supporting electrolyte. The removal efficiency was determined for copper and nickel separately. The results were: (1) <u>for copper removal</u>: The optimum pH was found to be in range of 5 – 6.5. Initial dye concentration should be low and supporting electrolyte increases the removal efficiency. (2) <u>For nickel</u>: The over all results showed that the removal of nickel was slightly low as compared to the copper. However the effect of initial nickel concentration and the additive addition was same as that of the copper removal. Current density was found to be directly proportional to the removal efficiency. The important difference found here was effect of pH, increase in pH lead to increase in the removal efficiency of the nickel. However 95% removal may also found in case of nickel also and 98 to 99% removal was found for copper.

lordachet *et al.* (2004) did work on the removal of cyanides ions in the presence of six types of electrodes (aluminum, titanium, nickel, copper, stainless steel and graphite). To increase the efficiency an ultrasound technology is used. The conductivity was maintained at 0.5 mS. The temperature was maintained at 30 – 35 C and current density was maintained at 0.03A/dm$^{2.}$ In order to highlight the influence of electrodes type on the remediation of cyanide, 3 types of experiments were performed for each electrode: electro –oxidation, sonoelectro–oxidation, and sonoelectro - chlorination. The results showed that in electro oxidation the maximum removal efficiency was done by graphite electrode. But in other both the cases (sono-electroxidation, sonoelectro–oxidation) the best electrode was aluminum one. The results also showed that by ultrasound technology, the removal efficiency increased up to 2 – 4 folds for each electrode in comparison to the simple electrochemical treatment. Generally for all types of electrodes used, the efficiency of cyanide treatment methods follows the following order: electro –oxidation < sonoelectro–oxidation < sonoelectro - chlorination.

Szpyrkowicz *et al.* (2005) worked on hydrodynamic effects on the performance of an electrochemical reactor for destruction of copper cyanide part -1. An electrochemical reactor with stainless-steel electrodes was used for cyanide destruction and copper electro deposition from dilute wastewater. With mechanical stirring, pumping or gas sparging, in situ deposition of a Cu oxyhydroxide film occurred on the anode at potentials > .7V vs. AgCl/Ag and had electrocatalytic properties for oxidation of cyanides. The Cu^{II}/Cu^{I} ratio in the electrocatalytic film was found to vary with the hydrodynamic conditions. The minimum mechanical energy dissipation, ranging from 1.5 to 7.2 W m^{-3} necessary to create sufficient turbulence for film formation, was of a similar order of magnitude for all three means of transport enhancement. However, shear rates > 410 s^{-1} and shear stresses >o.41Nm^{-2} at the anode resulted in shearing of the film from the stainless-steel support. **In another** experiment they worked on to determine the hydrodynamic effects on the performance of an electrochemical reactor for destruction of copper cyanide, Part 2—reactor kinetics and current efficiencies. An electrochemical reactor, with stainless-steel electrodes, was used for treatment of a wastewater containing dilute copper (I) cyanide. Both anodic cyanide oxidation and cathodic copper(I) reduction could be operated under mass transport control, when reactions rates and current efficiencies were influenced by hydrodynamic conditions created by pumping and gas sparging, used to enhance reactor performance. Pumping promoted the rate of Cu electro deposition to a greater extent than sparging with compressed air, whereas the latter slightly enhanced the rate of cyanide destruction. A hypothesis of cathodic O_2 reduction generating oxidizing species, which react homogeneously with cyanide, was verified experimentally. The specific electric energy consumption, calculated for typical values of current densities and current efficiencies, were 0.34 kWh mol^{-1} Cu and 0.24 kWh mol^{-1} CN^{-}).

3.3: Color removal by electro-chemical treatment

3.3.1 *Textile waste water:*

Ghalwa *et al.* (2005*)* worked on removal of acid green dye from textile wastewater. The electrode used for the treatment process was made up of titanium metal coated with lead oxide. During electrolysis the voltage was ranged from 1.5 to 1.8 V and current density applied was in range between 100 – 500 A / M^2. The results demonstrated that the optimum values of pH and current density for maximum removal were 2-5 and 200 – 250 A/M^2. The optimum electrolysis time and Nacl concentration was found to be 10 min and 500-mg/l. Optimum temperature was 30 C. Initial dye concentration also imposes the effect as until the concentration was below the 100mg/l the removal efficiency approaches to maximum. D**aneshvar** *et al.* (2006) did some work on decolorization of basic dye solutions. Iron plates were used as anode and steel plates were used as cathode. All the runs were performed at room temperature. The conductivity was maintained from 3.3 to 20.2 micro Simons /cm in results the optimum pH was found to be 6 to 8 and the optimum electrolysis time was found to be 5 minutes for the maximum color removal. The conductivity, current density and electrolysis time was found to be directly proportional to the removal efficiency. It was reported that conductivity also decreased the consumption of electrical energy. Initial dye concentration decreases the color removal efficiency from 99% to 85% as the concentration increases from 100-500 mg/l. Also by increasing the dye concentration, the value of electrode consumption or electrode dissolution decreases from 4.7 to 1.1Kg Al/kg dye respectively. **Can** *et al.* **(2006)** did some work on treatment of the textile waste water. They used four electrodes made up of aluminium. The run was conducted at constant temperature of 25C and constant pH 5.5. The wastewater was added in the reactor along with alum and **polyaluminum chloride solution (PAC).** The results demonstrated that the COD removal percentage becomes constant after the dosage of 0.32Kg/cu m of PAC. Optimum electrolysis time was found to be 12 minutes in the presence of PAC and 20 minutes in the absence of PAC. The minimum energy consumption was found to be at the dose of 1g/l of PAC.

Kobya *et al.* **(2005)** worked on treatment of levafix orange textile dye solution. In the experiment aluminum electrodes were used. The experiment was done at voltage 30V and 100A/M^2 current density. pH was maintained at 3and electrolysis time was 15 minutes. From The results demonstrated that almost complete removal of pollutants (99.9%) was obtained with typical operating conditions. The optimum conductivity was 250 – 750 uS/cm. The electrode and energy consumption during the electrolysis were 2.0 kg Al/kg and 43 kWh/ kg dye respectively. However 95% decorisation efficiency can also be obtained for same current density in 12 min and at pH 6.4. The electrode and energy consumption in that conditions were be 1.8 kg Al / kg dye and 35 kWh/kg dye. Similar type of work was done by (**Alinsafi** et al., **2005)** worked on removal of reactive textile dye and wastewater. The electrodes used ware of aluminum type. Conductivity was maintained at 4-5 micro Simons by adding the sodium chloride in the solution. The results showed that the maximum efficiency can be obtained at low pH in range from 4 – 6. Electrolysis time was found to be 10 – 12 minutes and current density was found to be directly proportional to the removal efficiency. **Kim** *et al.* (***2002***) worked on decolorization of disperse and reactive dyes present in textile wastewater. Aluminium, iron and stainless steel were used as electrodes. The results showed that dye removal from the solution was directly proportional to current density, electrode number, electrolyte concentration and it is inversely proportional to electrode gap, initial dye concentration and inlet flow rate. Dye removal was more efficiently achieved by A1 electrodes than those of stainless steel or iron. The optimum pH was found to be 4-6. The power consumption was found to be increased as we increase the current density, electrode gap, electrolyte concentration and number of pairs of electrodes. In addition, the effectiveness of electro coagulation according to dyestuff type was also studied. The disperse dyes had higher COD loading than the reactive dyes and disperse dyes were much more effectively removed than the reactive dye. **Fernandes** *et al.* (***2004)*** did work on removal of C. I. Acid Orange 7 dye by electro-chemical treatment. The electrodes used were boron doped diamond electrodes (BDD). Two different supporting electrolytes—KCl and Na_2SO_4 were also used and the results showed the complete removal of color and COD from the wastewater.

Roessler *et al*. (**2003**) worked on electrochemical methods for the reduction of vat dyes.Until now, in most industrial vat dyeing processes, vat dyes were reduced mainly using sodium dithionite. This process produces large amounts of sodium sulphate and sulphite as by-products which increase the costs for waste water treatment. Hence, many attempts are being made to replace the environmentally unfavorable sodium dithionite by ecologically more attractive alternatives, such as organic reducing agents or catalytic hydrogenation. In recent investigations to improve the biocompatibility of the vatting process even further, various electrochemical reducing methods have been described, such as indirect electrochemical reduction employing a redox mediator, direct electrochemical reduction of indigo via the indigo radical, electro catalytic hydrogenation and direct electrochemical reduction of indigo itself on graphite. These methods offer tremendous environmental benefits, since they minimize the consumption of chemicals as well as effluent load. However, most of these electrochemical processes are still in the development stage. This article gives an overview of the processes most commonly used and the state of development of recent electrochemical innovations.

Gurse *et al***. (2002)** worked on electro coagulation of some reactive dyes and did a statistical investigation of some electrical variables. In the experiment aluminum and iron electrode were used. During experiment stirring was done regularly at 200 rpm. Electrolyte concentration was kept constant at 8.5 mM by using Nacl as electrolyte. In all the experiments, cell voltages were kept constant, but a small variation was observed in case of current density. At the end of the experiments the treated solution was filtered and 5ml of that treated effluent was than centrifuged. Dye concentration was measured before and after the electrolytic treatment. Current density was adjusted by changing the cathode anode distances (2.0, 2.5 and 3.0 cm). They obtained the effects of four variables (electrolysis time, cell voltage, current density and mixing rate.) on the decolorization percentage.

Kobya ***et al. (2003)*** did work on treatment of textile waste waters by electro-coagulation. The composition of waste water was COD -3456mg/l, TSS -1112mg/l, TOC -900mg/l, Conductivity -3990mg/l, Turbidity -5700 NTU, pH 7.0. In experimental set up 4 electrodes were used out of them two was anode and two was cathode made up of aluminum as anode and iron as cathode respectively. All the runs were performed at constant temperature of 25C and stirring speed 200 rpm. At the end of the electrical treatment the solution was filtered. The same experiment was done for both electrode materials. COD, total organic carbon and total suspended solids were estimated of the treated water. .**It was found that as the pH increases the efficiency for, COD and turbidity removal decreases in case of aluminum electrodes. But in case of iron electrodes the results were different as nearly at neutral pH or basic pH the removal efficiency was maximum.** The effect of conductivity was investigated between 250-4000 micro Simons/cm and it can be concluded that maximum efficiency was found at 250 micro Simons and decreases as the conductivity increases in case of aluminum electrodes. But in case of iron electrodes the case is slightly different as with increase in conductivity the removal efficiency becomes increases. It was found that as the current density increases, removal efficiency increases. In both the cases they observed that current density was directly proportional to the removal efficiency. The effect of time was studied at constant current density and at constant pH (6.5). It is found that 12 minutes operating time is generally sufficient for one batch process. At this time the efficiency may reach up to 95%. It is found that increase in time from 5-20 minutes Increase the energy consumption from 22 to 50 kWh/Kg dye.

3.3.2 *Distillery:*

Areeetham *et al*. (2003) worked on the treatment of concentrated wastewater from distillery industry. They used graphite electrodes and titanium electrodes as cathode and anode respectively in the process. Wastewater was diluted to 10 times. The experiment was done at pH 1. The current density applied was ranged from 1A/M^2 to 9 A /M^2. The result demonstrated that the titanium electrode has more efficiency than that of the graphite electrode to remove the color and COD. It was also observed that at current density 9A/ M^2, pH 1, electrolysis time 6 hours and in the presence of electrolyte (0.1M Nacl), the removal efficiency was maximum : 92% for color, 89% for COD, 83% for BOD, 38% for TDS and 67% for TS. Similar type of work was also done by **Manishankar** *et al.* (2003) on electrochemical treatment of distillery effluent by using the catalytic anodes. Three types of electrodes were used in the process: (1) graphite electrode as cathode and anode (2) titanium substrate insoluble anodes (TSIA) coated with Lead oxide (PbO2) with steel as cathode and (3) titanium substrate insoluble anodes (TSIA) coated with ruthenium oxide (RuO2) with steel as cathode. Current densities applied was varied from 1.5 to 5.5 A /dm^2. In results complete decolorisation was obtained in all the cases but there was no significance removal in COD and BOD in case of graphite electrodes. While maximum 92% reduction in COD, 98% reduction in BOD and 99% reduction in total solids were found when ruthenium oxide titanium electrode as anode and steel electrode as cathode were used. The current efficiency and power consumption also showed the similar trends.

3.4: organic matter removal by electro-chemical treatment

Kobya *et al.* **(2005)** did some work on treatment of poultry slaughter house wastewaters. Two types of electrode materials were used in the experiment, iron and aluminum. The result demonstrated that aluminum electrode performance was better in reducing the COD (93%) from the waste water at pH 2-3, current density of 150

A/m^2 and the electrolysis time 2-5 minutes. On the other hand iron removes oil and grease (98%) better than that of aluminum. But when aluminum and iron both were used collectively as anode and cathode removal efficiency was found to be increased for both COD and oil and grease. **Kobya** *et al.* (**2005**) worked on treatment of potato chips manufacturing wastewater. Aluminum and iron electrodes were used. The results demonstrated that aluminum electrodes were more suitable than the iron electrode. The retention time and charge loadings both were found to be directly proportional to the removal efficiency. The removal efficiencies of COD and turbidity were high, being 60% and 98%, respectively. The operating costs were evaluated with respect to different values of current densities and time and it was found in the range of 0.48 to 5.42 \$/m3 and 0.62 to 6.32 \$/m^3 for the wastewater treated at 20–300 A/m^2 and 5–40 min, respectively. The power consumption was 4 kWh/m^3 for wastewater treated in typical conditions. **Feng** *et al.* **(*2004)*** worked on treating biological wastewater to know the performance of electrochemical treatment. The cathode was made up of titanium sheet and for anode, three types of materials was used: titanium, platinum and titanium coated with Ti/RuO_2-TiO_2. The performance of the treatment system was evaluated by treating domestic wastewater, pond water containing algae and wastewater from hog rising. The results showed that production of hydroxyl radicals at $Ti/RuO_2–TiO_2$ anode was larger than with a platinum anode, and hydroxyl radicals were not detected at Ti anode. However no difference was found in electrolytic activity for ammonia oxidation between the electrodes made up of platinum and Ti/RuO_2 – Ti/O_2. It was observed that the removal of T-N, T-P, NH_4–N and COD from domestic wastewater and pond water containing algae was approximately 90%, while the removal of chlorophyll-a (chl-a) of algae was approximately 100%. Although the electrochemical treatment system was effective on biologically treated wastewater from hog raising and the treatment of raw wastewater was not remarkable.

Koparal *et al. **(2002)*** worked on removal of nitrate from wastewater. The anode was made up of graphite rod and cathode was made up of carbon. It was found that higher the initial nitrate concentration lower the removal efficiency. The effect of pH was found as smaller the pH larger the removal efficiency. In electro reduction, maximum removal of nitrate was found to be at pH range of 5–7 with energy consumption value of 1×10^{-3} kWh g^{-1} and in electro-coagulation, the maximum removal of nitrate was found at pH range of 9–11 with energy consumption value of 0.5×10^{-4} kWh g^{-1}. The optimum voltage was found to be 2.9 V. It was also be found that the electro-coagulation seems to be more cost efficient method comparing to the electro-reduction.

Cossu *et al.* (**2007***)* did work on treatment of MSW landfill leachate having high COD and ammonical-N. The experiment was done in electrochemical cells having the electrodes made up of porous carbon and bi-dimensional Ti/PbO^2, Ti/SnO^2 as anode and stainless steel as cathode. The temperature was maintained at 25 C. Current density during electrolysis was kept in the ranges from 5 to 15 mA/cm^2 for cell (I) and from 2 to 20 mA/cm^2 for cell (II). In this case the pH of the solution was adjusted to a value of 6.8 and a fixed amount of Al (SO_4) was added. The results showed that a 75% of COD removal and 100% ammoniacal-N were found. Among the anode materials adopted in this study, Ti/PbO2 was the best electrode in electro catalytic behavior. **Nielson *et al.*** (**2005)** did work on municipal wastewater treatment by Ozone-enhanced electro-flocculation. Here they used a treatment technology termed as Electro-floc ^{PLUS,} where they did the pre-ozonation as a coagulation aid to improve the flocculation and reduce the pollutants by oxidation. The technology was effective in the reduction of certain water quality parameters, including total suspended solids (TSS) and total phosphorus (TP). The removals of chemical oxygen demand (COD) and biochemical oxygen demand (BOD5) were inadequate, as the test unit was unable to treat the wastewater adequately to meet regulatory guidelines. Energy requirements were also examined and the results showed that energy consumption was quite high relative to competing technologies. A laboratory study of Electro-coagulation–flotation was done by ***Jiang et al. (2002)*** for wastewater treatment. They used aluminum electrodes and a separation/flotation tank. The pH was maintained in range from 6.8 – 7.5. It was found that the specific electrical energy consumption of the reactor for drinking water treatment was 20 kWh (kg Al) $^{-1}$ which was less than ordinary conventional treatment. The performance of electro-coagulation process was found to be superior to that of conventional coagulation with 20% more removal of **dissolved organic carbon (DOC).**

Bergmann *et al.* **(2005)** worked on drinking water disinfection by the formation of chlorine dioxide from electrochemical treatment. They used titanium as anode coated with IrO_2/RuO_2. The current density and pH was maintained. The results showed that by electrochemical treatment the oxidation rate of the pollutants become increased and amount of chlorine consumption was also decreased. This also led to the decrease in the formation of by products formed during chlorination. **Vlyssides** ***et al.*** (***2002)*** worked on treatment of domestic wastewater. They used Ti/Pt as anode and stainless steel as cathode. Experiments were run in a continuous mode in a reactor at the temperature of 40 C. the current density was applied 0.075A/cm^2 and the electrolysis time was 1 hour. **The pH was maintained at 9.** In results, COD reduction was found to be about 89%, volatile solids were found to be reduced by 90%, ammonia nitrogen reduced by 82% and total phosphorus reduced by 98%. The energy consumption was found to be 12.4 kWh/kg of COD.

3.5. Treatment of Bleach effluent of Paper industry

Mansour *et al. (2007)* did work on treatment of wastewater of paper industry containing high amount of suspended solids, COD and BOD. The experiment was done in both batch and continuous modes by using electrodes and a flotation unit. The electrodes were made up of titanium coated with ruthenium oxide as anode and stainless steel as cathode. The voltage was varied between 7 to 9 volts and the current density was varied and not fixed. The batch mode aims to optimize coagulant concentration, pH and current density at fixed electrolysis time (20 minutes). Continuous mode aims to optimize the residence time. The results demonstrated that the removal efficiency of suspended solids in both the cases was more than 95%.

3.6. For rubber wastewater no paper has been yet found.

3.7: Miscellaneous:

Sok *et al. **(2004)*** worked on removal of ammonium from tannery wastewater. They used the electrodes made up of titanium coated with iridium oxide (IrO_2), Rubidium oxide (RuO_2) and platinum as anode and stainless steel as cathode. The voltage supplied was 50V and the pH was adjusted at 3, 7 and 11. The results showed that out of all three electrodes, Ti/IrO_2 electrodes were most suitable. A maximum 79% removal of ammonium was achieved after the 30 minutes electrolysis time. The optimum current density was found to be 40 A/ m^2. Free chlorine generation was also observed during the experiment which results in the degradation of organic matter present along with ammonium in wastewater. Similar type of work was also done by ***Szpyrkowicz et al.*** (**2005)** did work for the removal of tannery wastes like ammonium ions and sulfide ions. Ti/ Pt as anode and stainless steel as cathode were used. The current density and the voltage applied were in range of 20 – 40 A/ m^2 and from 1 – 10 volts. The pH was kept in range from 3 – 5. The results showed that the ammonium ions removed only by free chlorine while the other pollutants are removed by free chlorine as well as other hydrodynamic conditions like agitation. **In** another experiment he determined the influence of anode material on treatment of tannery wastewater. Parameters like chemical oxygen demand, nitrogen (TKN and ammonia), Cr and sulphides were monitored. The anodes were made up of noble metals and metal oxides (Ti/Pt–Ir, Ti/PbO_2, Ti/PdO–Co_3O_4 and Ti/RhO_x–TiO_2) and cathodes were made up of stainless steel. The current density was maintained at two values 200 and 400 A/m^2. Cell potential was kept in range between 5.4 to 11.6V. The results showed that best electrodes were Ti/Pt–Ir and Ti/PdO–Co_3O_4 which performed better than others with the highest rate of removal of ammonia.

Feng *et al.* **(2004)** did investigation on treatment of germinated brown rice (GBR) circulating water and disinfection by *Legionella* bacteria. Results showed the total aerobic plate counts (APC) in the treated GBR circulating water decreased significantly and the turbidity was largely improved at a pulse voltage of 1.0 kV; *Legionella* bacteria were also disinfected effectively at 1.0 kV.

Chen *et al.* (2000) did some work on separation of pollutants from restaurant wastewater containing high amount of oil and grease. Aluminum electrodes were preferred for the treatment. **The results demonstrated that pH, conductivity and current density do not impose the significant change in the removal efficiency**. The main factor, which affects the removal efficiency, was “Charge Loading”. The optimum charge loading was found to be 1.67 – 9.95 F/m^3 and optimum current density was found to be 30 – 80 A/m^2. The removal efficiency of oil and grease exceeded 94% for all wastewater tested. **Moulai** *et al.* (**2004**) worked out on treatment of oil/water emulsion by coupling flocculation. They used electrodes made up of stainless steel. The temperature was kept constant at 25 C. The results showed that pH and initial concentration of oil impose a great effect on the removal efficiency and by reducing the initial concentration of oil; the separation may reach up to 99%.

Gotsi *et al.* (***2005)*** worked on Electro-chemical oxidation of olive oil mill wastewater. Titanium–tantalum–platinum–iridium anode was chosen for the treatment. The results showed that conversion of total phenols, COD and decolorization was generally increased with increasing voltage, conductivity, recirculation rate and lower initial concentration. Nearly complete removal of phenols and decolorisation can be achieved with in the first 15 – 30 minutes. The pH in range from 3 – 10 does not show any significant effect on electrochemical degradation of organics. COD removal was never exceeded 40% even after prolonged (up to 240 min) electrolysis time. The acute toxicity to marine bacteria *Vibrio fischeri* decreased slightly during the early stages of the reaction and toxicity to *Daphnia magna* increased sharply at short treatment times and remained quite high even after prolonged oxidation.

Cañizares *et al.* ***(2005)*** did work on oxidation of phenolic wastewater. Boron-doped diamond materials were used as the anode. The results obtained were as chlorinated phenolic compounds were transformed into carbon dioxide and volatile organo-chlorinated compounds while nitro-substituted phenols converted into polymeric materials. The efficiencies of the process depend strongly on the organic pollutants concentrations and on their nature, and not on the current density, pH etc. Similar type of work was done by ***Rajkumar*** *et al.* (***2004)*** *et al* worked on the treatment of phenolic waste from industrial wastewater. $Ti/TiO_2–RuO_2–IrO_2$ electrodes were used in the experiment. The current density was maintained at of 5.4 $A/dm^{2.}$ Absorbable organic halogens (AOX) were detected at high concentrations during the electrolytic treatment of the effluents. However, it was observed that increasing the electrolysis time bring down the AOX concentration to lower levels. **Körbahti** *et al.* *(*2003*)* worked on treatment of phenolic wastewater. They used the carbon electrode as anode during the experiment. For initial phenol concentration of 450 and 3100-mg l^{-1}, the applied current densities was 61.4 and 54.7 mA cm^{-2} respectively. The results showed that for 450-mg/l concentration of phenol, 40 minutes residence time was sufficient for complete removal and for 3100mg/l 3hours-electrolysis time was needed for complete removal.

Kimbrough *et al***. (2002***)* did work on removal of **bromide and reduction of THM** formation which are the by-products formed during the chlorination of natural waters from drinking water. The basic theory is Bromide is oxidized by electrolysis to bromine and then the bromine is apparently volatilized due to which by-products such as bromate and haloacetic acids are not formed. This electrolyzed water also reduced the formation of THMs.

Bejankiwar *et al***. (2002)** did work on treatment of cigarette industry wastewater. The wastewater mainly contains the process wastewater. The electrodes were made up of cast iron. The current and electrolysis time was maintained at 3.5 Amp and 5 hours. After the experiment about 56% of COD and 84% of BOD removal was observed. The treated effluent was than subjected to chemical coagulation studies using $Ca\ (OH)_2$ as coagulant and then It was concluded that the electrochemical treatment followed by chemical coagulation could be opted as an alternate treatment scheme for the present industry.

Hu *et al.* **(*2005)*** worked on removal of fluoride from semiconductor wastewater. The electrodes chosen were made up of aluminum. The current density and temperature was kept constant. The pH was maintained from 4-6. An anodic surfactant, “sodium dodecyl sulfate (SDS)” was used to improve the flotation process. The electrochemical process was done after the chemical treatment of waste water by calcium hydroxide. Results showed that the dissolved fluoride ions and CaF_2 particles were effectively removed in the ECF process. The dosage of SDS required for ECF was much less than those for dispersed air flotation (DiAF) or dissolved air flotation (DAF) processes.

Holt *et al.* **(2001***)* did a quantitative comparison between chemical dosing and electro coagulation based on turbidity removal by using a clay pollutant. Chemical coagulation was evaluated via jar tests using aluminum sulphate (alum). This proved more effective than electro coagulation under acidic conditions (pH $\sim$4) and low coagulant levels (4 mg-Al l^{-1}). Highly effective coagulation was observed at intermediate alum dosage levels (4–20 mg-Al l^{-1}), where the isoelectric point occurred at pH 7.8. Three operating stages (lag, reactive and stable) were identified in a batch electro coagulation reactor. At the isoelectric point, which occurs during the reactive stage, the greatest turbidity reduction occurs because of neutralization of charge and precipitation of aluminium hydroxide, which was also continued in stable stage. The optimum current was found to be in between 0.25- 2A and the optimum time was found to be 30 minutes for the maximum removal. **In his** (2005) another experiment he carried out some work on treatment of clay suspension electrochemical treatment to describe the future of electro-coagulation. In his experiment he chose the electrodes made up of aluminum as anode and stainless steel as cathode. The current density was kept in range from 3.4 to 27 A/m2. The results demonstrated that lower the initial pollutant concentration higher will be the removal efficiency. Current density was identified as the key operational parameter as higher the current density higher will be the removal of the pollutants. Similar results were found for the electrolysis time.

CHAPTER-4

Materials and Methods

This chapter presents the methodology adopted for the study. For achieving the objectives, the work was planned on the following work elements:

- Conceptualization of laboratory scale electrochemical treatment system.
- Construction and assembly of laboratory scale treatment system (includes two components: the reactor and the power system).
- Treatment of bleach effluent from a pulp and paper industry in the assembled electrochemical treatment system.
- Treatment of rubber industry wastewater in assembled electrochemical treatment system.
- Monitoring of the treatment processes in terms of pollutant removal.

Wastewater from rubber reclaiming industry and first extraction stage effluent from a pulp and paper mill were worked in the present study.

For devulcanizing, rubber is added with devulcanizing chemicals and treated in a paddle stirred horizontal autoclave at 180-220°C through steaming. After the devulcanization, contents of the autoclave are steamed out. The vapors vented out are condensed in two surface condensers connected in series. The wastewater in question is actually the condensate generated at these surface condensers.

This wastewater is categorized as high strength wastewater because of having high chemical oxygen demand (COD) concentration ranging from 12000-15000mg/l, high concentration of volatile oil. On standing, a layer of floating oil is separated on the top and a layer of settled oil is separated at the bottom. Please see table-1, for the characteristics of the wastewater.

Table-1: Characteristics of the rubber reclaiming wastewater

Sr. No.	**Parameter**	**Value**
1	pH	8.5
2	Conductivity (in µS/cm)	100 - 150
3	Chemical oxygen demand (mg/L)	12000-14000
4	Total suspended solids (mg/L)	160
5	Total dissolved solids (mg/L) 100°C	420
6	Total solids (mg/l)	580
7	Oil and grease (in g/L)	0.18

First extraction stage effluent from a large integrated pulp and paper mill using $C_DE_{OP}HC_PD$ bleaching sequence and processing mixture of bamboo and hardwood into paper was the second wastewater used in the present study. The procured effluent was filtered through 0.5 mm sieve, to remove large suspended solids. Characteristics of this effluent are given in table-2

Table 2: Characteristics of Bleach effluent

Sr No.	Parameter	Untreated
1	pH	8.1
2	Color (PCU)	10135
3	Turbidity (NTU)	35.6
4	Sulphate (mg/l)	0.1
5	Total Solids (mg/l)	4330
6	Total Suspended Solids (mg/l)	200
7	Total Dissolved Solids (mg/l) 100° C	4130
8	Total solids (mg/l)	4330
9	COD (mg/l)	1900

4.1: Experimental Setup:

A laboratory scale unit was used to conduct the experiments in the present study. The unit includes two components: The Reactor and the Power system.

The reactor is made up of acrylic material and its capacity is of 500 ml. it includes two electrodes (a cathodes and an anode). Two types of electrodes Aluminum and Stainless Steel, each of 50mm width, 200 mm length and 2 mm thickness were used in the present study. In any single experiment, both the electrodes used were of same metal. A schematic of the experimental set-up is shown in fig. 1. Spacing between the two electrodes was 12 mm. Provisions were made in the reactor for the change of electrodes. Polarity of current was reversed at regular intervals in order to minimize the deposition on the electrodes.

The power system was used to supply Direct Current (DC) at desired voltage to the electrodes. The system converted the input Alternating Current (AC) into Direct Current (DC) of desired voltage. Provisions were made in the power system to regulate voltage of the output and to display it on a handy multimeter. An Ampere of 0-8A range was fitted in the power system to display the amperage of the power supplied. There was also a provision for polarity change in the power system at desired intervals.

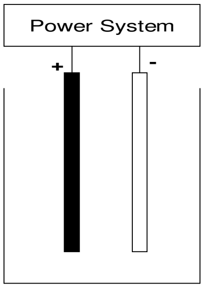


Fig: 3. Schematic diagram of experimental setup

Power System

Reactors

Stainless Steel Electrodes

Aluminum Electrodes

4.2: Rubber sample

The study on the effluents from the rubber reclaiming unit was conducted with both Stainless steel and Aluminum electrodes. Before each run the electrodes were washed with tap water and then dipped in chromic acid for 5 minutes to remove the impurities. The experiments were conducted after adjusting the effluent pH to different values with in the range of 2 to 8.5. Voltage is maintained constant throughout at 4V. For the adjustment of pH, 1N HCl was used. After adjusting pH, conductivity of the effluent was also measured. During each experiment, the amperage displayed on the ampere meter was noted down.

4.3: Bleach Effluent

In case of Bleach effluent also, the experiments were conducted with two types of electrodes: Stainless steel and Aluminum. Before each run the electrodes were washed with tap water and were dipped in chromic acid for 5 minutes to remove the impurities. All the experiments were conducted on the effluents, whose pH was adjusted to different values in range of 2-8. Voltage is maintained constant throughout at 5 V. for adjusting the effluent pH, 0.01 N Sulfuric Acid (H_2SO_4) was used. After adjusting the pH, prior to use, conductivity of the sample was also measured.

4.4: Analytical Techniques

4.4.1: Physical Parameters

pH was measured by electronic pH meter (CP-901) by CENTURY instruments after calibrating the pH meter with buffer solutions of pH 4.0, 7.0, and 9.2 *(Method no. 4500-B of Standard Method, 1989)*

Conductivity was determined by a conductivity meter (601-E) made by Deluxe instruments. The EC meter was calibrated with standard KCl solution of 0.1N strength. *(Method no. 2510-B of Standard methods, 1989)*

Turbidity of a sample was measured with Nephlometer which uses optical properties of light as the basis. *(Method no. 2130 -B of Standard Method, 1989)*

4.4.2: Chemical Parameters

Chloride was estimated by argentometric method (*Method no. 4500-B of standard methods, 1989*)

Chemical oxygen demand (COD) was determined by closed reflux (titrimetric) method, (*Method no 5220-C of Standard Methods, 1989*)

Total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS) were estimated by the method no. 2540-B, 2450-C and 2450-D respectively of Standard Methods, 1989

Oil-grease was determined by Partition-Gravimetric method (*Method No. 5520-B, 1989*)

The Color of the effluent samples was determined spectro-photometrically according to Canadian Pulp and Pulp Association (CPPA) Standard Method (1974)

Sulfate was estimated by gravimetric method ((*Method no. 4500-SO_4^{2-} D of standard methods, 1989*).

CHAPTER- 5

Results and discussion

5.1 Rubber wastewater

Wastewater from rubber reclaiming industry was studied for electrochemical treatment. Characteristics of these effluents are shown in table-1. A laboratory scale electro-chemical treatment unit with flexibility to use either stainless steel or aluminum electrodes was used in the study. Spacing between the electrodes was 12 mm and effective surface area of the electrodes was 200 cm^2. Electrochemical treatment of the wastewater was carried at different pH values for different durations of electrolysis and with different doses of electrolyte. For the pH adjustment of the wastewater Hydrochloric acid (HCl) was used and the acid consumed in the pH adjustment was estimated through constructing titration curve. Please see figure-4 for the titration curve. Conductivity at different pH was also measured and is shown in fig-4.. All the experiments were conducted on 400 ml of wastewater at 4 volts voltage using both the electrodes (stainless steel and aluminum). For avoiding fouling of the electrodes, current polarity reversals were practiced at 2 minute intervals. During the treatment, current measurements were made. Wastewater after the electro-chemical treatment was allowed to settle for 2 hours and in the supernatant COD was measured for assessing the treatment efficiency. A final experiment was conducted on the wastewater with the superior of the two types of electrodes, and the treated effluent obtained was characterized for different other parameters as well for assessing the treatment efficiency against the untreated wastewater

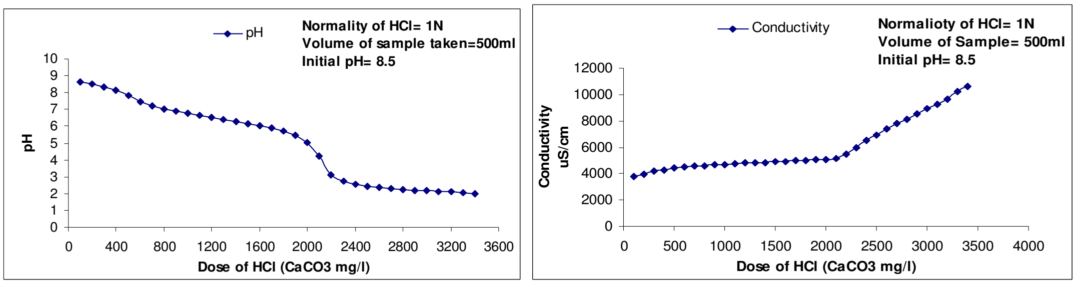


Figure 4: Titration curves showing acid consumed in the pH adjustment and conductivity value at different dose of acid

Results obtained from the electrochemical treatment experiments on the wastewater, after adjusting its pH to different values in the range of 2 to 8.5, are shown in table-3 and figure-5. Duration of electro-chemical treatment was maintained at 15 minutes in all these experiments. The results indicate that Stainless steel electrodes are superior to aluminum electrodes and best treatment efficiencies were obtained at 7 pH. At 7pH, with stainless steel electrodes COD was reduced by 63 %.

Table-3: Treatment efficiencies achieved through electro-chemical treatment of rubber wastewater at different pH values

pH	Current density		COD (mg/L)	
	SS elec.	Alum. Elec.	SS elec.	Alum. Elec.
2	290	330	3800	4100
3	275	310	4000	4200
4	220	285	4000	4200
5	215	275	5200	4300
6	195	250	5200	4300
7	190	230	**4400**	5000
8	80	30	9000	7000
8.5	75	26	9400	8000
Untreated effluent			12000	

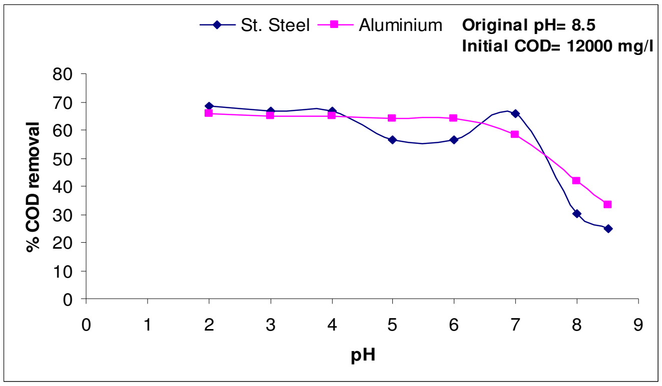


Figure 5: Treatment efficiency achieved through electrochemical treatment at different pH values of rubber wastewater

The experiments were conducted on the rubber reclaiming wastewater by stainless steel electrodes at pH 7 and with aluminum electrodes at pH 6 for different durations of electrolysis time. Results obtained are shown in table-4 and figure-X. The results indicate that duration of electrolysis is lower for stainless steel electrodes and optimum electrolysis time can be 15 minutes. For this duration at 4V voltage, electrical power consumption in the laboratory scale electrochemical treatment unit was found to be 2.875 kWh per cubic meter.

Table-4: Treatment efficiencies achieved through electro-chemical treatment of rubber wastewater at different time intervals

Voltage Applied= 4V

Time (Mins.)	COD (mg/l) (St. Steel)	COD (mg/l) (Aluminum)
5	9000	8500
10	7600	7500
15	**4400**	**4600**
20	4000	4400
25	3800	4400
30	3800	4200
35	4000	4200

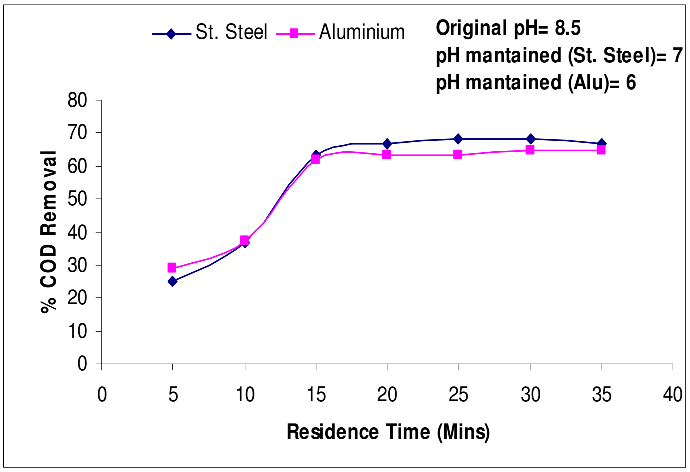


Figure 6: Treatment efficiencies achieved through electro-chemical treatment of rubber wastewater at different time intervals

Results obtained from the electrochemical treatment experiments on the wastewater, after adding the electrolyte at different concentrations ranging from 0.2 g/l to 2 g/l, are shown in table-5 and figure-7. The experiments were conducted by stainless steel electrodes at pH 7 and with aluminum electrodes at pH 6. Duration of electro-chemical treatment was maintained at 15 minutes in all these experiments. The results indicate that Stainless steel electrodes are superior to aluminum electrodes and best treatment efficiencies were obtained at 0.8 g/l of electrolyte dose. At 0.8 g/l of electrolyte dose, with stainless steel electrodes COD was reduced by 70 %.

Table-5: Treatment efficiencies achieved through electro-chemical treatment of rubber wastewater at different electrolyte doses

Voltage Applied= 4V

Dose of NaCl (g/l)	COD (mg/l) (St. Steel)	COD (mg/l) (Alu)
0.2	7000	6800
0.4	6800	6000
0.6	4800	**4200**
0.8	**3600**	4200
1.0	3600	4400
1.2	3640	4600
1.4	3640	4600
1.6	3800	4800
1.8	4000	4800
2.0	4000	4800

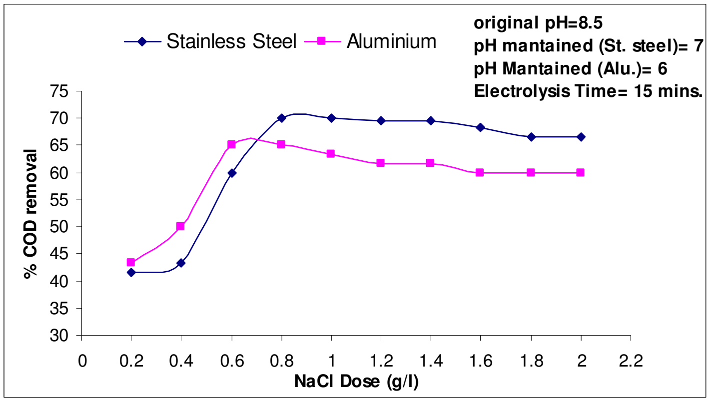


Fig. 7: Treatment efficiencies achieved through electro-chemical treatment of rubber wastewater at different electrolyte dose

Characteristics of the treated effluent after electro-chemical treatment, with aluminum electrodes at pH 7, electrolyte dose 0.8 g/l and voltage 4V for 15 minutes electrolysis time are shown in table-6. These results indicate that in addition to COD removal even oil and grease was getting removed by 78% efficiency. TDS is also getting removed significantly (50%). However the chloride concentration was found to increase. This has occurred from the hydrochloric acid used for adjusting the pH. pH of the treated effluent was higher (7.4), indicating that the electro-chemical treatment process has increased the pH.

Table-6: Table showing characteristics of untreated and treated wastewater

Sr. No.	Parameter	Untreated	Treated (St. Steel)
1	Alkalinity (mg/l) as $CaCO_3$	132	90
2	Acidity mg/l ($CaCO_3$)	Nil	750
3	COD mg/l	12000	3600
3	Chloride (mg/l)	100	1176.3
4	TDS (mg/l)	420	210
5	TSS (mg/l)	180	25
6	Oil and grease (mg/l)	180	38

5.2 Bleach Effluent

First extraction stage bleach effluents of an integrated pulp and paper mill were studied. Characteristics of these effluents are shown in table-2. A laboratory scale electro-chemical treatment unit with flexibility to use either stainless steel or aluminum electrodes was used in the study. Spacing between the electrodes was 12 mm and effective surface area of the electrodes was 200 cm2. Electrochemical treatment of the wastewater was carried at different pH values for different durations of electrolysis. For the pH adjustment of the wastewater sulfuric acid was used and the acid consumed in the pH adjustment was estimated through constructing titration curve. Please see figure-8 for the titration curve. All the experiments were conducted on 400 ml of wastewater at 5 volts voltage using both the electrodes (stainless steel and aluminum). For avoiding fouling of the electrodes, current polarity reversals were practiced at 2 minute intervals. During the treatment, current measurements were made. Wastewater after the electro-chemical treatment was allowed to settle for 2 hours and in the supernatant COD, colour and turbidity were measured for assessing the treatment efficiency. A final experiment was conducted on the wastewater with the superior of the two types of electrodes, and the treated effluent obtained was characterized for different other parameters as well for assessing the treatment efficiency against the untreated wastewater.

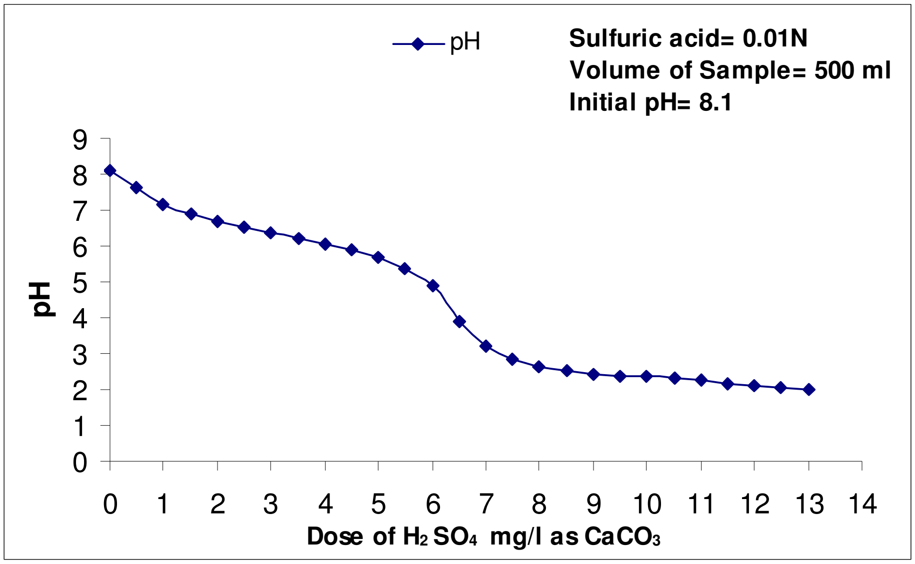
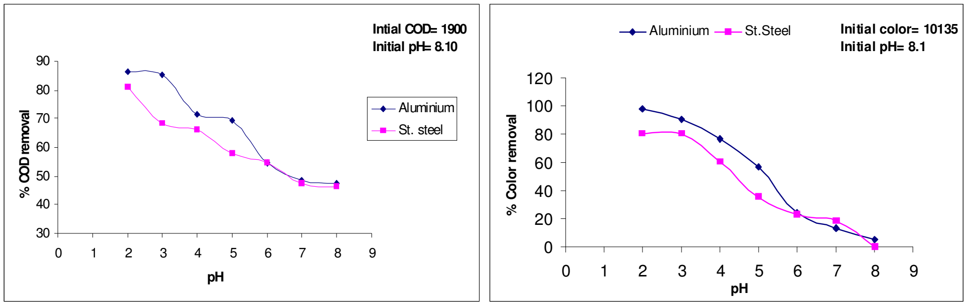


Fig. 8: Titration curve showing acid consumed in the pH adjustment of extraction stage bleach effluent

Results obtained from the electrochemical treatment experiments on the wastewater, after adjusting its pH to different values in the range of 2 to 8, are shown in table-7 and figure-9. Duration of electro-chemical treatment was maintained at 15 minutes in all these experiments. The results indicate that aluminum electrodes are superior to stainless steel electrodes and best treatment efficiencies were obtained at 2 pH. At 2 pH, with aluminum electrodes COD, colour and turbidity were reduced by 86%, 98% and 76% respectively. Initial turbidity of the wastewater was very low (35.7 NTU) and it was found increasing by electrochemical treatment at higher pH values.

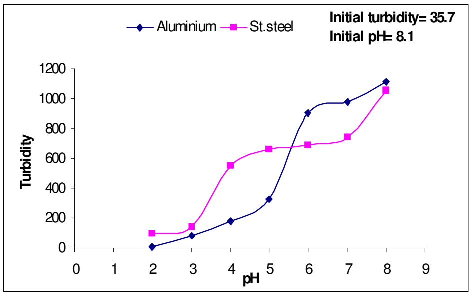
Table-7: Treatment efficiencies achieved through electro-chemical treatment of extraction stage bleach effluents at different pH values

pH	Current density		COD (mg/L)		Colour (PCU)		Turbidity (NTU)	
	SS elec.	Alum. Elec.	SS elec.	Alum. Elec.	SS elec.	Alum. Elec.	SS elec.	Alum. Elec.
2	262	274	360	**260**	1975	**199.3**	123.1	**8.5**
3	249	255	600	280	1993	926	140.5	79.5
4	200	240	640	540	4038	2395	550	180
5	190	210	800	480	7534	4353	660	326
6	188	200	720	960	7839	9650	690	906
7	180	170	1000	940	8250	9825	740	980
8	158	165	1020	1000	10125	9625	1100	1010
Untreated effluent	---		1900		10135		35.6	



9.a: COD removal

9.b: Colour removal



9.c: Turbidity removal

Figure-9: treatment efficiencies achieved through electro-chemical treatment at different pH values of the extraction stage bleach effluent.

Results obtained form the experiments conducted on the extraction stage bleach effluent at 2 pH for different durations of electrolysis are shown in table-8 and figure-X. the results indicate that duration of electrolysis is lower for aluminum electrode and optimum electrolysis time can be 15 minutes. For this duration at 5V voltage, electrical power consumption in the laboratory scale electrochemical treatment unit was found to be 3.425 kWh per cubic meter.

Table-8: Treatment efficiencies achieved through electro-chemical treatment at different time intervals of the extraction stage bleach effluent

Voltage Applied= 5V

Time (Mins.)	COD (mg/l) (Aluminum)	COD (mg/l) (St. Steel)
5	980	1020
10	440	540
15	280	360
20	280	320
25	260	300
30	260	280
35	260	280

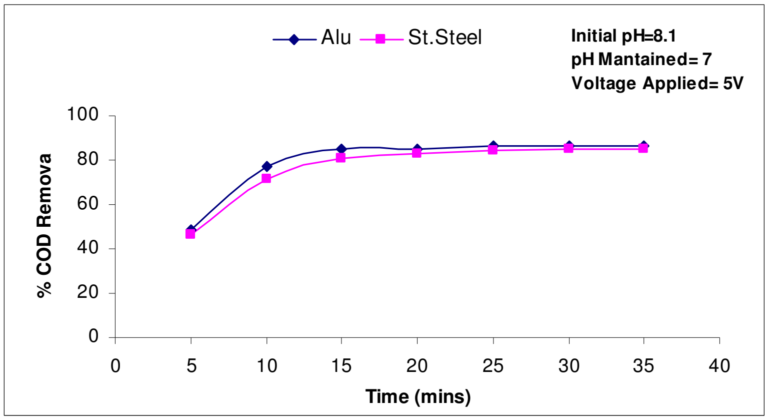


Figure 10: Treatment efficiencies achieved through electro-chemical treatment of the extraction stage bleach effluent at different time intervals

Characteristics of the treated effluent after electro-chemical treatment, with aluminum electrodes at pH 2 and voltage 5V, for 15 minutes electrolysis time are shown in table-9. These results indicate that in addition to colour and COD removal even AOX was getting removed by 86% efficiency. TDS is also getting removed significantly (23%). However the sulfate concentration was found to increase. This has occurred from the sulfuric acid used for adjusting the pH. pH of the treated effluent was higher (4.3), indicating that the electro-chemical treatment process has increased the pH and neutralized partially the acidity of the wastewater.

Table-9: Treatment efficiencies achieved through electro-chemical treatment of extraction stage bleach effluent

S No.	Parameter	Untreated	Treated (Al)
1.	pH	8.1	4.3
2.	COD (mg/l)	1900	260
3.	Color	10135	199.3
4.	AOX (mg/L)	96	12.6
5.	Turbidity	35.6	8.5
6.	TDS (mg/l)	4130	3200
7.	Sulphate (mg/l)	0.1	12.2

CHAPTER- 6

Conclusion

The electro-coagulation and flocculation process was used to treat the wastewater from a rubber reclaiming industry and the first extraction stage bleach effluent from an integrated pulp and paper mill. Treatment was optimized for the operational variables such as electrode type, influent pH, electrolyte dose and treatment time. Treatment efficiencies were assessed on the basis removal of color, turbidity, chemical oxygen demand (COD), oil and grease and total solids from the effluents.

In case of rubber sample, maximum removal efficiency was found with Stainless steel electrodes. Effluent pH of 7, voltage of 4 V, an electrolysis time of 15 minutes and electrolyte dose (NaCl) of 0.8 g/l gave best results when stainless steel electrodes were used. Under optimal conditions, COD, total solids and oil and grease of the effluent were removed by 70%, 50% and 80% respectively.

In case of bleach effluent, maximum removal efficiencies were found with Aluminum electrodes. Best results were obtained with aluminum electrodes at the voltage of 5V and at the pH of 2, for the electrolysis time of 15 minutes. Color, turbidity and COD of the first extraction stage effluent were removed by 98%, 76% and 86% respectively.

Power consumed was found to be high in both the cases of wastewaters. in case of rubber wastewater it was found to be 2.87kWh/m^3 and in bleach effluent it was 3.84kWh/m^{3} .

In respect to power consumption, it was concluded that this technology is costly for wastewater treatment but for some of the difficult wastewaters for which the alternative technologies are not feasible, this technology may proves to be appropriate for treatment.

It is also concluded that if this technology is used in large scale, then it may be cheaper or less costly in comparison to the lab scale observations.

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