TREATMENT OF AGRO BASED PAPER MILL EFFLUENT USING ELECTROCOAGULATION

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
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(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitle"**TREATMENT OF AGRO BASED MILL EFFLUENT USING ELECTROCOAGULATION**" in the partial fulfillment of the requirements of the award of the degree of **Master of Technology** in **Chemical Engineering** with specialization in **Industrial Pollution Abatement**, submitted in the **Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee,** is an authentic record of my own work carried out during the period from June 2004 to June 2005 under the supervision of **Dr. I. D. Mall,** Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter, embodied in this dissertation has not been submitted by me for the award of any other degree.

Date: 30 June, 2005
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This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

Paper industry consumes large amount of water and generate an equal amount of wastewater having high BOD, COD, pH, turbidity, high temperature, color etc. The environmental pollution problem for agro based paper mills is, however, different from the large integrated paper mills due to lack of recovery systems and use of short fiber.

Some of the conventional methods of treatments like activated sludge, trickling filters, stabilization lagoon, etc., are well known. However because of the color and presence of refractory organics, physico-chemical methods are being used in the polishing stage to meet the stringent environmental standards. Amongst various tertiary treatment processes, coagulation using lime, alum etc. are also being used.

Treatment of Paper mill wastewater from an Agro based Paper Mill by electrocoagulation is investigated. Laboratory scale Electrocoagulation experiments have been conducted using Aluminum electrodes, as anode and cathode for removal of COD and color. It has been found to be very effective in the COD and color reduction. Up to 90 %COD and 99 % color removal was achieved. Effects of various operating parameters like pH, number of electrodes, current density, electrode submergence, inter electrode spacing for electrocoagulation have been studied.

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CHAPTER 1

INTRODUCTION

1.1 General

Paper is an essential component of a modern society. Paper consumption for any country closely follows the growth economics of that country. As a component of people's consumption, paper contributes about 1% to the annual value of world economic activity- gross domestic product (GDP). For developing countries like India, the consumption of paper per unit of income has increased over the years.

India has over 16% of the world's population but consumes only 1% of world's paper and paperboard. But with the liberalization of the market economy, there has been an export and domestic growth rate of 6 %. As India enters the world of market the demand is high for paper and paperboards particularly the packaging grades, fine paper and other varieties (Rao et al., 1996).

Environmental degradation due to rapid industrialization has emerged as a major challenge world over in recent years. Paper industry that represents an important segment of the world economy has not remained unaffected with this phenomenon and is amongst the highly polluting industries. In addition to global competitiveness, a major issue that the paper industry all over the world is facing is the environmental problem. Environmental issues have become one of the important factors controlling the growth of paper industries during recent years.

1.2 Profile of Pulp and Paper Industry

Paper consumption for any country closely follows the growth economics of that country. As a component of people's consumption, paper contributes about 1% to the annual value of world economic activity- gross domestic product (GDP). World paper industry assumes nearly 3.5 % of the world industrial production and 2% of world's trade. Demand of paper and boards worldwide will reach 470 million tones in 2010 with an average annual increase of paper demand of about 3.7%. Paper and boards demand is estimated to reach 640 million times in 2020.

In India, paper mills manufacture paper and board, newsprint, rayon grade pulp etc. For developing countries like India, consumption of paper per unit income has increased over the years. India has over 16% of the world's population but consumes only 1% of the world's paper and paperboard. The modern paper industry in India was in a nascent state of development till the late 1950's. A thrust was given to boost capacity in the early 1960's. Several large integrated mills came on stream during the late 1970's but the growth apart from the expansion of existing capacity, has mainly been the result of creating new small mills. The average size of paper mills in India is now about 15,000 tpa (45 tpd) compared to 85,000 tpa (260 tpd) in Asia and 300,000 tpa (900 tpd) in Europe and North America. With merely 17 units in 1950 with production of 0.11 million tones paper, presently in India we have about 380 mills with a total installed capacity of around 4.2 million tones. There are 28 large mills and the remaining are small paper mills.

Non-availability of forest based raw materials and lower capital investment has resulted in the growth of small paper mills using non-conventional raw materials. The share of the agro-based mills is about 62% of the total production. However due to lack of recovery section in most of the agro based mills pollution load has become alarming especially with the new stringent environmental standards.

Per capita consumption of paper in India is the lowest at 6 kg compared to the South Asian and the world average of 11kgs and 53kgs respectively. The Indian paper industry has an installed capacity of 6.7mn tons while, the effective capacity is estimated to be lower at 6.15mn tons. The industry produced 5.26mn tons of paper in 2003-04. Newsprint capacity in India is estimated at 1.12mn tons however, domestic production is only 0.59mn tons, while consumption of newsprint is 1.1mn tons. With the entry of India into the world market, the demand for paper and paperboards particularly the packaging grades, fine paper and other varieties has gone up. (http://www.indiainfoline.com/nevi/pain.html)

Major raw material used by paper industry is bamboo, wood, bagasse, waste paper and agricultural residue like wheat straw, rice straw, jute sticks etc. and other unconventional non-woods from farms/ grassland besides waste paper and market pulp. Apart from this, paper industry consumes large amount of chemicals like caustic soda, sodium sulfide, sodium carbonate, chlorine, hypochlorite, mineral acid; coal, talcum powder etc. Process technology used is Kraft pulping, mechanical pulping, and semi chemical pulping. Majority of mills use CEH and CEHH bleaching sequences while very few mills use chlorine dioxide bleaching and oxygen delignification.

Table 1.1: Zone-Wise Installed Capacity for Manufacturing Paper and Paper Board in India

	Forest based		Agro based		Others		Total	
Zone	No. of Units	I.C.(000'T)	No. of Units	I.C.(000'T)	No. of Units	I.C.(000'T)	No. of Units	I.C.(000'T)
East	13	644	8	101	16	45	37	790
North	3	126	38	347	85	351	126	824
South	10	524	19	239	29	153	58	916
West	3	191	24	287	92	455	119	933

(I.C. = Installed Capacity) (Source: http://www.cpcb.nic.in/dec944.htm)

1.3 Need Cum Importance Of Small Agro Based Paper Mills

To understand the current drive for small paper mills based on agricultural residues principally bagasse along with wheat straw, rice straw, jute etc. one has to look at the following aspects

1.3.1 Depleting Forest Resources

Indian forestry is at cross road only 12% land area has good forest cover against the official figure of 19%. With fast depletion of forest resources large integrated mill that account for 38% of the total production are facing serious challenge (Rao et al., 1996).

1.3.2 National Forestry Policy Recommendations

The recommendations of national forest policy for forest-based industries very firmly illustrate that no forest supply would be forthcoming for the paper industry in the future. When demand will increase the raw material requirement cannot be sustained from the forest-based materials and the paper industry will have to increase the usage of agricultural residues mainly bagasse, straw, and other agro-based annual plants like kenaf and jute etc. National forest policy has forced the paper mills to look for alternative solutions (Rao et al., 1996).

1.3.3 Availability of Agricultural Residues

The present agro-based mills are using only small amount of the total available agricultural based raw material, so there exist a huge potential raw material waiting to be tapped which can be done only by small paper mills based on agricultural residues.

1.4 Major Challenges and Shortcomings

Paper industry is passing through bad times due to market recession. Energy, chemical and raw material cost in Indian paper industry is quite high as compared to the paper mills in developed countries. Some of the major problems which paper industry is facing today are poor infrastructure, too many administrative hurdles, tedious bureaucratic methods, recent setback from raising capital through equities for new companies/developing projects, uneconomic size and obsolete technology in many mills, high cost of production, poor productivity, poor instrumentation, low availability of forest raw materials, poor recycling of waste paper, non existence of recovery system in agro-based mills, decolorisation and detoxification, emission of odour and other air pollutants, high energy consumption.

1.5 Pollution Problem and Various Control Measures

Paper industry is one of the major polluting industries and is amongst top twenty-nine industries for which environmental impact assessment (EIA) has been made mandatory. Paper industry consume large amount of water (about 250-300 cu. m. per tones of water) and generate an equal amount of wastewater having high BOD, COD, pH, turbidity, high temperature and color. According to demand projections, the amount of waste water generated by the pulp and paper industry by the year 2015 will be 1197.15 m^3 per tones of paper, and the corresponding quantities for suspended solids, BOD and COD will be 12.37 lakh tones, 13.96 lakh tones and 56.05 lakh tones respectively.

1.5.1 Environmental Pollution of Agro Based Pulp and Paper Mills

In India, majority of the agro-based paper mills don't have chemical recovery systems. Therefore, these mills are facing serious problems. Due to high silica content of the agricultural residues, recovery of chemicals from the agro-based mills has caused a major concern. Black liquor from cooking residues has high silica content and cannot be concentrated to high solid contents to enable burning in conventional recovery systems. In small paper mills without recovery system, lignin content in wastewater is about 215-225 kg per ton of paper. Pollution load from small paper mill is nearly equal to that of big mills although paper production in small mills is only 20% of the total production of large mills. BOD load of the small paper mill without recovery is about 3-4 times that of integrated pulp mills having recovery systems.

1.5.2 Control Measures

Due to recent changes in environmental regulations for reducing chlorinated organic compounds, especially AOX, pulp mill all over world have shifted to elemental chlorine free or total chlorine free and even totally effluent free bleaching process. However, environmental issues in Indian paper industry are quite different from those in developed countries, due to poor infrastructure, poor economy, and uneconomic size of large number of mills. Moreover, these mills are still using conventional bleaching sequences using chlorine and hypochlorite. Large numbers of small agro based paper mills still do not have proper recovery and wastewater treatment facilities.

The biological treatment considerably improves the characteristics of the effluent in terms of DO, BOD, COD to safe limits. Anaerobic treatment is an attractive treatment alternative for pulp and paper mills effluents as the organic load in the effluents could be recovered partially as methane, a valuable energy source. Furthermore, less energy would be needed for aeration in the secondary and tertiary treatments to meet the discharge standards and the excess sludge production will also be low.

Biological processes are cost effective in comparison to physico-chemical processes; however, biological processes may not be sufficient for the removal of the toxicity desired permissible limit. In general, aerobic microbial processes become less effective in biodegrading compounds as the degree of chlorination increases (Vogel et al., 1987). Therefore, tertiary treatment of the segregated bleach plant effluents, which contains a majority of the chlorinated compounds, is a potential option for removal of chlorinated organics.

Physico-chemical methods have been used in full scale or large-scale pilot plants but none of these methods can be considered commercially viable technology. These methods can be divided into the following: (a) adsorption and ion-exchange methods, (b) flocculation and chemical precipitation methods, (c) membrane methods, (d) oxidation and other methods (Avijit et al., 1991).

1.6 Environmental Standards

For the preservation of natural resources of earth and protection and improvement of human environments, several acts, rules, regulations, and standards have been enforced. Environmental standards for pulp and paper industry all over the world have also been modified. Minimal national standards and emission standards for pulp and paper industry are given in Table 1.1.

Table 1.2: Small Pulp & Paper Industry: Standards For Liquid Effluents

Mode of Disposal	Parameter	Concentration not to exceed, mg/l (except for pH and sodium absorption ratio)
Inland Surface Water	pH	5.5 to 9.0
	Suspended solids	100
	BOD at 27°C, 3 days	30
Land	pH	5.5 to 9.0
	Suspended solids	100
	BOD at 27°C, 3 days	100
	Sodium absorption ratio	26
c) Raw meat from other sources	disposal via screen and septic tank	

Source: EPA Notification

S.O. 64(E), dt. 18th Jan 1998

Small Pulp & Paper Industry: Waste Water Discharge Standards*

CATEGORY

A: Agro based	200 cum/ton of paper produced
B: Waste Paper Based	75 cum/ton of paper produced

* The agro based mill to be established from January, 1992 will meet the standards of 150 cum/ton of paper produced.

** The waste paper mills to be established from January, 1992 will meet the standards of 50 cum/ton of paper produced.

Large Pulp & Paper/News Print/Rayon Grade Pulp Plants of Capacity above 24000 Ton/Annum: Wastewater Discharge Standards

Parameter/ Flow	**Concentration not to exceed**
(i) Large pulp & paper	200 cum/ton of paper
(ii) Large rayon grade/news print	175 cum/ton of paper
pH	6.5 to 8.5
SS	100 mg/l
BOD at 27°C for 3 days	30 mg/l
COD	350 mg/l
TOCL*	2.0 kg/ton of paper produced

- The standards for TOCL will be applicable from January, 1992.

Source: EPA Notification [GSR 93(E), dt. Feb. 21, 1991]

Large Pulp & Paper: Emission Standards

Parameter	**Concentration in mg/Nm^3**
Particulate Matter	250**
H_2S	10

** This standard of 250 mg/m^3 (normal shall apply only for a period of 3 years with effects from the date on which the Environmental (Protection) Second Amendment Rules, 1989, came into force.

After three years the standards to be applicable is 150 mg/m^3 (normal).

SO_2 in kilns above 5 ton/day capacity.

Source: EPA Notification [G.S.R. 913(E), dt 24th Oct., 1989]

1.7 Objective of Study

The objective of the project is to carry out Electrocoagulation for the removal of color and COD of the agro based paper mill wastewater using Aluminum electrode.

The effect of following parameters on COD and color removal from effluent has been studied:

(1) Effect of pH.
(2) Effect of number of electrodes.
(3) Effect of current density.
(4) Effect of electrode submergence.
(5) Effect of inter electrode spacing

SEM and TGA of the sludge generated during electrocoagulation has been studied.

CHAPTER 2

PROCESS TECHNOLOGY OF PULP AND PAPER MILL

2.1 General

Although the history of papermaking dates back to the first century B'C the modern process dates back to the opening of the Frog more Mill in England in 1798 producing paper from rags. The extreme short supply of rags was alleviated in the late 1870s when it became technically feasible to produce pulp from wood. This was a turning point in the development of the industry, which subsequently evolved to a fully mechanized industry. Subsequently, paper mills came to be located by rivers with afforested catchments, facilitating transport of the mill wood furnish and the use of the rivers for power and process water.

2.1.1 Wood Fiber

Wood is a natural composite material consisting of hollow, flexible tubes of cellulose bonded together and rigidified by glue called lignin.

Trees can be divided into two general classes - softwoods and hardwoods. Softwood trees are conifers - e.g., southern pine, douglas fir, spruce. Hardwood trees lose their leaves every year- e.g., birch, aspen, and red gum.

Softwood fibers with their length and coarseness are generally used to provide strength to a sheet of paper. Hardwood fibers, being finer and more conformable, give a sheet of paper its smooth printing surface and opacity. Hardwood fibers are also easier to bleach to high brightness because they have less lignin.

2.1.2 Non-Wood Fiber

Bamboo is the major raw material of paper industry, however, due to depletion in bamboo resources, various raw materials started in early seventies. According to their origin, the non-wood fibers are divided into agricultural by-products, industrial crops and naturally growing plants.

Agricultural by-products are the secondary products of the principal crops (usually cereals and grains) and characterized by low raw material price and moderate quality such as rice, straw and wheat straw. Industrial crops such as hemp and kenaf can produce high quality pulps with high expense of the raw material cost, but the source of the pulp is limited and these materials come from crops planted specifically to yield fiber. Naturally growing plants are also used for the production of high quality pulps. This includes some grass fibers such as elephant grass, reed and sabai grass. Unlike the conventional Kraft process (sulfate process), these mills do not generate hydrogen sulfide and mercaptans (organic sulfides), as sodium sulfide is not used in pulping. The pollution is mostly confined to the surrounding of the mill.

The proximate analysis of various raw materials is given in Table 2.1 (Mall et al. 1989).

2.2 Raw Materials

2.2.1 Rice and Wheat Straw

Rice and wheat straw are by product of agricultural operations and are available in huge quantity, and are major raw materials for small paper mills. About 1.5 ton rice straw pr ton of rice and 2.5 tones of wheat straw per ton of wheat is produced in our country (Mall, Upadhyay, 1989).

Straws contain higher percentage of silica and hemi-cellulose compared to other conventional raw materials. Presence of silica, extraneous materials like grain, husk, leaves etc. affect pulp quality. As the straws have short fibers, the area required for washing straw pulp in vacuum washer is three times that required for bamboo due to its allow drainage problem.

2.2.2 Bagasse

The bagasse has enormous potential in papermaking. 95 % of total bagasse produced is presently wasted for uneconomical use as fuel. Bagasse forms about 30 % of sugarcane, consists of 50 % moisture and 50 % fiber along with the cells. The fiber content of bagasse is about 65 %, pith 30 % and soluble 5 %. Pith is undesirable fraction because it contains non-fibrous cells below 0.4 mm length. Removal of pith is done by dry, moist or wet depithing. Depithing reduces the drainage characteristics of the pulp and increases the fiber pick up problem. Depending on the degree of depithing the pulp may have 5-12 % pith. Bagasse pulp has high degree of hydration and requires higher washing area. Higher dilution factor is used resulting in weak black liquor strength. Bagasse pulp has slower drainage characteristic and requires mild refining. Bagasse has higher water holding capacity and requires special design considerations in press and drying section (Mall, Upadhyay, 1989).

2.2.3 Jute Sticks

They are available in huge quantity and have good potential. About 2.5 kg of jute sticks is produced per kg of jute fiber. Jute stick pulp has slow drainage characteristics resulting in higher dilution factor and reduced washer capacity, the pulp require blending with long fiber to have satisfactory drainage and strength properties (Mall, Upadhyay, 1989).

2.3 Chemical Requirement

Sodium hydroxide, lime, chlorine, hypochlorite, sulfites are the normally used chemicals in paper industry. Sodium hydroxide requirement is essentially for agriculture residue based industry and it varies with the raw material. However when bagasse is used the requirement for alkali would be as high as 12 % of the raw material used. Lime is used as the supplement to sodium hydroxide. Chlorine and calcium hypochlorite are used as bleaching chemicals. Sizing chemicals such as alum, starch, talc, rosin are used (Comprehensive Industry Document for Small Pulp and Paper Industry, 1986).

2.4 Process Technology for Pulping, Bleaching and Papermaking

Pulp and papermaking is a combination of following major steps.

Raw Material Preparation	
Bamboo and wood	Debarking, washing, chipping, screening
Bagasse	Depithing (wet/dry), cutting screening
Straw	Cutting and screening
Pulping	
Bamboo and wood	Cooking of the chips with cooking liquor containing Na_2S, NaOH, Na_2CO_3, $Na_2S_2O_3$ etc., temperature 170-180^{0}C, pressure 7-7.5 Kg/cm^2
Agricultural residues	Cooking at 130^{0}C and 3.5-5 Kg/cm^2 pressure using 8-10% caustic soda.
Mechanical pulping	Mechanical pulping use thermo mechanical pulping, stone ground pulping, chemi-mechanical pulping, refiner mechanical pulping, cold soda refiner mechanical pulping
Washing And Screening Cleaning	Washing of the cooked pulp in a 3 or 4 stage brownstock washers for the recovery of black liquor, two stage screening and 3-4 stage centricleaning for the removal reject sand and other foreign material.
Bleaching	Bleaching of the pulp using chlorine, caustic soda, calcium hypochlorite, chlorine dioxide, oxygen ozone, hydrogen peroxide.
Stock Preparation And Paper Making	Imparting suitable property for paper making by heating, refining, additives of dyes, additives and rosin size conversion of pulp from stock preparation into a sheet of paper.
Chemical Recovery	Concentration of spent black liquor in multiple effect evaporators, burning of concentrated black liquor, clarification of black liquor, causticising of black liquor with lime for production of white liquor, reburning of lime sludge to produce lime.
Power Generation	Generation of steam and power using coal, fuel oil, bagasse, rice husk, etc.

Processes of pulp and paper manufacture in a large integrated kraft mill and in an agro based paper mill are shown Fig. 2.1 and 2.2 respectively.

2.4.1 Pulping

All pulping processes are designed to separate the wood fibers present in the wood. In principle, there are two ways of pulping, mechanical and chemical pulping. A summary of key comparisons is given in Table 2.2.

2.4.1.1 Mechanical Pulping

In mechanical pulping, cellulose fibers are removed from the wood matrix by thermal softening of lignin and micro-abrasion. There are two basic types of mechanical pulping stone ground wood and chip refining. Both of these mechanical pulp processes produce pulp, which has quality, and cost factors that differ from those of chemical pulp.

(a) Stone Ground Wood (SGW)

In this process, logs are subjected to repeated shear and compression at high loading rates and temperature to produce fibers suitable for papermaking. Sizable amount of electrical energy is required to produce mechanical pulp. This energy is referred to as "specific energy", i.e., the energy required per unit mass of dry fiber. Power consumption depends on quality of pulp (freeness) needed. Higher quality (lower freeness) requires higher energy consumption.

These processes essentially grind the raw wood to produce a pulp yield of between 90 and 98% in modern systems. Modifications to the process include the use of steam as a lignin-softening agent and carrying out the process under positive pressure. Uses of this pulp are generally restricted to applications such as newsprint, toilet tissues and paperboard since it tends to yellow on age due to the content of residual lignin.

(b) Refiner Mechanical Pulping (RMP)

This process differs from ground wood pulping principally in the use of chips, wafers and sawmills wastes as feedstock. The dominant process is thermo-mechanical pulp where the wood chips are preheated and steamed before being fed to one of the three standard disc-refiner systems. The resulting pulps are somewhat less bright for a given wood species than ground wood pulps.

There are many types of chip refining. The basic type is open discharging refiner; here the refiner is operated without externally applied pressure in the refining zone. Pulp passes through the eye of the refiner and radially outward between a bar pattern.

(c) Thermo Mechanical Pulping (TMP)

In thermo mechanical pulping, wood chips are pre-steamed to raise their temperature. They then pass into a refiner, which is externally pressurized at the same pressure as the steamer. Thus, the refining process is carried out at elevated temperature. In most TMP processes, chips are passed to a second open discharge refiner for further fiber development.

The original objective of TMP refiners was to lower the energy consumption in refining and improve fiber quality, instead, the mechanical energy to produce TMP is larger than that required for stone ground wood, and producing longer fibers since fibers are more easily removed from the wood matrix.

2.4.1.2 Semi-Chemical Pulping

Semi-chemical pulping processes are characterized by a chemical pretreatment stage followed by a mechanical refining step. The process uses predominantly hardwoods and can accommodate wood of relatively inferior quality and wood obtained from mixed stands. The best known of these processes is the neutral sulphite semi-chemical process and it involves impregnation of the chips with sodium sulphite liquor, followed by cooking at 160-190^{0}C and a subsequent disc refining stage. The pulps produced typically have 10-15% residual lignin, much higher than the full chemical pulps. The pulp has high rigidity and stiffness and is used in corrugated boards as well as printing papers, greaseproof papers and bond papers. There is no clear differentiation between the semi-chemical processes and the high yield chemical processes, which are generally modifications of the normal kraft and sulphite pulping methods.

2.4.1.3. Chemical Pulping

(a) Alkaline Chemical Pulping

The two major alkaline processes for producing chemical pulps are the alkaline sulfate or "Kraft" process and the soda process. In both these processes, wood chips are cooked with sodium hydroxide in order to dissolve the lignin that binds the fibers together. Sodium sulfide is an additional component of the pulping chemical mix in the kraft process. Both processes are named according to the regeneration chemicals used to compensate for sodium hydroxide: sodium sulfate and sodium carbonate.

The kraft process is not only the dominant chemical pulping process but also the most important overall in terms of the various production methods. The soda process is important largely in the production of non-wood pulps.

The pulps produced by the Kraft process are characterized by good strength properties. They are, therefore, the preferred grades in strong paper grades such as the liner in corrugating boards or bag and wrapping papers. Hardwood Kraft pulps are used in many printing papers for bulking purposes, in mixture with softwood pulps.

Various modifications to the Kraft and soda processes have been devised in order to attempt to overcome low pulp yields and environmental problems. These generally involve the addition of chemicals to the digest liquor. The most important of these is anthraquinone (AQ). The benefits of AQ pulping include increased delignification rates together with reduced alkali charges and improved pulp properties.

Regeneration of the Cooking Liquors

An integral and economically vital part of alkaline pulping mill operations is the regeneration of the cooking liquors. The main steps in the process are the evaporation of the black liquor drained from the digester after wood chip digestion, combustion of the concentrated liquor to produce a mineral "smelt", causticization of the smelt and regeneration of the lime used in the process. The energy content of the black liquor is high.

The heart of the process is the recovery furnace. The black liquor is evaporated to a solid content of between 60-75% using a 5-6 stage system and this is followed by direct contact evaporation in which flue gas from the recovery boiler is brought directly into contact with the liquor. Tall oil soaps are recovered during the evaporation stages. Oxidation of the liquor prior to evaporation can be carried out to reduce the emission of malodorous compounds.

When the black liquor is concentrated, sodium sulfate and other chemicals are added to compensate for those lost in the pulping process. In the recovery boiler, the organic content is combusted to produce heat. Carbon dioxide reacts with sodium hydroxide to produce sodium carbonate. The added sodium sulfate is reduced to sodium sulfide and hence the solid smelt produced by the boiler contains largely sodium carbonate and sodium sulfide. This is dissolved in a tank to produce the green liquor, which is subsequently filtered and treated with calcium hydroxide (slaked lime) to convert the sodium carbonate to sodium hydroxide. The resulting white liquor is then returned to the digestion process. Heating and mixing with water removed from the green liquor regenerate the lime. This process is, therefore, theoretically closed in relation to water use but not with respect to atmospheric emissions, spills and condensate generation.

Kappa Number

The residual lignin present in the pulp is expressed in terms of the "kappa number" which is determined by the oxidation of lignin by potassium permanganate under acidic conditions. The lower the kappa numbers of a pulp, the lower the level of residual lignin.

Kappa number x 0.15% = % Lignin in pulp

(b) Sulfite Chemical Pulping

These are the acidic sulphite process, bisulfite process, multi-stage sulphite process, neutral sulphite process and alkaline sulphite process. All are described in terms of the composition of the cooking liquor that in turn defines the process pH and the choice of basic chemicals used. The gas sulfur dioxide is used to generate the sulphite chemicals used in digestion. Pulping conditions vary widely according to the mill furnish and the different processes produce pulps of differing chemical composition and papermaking application.

(c) Organosolv Pulping

This pulping method has been receiving increased attention in recent years. Solvent pulping offers a number of potential advantages over conventional pulping techniques such as relatively low chemical and energy consumption coupled with low capital costs and low environmental impact.

Aqueous organic solvents such as methanol and ethanol are used for delignification to produce a bleachable pulp, which can be bleached with non-chlorine chemicals. Pilot scale tests have given high pulp yields with strength properties similar to sulphite and Kraft pulps.

In most pulp and paper processes, some type of stock screening operation is required to remove oversized, troublesome, and unwanted particles from good papermaking fibers.

2.4.2 Pulp Processing

2.4.2.1 Pulp Washing

Chemically digested pulp is discharged into a blow pit or on a perforated floor where part of the black liquor (BL) also known as spent liquor drains out. In some mills the cooked materials is directly taken for washing in pouchers where washing is done by vacuum rotary drum. The washing continues for 2-3 hours and is in series if more than one poucher is used. The pulp wash is one of the major sources of wastewater besides black liquor. The drained out black liquor joins the pulp wash water before leaving the unit. The wastewater leaving this section is very strong initially and weak in final stages of washing.

2.4.2.2 Beater, Centri-Cleaner, Thickner

Pulp from the poucher is dumped to beater either directly or through storing chest depending on the operation schedule. Pulp is beaten to separate the fibers and remove adhering dirt, chemicals and color. Some mills employ washing along with beating thus creating a source of wastewater. From beater, the pulp is screened and then taken to centri-cleaner for removal of heavy inorganic particles (mostly sand), it is then pumped to thickner where water is sucked by rotary drums and discharged as wastewater. The pulp in this section still contains some color but it can be used to make boards and unbleached paper.

2.4.3 Bleaching

Pulp, especially dark Kraft pulp requires bleaching in order to be bright enough for many paper grades. In bleaching, residual lignin, which is the main reason for dark color of pulp, is removed by bleaching chemicals.

The bleaching is carried out in a sequence that consists of many stages. In these stages, oxidative and extractive treatment of pulp alternates with each other. After each stage, washing is done and the wash water is used for dilution in previous bleaching stage and finally led to wastewater treatment plant. This is the main source of water pollution in chemical pulp mills. Classes of bleaching chemicals used are strong oxidizing agents, alkali and metal removal agents

(a) Chlorination

Oxidizing chemicals can either degrade the lignin or remove color from the pulp depending on operating conditions

Elemental chlorine (Cl_2) is an effective delignifying agent. As it breaks lignin bonds, it adds chlorine atoms to the lignin degradation products, thus producing significant amounts of chlorinated organic material.

$$\textbf{Lignin} + Cl_2 \Rightarrow \textbf{Chlorinated organic compounds}$$

Chlorine dioxide (ClO_2) is a highly selective chemical that can both delignify and brighten pulp. It oxidizes lignin, but does not add chlorine atoms onto lignin fragments; however, small amounts of elemental chlorine and other chlorine compounds formed during the chlorine dioxide bleaching process react with degraded lignin to form chlorinated organic compounds.

$$\textbf{Lignin} + ClO_2 \Rightarrow \textbf{Oxidized Lignin} + HOCl \Leftrightarrow Cl_2$$

Important point to note is that the elemental chlorine and chlorine dioxide react differently with lignin. Elemental chlorine breaks up the lignin molecule by adding chlorine to the lignin. Chlorine dioxide transfers oxygen to the lignin to break up the rings. Hypochlorous acid is also formed. It can react directly with the aromatic rings on the lignin or be converted to elemental chlorine. Thus, the only way to be sure that chlorinated organic compounds including dioxins are not formed in the bleaching process is to eliminate all chlorine-based bleaching chemicals.

Ozone (O_3) is an effective delignifying agent and also brightens the pulp as well. Ozone has not been used in the past because mills have not been able to improve its selectivity - ozone attacks the cellulose fiber as well as the lignin. Recent technological developments, however, have solved this problem and have allowed mills to take advantage of this cost-effective bleaching agent.

Oxygen (O_2) is an inexpensive, highly effective delignifying agent that is usually used at the beginning of the bleaching process. It has intermediate selectivity.

Sodium hypochlorite ($NaOCl$) is an inexpensive delignifying agent formed by mixing elemental chlorine with alkali at the mill. Mills are phasing out the use of hypochlorite because it generates large quantities of chloroform when it is used to bleach pulp.

Hydrogen peroxide (H_2O_2) is mainly used to brighten pulps in the final bleaching stages. Peroxide is often used at the end of a conventional bleaching sequence to prevent the pulp from losing brightness over time. Researchers have found operating conditions under which peroxide will delignify pulp, and are working on technologies that will consume less.

Chlorine, chlorine dioxide and ozone work best when they are run in acidic conditions at pH that range from 1.5 to 4. Once the bleaching reactions are finished, the pulp is washed to remove the degraded lignin or other organic waste that has been dissolved in the wastewater. Much of the organic waste, however, consists of organic acids and alcohols. These compounds are not soluble in acidic water so they remain with the pulp during washing.

(b) Alkali Extraction Process

In the alkali extraction stage, these organic acids and alcohols (degraded lignin products) react with the caustic (sodium hydroxide) to form organic sodium compounds and water. These organic substances do dissolve in water. In fact, most of the color and organic waste in mill effluent comes from this first extraction stage. There is much less organic waste in the second extraction phase, if one is used, because very little lignin is removed in the later stages of the bleaching process.

R-COOH	+	**NaOH**	=>	**R-COO-Na**	+	**H_2O**
Organic acid insoluble in water		Caustic soda (sodium hydroxide)		Organic sodium salt soluble in water		Water

Oxygen, hydrogen peroxide or both are often added to the caustic solution to enhance the removal of organic waste.

After bleaching or in case of production of unbleached pulp after screening, the pulp is pumped to paper mill or dried and then transported to end-use site.

2.4.4 Stock Preparation for Papermaking

The objective of this step is to process the pulp, and then combine it with additives into the papermaking furnishes. The following operations are practiced in the paper mills:

2.4.4.1 Dispersion

Pulpers are used to disperse dry pulp into water to form slush or slurry. The stock in the pulper is accelerated and decelerated repeatedly, and hydrodynamic shear forces are produced by the severe velocity gradients. The resulting forces serve to loosen fibers and reduce any flakes into individual fibers.

2.4.4.2 Refining

The term beating or refining means mechanical treatment of chemical pulp at low consistency (1.5-8%). Beating and refining are synonymous, since refiners are commonly used to beat pulp stock. While little is known about the physical processes that occur in refining, much is known about how they affect fiber structure. External and internal fibrillation, creation of fines and loss of cell wall materials are changes that have been observed in fibers following beating.

Refining is arguably the most important papermaking step, incorrect practices at this stage are very difficult to rectify later in the process. In old days, refining of fiber was a batch process and, in a sense, an art form. The beatermans' knife was often the primary subjective tools used to judge proper beating. The continuous process replaced the batch process, thus the ability to feel the stock disappeared.

2.4.4.3 Metering and Blending Of Furnishes

Blending provides required pulp to water ratio before sending it to paper machine. Further conditioning by chemicals such as alum, rosin, talc and acid to suit requirements of final paper quality and addition of dyes to make colored paper are also adopted.

The pulp components are supplied from a high-density storage tank. Therefore, a series of controlled dilution steps and mixing stages are necessary to achieve a uniform consistency. Accurate proportioning of pulps and additives into a blend is the major task of this stage.

2.4.5 Papermaking Process

Paper making process starts from preparing stock, refining and mixing long and short fibers, fillers and chemicals. Impurities are removed by screening before entering to flows spreader.

Flow spreader takes the incoming stock flow and distributes it evenly across the machine from back to front. The head box gives high turbulence into the stock and discharges a uniform jet of papermaking stock onto the forming fabric. Consistency of the stock is 0.2-1 %. Endless rotating fabric forms a continuous matted web while the water removal elements drain the water by pressure or suction forces.

Original fourdrinier former has one fabric only. Hybrid formers have two fabrics and it forms a less two-sided web. Latest development is gap former where jet from head box enters directly into the gap former by two fabrics.

The sheet (dry content 15-22 %) is conveyed through a series of roll presses where additional water is removed and the web structure is consolidated. After press section, dry content of the web is 45-55 %. In the drying section water is removed by heating the web on steam heated drying cylinders. During drying fiber to fiber bonds are formed and paper gets its strength. By calendaring, the thickness of paper is adjusted at target value and web is reeled on the pope. Jumbo reels are winded and packed to be shipped to end-users.

Table 2.1: Proximate Analysis of Various Raw Materials

Raw Material	Ash%	Solubilities			Ponto-sans	Lignin	Cellu-lose	Hemi-cellulose	Holo-cellulose
		Hot water	1% NaOH	Alcohol-benzene					
Bamboo	2-3	5-9	15-20	1-3	18-21	15-30	40-49	19-21	70-80
Softwood	0.2-0.5	3-5	10-20	2-4	8-9	23-33	55-60	10-15	72-80
Hardwood	0.3-0.5	5-6	10-20	2-4	18-20	16-25	45-50	20-25	75-88
Rice Straw	8-16	10-15	40-48	3.8-6	24-30	10-22	26-28	24	60-74
Wheat Straw	8-10	8-12	-	3.2-5.5	23-28	21.0	32	21	-
Bagasse	1.8	3.5-3.8	27-36	1.2	27-30	16-22	30-35	28	72
Jute sticks	0.6-1.2	1-1.5	25-30	1.2-1.8	18	18-21	41	25	76
Sabai grass	6.0	9.5	38.90	4.0	23.9	22.0	3	-	66.4
Kenaf	2.4	7.9	27	1.86	-	21.5	38	-	72

Source: Mall et al. (1989)

Table 2.2: Comparison Of Mechanical And Chemical Pulping Processes

General Parameters	**Chemical/ Semi-Chemical**	**Mechanical/Chemi-Mechanical**
Yield fiber/Wood	Low 40-70%	High 90-98%
Cellulose purity	High	Low
End Uses	High quality paper Reinforcement Dissolving pulp	Lower quality paper High volume (Newsprint, Magazines)
Raw material sensitivity	Low	High
Quality Parameters		
Strength	High	Low
Bulk	Low	High
Optical	Dark but bleachable Poor opacity	Bright but hard to bleach High opacity
Drainability	Good (few fines)	Poor (many fines)
Permanence	Good	Poor
Cost Parameters		
Raw material capital	High	Low
Operating (chemicals, energy etc.)	High	Low
Auxiliary (pollution etc.)	High	High
Total	High	Low

Source: Cleaner Production at Pulp & Paper Mills: A Guidance Manual UNEP I&E

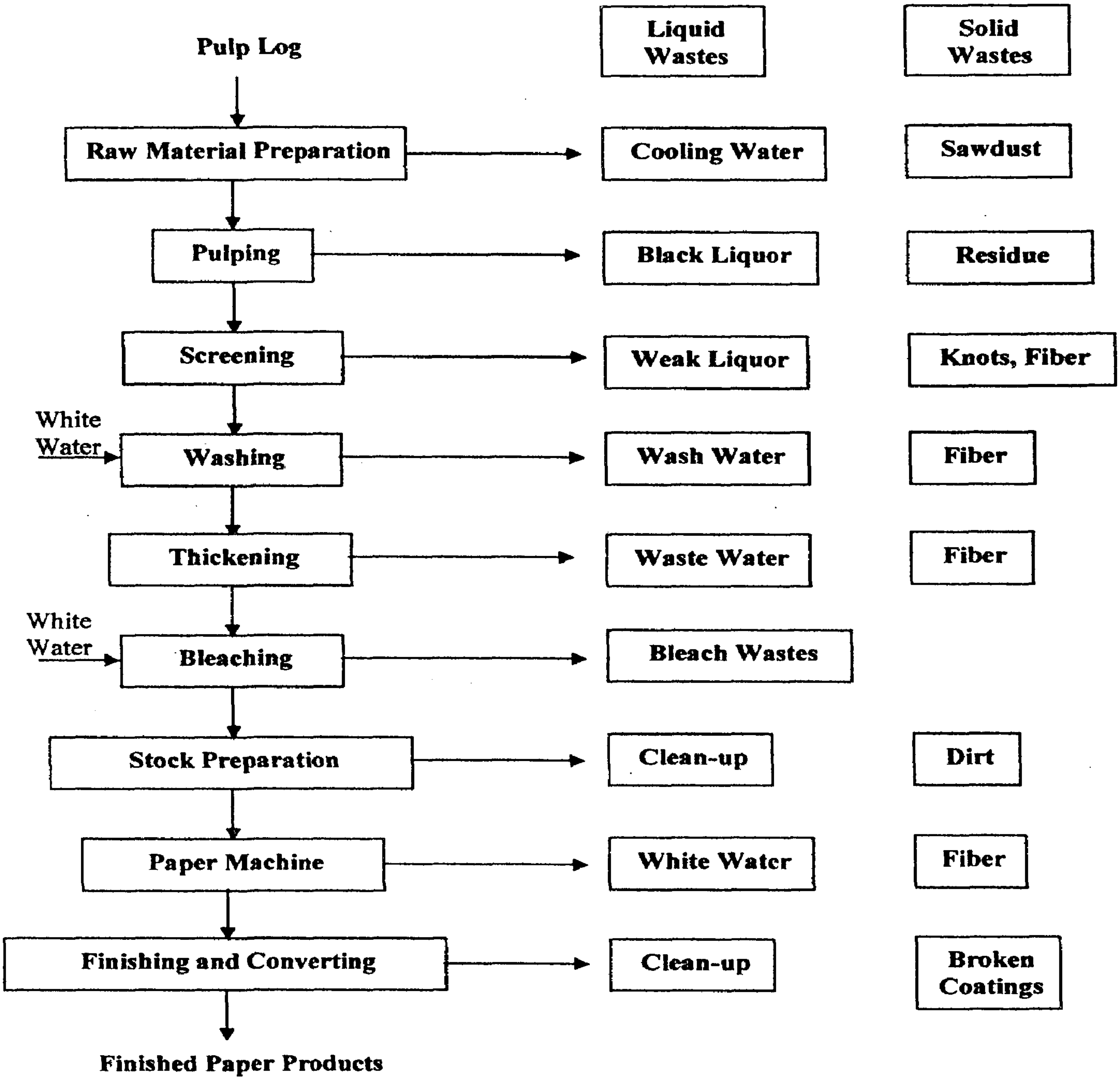


Fig. 2.1: Process flow diagram indicating waste streams

contaminated streams from uncontaminated or less contaminated streams to determine the correct size of the effluent treatment plant.

Typically, wastewater treatment requires a two-stage process i.e. primary (physical) and secondary (biological) treatment. The purpose of *primary treatment* is to remove the suspended solids from the effluent. This is usually done in a clarifier, which is a circular tank where the particles (fibers) are allowed to settle under gravity. The sludge collected at the bottom is withdrawn from the clarifier and can be handled by a variety of methods. Most commonly the sludge is dewatered through belt presses.

Wastewater Treatment Plant

Major steps in the wastewater treatment include the following steps:

- Flow Equalization
- Physico-chemical Treatment
- Primary Treatment for reduction in organic load (Aerobic or Anaerobic Treatment)
- Secondary Treatment to reduce the organic load (Aerobic Treatment)
- Tertiary Treatment for treatment of Residual Refractory Organics

A number of technologies exist for *secondary treatment*. Table 3.4 gives the details of the major technologies that are available for dealing with the wastewater from pulp & paper mills.

Air Pollution Control Schemes

Table 3.5 summarizes different air pollution points and treatment majors usually adopted in the Pulp and Paper industry.

3.5 Strategies and Possible Solutions for Pollution Control in Small Agro Based Mills

(Jain et al., 1996)

3.5.1 Increased Use of Recycled Paper

Replacing virgin pulp with recycled waste paper decreases the overall pollution load in the mill and at the same time energy demand in terms of raw material, input chemicals, and waste materials also gets reduced.

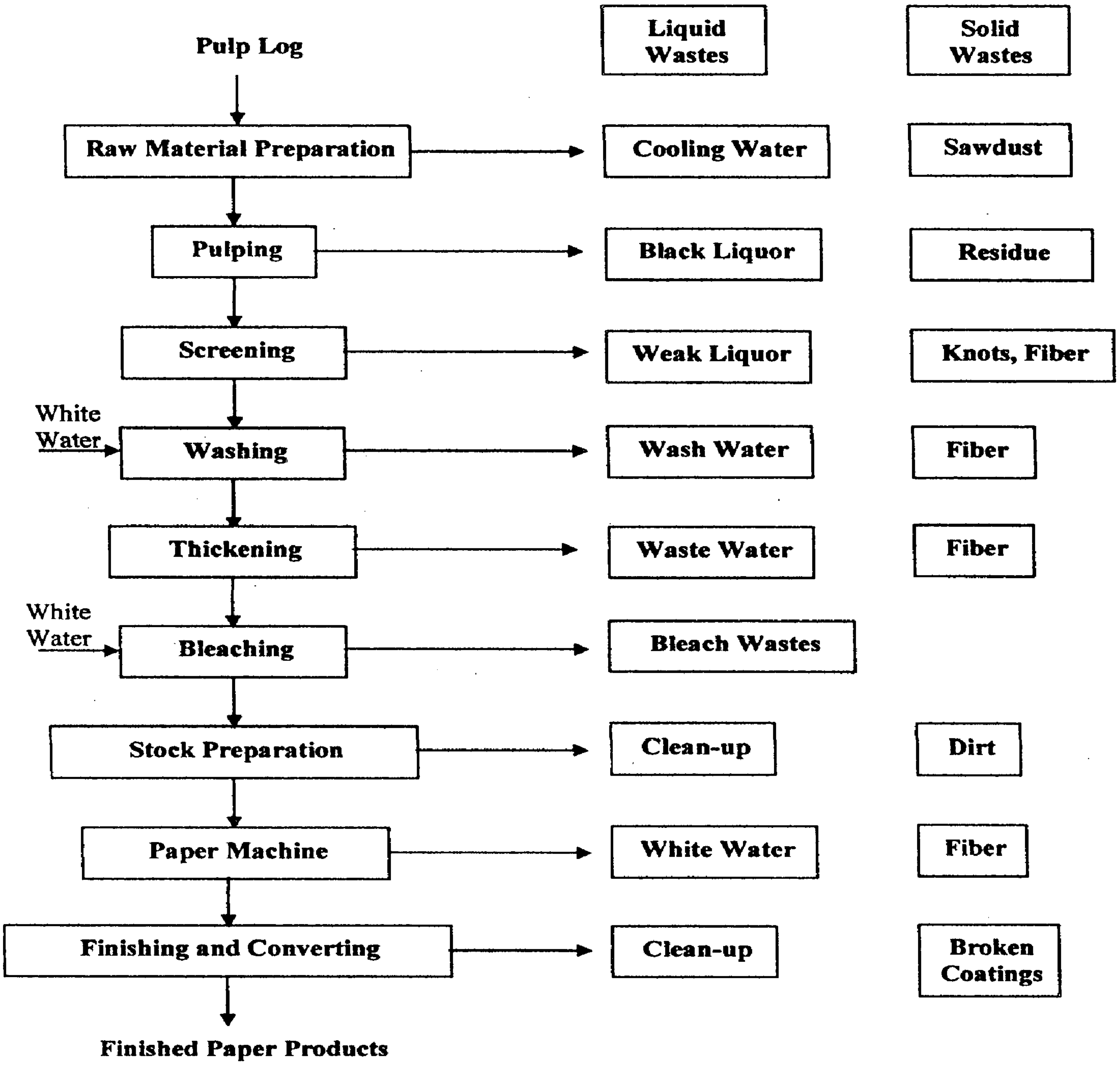


Fig. 2.1: Process flow diagram indicating waste streams

Chapter 3

Environmental Challenge in Pulp and Paper Industry

Pulp and Paper industry is an intensive industry. It is intensive in terms of raw material consumption, chemical consumption, energy consumption, water consumption, capital requirements besides pollution load generation.

3.1 Process wise Pollution Sources

This section looks at different sources of pollution in an integrated pulp and paper mill. Figure 3.1 represents the pollution sources in terms of solid, liquid and gaseous phase. Major pollutants and solid wastes from pulp and paper industry is given in Table 3.1 .The potential pollutants from a pulp and paper mill fall into four principal categories as under:

(i) Water Effluents:

(a) Suspended solids including bark particles, fiber, pigments, dirt, and the like.

(b) Dissolved colloidal organics like hemicelluloses, sugars, lignin, compounds, alcohols, turpentine, sizing agents, adhesives like starch and synthetics, which create BOD load.

(c) Color bodies, primarily lignin compounds and dyes.

(d) Dissolved inorganic such as NaOH, Na_2SO_4 bleach chemicals etc.

(e) Thermal loads

(f) Micro-organisms such as coliform group.

(g) Toxic chemicals if present.

(ii) Particulates:

(a) Fly ash from coal fired power boilers

(b) Chemical particles primarily Na and Ca based

(c) Char from bark burners

(iii) Gases:

(a) Malodorous sulfur gases such as mercaptans and H_2S released from various stages in Kraft pulping and recovery processes

(b) Oxides of sulfur from power plants, Kraft recovery furnace, and lime kiln

(c) Steam since it can be hazardous when visibility is impaired

(iv) Solid Wastes:

(a) Sludge from primary and secondary treatment and causticizing in kraft mill recovery section.

(b) Solids such as grit, bark and other mill wastes.

(c) Ash from coal fired boilers

The gaseous emissions released from digesters, chemical recovery furnace, steam boiler are H_2S, SO_2, SO_3 and malodorous gases (like mercaptans Dinethyl sulfide, Dimethyl Disulphide). The odor problem in Kraft mills is essentially due to reduced sulfur compounds.

3.2 Environmental Issues in Indian Pulp and Paper Industry

Due to environmental pressure and strict regulatory parameters, and market pressure for eco-friendly product environmental issues has emerged as a major challenge and will continue to be single most important factor influencing the technological change in pulp and paper industry. Environmental issues have been cause of major concern in pulp and paper mills especially with discovery of dioxins and furans all over the world. However, the problem in Indian paper mills is quite complex due to low average capacity of the mills in India especially the agro-based mills. Majority of India mills are still using the conventional pulping and bleaching process which has higher consumption of fibrous raw material, water, chemicals, steam etc. resulting in higher generation of wastewater. Major environmental issues in Indian paper mills are:

- Deforestation
- Large use of water and generation of large volume of wastewater.
- Generation of toxic and color effluents.
- Lack of recovery system in agro-based paper mills.
- Emission of odours and toxic chemicals.

- Emission of particulate matter.
- Generation of large amount of solid waste
- Poor recycle of waste paper.

3.2.1 Deforestation

Although the paper industry in India is primarily tree free as about 62% of the market is catered by paper products from non-conventional raw materials like agro waste, agro residues and recycle paper. However, the industry is also held uncharitably responsible for the denudation of forests. Total wood requirement of wood for paper industry is projected at 5-7 million tonnes by 2010 which is 1.5% of the total wood required for fuel, wood industry, and timber paper industry. However, in spite of small portion of total wood consumption by paper industry, Indian paper needs sustainable forest management to meet the future demand of paper industry for maintenance of environmental stability. Through preservation and restoration of ecological balance, there is a need to evolve a comprehensive policy which should aim at allocation of forestland to industry where feasible and promotion of agro based mills through incentives.

3.2.2 Waste Water Generation

Water is a prime natural resource, a basic human need and a precious national asset and optimum development and efficient utilization of water resources assumes great significance. Paper industry is highly water-intensive. Water consumption and wastewater generation in Indian paper mills is considerably higher than their counter part. Paper industry discharges large amount of wastewater containing high pH, color, suspended solids, BOD, COD, chlorinated organic compounds, dioxins, furan etc. Washing efficiency in case of agricultural residue pulp is poor due to slow drainage resulting in higher wastewater generation. Wastewater generation and characteristics of effluent from large integrated mill, agro based paper mill and waste paper mill is given in Table 3.2 [Mall & Prasad, 1998].

Being a large mill with different types of stages, paper industry discharges a lot of liquid effluent from different stages of the processes. The sources of liquid waste are shown in the Table 3.3. Figure 3.3 shows the wastewater generated from different sections of a large integrated mill.

3.2.3 Generation of Toxic and Color Effluent

A relatively large number of pollutants have been identified in pulp and paper mill effluent which are responsible for toxicity and color. Bleach plant effluents present the highest pollution load and are responsible for generation of toxic and colored effluent. During bleaching using chlorine and chlorine dioxide, absorbable organic halides (AOX) which include series of chlorophenols dioxin, and furan are formed which are highly toxic and carcinogenic. Most of the mills in other parts of world have shifted over from even CEDED or CEHDED sequences to DEDED or relate sequences reinforced with oxygen and peroxide such as DCEOPDED. However, majority of the mills in India are still using traditional CEH or CEHH bleaching sequences except few large mills which have gone for chlorine dioxide bleaching and oxygen delignification. Effluent color is largely as a result of lignin and lignin degradation products such as aromatics and quinoid nuclei, carbonyl and ethylenic groups. Structures involved in formation of color are large molecular weight compounds. Caustic extraction stage in bleaching is responsible for 60-70% of kraft mill effluent color loading. In view of the great variety of reactions involved in the various stages of bleaching, large number of chlorinated organic matters are produced the amount of which depend on types of raw material, bleaching chemical, bleaching condition and extent of bleaching. Due to increasing public awareness and decreasing tolerance levels towards color discharged into natural water, stream decolorisation of paper mill effluent is also becoming important issue along with detoxification.

3.2.4 Recovery of Chemicals from Agro-based Paper Mill

Although paper mills based on agricultural residues are playing important role in sustainable development of paper industry in India through utilization of non-conventional fibrous raw materials, however, agro-based paper mills are cause of major concern for Indian paper industry due to lack of recovery section in large number of mills. Black liquor from cooking of agricultural residues has high silica content and cannot be concentrated to high solid content to enable its burning in conventional recovery system. Pulp crushing in agro-based mill contributes more than 60% of the total pollution load. Apart from pulp washing, bleach plants from agro-based mills also contribute significant toxicity as majorities of mills are using either CEH or only hypobleaching.

3.2.5 Emission of Odorous Gases and Particulate Matter

Emission of odour is a major problem in the kraft mills as highly malodorous gases hydrogen sulphide, mercaptans, dimethyl sulphide, dimethyl disulphide are emitted at various stages of operation in pulping and recovery section. Emission of chlorine and chlorine dioxide is also a problem from various sections of caustic chlorine and bleaching plants. Particulate emission from recovery furnace and power plants are also cause of concern due to poor performance of control equipments. In agro-based mill, air pollution occurs from straw cutters, digester blow tanks, steam boilers, hypo preparation plant, bleaching plants etc.

3.2.6 Solid Waste Generation

Large amounts of solid waste are generated at various stages of pulp and paper manufacture. Solid waste generated and their source is given in Table 3.1.

3.3 Pollution Control in Pulp and Paper Industry

The pollution from pulp and paper industries is a major environmental challenge worldwide. The most polluted effluents originate from the pulping and bleaching section of the mill and constitute more than 90% of the total pollution load.

The conventional treatment of pulping effluent could be a wastewater treatment plant. The wastewater treatment technologies can remove pollutants up to 90%. This means that a mill with BOD_5 of 6500 mg/l will end up with 650 mg/l BOD5 that is still higher than the MINAS permissible limit.

Other possible solution, which is widely being implemented in the large and medium sized paper mills world wide, is the Chemical Recovery Plant (CRP). However, this also requires huge investments.

These technological and financial limitations ask for alternate approach, which are technologically simple and financially cost effective. These are possible with Cleaner Production (CP) techniques, which will considerably reduce pollution load and water consumption. CP techniques have higher rate of return.

3.3.1 End-of-Pipe Treatment Options

Whether or not the above CP options are implemented (including or excluding Chemical Recovery Plant) end-of-pipe treatment is required to meet the effluent quality standards. For end-of-pipe treatment, it is essential to segregate all the contaminated streams from uncontaminated or less contaminated streams to determine the correct size of the effluent treatment plant.

Typically, wastewater treatment requires a two-stage process i.e. primary (physical) and secondary (biological) treatment. The purpose of *primary treatment* is to remove the suspended solids from the effluent. This is usually done in a clarifier, which is a circular tank where the particles (fibers) are allowed to settle under gravity. The sludge collected at the bottom is withdrawn from the clarifier and can be handled by a variety of methods. Most commonly the sludge is dewatered through belt presses.

Wastewater Treatment Plant

Major steps in the wastewater treatment include the following steps:

- Flow Equalization
- Physico-chemical Treatment
- Primary Treatment for reduction in organic load (Aerobic or Anaerobic Treatment)
- Secondary Treatment to reduce the organic load (Aerobic Treatment)
- Tertiary Treatment for treatment of Residual Refractory Organics

A number of technologies exist for *secondary treatment*: Table 3.4 gives the details of the major technologies that are available for dealing with the wastewater from pulp & paper mills.

Air Pollution Control Schemes

Table 3.5 summarizes different air pollution points and treatment majors usually adopted in the Pulp and Paper industry.

3.5 Strategies and Possible Solutions for Pollution Control in Small Agro Based Mills

(Jain et al., 1996)

3.5.1 Increased Use of Recycled Paper

Replacing virgin pulp with recycled waste paper decreases the overall pollution load in the mill and at the same time energy demand in terms of raw material, input chemicals, and waste materials also gets reduced.

3.5.2 Segregation of Spent Liquor

The prevailing system practiced in small agro based mill is batch pulping followed by washing. Because of lack of chemical recovery systems these mills don't care about effective washings. Normally the mills employ poacher washers followed by one or two drum washers. Often the drum washers do not work at the desired efficiency levels due to lack of required pulp mat formation and thereby the desired vacuum is not achieved. This results in use of high quantities of water for black liquor extraction. Introduction of belt washer after the blow tank before existing washing system may help in extracting the black liquor in the concentrated form.

3.5.3 Incineration of Segregated Stream

One option of immense practical application is that these mills evaporate the segregated stream to solids concentration up to 30-35 % at the mill site itself using a single/two stage system. This spent liquor in semi-concentrated form at the solids concentration of 30-35% w/w may be transported to a nearby integrated paper mill where it can be treated along with the black liquor of the wood. Adoption of this practice may help the small mills to gat rid of more than 50% of pollution load in terms of BOD and COD and at the same time achieve the desired standards.

3.5.4 Partial Lignin Removal Followed by Anaerobic Treatment of Combine Effluent

In this method there is pretreatment of black liquor in which lignin could be recovered partially from segrated concentrated weak liquor stream. This may result in 50% reduction in COD load and color load. The resultant liquor rich in carbohydrates and low molecular weight becomes more prone to bio-methanation.

3.5.5 Bio-methanation of Effluent Resulting After Lignin Removal

The anaerobic treatment system is more popular now due to its ability to handle effluents with high concentration of COD and generation of bio-gas as a source of bio-energy from the effluents generated in small pulp and paper mills such as waste paper, chemi-mechanical, thermo-mechanical and after removal of lignin can be successfully treated by anaerobic means which could be further treated by conventional aerobic process to get the desired discharge limits.

3.5.6 Corporate Chemical Recovery System for Mills with a Capacity of 30 TPD and Above

To have such a corporate recovery systems certain modalities have to be work out for the participating mills such as:

1) Cooking conditions have to be optimized so that the resulting spent liquor in each mill has minimum solids concentration of around 8% with minimum required active alkali.
2) The spent liquor from the mills may be transported to common site by means of pipelines.
3) Proper facilities of storage of different types of liquor at common site choosen.

With such an arrangement, received chemical can be shared by the participating mills.

3.5.7 Common Effluent Treatment Plant

For mills of very small capacities in the range of between 5-30 TPD if located in close proximity of each other can have combined effluent plant based on lignin removal followed by biomethanation and activated sludge process. In this process, lignin removal can be brought to the common treatment plant to treatment the effluent by bio-methanation process followed by conventional activated sludge process.

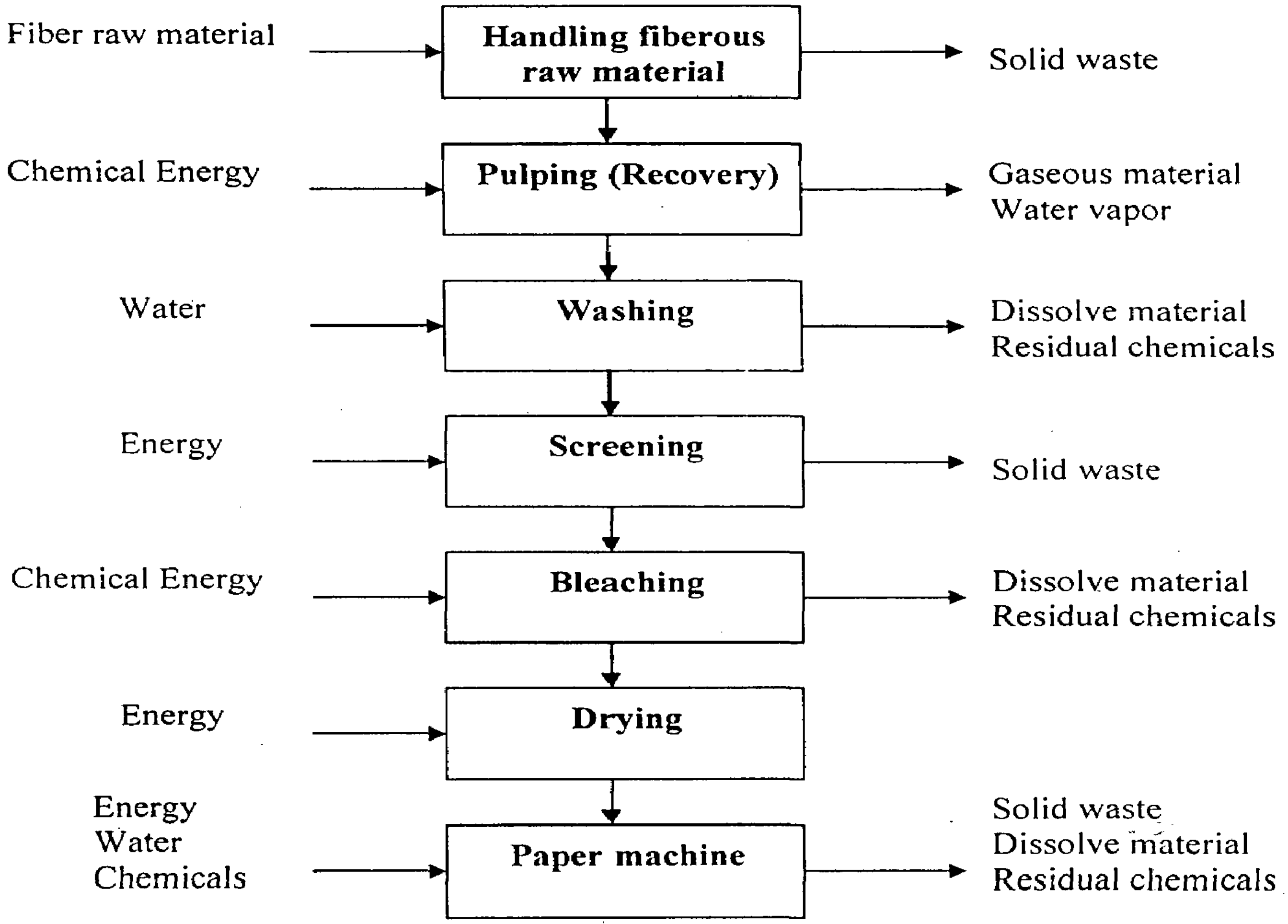


Fig. 3.1: Pollution Sources (UNEP IE, 1996)

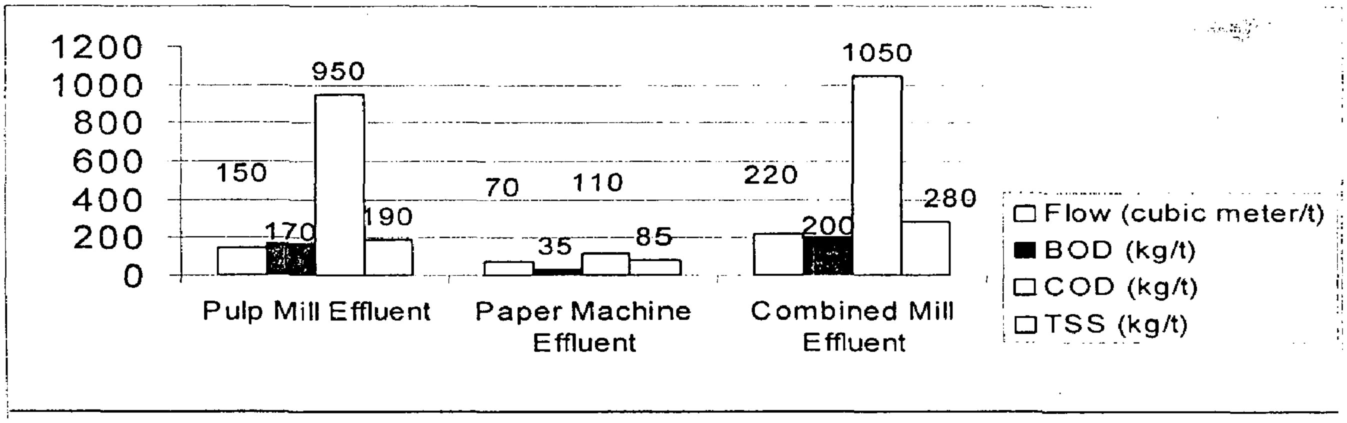


Fig. 3.2: Waste Water Generation in a Large Integrated Mill

Table 3.1: Characteristics of Effluent Generated From Large Integrated Mill, Agro Based Paper Mill and Waste Paper Mill

Parameter	Large Integrated Mill	Agro Based Mill	Waste Paper Based Mill
COD, mg/l	150-300	1000-2000	50-100
BOD, mg/l	50-80	200-400	20-50
Suspended solids, mg/l	150-300	300-400	250-350
Wastewater generation m^3/ton of paper	200-350	200-250	70-150
Lignin, kg/ton of paper	40-50	200-350	-
Sodium, kg/ton of paper	-	60-150	-

Table 3.2: Wastewater Sources in Pulp and Paper Mill

Section	Source
Raw material preparation	Conveying wash of wood/bamboo, deplithing, debarking, chip washing.
Pulping	Digester steam condensate, leakage from digester condensate, floor washings, screening, and washing.
Bleaching	Bleaching stage, bleach liquor pump leakage, bleach liquor spillage, and floor washing.
Stock preparation	Refiner/beater, centricleaners, saves all spillage floor washing.
Paper machine	White water over flow, condensate, floor washing, cooling water.
Power plant	Coal washing, condensate, and cooling tower, blow down.
Recovery plant	Lime slacker, evaporator, condensate cooling water in furnace, caustising, clarifiers, and blow down.

Table 3.3: Technologies for Wastewater Treatment in Pulp and Paper Mills

Solutions	Technical Characteristics	Operational Characteristics
Aerated Lagoons	Anaerobic lagoons are deep earthen basins used for high strength organic wastewater with high solid concentration. Facultative lagoons are earthen basins filled with screened or primary effluent in which stabilization of waste is brought about by a combination of aerobic, anaerobic and facultative bacteria. Aerobic lagoons are large, shallow earthen basins used for treatment of wastewater by natural processes involving both algae and bacteria. Maturation ponds are low rate stabilization ponds usually designed to provide for secondary effluent polishing and seasonal nitrification.	• BOD loading kg/m3/d – least efficient • BOD removal efficiency – 85 -90% • Energy requirement for aeration kWh/kg BOD treated – moderately efficient • Hydraulic detention time—very high • mechanical complexity – low • Reactor resilience for power failure and shock loads – moderate to high • By product – nil • On-site environmental impacts - soil infiltration and aerosols dispersion • Land requirement --- large • Man power requirement – skilled • Frequency of repair & maintenance -medium
Activated Sludge Treatment (Single and Two Stage Reactor)	Many variations of activated sludge treatment exist, depending on load characteristics. In case of high organic loading conventional, one-stage activated sludge will not yield the required results. Two Stage Activated Sludge System consists of two aeration tanks and mechanical surface aerators. This arrangement is in order to achieve to treat effluent with BOD and COD in the ranges of 4000-8000 mg/l and 6000-14000 mg/l respectively.	• BOD loading kg/m3/d – very efficient • BOD removal efficiency – 85-95% • Energy requirement for aeration kWh/kg BOD treated – least efficient • Hydraulic detention time — moderately efficient • mechanical complexity – high • Reactor resilience for power failure – low and for shock loads – moderate • By product – Sludge • On-site environmental impacts - aerosol dispersion and noise • Land requirement --- moderate

		• Man power requirement – highly skilled • Frequency of repair & maintenance - very high
Up-flow Anaerobic Sludge's Blanket (UASB) Reactor	Per-sedimentation, anaerobic treatment and final sedimentation are essentially combined in one reactor. No sedimentation tank is necessary. Flocs of anaerobic bacteria tend to settle under gravity (when applying moderate up-flow velocity); anaerobic bacteria develop and settle in reactor compartment; organic compounds are consumed by the bacteria during passage of wastewater through sludge layer. During anaerobic degradation, biogas is formed (principally composed of methane). This is collected in gas collectors and can be used as an energy source.	• BOD loading kg/m3/d – very efficient • BOD removal efficiency – 80-90% • Energy requirement for aeration kWh/kg BOD treated – most efficient (only for pumping) • Hydraulic detention time—most efficient • mechanical complexity – low • Reactor resilience for power failure and shock loads – moderate • By product – bio-gas • On-site environmental impacts - nil • Land requirement --- small • Man power requirement – highly skilled • Frequency of repair & maintenance -low • Problem of H_2S formation in case of high sulphide contents in effluent

Table 3.4: Air pollution control devices used at various air pollution points

Process	Air Pollution control Device
Raw Material Preparation	Dust Collection System, Scrubbers, Collection and burning of odorous gases
Utilities (Boiler)	Scrubbers, Electrostatic Precipitators
Paper Making Machines	Dust Collection System
Paper Cutting Machines	Dust Collection System

CHAPTER 4

FUNDAMENTALS OF ELECTROCOAGULATION

Treatment of wastewater by electrocoagulation has been practiced for most of the 20th century with limited success and popularity. In the last decade, this technology has been increasingly used in South America and Europe for treatment of industrial wastewater containing metals. It has also been noted that in North America EC has been used primarily to treat wastewater from pulp and paper industries (Bhabha et al., 2004), mining and metal-processing industries. In addition, electrocoagulation has been applied to treat water containing foodstuff wastes (Chen et al., 2000), oil wastes (Bergmann et al., 2003), dyes (Daneshvar et al., 2004), suspended particles, chemical and mechanical polishing waste (Lai & Lin, 2003), and organic matter from landfill leachates, defluorination of water (Shen et al., 2003), synthetic detergent effluents, mine wastes and heavy metal-containing solution (Adhoum et al., 2004). Typically, empirical studies are done on electrocoagulation to define major operating parameters for broad classes of contaminated water or waste streams. The technology has been optimized to minimize electrical power consumption and maximize effluent throughput rates. This approach, which provides little insight into the fundamental chemical and physical mechanisms, does not allow modeling of the process or the design of improved systems, process control, and optimization from fundamental physico-chemical principles (Mollah et al., 2001).

4.1 Coagulation and Electrocoagulation

Coagulation is a phenomenon in which the charged particles in colloidal suspension are neutralized by mutual collision with counter ions and are agglomerated, followed by sedimentation. The coagulant is added in the form of suitable chemical substances. Alum [$Al_2(SO_4)_3 \cdot 18H_2O$] is such a chemical substance which has been widely used for ages for wastewater treatment. The mechanism of coagulation has been the subject of continual review. It is generally accepted that coagulation is brought about primarily by the reduction of the net surface charge to a point where the colloidal particles, previously stabilized by electrostatic repulsion, can approach closely enough for the van derWaal's forces to hold them together and allow aggregation. The reduction of the surface charge is a consequence of the decrease of the repulsive potential of the electrical double layer by the presence of an electrolyte having opposite charge. Electrocoagulation is the process of destabilizing suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electrical current into the medium. The electrical current provides the electromotive force to drive the chemical reactions. When reactions are driven or forced, the elements or compounds will approach the most stable state. Generally, this state of stability produces a solid that is either less colloidal and less emulsified (or soluble) than the compound at equilibrium values. As this occurs, the contaminants form hydrophobic entities that precipitate and can be easily be removed by a number of secondary separation techniques. In the Electrocoagulation process, the electrical current is introduced into water via parallel plates constructed of various metals that are selected to optimize the removal process. The two most common plate materials are iron and aluminum. In accordance with Faraday's Law, metal ions will be split off or sacrificed into the liquid medium. 'These metal ions tend to form metal oxides that electromechanically attract to the contaminants that have been destabilized.' (http://www.powellwater.com/ec-overview.htm).

In this process, charged ionic species—metals or otherwise—are removed from wastewater by allowing it to react (i) with an ion having opposite charge, or (ii) with floc of metallic hydroxides generated within the effluent. The electrocoagulation technology offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions. The technology removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species. These species neutralize the electrostatic charges on suspended solids and oil droplets to facilitate agglomeration or coagulation and resultant separation from the aqueous phase. The treatment prompts the precipitation of certain metals and salts. The advantages and disadvantages of EC technology are discussed follows.

4.2 Advantages of Electrocoagulation (Mollah et al., 2001)

1. Electrocoagulation requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running.
2. Wastewater treated by electrocoagulation gives palatable, clear, colorless, and odorless water.
3. Sludge formed by electrocoagulation 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 electrocoagulation are similar to chemical floc, except that electrocoagulation floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.
5. Electrocoagulation 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 electrocoagulation 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. The electrocoagulation 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 electrocoagulation cell are controlled electrically with no moving parts, thus requiring less maintenance.
10. The electrocoagulation 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.

4.3 Disadvantages of Electrocoagulation

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 the electrocoagulation unit.
4. High conductivity of the wastewater suspension is required.
5. Gelatinous hydroxide may tend to solubilize in some cases.

4.4 Theory of Electrocoagulation (Mollah et al., 2001)

Electrocoagulation (EC) is a complicated process involving many chemical and physical phenomena that use consumable electrodes to supply ions into the wastewater stream. In an EC process the coagulating ions are produced 'in situ' and it involves three successive stages:

(i) Formation of coagulants by electrolytic oxidation of the 'sacrificial electrode',

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

(iii) Aggregation of the destabilized phases to form flocs.

The destabilization mechanisms of the contaminants, particulate suspension, and breaking of emulsions have been described in broad steps and may be summarized as follows:

- Compression of the diffuse double-layer around the charged species, which is achieved by the interactions of ions generated by dissolution of the sacrificial electrode, due to passage of current through the solution.
- Charge neutralization of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic inter particle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
- Floc formation; the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles still remaining in the aqueous medium. The solid oxides, hydroxides, and oxyhydroxides provide active surfaces for the adsorption of the polluting species.

Electrocoagulation has been successfully employed in removing metals, suspended particles, clay minerals, organic dyes, and oil and greases from a variety of industrial effluents. In this process, a potential is applied to the metal anodes, typically fabricated from either iron or aluminum, which causes two separate reactions:

- Fe/Al is dissolved from the anode generating corresponding metal ions, which almost immediately hydrolyze to polymeric iron or aluminum hydroxide. These polymeric hydroxides are excellent coagulating agents. The consumable (sacrificial) metal anodes are use to continuously produce polymeric hydroxides in the vicinity of the anode. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion. Contaminants present in the wastewater stream are treated by either chemical reactions or precipitation or physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electro-flotation, or sedimentation and filtration. Thus, rather than adding coagulating chemicals as in conventional coagulation process, these coagulating agents are generated in situ.
- Water is also electrolyzed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attract the flocculated particles and, through natural buoyancy, float the flocculated pollutants to the surface.

In addition, the following physiochemical reactions may also take place in the electrocoagulation cell:

- Cathodic reduction of impurities present in wastewater.
- Discharge and coagulation of colloidal particles.
- Electrophoretic migration of the ions in solution.
- Electroflotation of the coagulated particles by O_2 and H_2 bubbles produced at the electrodes.
- Reduction of metal ions at the cathode.
- Other electrochemical and chemical processes.

4.5 Reaction Types Involved In the Electrocoagulation Process

The mechanism of electrocoagulation is highly dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the electrocoagulation process. The mechanisms of removal of ions by electrocoagulation will be explained with two specific examples involving aluminum and iron, since these two metals have been extensively used to clarify wastewater.

Aluminum

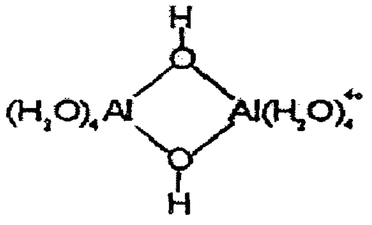
The electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as Al3+ and Al(OH)2+ at low pH, which at appropriate pH values are transformed initially into Al(OH)3 and finally polymerized to Al*n*(OH)3*n* according to the following reactions:

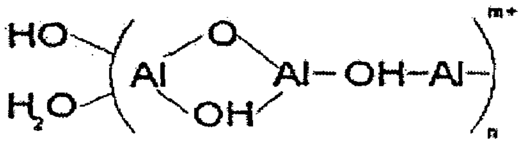
$$Al \rightarrow Al^{3+}{}_{(aq)} + 3e^- \qquad (1)$$

$$Al^{3+}{}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+{}_{(aq)} \qquad (2)$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \qquad (3)$$

However, depending on the pH of the aqueous medium other ionic species, such as $Al(OH)^{2+}$, $Al_2(OH)_2{}^{4+}$ and $Al(OH)^{4-}$ may also be present in the system. Examination of the pE–pH equilibrium diagram reveals that under appropriate conditions various forms of charged multimeric hydroxo Al^{3+} species may be formed. For example, the structures of dimeric and polymeric Al^{3+} hydroxo complexes are shown below:





These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization, and by enmeshment in a precipitate. According to the proposed mechanism the Al^{3+} ions under high F^- concentration may be induced to form $AlF_6{}^{3-}$ which was transformed to insoluble salt Na_3AlF_6 by adding sodium ions according to the following reactions:

$$Al^{3+} + 6F^- \rightarrow AlF_6^{3-} \qquad (4)$$

$$AlF_6^{3-} + 3Na^+ \rightarrow Na_3AlF_6 \qquad (5)$$

The insoluble Na_3AlF_6 salt was then separated by decantation. Mameri et al. (1998) have successfully applied this technology to defluoridation of septentrional Sahara water of North Africa.

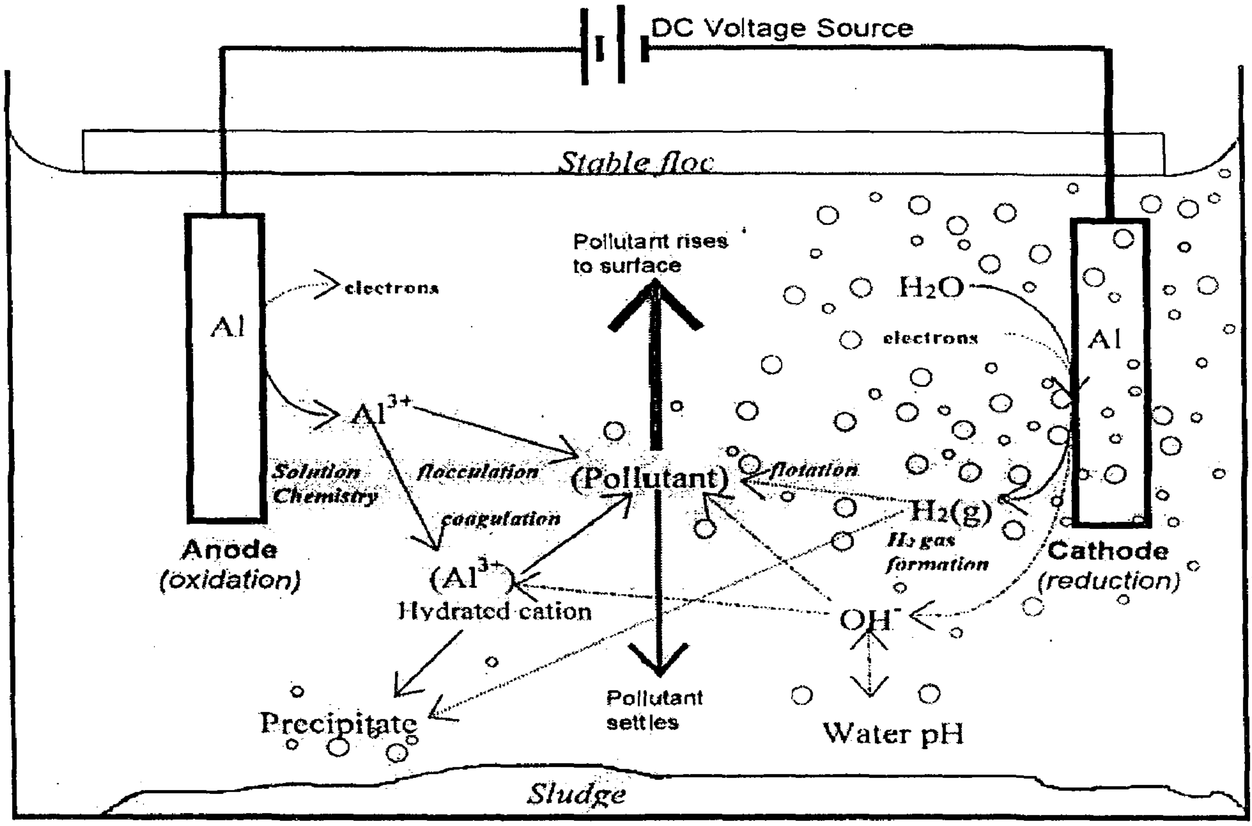


Fig. 4.1: Schematic diagram of a bench-scale two-electrode electrocoagulation cell.

Iron

Iron upon oxidation in an electrolytic system produces iron hydroxide, Fe $(OH)_n$, where $n = 2$ or 3. Two mechanisms have been proposed for the production of $Fe(OH)_n$.

- Mechanism 1

Anode:

$$4Fe_{(s)} \rightarrow 4Fe^{2+}{}_{(aq)} + 8e^- \qquad (6)$$

$$4Fe^{2+}{}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+{}_{(aq)} \qquad (7)$$

Cathode:

$$8H^{+}_{(aq)} + 8e^{-} \longrightarrow 4H_{2(g)} \qquad (8)$$

Overall:

$$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \longrightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \qquad (9)$$

- Mechanism 2

Anode:

$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^{-} \qquad (10)$$

$$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Fe(OH)_{2(s)} \qquad (11)$$

Cathode:

$$2H_2O_{(l)} + 2e^{-} \longrightarrow H_{2(g)} + 2OH^{-}_{(aq)} \qquad (12)$$

Overall:

$$Fe_{(s)} + 2H_2O_{(l)} \longrightarrow Fe(OH)_{2(s)} + H_{2(g)} \qquad (13)$$

The $Fe(OH)_{n(s)}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation. In the surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron:

$$L - H_{(aq)}(OH)OFe_{(s)} \longrightarrow L - OFe_{(s)} + H_2O_{(l)} \qquad (14)$$

The prehydrolysis of Fe^{3+} cations also leads to the formation of reactive clusters for water treatment. Wastewater containing Cr^{6+} (CrO_4^{2-}) ions can be removed by the EC technique using iron as the sacrificial anode. The ferrous ion (Fe^{2+}) generated by electroxidation of the iron anode can reduce Cr^{6+} to Cr^{3+} under alkaline conditions and is itself oxidized to ferric (Fe^{3+}) ion according to

$$CrO_4^{2-}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + 4H_2O_{(l)} \longrightarrow 3Fe^{3+}{}_{(aq)} + Cr^{3+}{}_{(aq)} + 8OH^{-}{}_{(aq)} \qquad (15)$$

or

$$CrO_4^{2-}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + 4H_2O_{(l)} + 4OH^{-}{}_{(aq)} \longrightarrow 3Fe(OH)_3 \downarrow + Cr(OH)_3 \downarrow \qquad (16)$$

The $Cr^{3+}_{(aq)}$ ion is then precipitated as $Cr(OH)_{3(s)}$ by raising the pH of the solution. The $Fe^{2+}_{(aq)}$ ions can also reduce $Cr_2O_7^{2-}{}_{(aq)}$ under acidic conditions according to the following reaction:

$$Cr_2O_7^{2-}{}_{(aq)} + 6Fe^{2+}{}_{(aq)} + 14H^{+}{}_{(aq)} \longrightarrow 2Cr^{3+}{}_{(aq)} + 6Fe^{3+}{}_{(aq)} + 7H_2O_{(l)} \qquad (17)$$

The H_2 produced as a result of the redox reaction may remove dissolved organics or any suspended materials by flotation. However, the Fe^{3+} ions may undergo hydration and depending on the pH of the solution $Fe(OH)^{2+}$, $Fe(OH)^{2+}$ and $Fe(OH)_3$ species may be present under acidic conditions. The reactions involved are:

$$Fe^{3+}{}_{(aq)} + H_2O_{(l)} \rightarrow Fe(OH)^{2+}{}_{(aq)} + 2H^{+}{}_{(aq)} \qquad (18)$$

$$Fe^{3+}{}_{(aq)} + 2H_2O_{(l)} \rightarrow Fe(OH)^{+2}{}_{(aq)} + 2H^{+}{}_{(aq)} \qquad (19)$$

$$Fe^{3+}{}_{(aq)} + 3H_2O_{(l)} \rightarrow Fe(OH)_3 + 3H^{+}{}_{(aq)} \qquad (20)$$

Under alkaline conditions, $Fe(OH)^{6-}$ and $Fe(OH)^{4-}$ ions may also be present. It is, therefore, quite apparent that electrocoagulation of both anionic and cationic species is possible by using an iron plate/rod as a sacrificial electrode.

4.6 Description of the Technology

In its simplest form, an electrocoagulating reactor may be made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. However, this arrangement is not suitable for wastewater treatment, because for a workable rate of metal dissolution, the use of electrodes with large surface area is required. This has been achieved by using cells with monopolar electrodes either in parallel or series connections. A simple arrangement of an electrocoagulation cell with a pair of anodes and a pair of cathodes in parallel arrangement is shown in Fig. 1.

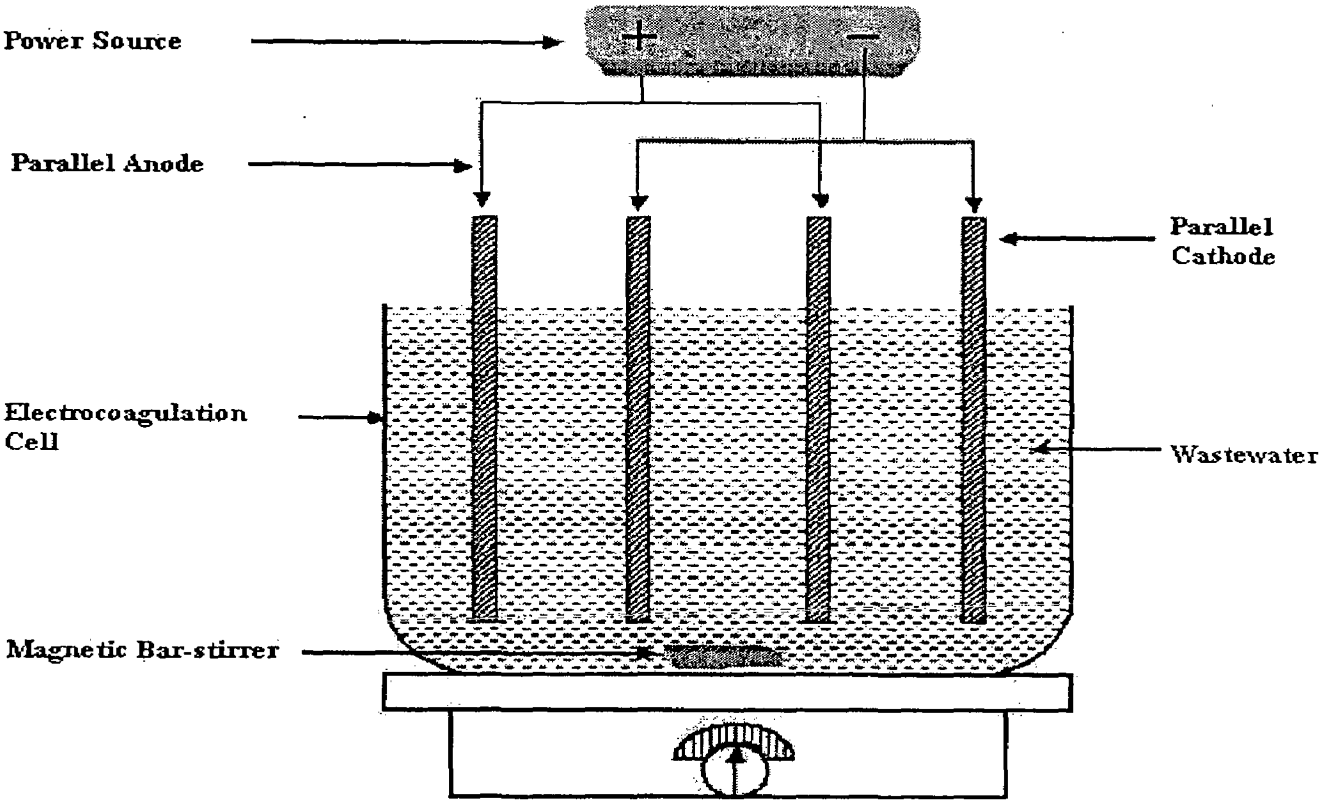


Fig. 4.2: Schematic diagram of a Bench-scale electrocoagulation reactor with monopolar electrodes in parallel connection

It essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a dc power source as shown in Fig. 4.2. The experimental set up also requires a resistance box to regulate the current density and a multimeter to read the current values. The conductive metal plates are commonly known as 'sacrificial electrodes'. The 'sacrificial anode' lowers the dissolution potential of the anode and minimizes the passivation of the cathode. The sacrificial electrodes may be made up of the same or of different materials as the anode.

An arrangement of an electrocoagulation cell with monopolar electrodes in series is shown in Fig. 4.3.

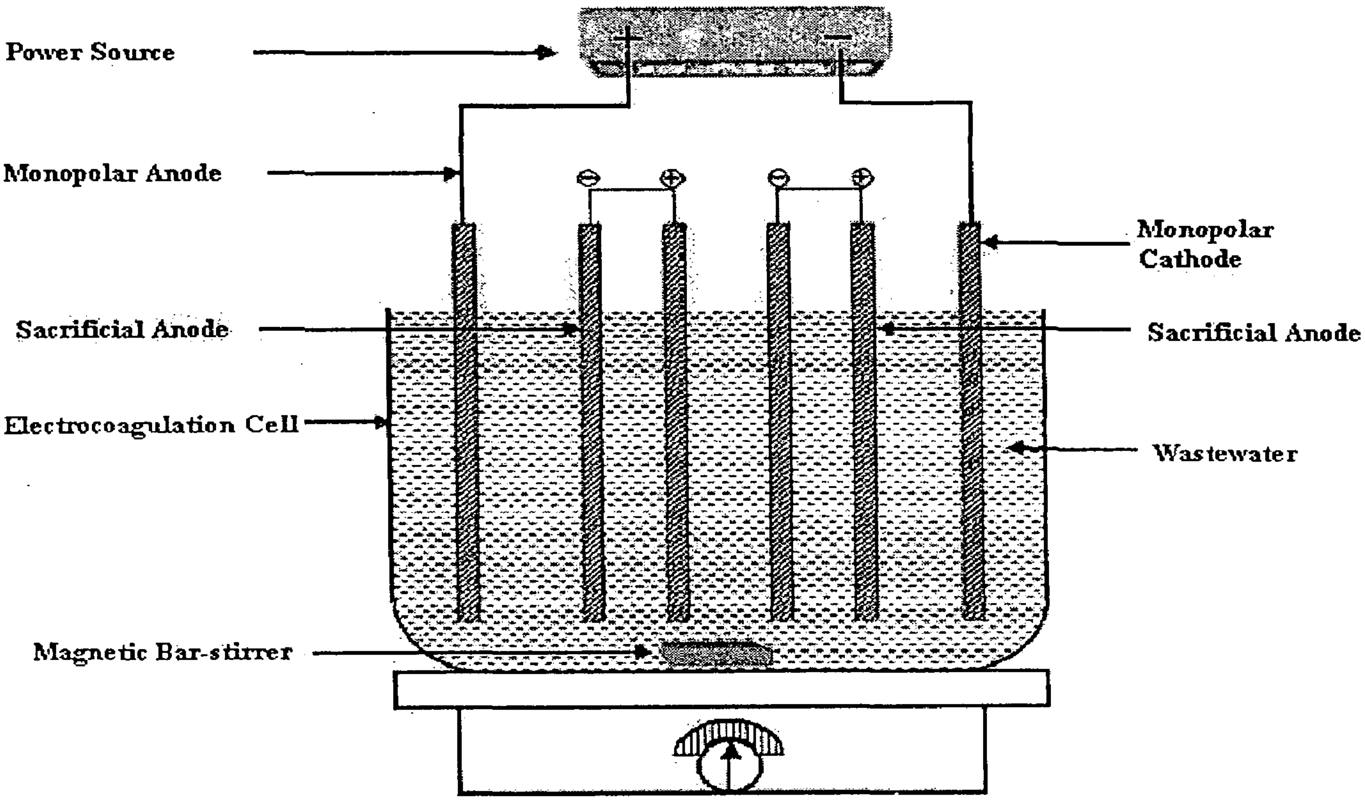


Fig. 4.3: Schematic diagram of a bench-scale EC reactor with monopolar electrodes in series connections

As can be seen from Fig.4.3 each pair of 'sacrificial electrodes' is internally connected with each other and has no interconnections with the outer electrodes. This arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections. In series cell arrangement, a higher potential difference is required for a given current to flow because the cells connected in series have higher resistance. The same current would, however, flow through all the electrodes. On the other hand, in parallel arrangement the electric current is divided between all the electrodes in relation to the resistance of the individual cells. Mameri et al. (1998) have, however, used bipolar electrodes with cells in parallel. In this case, the sacrificial electrodes are placed between the two parallel electrodes without any electrical connection as shown in Fig. 4.4.

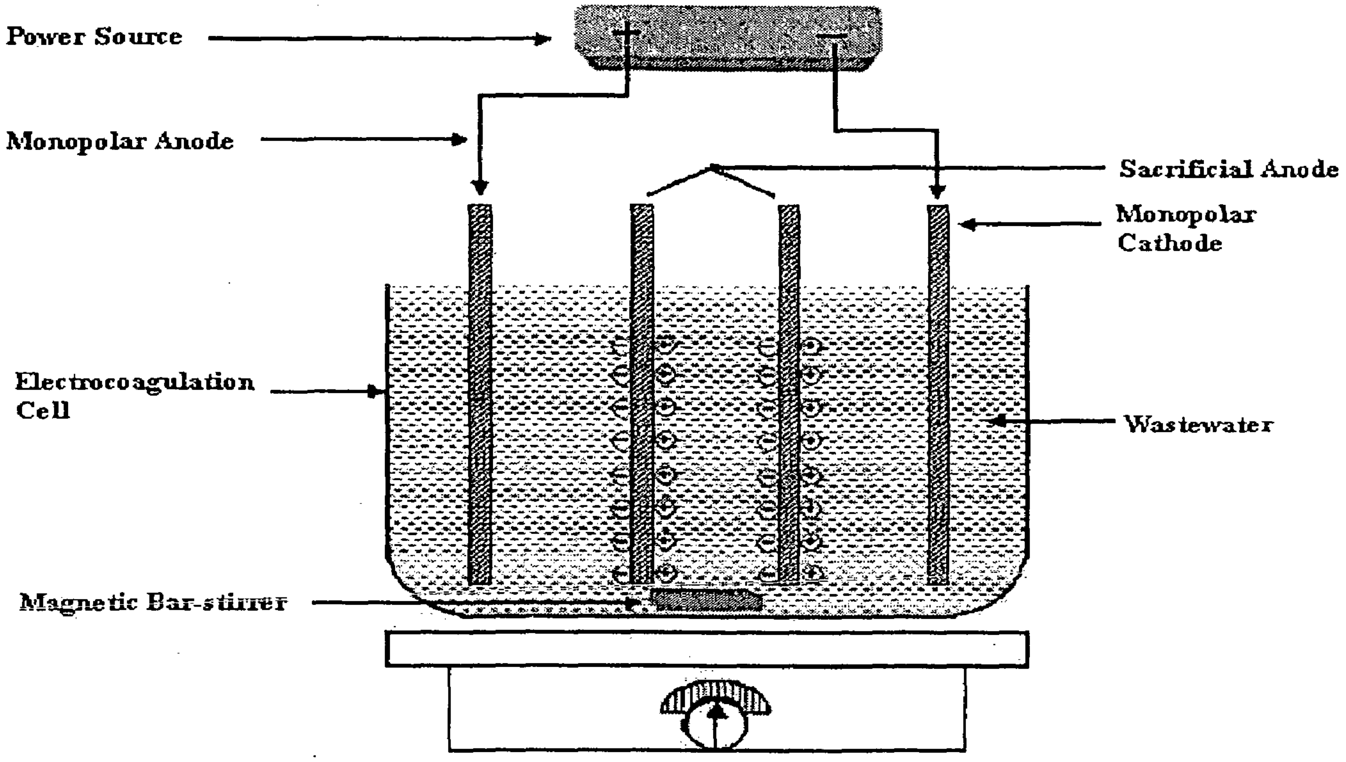


Fig. 4.4: Schematic diagram of a bench-scale EC reactor with dipolar electrodes in parallel connections

Only the two-monopolar electrodes are connected to the electric power source with no interconnections between the sacrificial electrodes. This cell arrangement provides a simple set-up, which facilitates easy maintenance during use. When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared to the parallel side beside it. The sacrificial electrodes in this case are also known as bipolar electrodes. Thus, during electrolysis, the positive side undergoes anodic reactions, and on the negative side, cathodic reaction is encountered. Consumable metal plates, such as iron or aluminum, are usually used as sacrificial electrodes to continuously producing ions in the system. The released ions neutralize the charges of the particles and thereby initiate coagulation. The released ions may remove the undesirable contaminants either by chemical reaction and precipitation, or by causing the colloidal materials to coalesce and then removed by electrolytic flotation. In addition, as water containing colloidal particulates, oils, or other contaminants move through the applied electric field, there may be ionization, electrolysis, hydrolysis, and free-radical formation which may alter the physical and chemical properties of water and contaminants. As a result, the reactive and excited state causes contaminants to be released from water and destroyed or made less soluble. Inert electrodes, such as titanium and the passage of alternating current, have been observed to remove metal ions from solution and to initiate coagulation of suspended solids. To ensure more effective removal of the undesirable ions, wastewater may be passed through a series of cells containing electrodes made up of various metals. In such cases, the contaminated wastewater is passed through the annular spaces between the electrodes and is exposed to sequential positive and negative electrical fields. To optimize the removal efficiencies, the water characteristics such as pH, oxidation–reduction potential, and conductivity can be adjusted for specific contaminants. In the electrocoagulation process, an electric field is applied to the medium for a short time, and the treated dispersion transferred to an integrated clarifier system where the water–contaminant mixture separates into a floating layer, a mineral-rich sediment, and clear water. The aggregated mass settles down due to gravitational force. The clear water can be extracted by conventional methods.

CHAPTER 5

LITERATURE REVIEW

Sr. No.	Reference	Waste Characteristics/ Purpose of Study	Dosing Agent/ Electrode Used	Operating Condition	Result
1	Hu et al. (2005)	Effects of the molar ratio of hydroxide and fluoride to Al(III) on fluoride removal by coagulation and electrocoagulation	Aluminum	Concentration, acidity, charge loading, Effect of co-existing anions	Wastewater from semiconductor manufacturers that contains large amounts of fluoride can be effectively treated by EC F with sodium dodecyl sulfate (SDS). SDS can improve the treatment efficiencyof the SS. The optimum initial acidity for ECF is close to the initial fluoride concentration after calcium precipitation; the amount of SS removed dropped rapidly if the initial acidity exceeded the optimal value because the surface charge of the hydro–fluoro–aluminum particles increased.
2	Daneshvar et al. (2004)	Decolorization of dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections	Iron (ST 37-2) anode and steel (grade 304) cathode		(1) For dye solutions with COD of approximately 30 ppm and dye concentrations less than 150 ppm, high color removal (93%) was obtained when the pH ranged from 6 to 9, time of electrolysis was approximately 4 min, current density was approximately 80 A/m2, the temperature was approximately 300 K, and inter electrode distance was 1 cm. During

					the EC process under these conditions, the COD decreased by more than 85%. (2) The experimental results showed that an EC cell with several electrodes was more effective than a simple electrochemical cell in color removal. (3) EC cell with mono polar electrodes had higher color removal efficiency than an EC cell with bipolar electrodes.
3	Kumar et al. (2004)	Studied the removal of arsenic from water by electrocoagulation	iron, aluminum and titanium	Current density, pH	(1) Arsenic removal efficiencies with different electrode materials follow the sequence: iron > titanium > aluminum. (2) The process was able to remove more than 99% of arsenic from an As contaminated water and met the drinking water standard of 10 µg/l with iron electrode. (3) The aqueous phase pH did not have significant effect on both As(III) and As(V) removal in the pH range 6–8. As(III) was more efficiently removed in electrocoagulation than chemical coagulation, whereas, As(V) removal performance of both EC and CC was nearly same.
4	Bhabha et al. (2004)	Studied the electrochemical treatment of pulp and paper mill effluent.	$RuO_2/TiO_2/$ Ti as anode and stainless steel as cathode	Current density, concentration of mediator, flow rate	Optimum result came at the Sodium chloride concentration of 5 g/l, reactor volume of 200 ml and current density of 2.5 A/dm^2.
5	Adhoum et al. (2004)	Studied the treatment of electroplating wastewater containing Cu^{2+}, Zn^{2+} and	Aluminum	pH, current density, metal ion	The most effective removal capacity was achieved in the pH range between 4 and 8. The treatment rate was shown to increase

		Cr(VI) by electrocoagulation.		concentration	upon increasing the current density. Indeed, the highest current produced the quickest treatment with an effective reduction of Cu and Zn concentrations in the industrial wastewater under the admissible level, after only 5 min. Whereas, 20 min. were needed to achieve an equivalent removal of Cr (VI). The slower removal of chromium compared to copper and zinc is attributed to a difference in the removal mechanisms. Moreover, the charge loading required to achieve an effective treatment, increased with initial concentration.
6	Jiantuan et al. (2004)	Studied the bipolar electrocoagulation–electroflotation process for the treatment of laundry wastewater.	Ti as anode and Aluminum as cathode	pH, hydraulic residence time (HRT) and current density	The process successfully removed turbidity, COD, phosphate and MBAS simultaneously in the pH range of 5–9. The laboratory results showed that the removal of COD was greater than 70%. Moreover, the removal efficiencies of MBAS, turbidity and P-phosphate could be reached above 90%. The 1.5 m3/h pilot scale tests proved that the process was competitive for the treatment of laundry wastewater.
7	Guohua Chen (2004)	Reviews the development, design, and applications of electrochemical technologies in water and wastewater treatment.	Aluminum, iron	Electrode material, pH, current, temp., conductivity	Electrocoagulation has been used industrially and demonstrated its superior performances in treating effluents containing suspended solids, oil and grease, and even organic or inorganic pollutants that can be flocculated.
8	Shen et al. (2003)	Electrochemical removal of fluoride ions from industrial wastewater	Aluminum	pH, charge loading, other chemicals	The combined EC–EF process was successfully applied in treating wastewater-containing fluoride. The experimental results showed that weakly acidic condition is

					favored in this treatment, while too high or too low pH can affect the formation of the Al(OH)3 flocs. The optimal retention time in our case was 20 min. Higher charge loading resulted in good fluoride removal e3ciency. A feasible charge loading for 15 mg=l fluoride wastewater was 5 F=m3 water.
9	Lai & Lin (2003)	Studied on the electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication	Aluminum, iron	electrocoagulation time, type of electrode pair and electrolyte dosage	(1)For electrocoagulation of the CMP wastewater, cast iron cathode and aluminum anode were found to form a better electrode pair due to good COD, copper ion and fine suspended particle removal and relatively low sludge production. Adopting this electrode pair, electrocoagulation of the CMP wastewater was able to realize a 96% NTU reduction and 99% copper removal. The COD removal achieved was better than 75% with a final wastewater COD concentration below the discharge standard (100 mg/l). The final wastewater effluent was clear and can be considered for reuse. (2) Addition of electrolyte (i.e. NaCl) was found to be very effective in enhancing the fine oxide particle and copper removal and in improving the wastewater turbidity. A small NaCl dosage of 25 mg/l yielded the best overall performances. (3) In terms of low electrocoagulation time to reach 99% copper removal, low final wastewater NTU below 10 and low power expenditure, a 20V power supply was found to offer the best overall results within the test

					range of power supply between 10 and 30V.
10	Feng et al. (2003)	Development of a high performance electrochemical wastewater treatment system	Platinum, Ti/RuO$_2$–TiO$_2$	Electrode material, concentration	(1) No difference in electrocatalytic activity for ammonia oxidation between platinum and Ti/RuO2–TiO2 was observed from the cyclic votammogram; (2) Hydroxyl radicals formed in the electrochemical process were detected using a *p*-nitrosodimethylaniline (RNO) solution and the production of hydroxyl radicals with Ti/RuO2–TiO2 anode was larger than found using platinum and titanium anode; (3) Excellent removal of T-N, NH4–N, T-P, and COD from domestic wastewater and pond water containing algae was achieved by the pilot plant of electrochemical treatment system.
11	Barrera-Diaz et al. (2003)	Studied on a combined electrochemical-irradiation treatment of highly colored and polluted industrial wastewater	Carbon steel disc	Time, pH	The use of electrochemical methods has proved to be effective to reduce significantly the amount of pollutants present in industrial highly colored wastewater. The main mechanism responsible for particle destabilization is ascribed to the liberation of iron ions into the solution containing the pollutants, which under the pH conditions established as a result of the thermodynamic study, gave rise to hydro complexed chemical species capable of fixing the contaminants. Using electrochemical means combined with g-irradiation in industrial wastewater treatment process resulted in an improved water quality method as compared with biological methods alone.

12	Ranjbar & Moradian (2003)	Studied on the Characteristics and deposition behavior of epoxy-amine adducts in cathodic electrodeposition as a function of the degree of neutralization (DN)	Stainless steel	Current, pH, conductivity, particle size, viscosity	DN of the resin drastically affects many properties of the electrodeposition coatings. By increasing the DN, the ionic sites on the surface of the particles will increase which leads to the breaking of the particles to smaller ones. Increasing the DN also results in decreasing the probability of the ionic sites being present within the bulk of the particles, so the behavior of the system tends to change from primary dispersions to a more near true solutions, behavior. By increasing the DN, the film grows in a porous like manner, which can be attributed to the fact that the rate of hydrogen gas evolution is much higher than the rate of electrocoagulate deposition of the particles on the surface.
13	Bergmann et al. (2003)	Studied electrochemical treatment of cooling lubricants	Anode formed by an expanded mesh of titanium coated with iridium mixed oxide (diameter= 50 mm) and copper as cathode	Current density, concentration, time	1) Direct electrolysis is possible. The cathodic polarization curves indicate a mass-transfer controlled process. Anodic polarisation curves indicate a slowing down of the oxygen evolution reaction in the potential range up to about 2.0 V (SHE). 2) Under conditions of slow electrolyte convection and enhanced anodic current densities the anode tends to be blocked by a layer of deposit. 3) Copper concentration can be successfully reduced by cathodic deposition to the range of units of mg dm^{-3}. Deposition efficiency increases with a decreasing electrode boundary layer and increasing current density.

					4) In cells with separators a blocking layer was formed on the ion exchange membrane, probably due to changes in the local pH value. 5) The combination of electrolysis and electrocoagulation resulted in transparent solutions with a low content of copper and organic matter.
14	Jia et al. (2002)	The electrocoagulation-flotation for water treatment on lab scale, by using Thames river water.	Aluminum	pH, Current density	(1) Specific Electrical Energy Consumption was about 20-80 KWh per kg Al for current density of 10-60 Am^{-2} and was essentially independent of whether monopolar or bipolar electrode were used. (2) Electrocoagulation performs better than conventional coagulation with ammonium sulfate for treating model color water 20% more COD removed from the same Al (III) dose. (3) Lowering the water pH to 6.5 resulted in the removal of 20% and 14% more color and $UVasb_{254}$, respectively, for coagulation with aluminum sulfate and electrocoagulation.
15	Holt et al. (2002)	Studied on a quantitative comparison between chemical dosing and electrocoagulation	Aluminum	Charge loading, current	The mechanism of coagulant delivery is a key difference between chemical dosing and electrocoagulation performance. In the alum dosing studied here, coagulant addition is a discrete event with the system then moving towards an acidic equilibrium. Modification of pH was shown to be able to improve turbidity reduction under some conditions. By contrast, in electrocoagulation the continuous addition of aluminum and hydroxyl ions (with the multi-step hydrolysis

					of the former) results in a non-equilibrium state. Somewhat surprisingly, however, the system appears stable, at least with respect to pH, during the reactive and stable stages.
16	Mollah et al. (2001)	Studied the electrocoagulation (EC) science and application by giving advantages and disadvantages of the EC process and gave a brief description of the EC technology in three modes: 1. Monopolar electrodes in parallel connection. 2. Monopolar connection with series connection. 3. Bipolar electrode in parallel connection.	Aluminum and iron	pH, Particle size, chemical constituent, concentrations.	The mechanism of removal of ions by EC explained with two specific examples involving aluminum and iron, since these two metals have been extensively used to clarify wastewater.
17	Tsouris et al. (2001)	Studied on the electrocoagulation for magnetic seeding of colloidal particles	Iron	pH, temperature, voltage, and solution conductivity	Electrocoagulation (EC) was investigated as a magnetic seeding method to be used prior to a high-gradient magnetic separation (HGMS) process. Experimental results showed that particulates with significant magnetic susceptibility were formed by EC with steel electrodes. Magnetite was specifically formed most readily in a sodium chloride solution, in the absence of other ions, but also in surrogate wastewater under controlled conditions. These results suggest that EC could be employed in a magnetic seeding process in which paramagnetic particles are formed and then removed through high-gradient magnetic filtration (HGMF).

18	Mameri et al. (2001)	Studied on the defluoridation of Sahara water by small plant electrocoagulation	Aluminum	Flow rate, current	Water defluoridation in a small plant by electrocoagulation appeared very promising for in depth development studies. Moreover, this process, which consumes 40 kg of aluminum for 1000 m3 of treated water, does not require technically qualified personnel, and the equipment is easy to maintain.
19	Ciorba et al. (2000)	Correlation between organic component and electrode material: consequences on removal of surfactants from Wastewater	Aluminum	Curmet density, pH, COD conc., NaCl conc., surfactant type	The efficiencies of treatment ranged between 40 and 60% (as COD removal) depending on the working parameters.
20	Phutdhawong et al. (2000)	Studied the EC to recovery of Phenolic compounds.	Aluminum	Electrolysis time	More than 94 % precipitation for pyrocatechol, pyrogallol, n-propyl 3,4,5-trihydroxybenzoate, and tannin is achieved.
21	Chen et al. (2000)	Sutdied on separation of pollutants from restaurant wastewater by electrocoagulation	Aluminum, iron	Electrode material, pH, current density, charge loading, conductivity	Electrocoagulation is a feasible process for treating the restaurant wastewater, characterized by high oil and grease content, fluctuated COD,BOD_5 and SS concentrations. Aluminum electrodes are preferred for this application. The influent pH, conductivity, and electrical current density do not affect the pollutant removal efficiency significantly. Charge loading is the most important operational variable. The optimal charge loading and current density are 1.67–9.95 F/m3 and 30–80 A/m2, depending on wastewater characteristics. The aluminum electrode consumption ranges from 17.7 to 106.4 g/m3, and the power requirement is usually B1.5 kW h/m3. The removal efficiency of oil and grease is over 94% for all

					the wastewaters tested. The EC can neutralize wastewater pH.
22	Paul et al. (1996)	Studied the electrolytic treatment of turbid water in packaging plant.	aluminum	pH	(1)Narrow gap between plates enhanced the mass transfer and decreased ohmic loss. (2) However, when a gas product is present a decrease in gap results in an increase in electrolyte resistance. (3) The EC was found to be most effective at pH 6.5 to 7.5 and poor at high pH (>9) as well as at low pH (<5).
23	Baklan & Kolesnikova (1996)	Studied the influence of the electrode material on the electrocoagulation.	Aluminum and iron		The higher efficiency of the Fe electrode is connected with larger size of initial particles (10-30 µm for three-valent Fe against 0.05-1 µm for the aluminum electrode.
24	Barkley et al. (1993)	Tested ACE Technology using two designs of the ACE separator.	Aluminum	pH, particle size, chemical constituent, concentration	(1) Optimum operating conditions for parallel electrode unit as a result of bench unit scale tests were electrode spacing 0.5 inch (12.5 mm); current, 4A, retention time, 3 to 5 min., frequency, 10 Hz, and fully submerged. Similarly, based on the bench scale testing of the fluidized bed design, the optimum operating conditions established were electrode spacing, 1 inch (25.4 mm); aluminum pellets size, -8 to +16 mesh; and current, 20A. (2) TSS values for the alum treatment were four to five times greater than those for ACE separator treatment or polymer treatment. (3) Removal efficiency of COD was two to four times higher than removal efficiency for either alum treatment or polymer treatment.
25	Vik et al. (1984)	Studied the electrocoagulation	Aluminum	pH, particle	(1) The electrochemical treated water contains

		of potable water.		size	higher residual aluminum concentration than the conventional treated water due to higher pH values. (2) The amount of chemical which has been to be transported was lower than the conventional treatment (approx. 1/10 of the amount) and a lesser amount of sludge was formed because of the higher dry solids content.

CHAPTER 6

EXPERIMENTAL PROGRAMME

6.1 General

Electrocoagulation studies for the removal of COD and color from wastewater prepared from black liquor of agro based pulp and paper mill based on wheat straw was conducted using aluminum electrode. Effect of various parameters such as pH, current density, number of electrodes, electrode submergence, inter-electrode spacing was studied.

6.2 Characterization of Effluent

Wastewater prepared from black liquor of agro based pulp and paper mill based on wheat straw was used in present investigation.

wastewater sample was characterized for the BOD, COD, pH, total solids, dissolved solids, suspended solids as per the standard methods (IS: 2488). COD and color of the treated effluent was analyzed to evaluate the performance of electrocoagulation.

6.2.1. COD Estimation

The COD of the samples were determined as per ISI (IS: 3025). The COD of the sample was calculated by the formula.

$$\text{COD (mg/l)} = [(A-B) \times C \times 8000] / \text{ml of sample}$$

Where,

A= Volume (ml) of Ferrous Ammonium Sulfate for the blank solution.

B= Volume (ml) of Ferrous Ammonium Sulfate for the solution.

C= Normality of the Ferrous Ammonium Sulfate solution.

6.2.2 Analytical Measurements

The determination of the color concentration of effluents was done using UV-spectrophotometer (Shimadzu, Japan) in terms of Pt-Co units as per standard method. A standard solution of Pt-Co was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance $\lambda_{\max}$ was determined from this plot. The $\lambda_{\max}$ for Pt-Co was found to be 263 nm. Calibration curves were plotted between absorbance and solution concentration. The linearity of calibration curve indicates applicability of the Lambert-Beer's Law. The linear portions of the standard calibration curves were used for the determination of residual concentration of color.

6.3 Electrocoagulation Studies

6.3.1 Experimental Set up

The batch electrocoagulation experimental set up is shown in fig. 6.2. The experiment set up consists of a rectangular plexi glass container of size 15cm x 15cm x 20cm. Electrode plates were 1mm thick, 9cm wide and 14cm long. 12 aluminum electrode plates were used for electrocoagulation. A regulated DC power supply 15V/5A was used to maintain the potential difference between the anode and cathode plate. A rheostat (26 ohm / 5A) was used for the regulation of current.

6.3.2 Experimental Method

The various steps in the electrocoagulation study are given below:

(1) Measurement of initial COD and color using the methods described earlier.

(2) Measurement of pH of the effluent was measured with a digital pH meter.

(3) Acidification of the effluent using sulfuric acid till the pH was in the desirable range. It allowed to settle for 2-3 h., after that the supernatant wastewater was used for electrocoagulation.

(4) Electrocoagulation studies were carried out by using regulated DC power supply. Voltage and current were maintained by rheostat.

(5) In all cases the continuous mixing was done by magnetic stirrer at constant speed to distribute the ions thoroughly in the water. 25 ml sample at regular time interval was taken for analyzing COD and color.

(6) After electrolysis the scum at the top was skimmed off and the remaining supernatant liquid was left for flocculation. After 1 h clean sample was decanted and sludge was further analyzed.

(7) Finally COD and color of the clear supernatant were measured and the changes in these parameters were evaluated.

(8) Same procedure was repeated for evaluation of various parameters.

(9) Graphs were plotted between the percentage COD and color removal versus time for each parameter.

(10) Sludge was dried and did SEM and TGA analysis.

6.3.3 Scanning Electron Microscope (SEM) Analysis

SEM analysis of dried sludge was carried out using LEO 435 VP Scanning Electron Microscope.

6.3.4 Thermal Degradation Studies

The thermal degradation (pyrolysis) of the dry sludge was studied using the thermogravimetric and differential analysis techniques. The thermal decomposition of dry sludge was carried out non-isothermally in a Pyris diamond TG/TGA of Perkin Elmer Instruments. A sample size of 10.29 mg was used for each run. The samples were prepared carefully after crushing and sieving so as to obtain homogenous material properties. The degradation runs were taken at heating rate of 25^0C min^{-1} under an inert atmosphere (flowing nitrogen) for pyrolysis. The tests were conducted from the ambient temperature to 1000^0C. Flowing rate was kept constant at 400 ml/min. The TG%, DTG and DSC curves obtained were analyzed to understand the behavior of thermal degradation.

Table 6.1: Variation of Absorbance with Concentration of Pt-Co Standard solution

~~Conc., NTU~~ Pt-Co Color Unit	Absorbance, nm
5	0.05
10	0.1
15	0.15
20	0.2

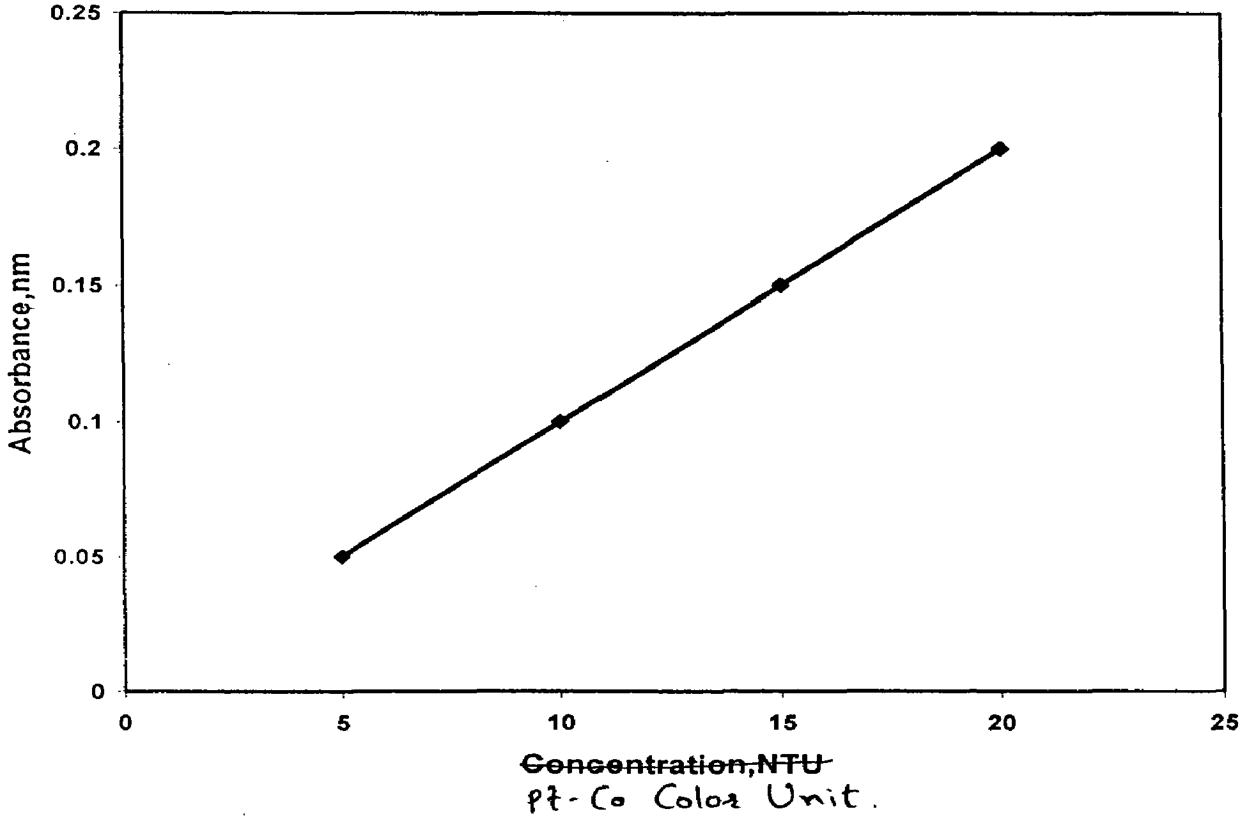


Fig. 6.1: Standard Graph for Pt-Co Color Determination

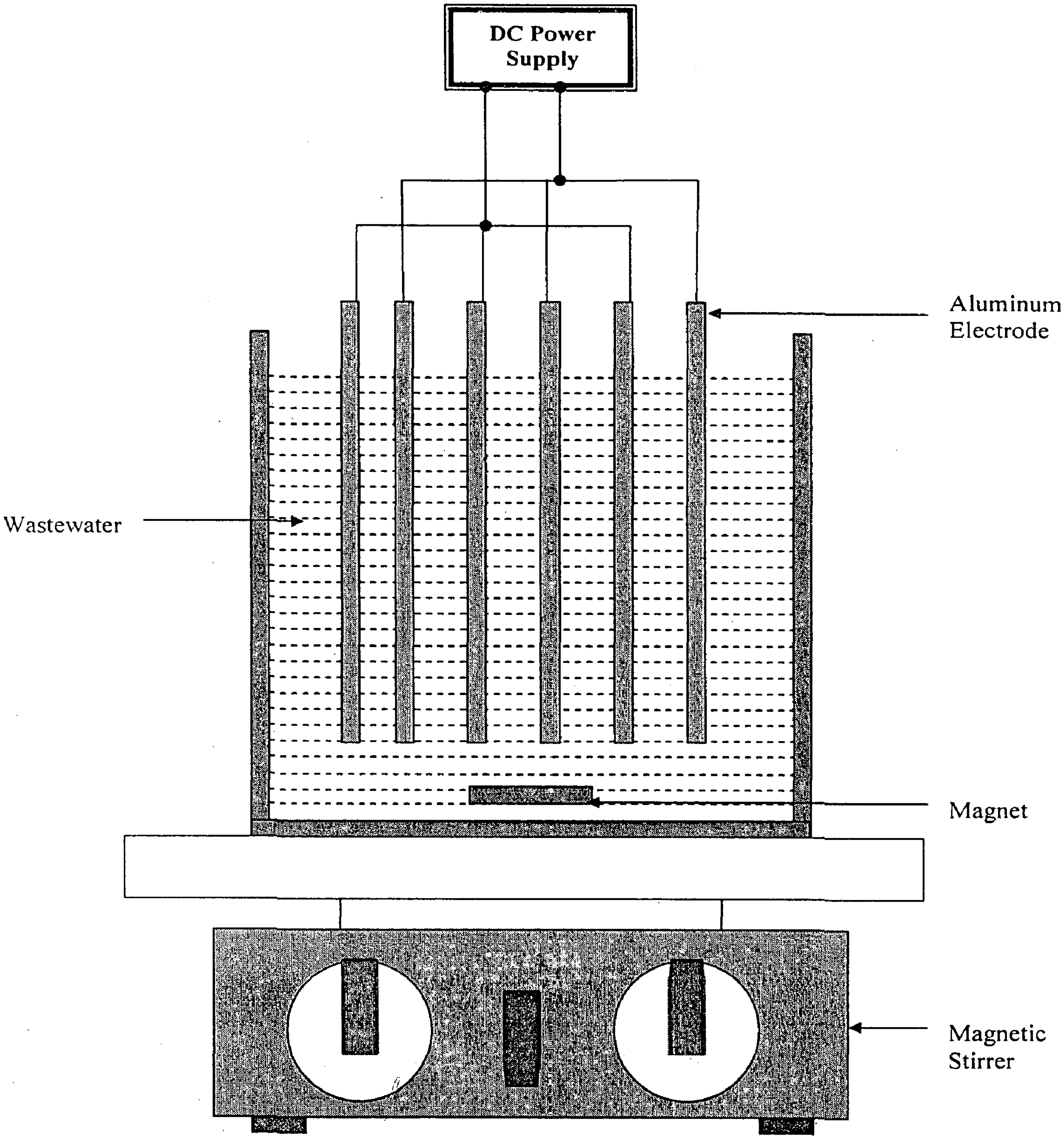
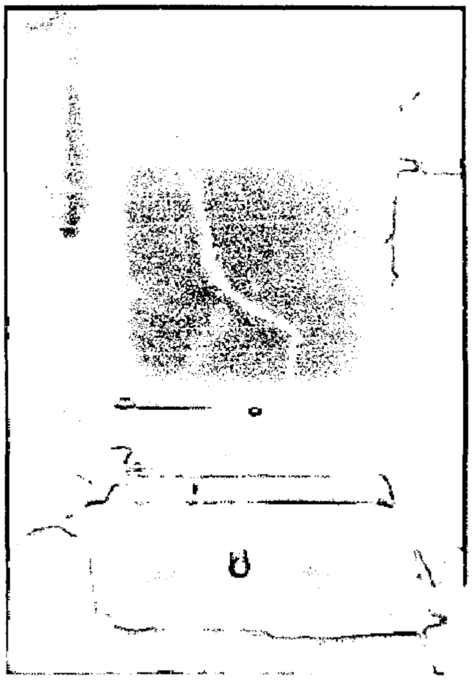
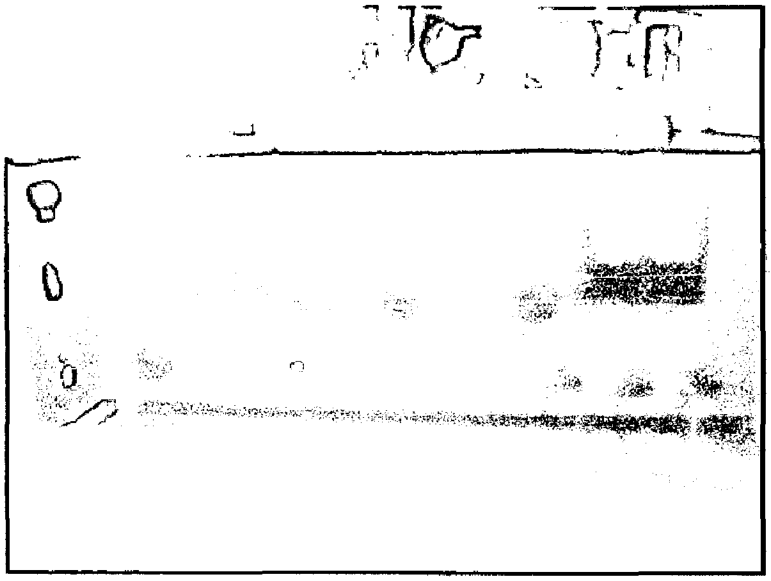


Fig. 6.2 : Schematic Diagram of Electrocoagulation





(b)

(a)

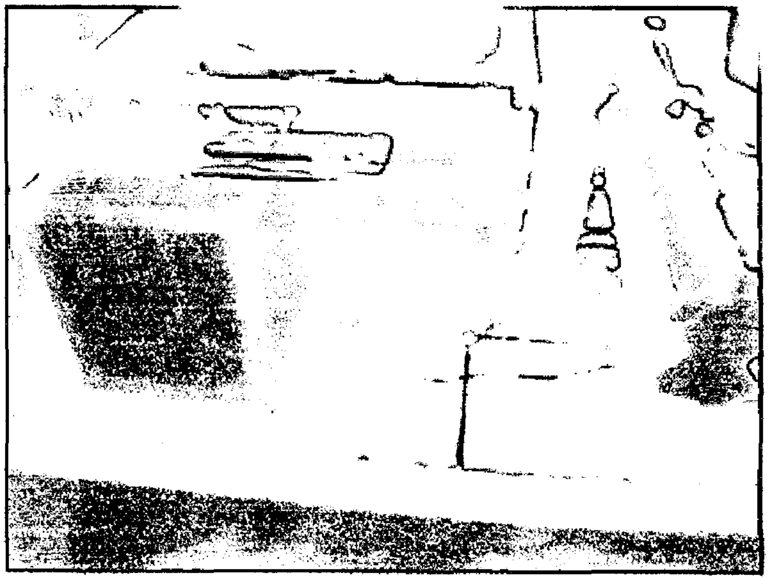


Fig. 6. 2: Actual assembly of Experimental Set Up at Pollution Abatement Research Lab., IIT Roorkee. (a) Batch Scale Electrocoagualation Assembly with Magnetic Stirrer, (b) DC Power Supply

CHAPTER 7

RESULTS AND DISCUSSION

7.1 General

The detailed discussion on the results of the electrocoagulation experiments conducted is given below.

7.2 Wastewater

Synthetic wastewater prepared from black liquor of agro based paper mill based on wheat straw as a raw material was used for present investigation.

7.3 Electrocoagulation Study

Detailed electrocoagulation studies had been conducted for the removal of COD and color of the wastewater prepared from black liquor of agro based paper mill. Effect of various operating parameters like pH, number of electrode, current density, electrode spacing, inter electrode spacing have been studied and are shown in Tables A1 to A10 and Figs. 7.1 to 7.20

7.3.1 Effect of pH

It has established that the initial pH has a considerable influence on the performance of electrocoagulation process (Adhoum et al., 2004). To evaluate its effect, a series of experiments were performed, with an initial pH varying in the range 3–10.8.

Fig 7.1 to 7.10 shows the effect of pH on the removal efficiency of COD and color using Aluminum electrodes. Initial COD in the effluent was about 1300 mg/l, and the potential difference across the electrode was keep at 5 volt and current density 47.62 A/m^2. The number of electrode were 8, the inter electrode spacing was 1 cm and fully submerged in the wastewater. After 2 h of treatment, the percent COD removal was plotting against the time for different pH. The initial pH was varying between 3 and 10.8 with the help of aqueous solution of sulfuric acid.

Fig 7.1 to 7.10 show that the COD and color removal efficiency increases with the decrease of the pH. Higher removal efficiency was observing at pH 3 for aluminum electrodes, about 83% COD and 92.26% color removal achieved. Removal percentage does not increase much after the lowering of the pH below 3. The initial pH was adjusted to 3 for all subsequent studies.

7.3.2 Effect of Number of Electrodes

Removal efficiency is also dependent upon the number of electrodes used in the electrolysis process. Fig 7.11 to 7.16 and Tables A3 to A4 show the effect of number of electrodes on COD and color removal, at current density 47.62 A/m^2 for aluminum electrodes. It was found that electrocoagulation gives the best result with increasing the number of electrodes. Several experiments have been carried out at constant current density of 47.62 A/m^2 with 4,6,8,12 electrodes system. From Fig 7.11 to 7.16 and Tables A3 to A4 it is clear that the COD and color removal efficiency increases sharply with the increases in the number of the electrodes for the same current density. Time requirement is less for higher number of electrode system for achieves definite removal efficiency.

Table 7.1 % COD and Color Removal at Different Number of Electrodes

Number of Electrodes	%COD Removal	%Color Removal
4	75.38	88.67
6	80.38	90.81
8	83	92.26
12	90.77	99

7.3.3 Effect of Current Density

The current density not only determines the coagulant dosage rate, but also the bubble production rate and size. Thus, this parameter should have a significant impact on pollutants removal efficiencies. To investigate the effect of current density and charge loading on the removal yield, a series of experiments were carried out on solutions containing a constant pollutants loading with current density being varied from 47.62 to 198.41 A/m^2. Figs 7.17 to 7.22 show percent removal of COD and color with time for typical electrocoagulation runs, where the initial pH was fixed at 3. The removal rate of COD and color increased upon increasing current density.

The highest current (198.41A/m^2) produced the quickest removal rate of COD and color, 90.62% and 99.17% removal in COD and color was observed after 2 h in

COD and color respectively. This expected behavior can be easily explained by the increase of coagulant and bubbles generation rate, resulting in a more efficient and faster removal, when the current is increased. At high current, the bubble density and upwards flux increased and resulted in a faster removal of the coagulant by flotation. Hence, there is a reduction in the probability of collision between the coagulant and pollutants.

7.3.4 Effect of Electrode Submergence

The effect of electrode submergence on removal of COD and color are shown in fig 7.23 to 7.28 and table A7 to A8. Maximum removal of COD and color observed when electrodes were fully submerged. With the increase in submergence of electrode, the surface area of anode increases which gives higher rate of aluminum ions production and so the reaction rate in the reactor increase resulting in increase coagulation. In view of the above observations, the rest of the experiments were performed for fully submerged electrode in the wastewater.

7.3.5 Effect of Inter-Electrode Spacing

Removal efficiency of COD and color depends on the inter electrode spacing. It is found that electrocoagulation gives the best result when inter-electrode spacing is the least. In addition, the ohmic resistance is low for short inter-electrode spacing (Eilen et al, 1984). The resistance between the electrode decreases with decreasing electrode spacing. So the aluminum ions generated from the anode is quickly reach the cathode and it react, there resulting formation of aluminum hydroxide which subsequently work as a coagulant. From fig 7.29 to 7.34 and Table A9 to A10, it is observed that the COD and color removal is greater when the spacing is low but the removal rate is affected by increasing the inter-electrode spacing, due to generation of hydrogen bubbles at the anode. The optimum inter-electrode distance was 1 cm.

7.3.6 Effect of Residence Time

With increase of the residence time, the dissolving of the aluminum ions is increasing which in turn increase the removal efficiency. However, with time the film generated on the electrodes decrease the rate of ions generated so the removal rate decreases. From the graphs it can be seen that with increase in the residence time of the wastewater in the reactor, the removal of COD and color is increased but after 2 h the removal was not significant, so further study of effect of different parameters, experiments were conducted for 2 h only.

7.3.7 Sludge Characteristics

Sludge obtained after treatment of effluent by acidification and electrocoagulation was dried and then analyzed in Scanning Electron Micrographs and in thermal gravimetric analysis. The Fig. 7.35 and Fig. 7.36 shows SEM photograph after acidification and Fig. 7.37 and Fig. 7.38 shows SEM photograph after electrocoagulation.

The degradation characteristics of sludge after acidification and electrocoagulation treatment under nitrogen, as obtained by TG, DSC and DTG for the heating rate of 25^0C min^{-1} are shown in Figs. 7.39 and 7.40 respectively. The degradation runs were taken under an inert atmosphere (flowing nitrogen) for pyrolysis. The test for sludge of after acidification was conducted from the ambient temperature to 1000^0C. Flowing rate was kept constant at 400 ml/min. Under nitrogen atmosphere, moisture removal of about 6.86% is observed to occur up to 199^0C followed by removal of light volatiles up to 466^0C. This initial zone is followed by the active pyrolysis (second degradation) zone from 466^0C to 810^0C with total degradation of 12.94%. The subsequent degradation is found to proceed very slowly beyond 1000^0C with total degradation of 1.99%. Residue left at 1000^0C is ash and is about 40.01% of the original sample weight. The highest activation energy was found at 347^0C and it was $0.26\%/^0$C.

Another test was run for sludge of after electrocoagulation was conducted from the ambient temperature to 1000^0C. Flowing rate was kept constant at 400 ml/min. Under nitrogen atmosphere, moisture removal of about 6.81% is observed to occur up to 98^0C followed by removal of light volatiles up to 500^0C. This initial zone is followed by the active pyrolysis (second degradation) zone from 500^0C to 800^0C with total degradation of 9.55%. The subsequent degradation is found to proceed very slowly beyond 1000^0C with total degradation of 19%. Residue left at 1000^0C is ash and is about 47.11% of the original sample weight. The highest activation energy was found at 113^0C and it was $0.21\%/^0$C.

Table 7.1: Characteristics of agro based pulp and paper mill effluent

Characteristics	Black Liquor	Effluent
COD, mg/l	590000	1300
BOD, mg/l	120500	320
pH	11	10.8
Total Solids, g/l	-	1.6
Suspended Solids, g/l	-	0.218
Dissolved Solids, g/l	-	1.4
Conductivity, mMHOS	-	1.9

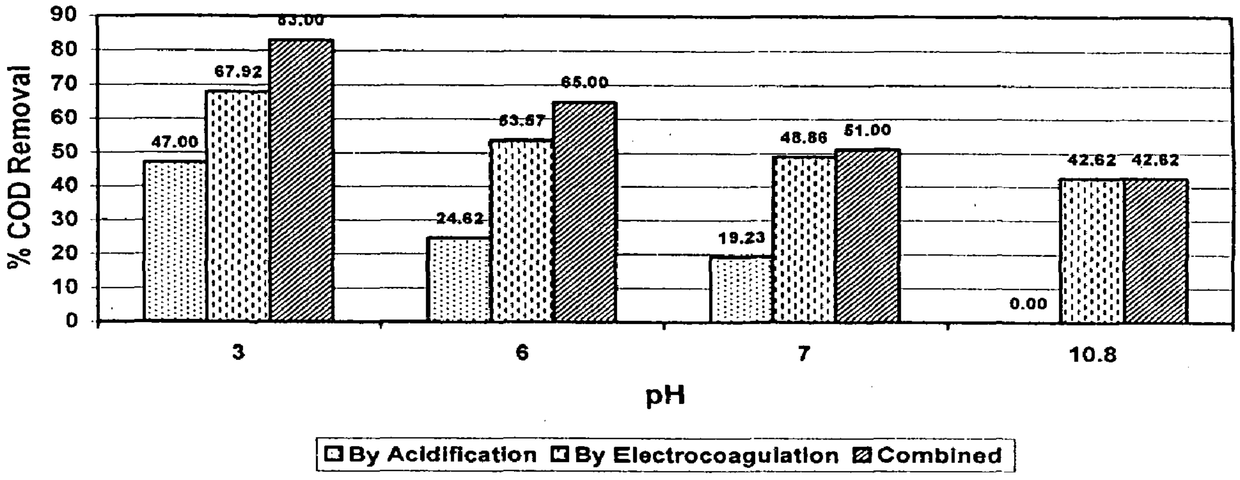


Fig. 7.1 : **Effect of pH on Percentage COD Removal**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

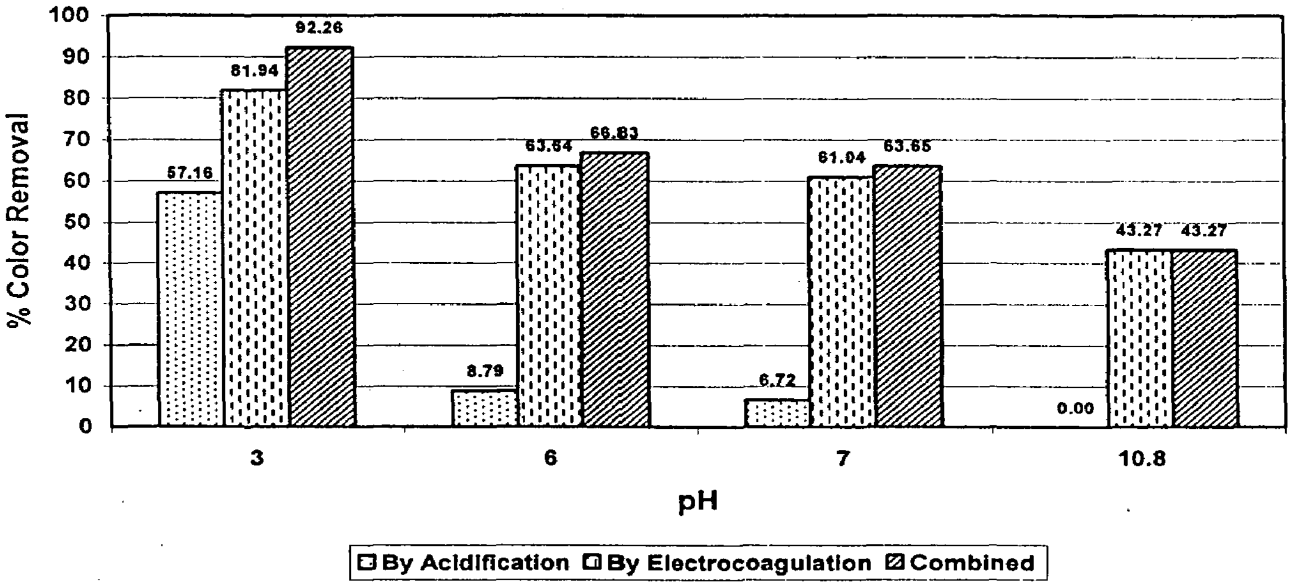


Fig. 7.2 : **Effect of pH on Percentage Color Removal**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

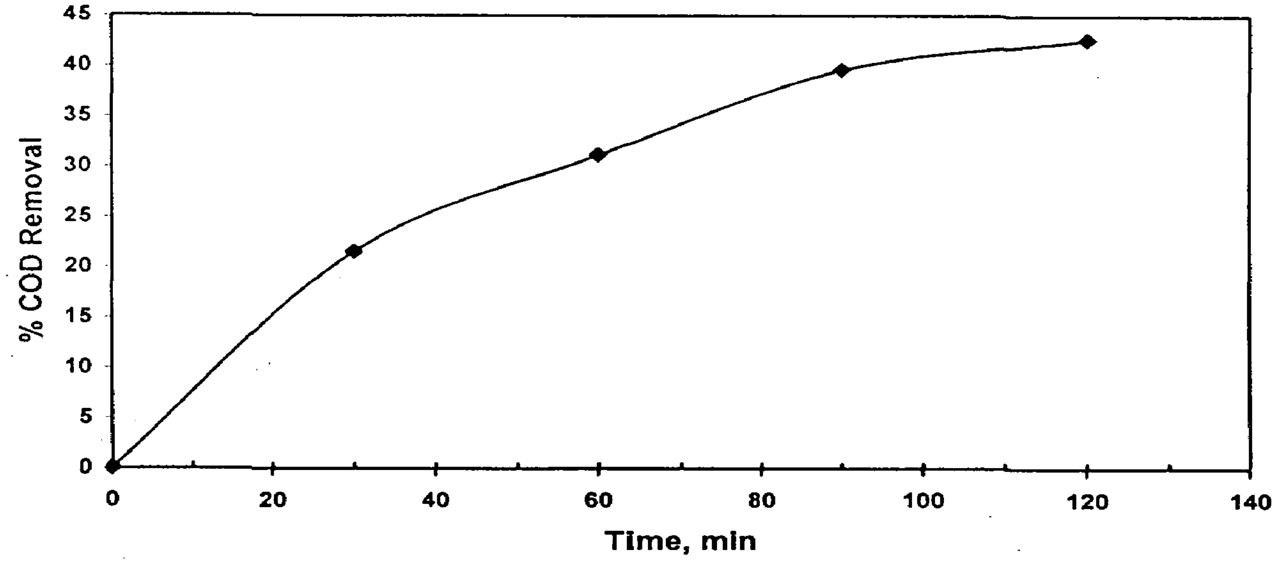


Fig. 7.3 : **Percentage COD Removal by Electrocoagulation at pH= 10.8**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

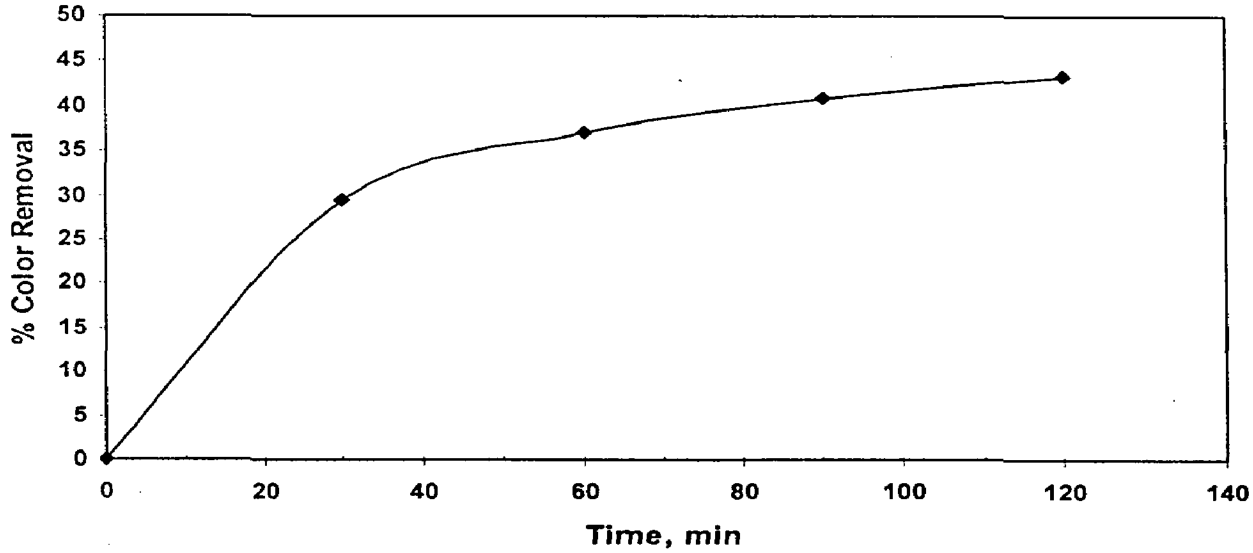


Fig. 7.4 : **Percentage Color Removal by Electrocoagulation at pH= 10.8**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

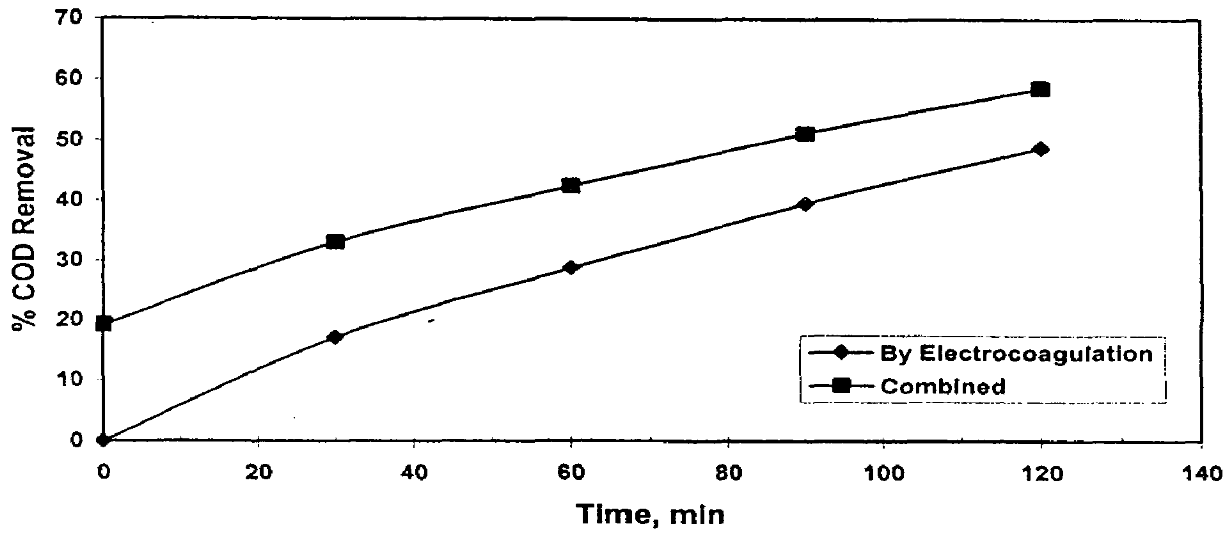


Fig. 7.5 : Percentage COD Removal by Electrocoagulation and Combination of Acidification & Electrocoagulation at pH= 7
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

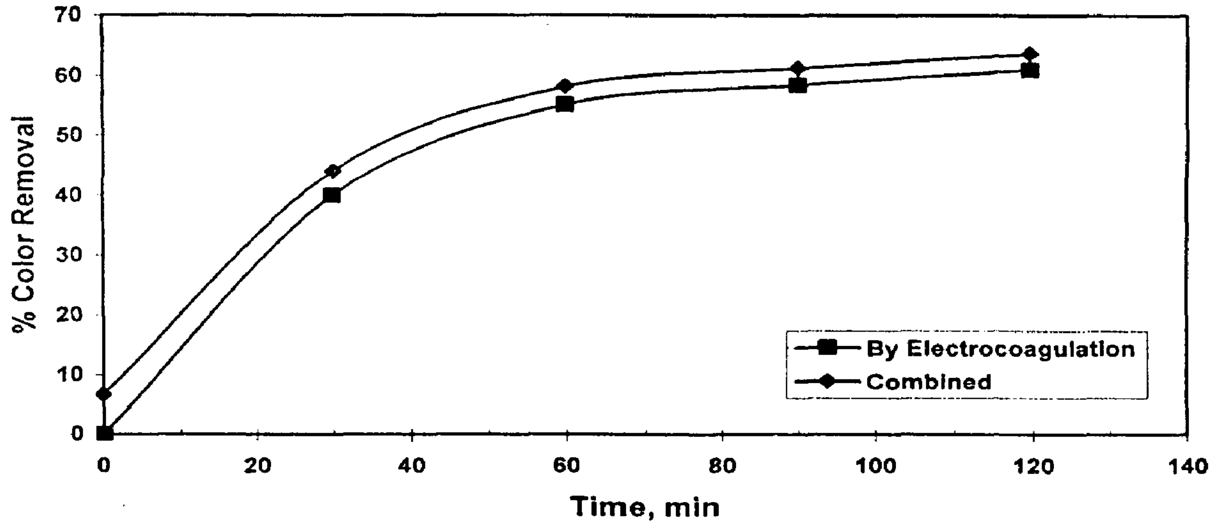


Fig. 7.6 : Percentage Color Removal by Electrocoagulation and Combination of Acidification & Electrocoagulation at pH= 7
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

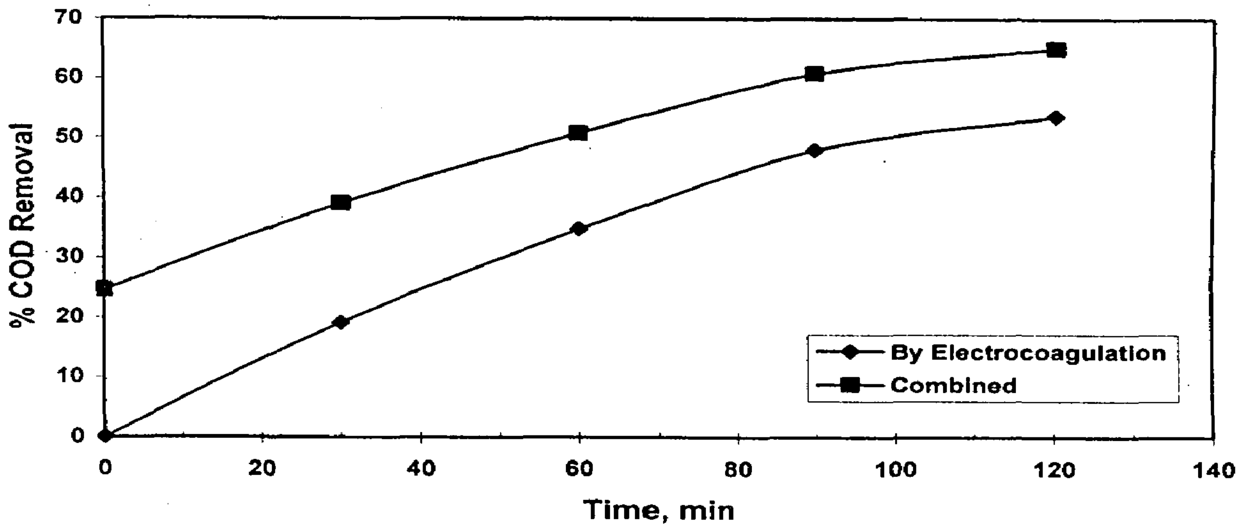


Fig. 7.7 : **Percentage COD Removal by Electrocoagulation and Combination of Acidification & Electrocoagulation at pH= 6**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

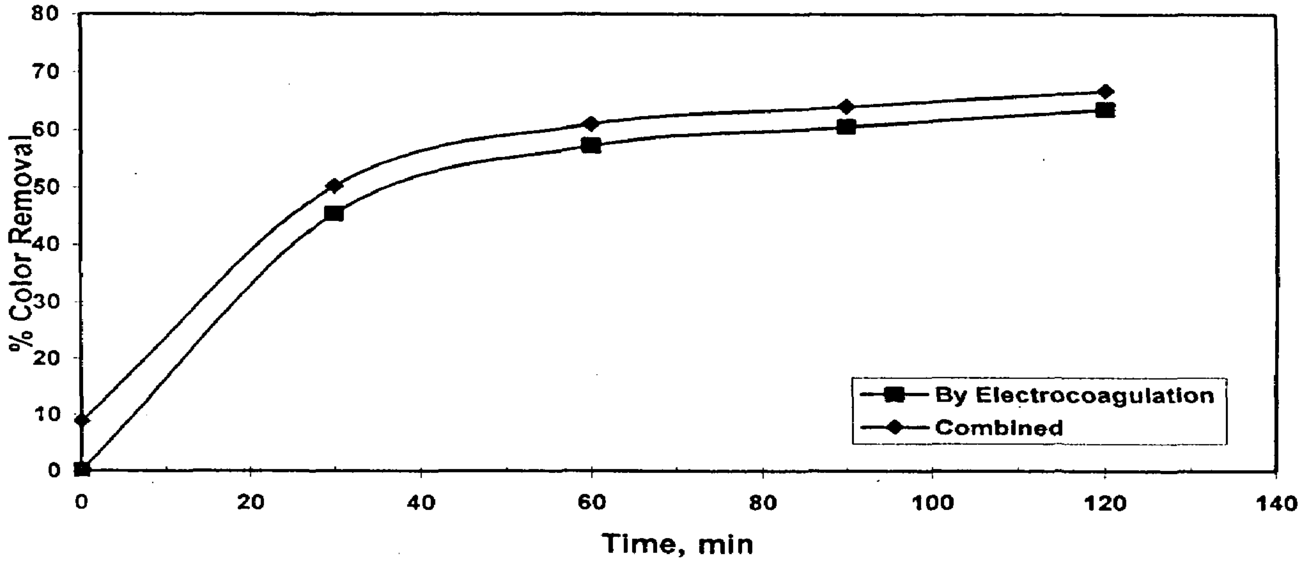


Fig. 7.8 : **Percentage Color Removal by Electrocoagulation and Combination of Acidification & Electrocoagulation at pH= 6**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

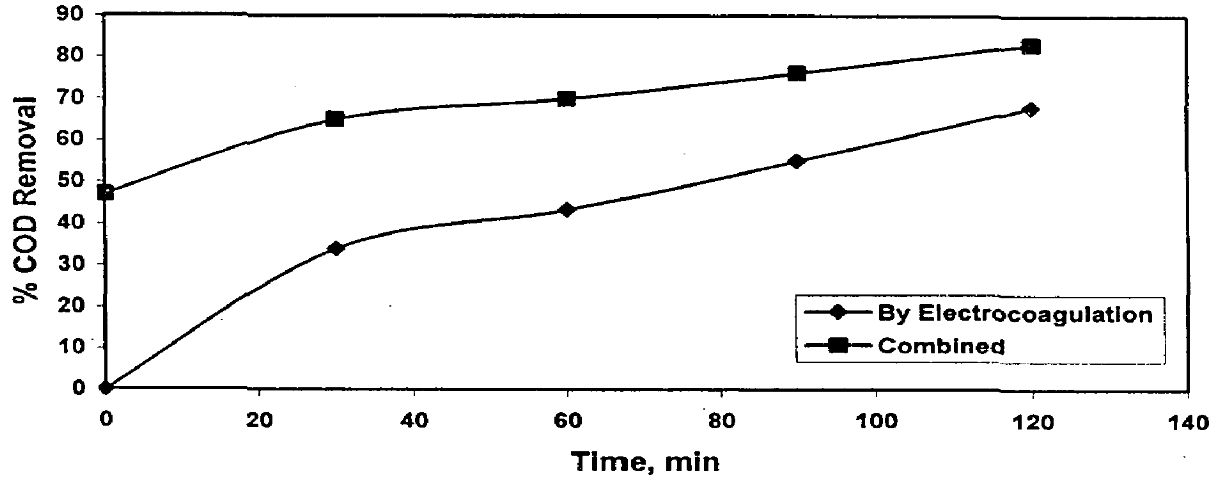


Fig. 7.9 : **Percentage COD Removal by Electrocoagulation and Combination of Acidification & Electrocoagulation at pH= 3**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

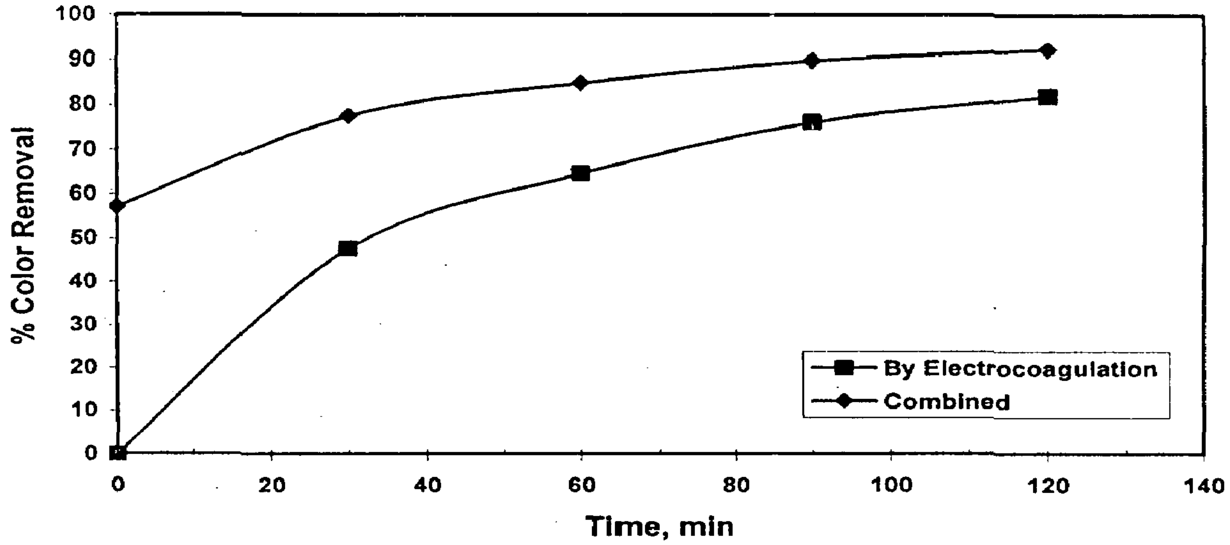


Fig. 7.10 : **Percentage Color Removal by Electrocoagulation and Combination of Acidification & Electrocoagulation at pH= 3**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

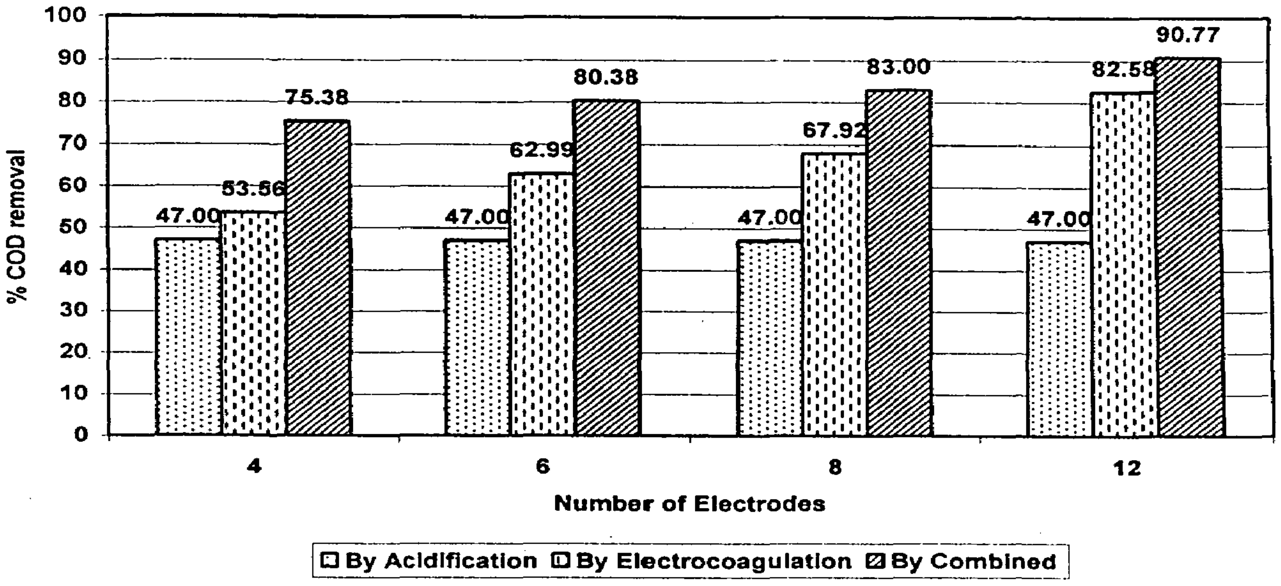


Fig. 7.11 : **Effect of Number of Electrodes on Percentage COD Removal**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

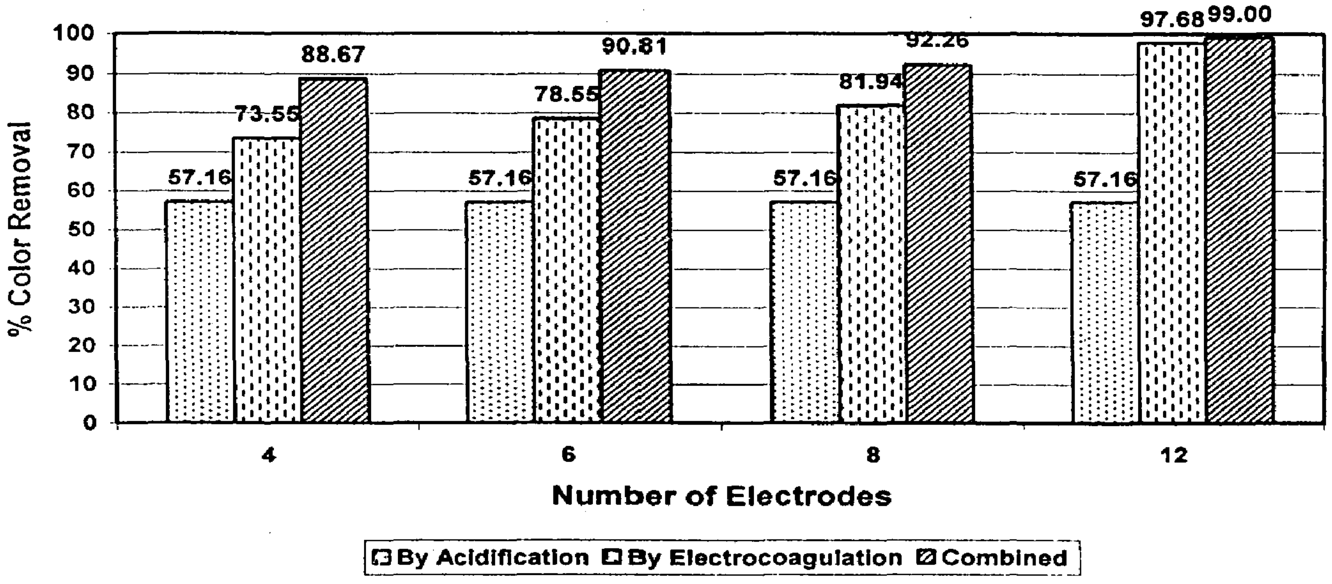


Fig. 7.12 : **Effect of Number of Electrodes on Percentage Color Removal**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 1.2A, Number of electrode=8, Electrode spacing=1cm, Electrodes are fully submerged

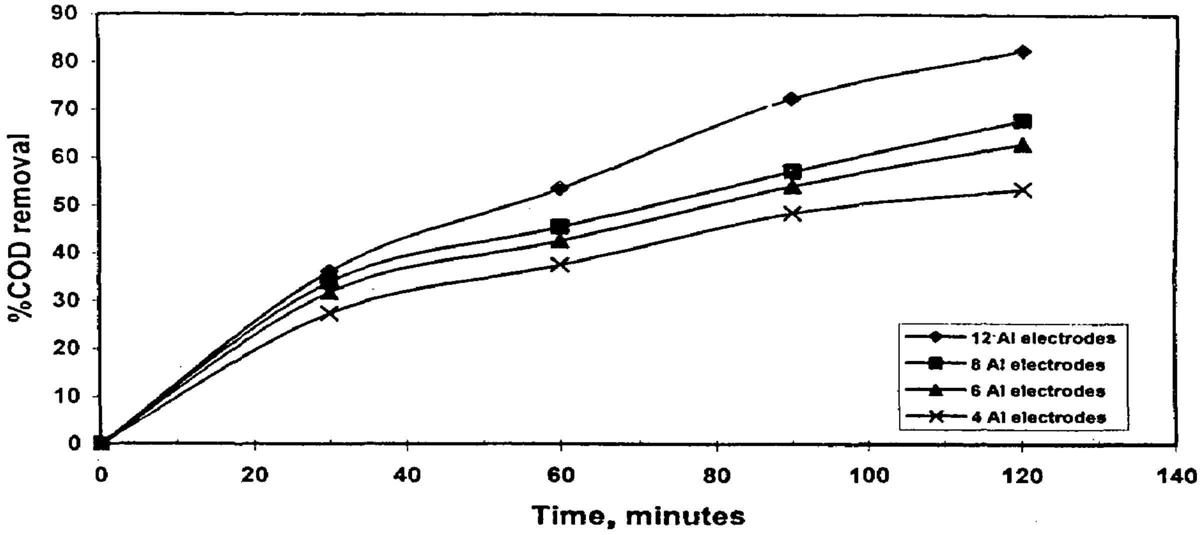


Fig. 7.13 : Effect of Number of Electrodes on Percentage COD Removal by Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Current= 1.2A, Electrode spacing=1cm, Electrodes are fully submerged

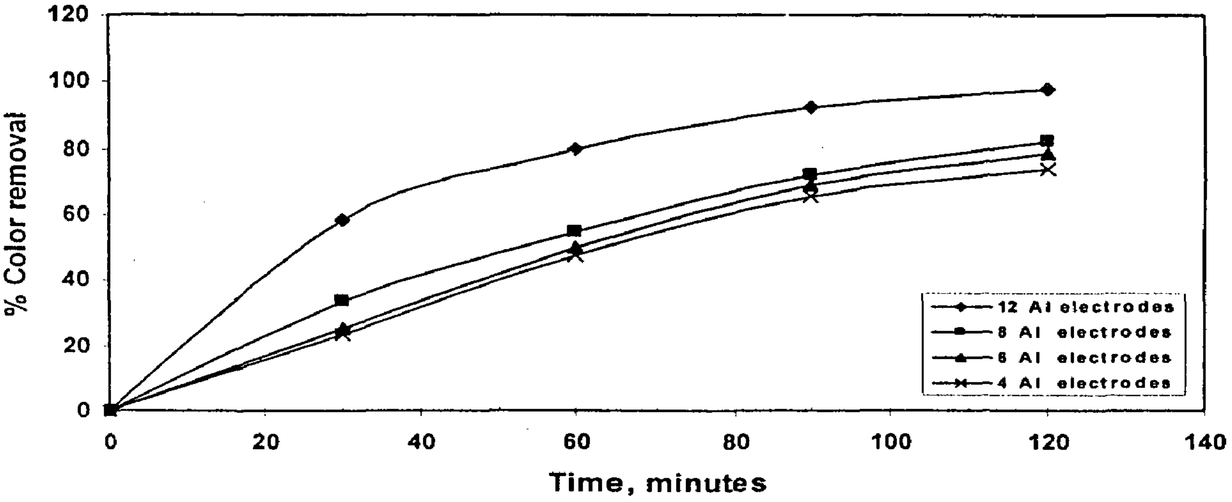


Fig. 7.14 : Effect of Number of Electrodes on Percentage Color Removal by Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Current= 1.2A, Electrode spacing=1cm, Electrodes are fully submerged

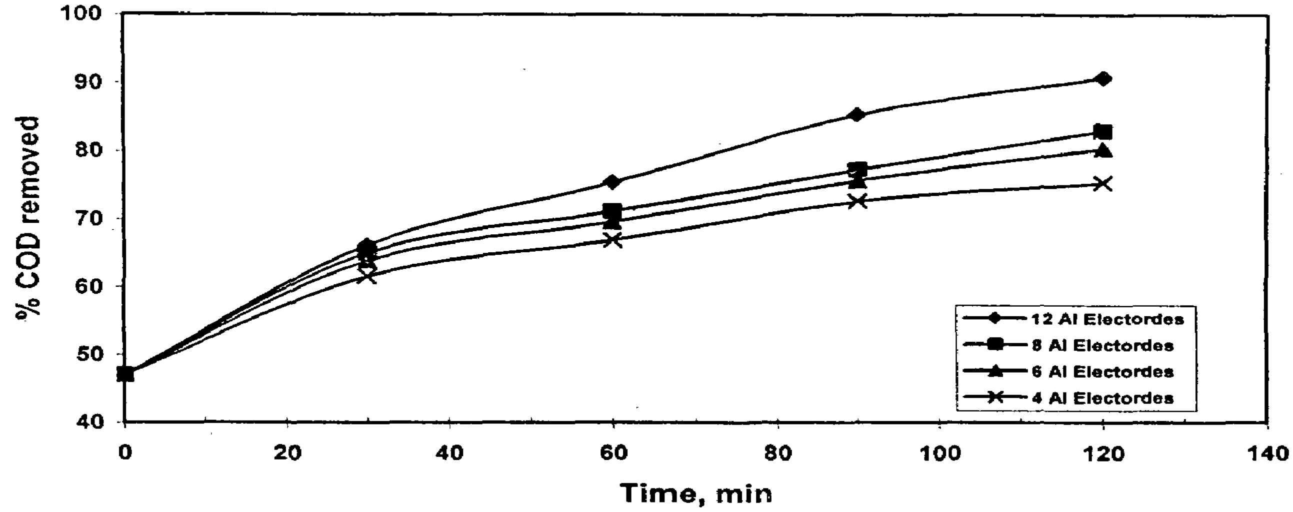


Fig. 7.15 : Effect of Number of Electrodes on Percent COD Removal by Combination of Acidification & Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Current= 1.2A, Electrode spacing=1cm, Electrodes are fully submerged

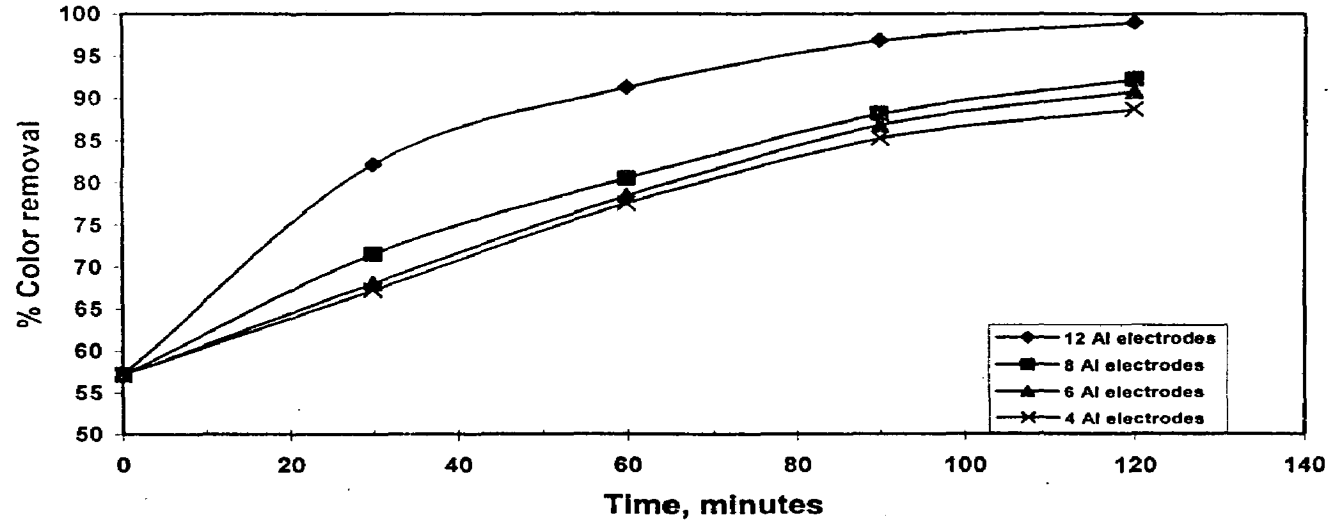


Fig. 7.16 : Effect of Number of Electrodes on Percentage Color Removal by Combination of Acidification & Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Current= 1.2A, Electrode spacing=1cm, Electrodes are fully submerged

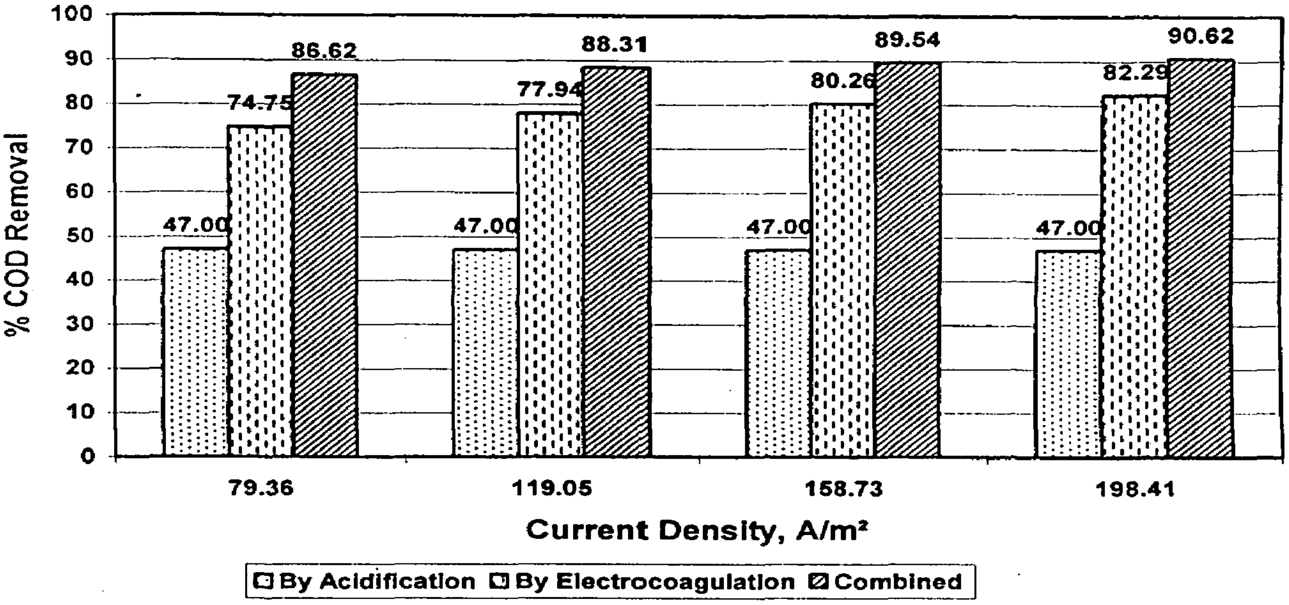


Fig. 7.17 : **Effect of Current Density on Percentage COD Removal**
Initial COD= 1300 mg/l, Voltage= 5V, Number of electrode=6,
Electrode spacing=1cm, Electrodes are fully submerged

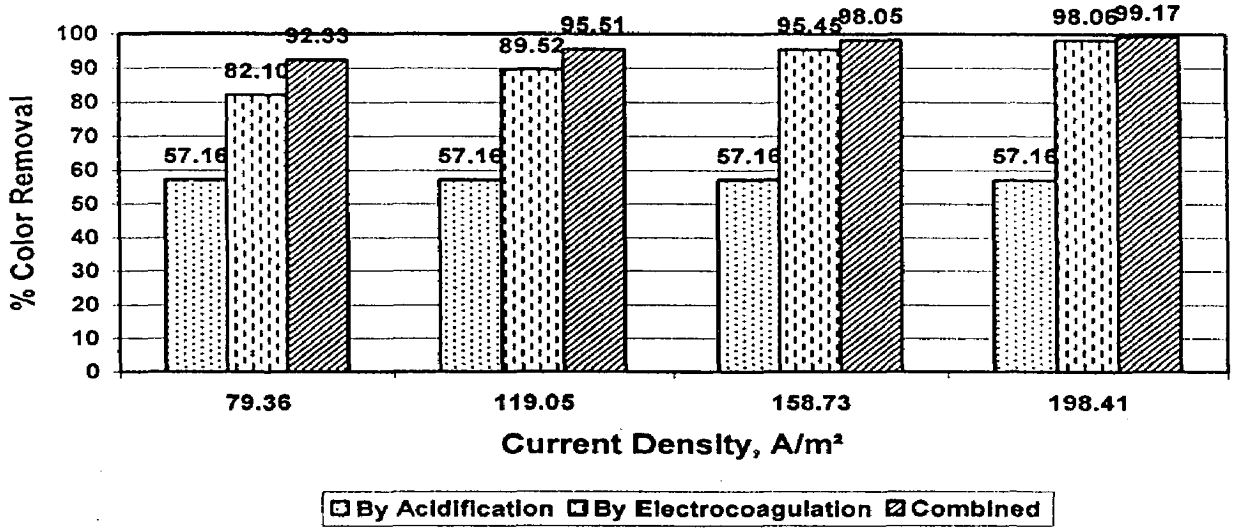


Fig. 7.18 : **Effect of Current Density on Percentage Color Removal**
Initial COD= 1300 mg/l, Voltage= 5V, Number of electrode=6,
Electrode spacing=1cm, Electrodes are fully submerged

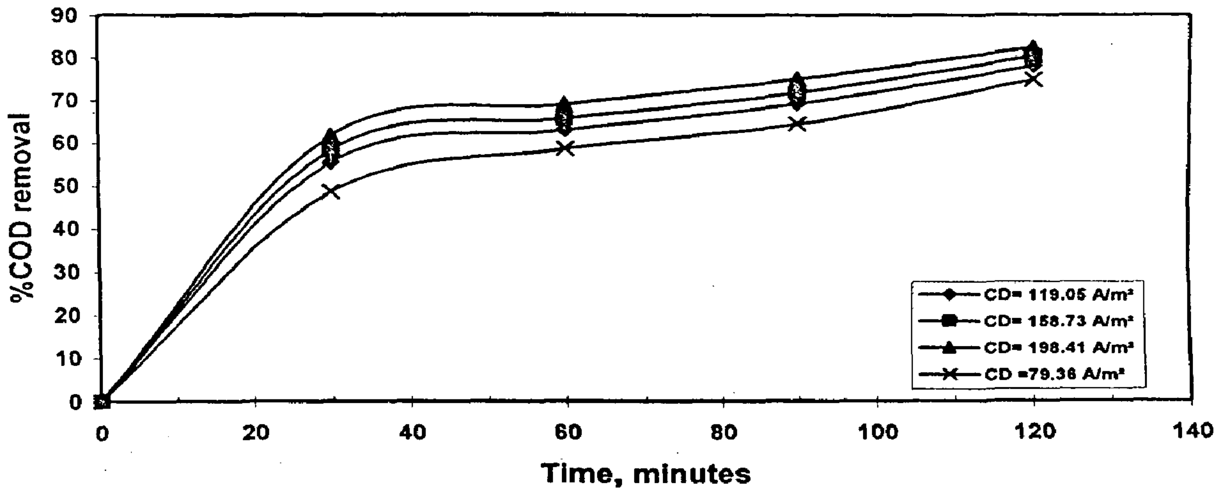


Fig. 7.19 : Effect of Current Density on Percentage COD Removal by Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Number of electrode=6,
Electrode spacing=1cm, Electrodes are fully submerged

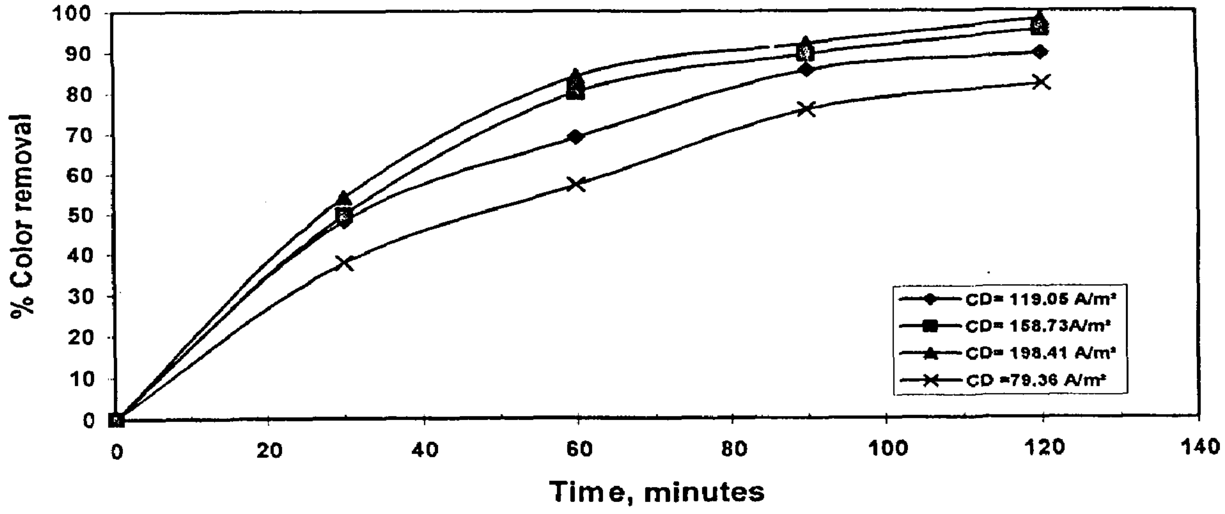


Fig. 7.20 : Effect of Current Density on Percentage Color Removal by Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Number of electrode=6,
Electrode spacing=1cm, Electrodes are fully submerged

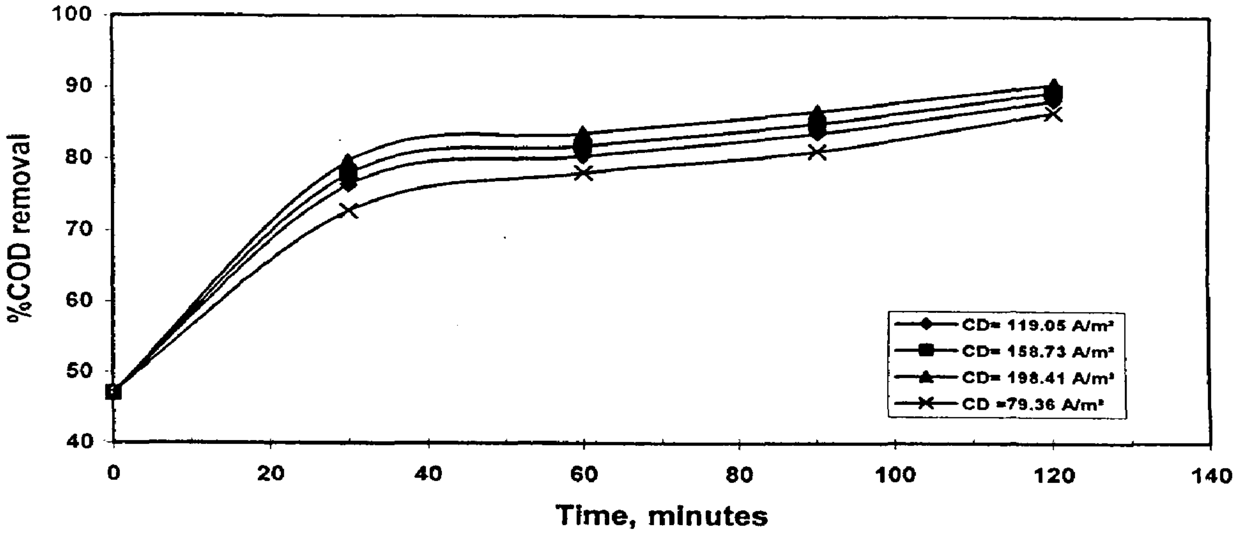


Fig. 7.21 : Effect of Current Density on Percentage COD Removal by Combination of Acidification & Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Number of electrode=6,
Electrode spacing=1cm, Electrodes are fully submerged

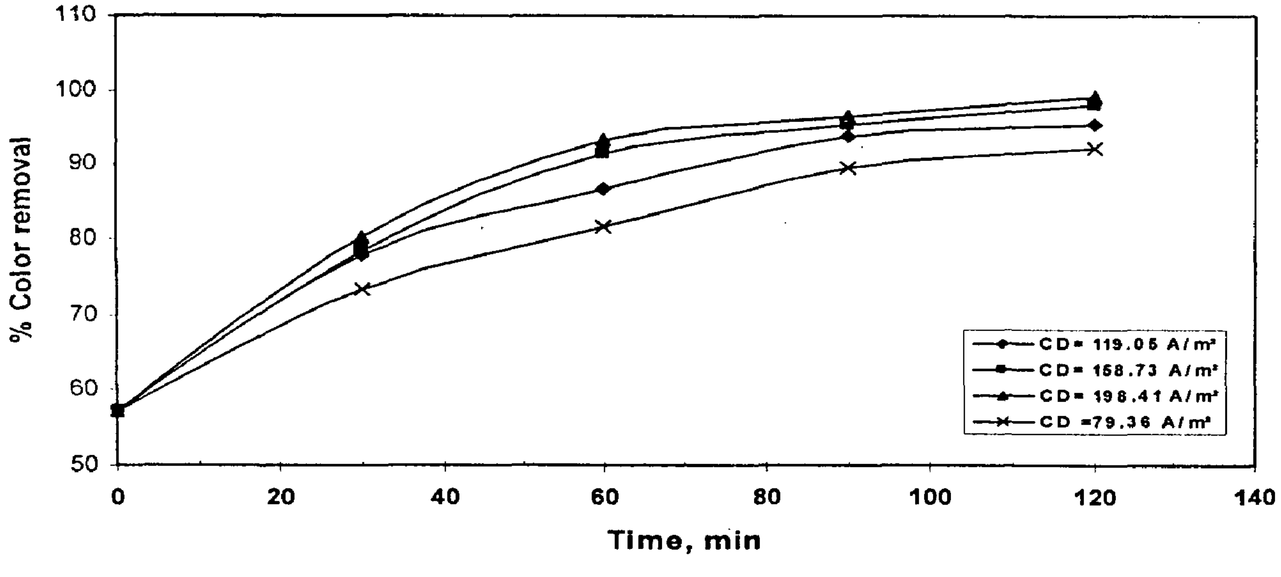


Fig. 7.22 : Effect of Current Density on Percentage Color Removal by Combination of Acidification & Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Number of electrode=6,
Electrode spacing=1cm, Electrodes are fully submerged

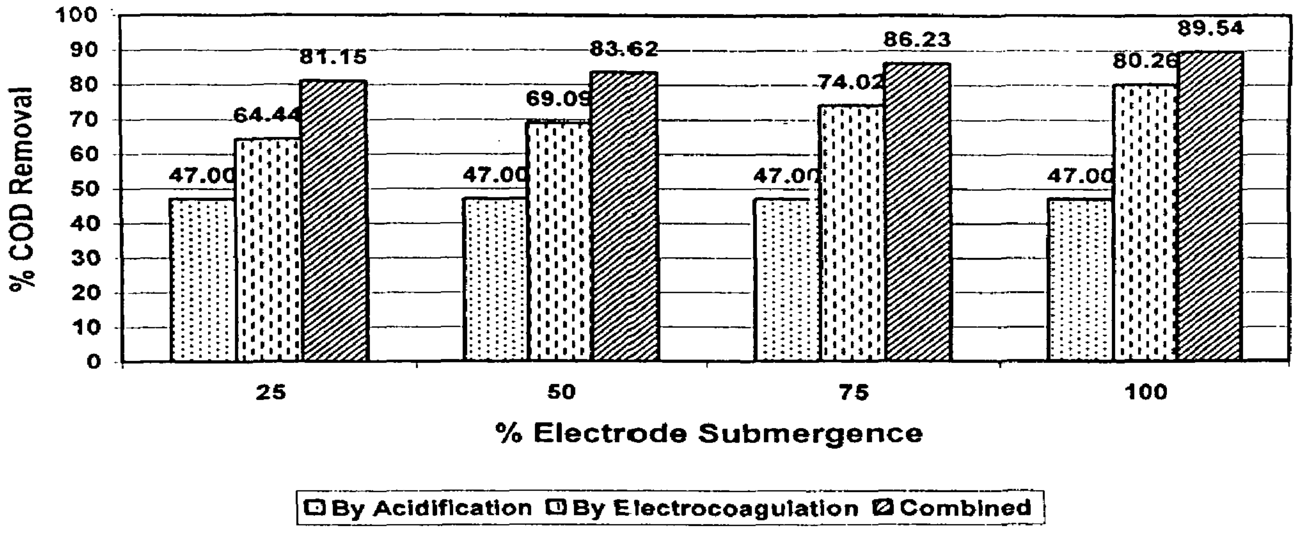


Fig. 7.23 **: Effect of Electrode Submergence on Percentage COD Removal** Initial COD= 1300 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6, Electrode spacing=1cm

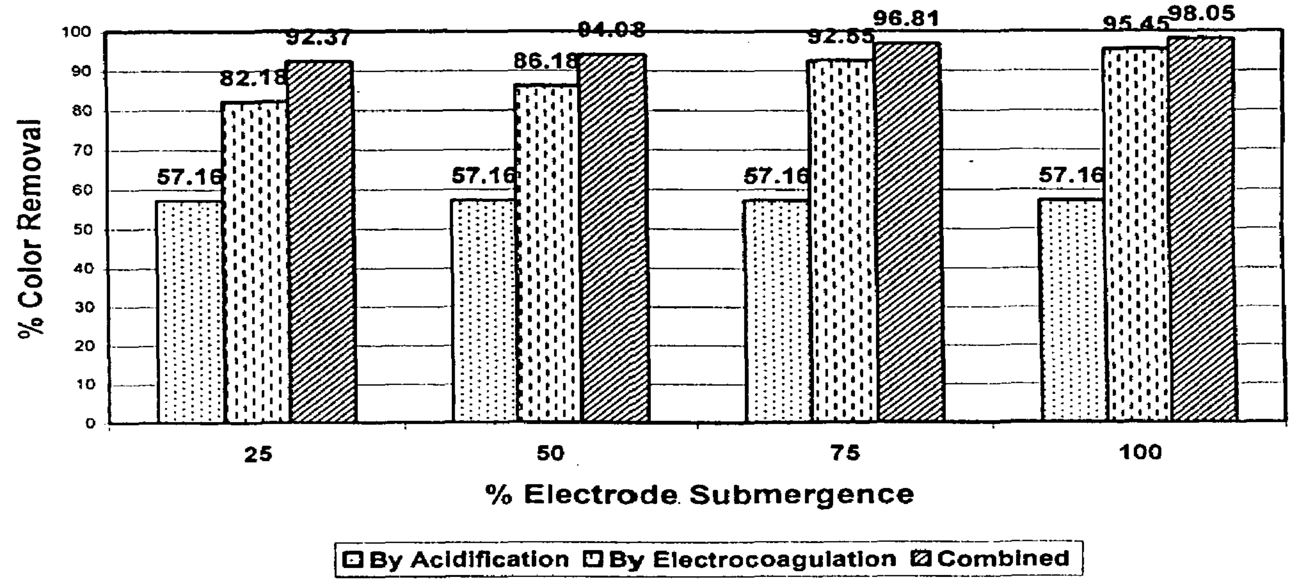


Fig. 7.24 **: Effect of Electrode Submergence on Percentage Color Removal** Initial COD= 1300 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6, Electrode spacing=1cm

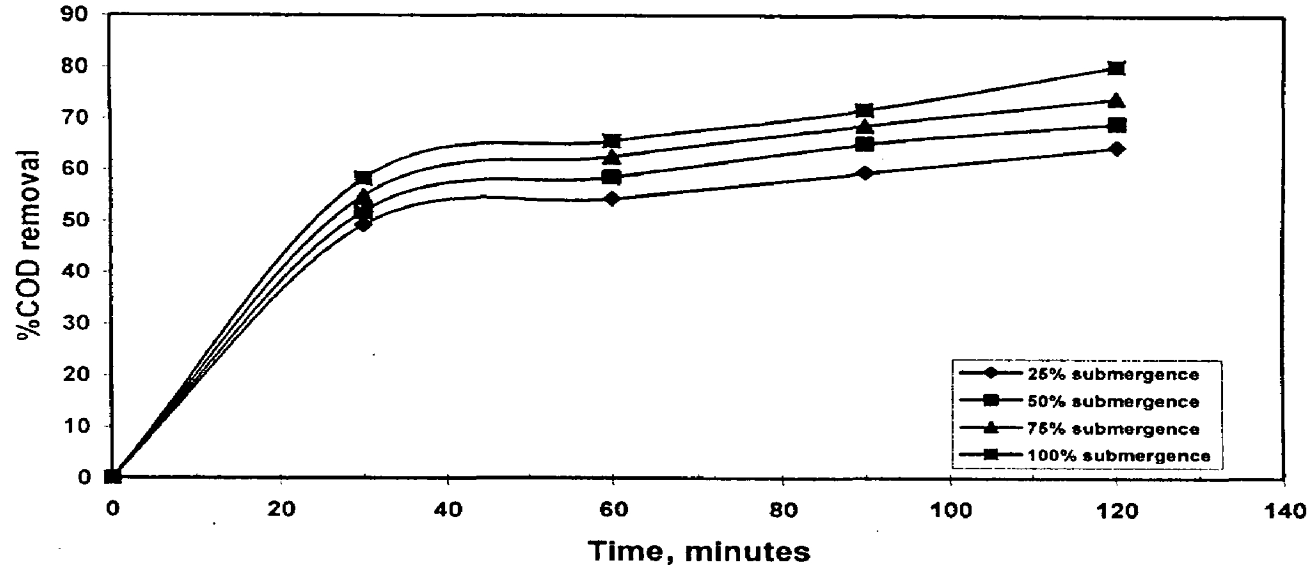


Fig. 7.25 : Effect of Electrode Submergence on Percentage COD Removal by Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6, Electrode spacing=1cm

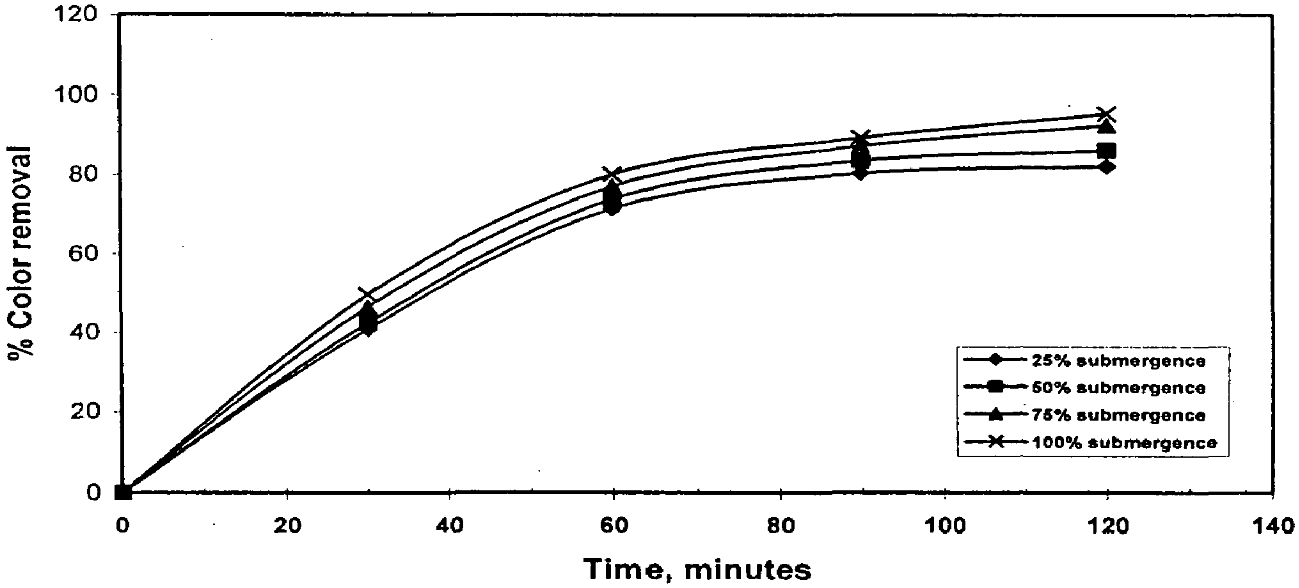


Fig. 7.26 : Effect of Electrode Submergence on Percentage Color Removal by Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6, Electrode spacing=1cm

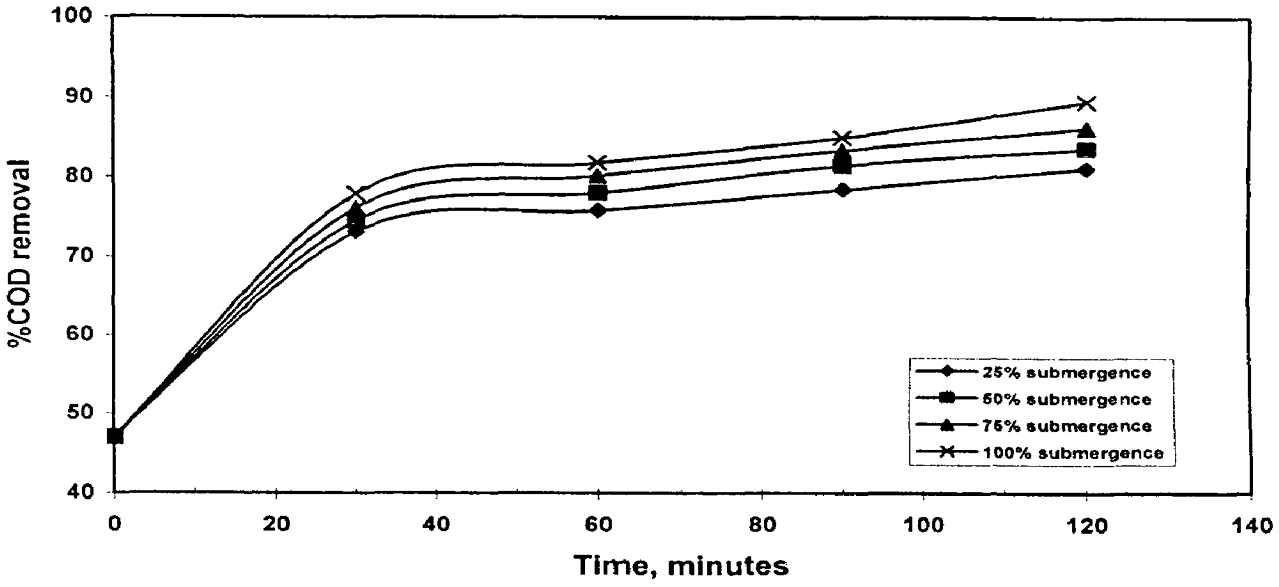


Fig. 7.27 : **Effect of Electrode Submergence on Percentage COD Removal by Combination of Acidification & Electrocoagulation**
Initial COD= 689 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6, Electrode spacing=1cm

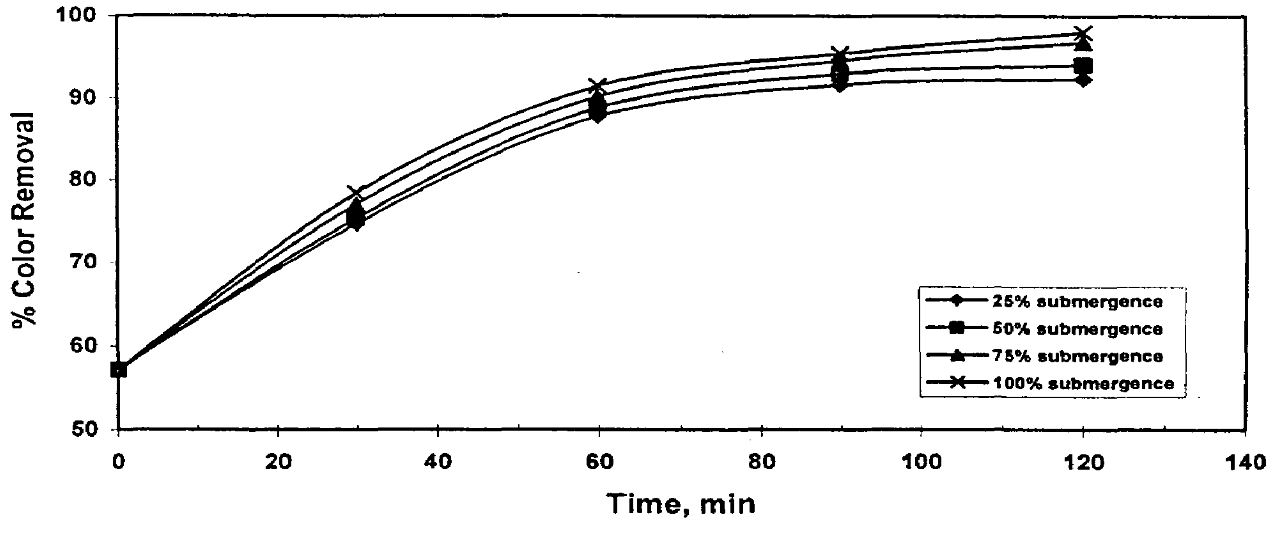


Fig. 7.28 : **Effect of Electrode Submergence on Percentage Color Removal by Combination of Acidification & Electrocoagulation**
Initial COD= 689 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6, Electrode spacing=1cm

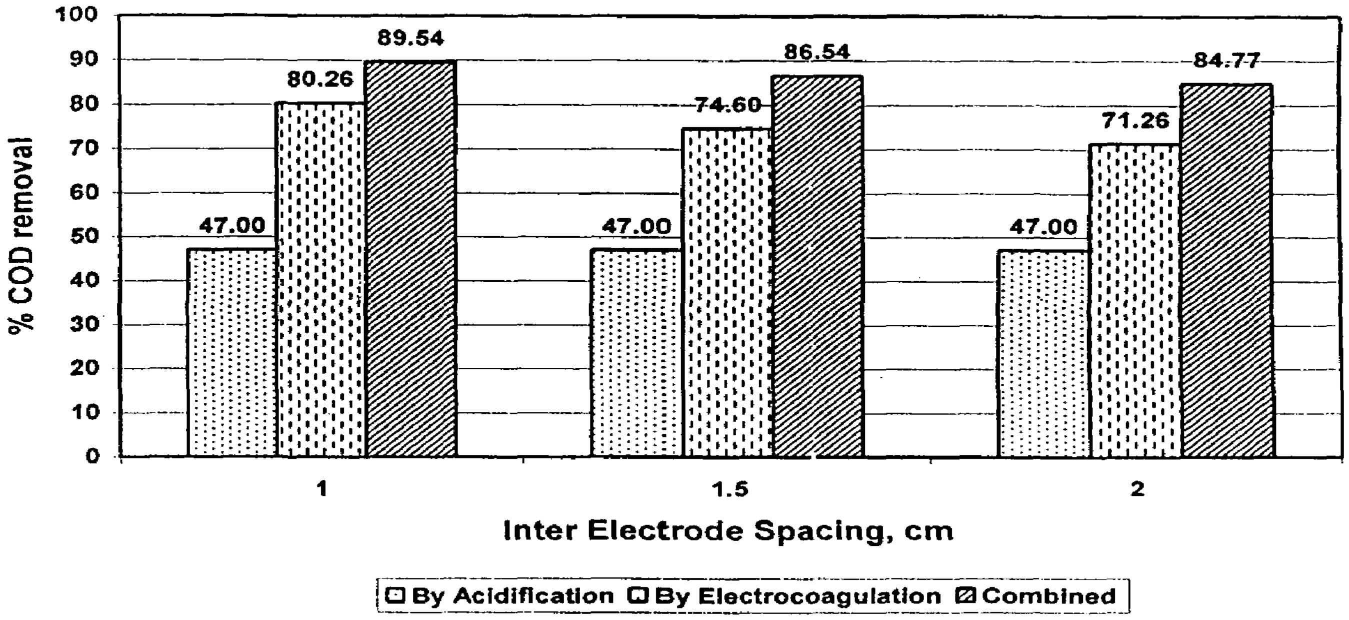


Fig. 7.29 : **Effect of Inter-Electrode Spacing on Percentage COD Removal**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 4A, Number of electrode= 6, Electrodes are fully submerged

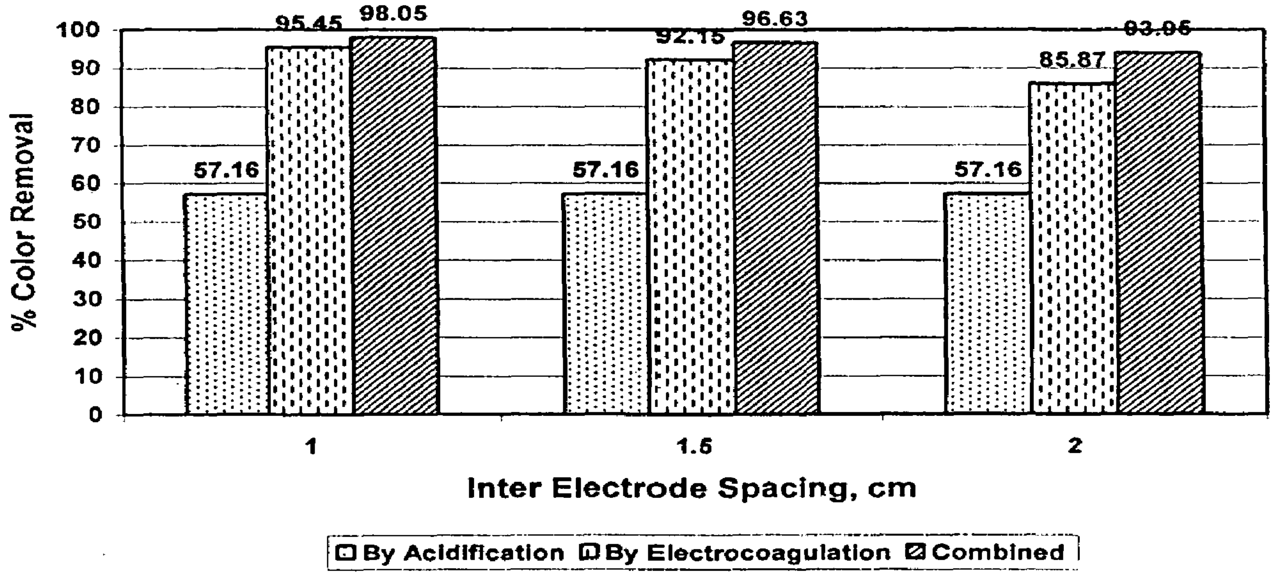


Fig. 7.30 : **Effect of Inter-Electrode Spacing on Percentage Color Removal**
Initial COD= 1300 mg/l, Voltage= 5V, Current= 4A, Number of electrode= 6, Electrodes are fully submerged

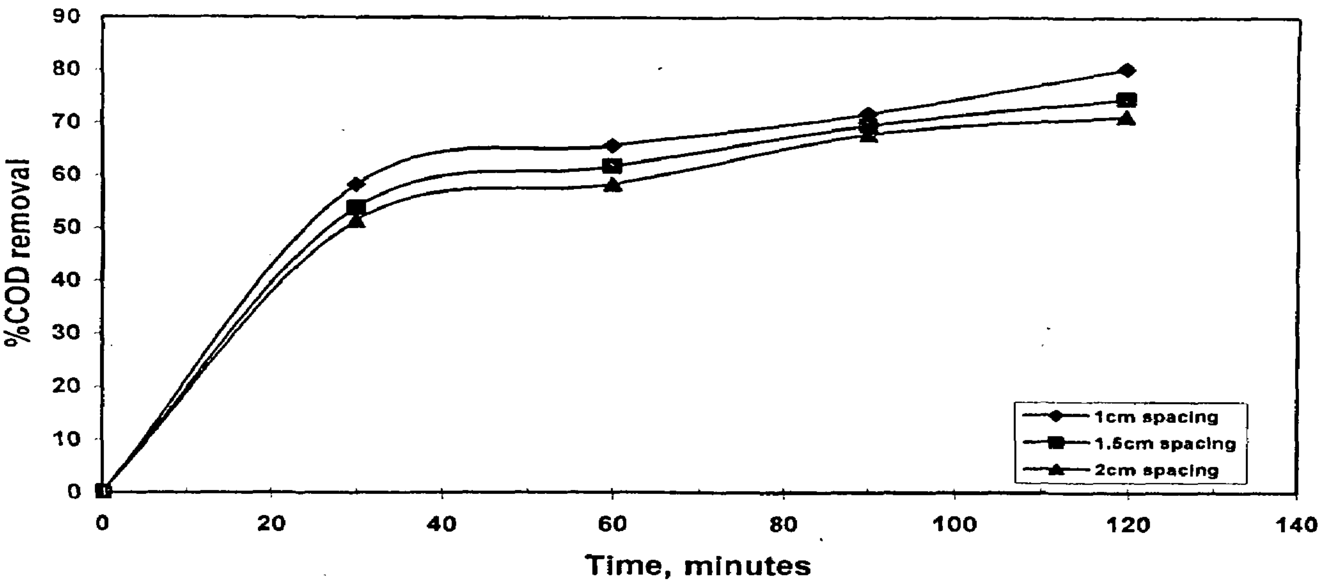


Fig. 7.31 : Effect of Inter-Electrode Spacing on Percentage COD Removal by Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6
Electrodes are fully submerged

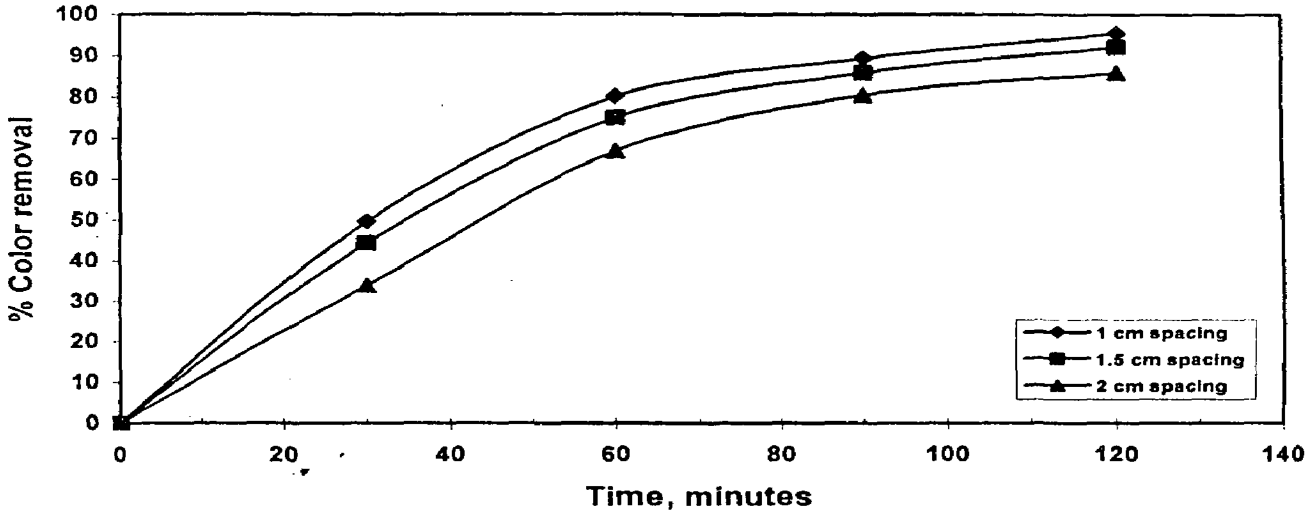


Fig. 7.32 : Effect of Inter-Electrode Spacing on Percentage Color Removal by Electrocoagulation
Initial COD= 689 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6,
Electrodes are fully submerged

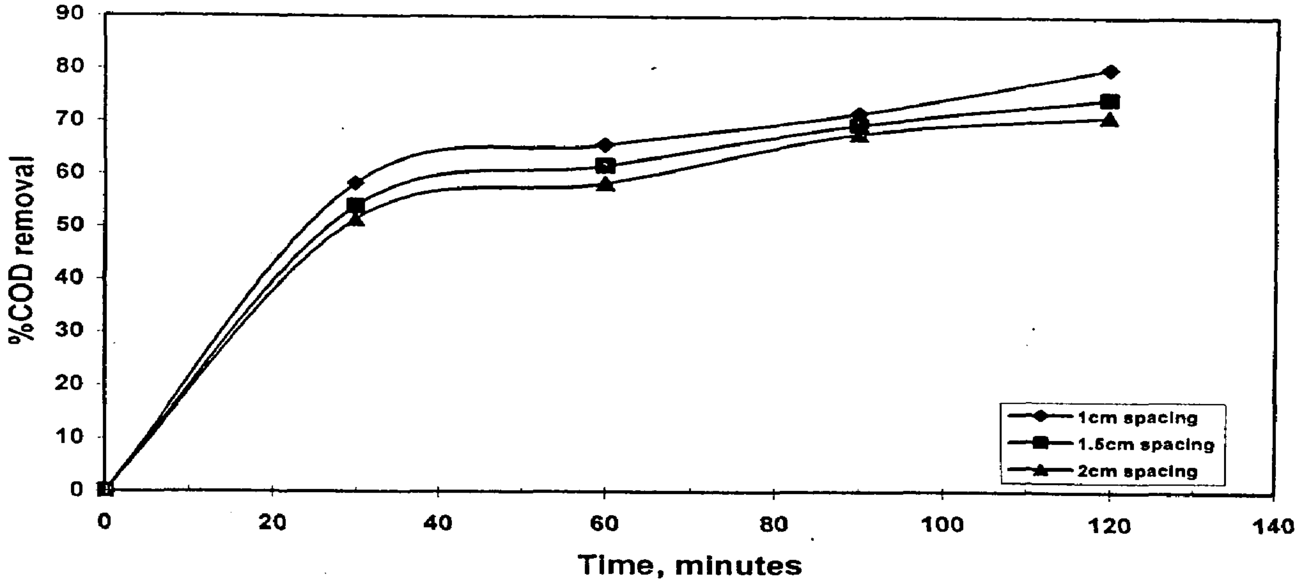


Fig. 7.31 : **Effect of Inter-Electrode Spacing on Percentage COD Removal by Electrocoagulation**
Initial COD= 689 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6, Electrodes are fully submerged

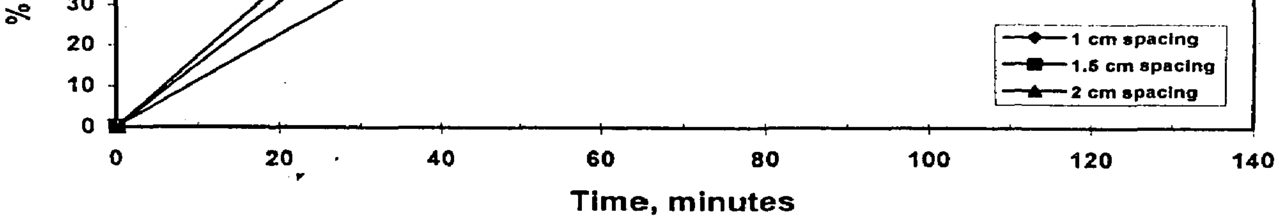


Fig. 7.32 : **Effect of Inter-Electrode Spacing on Percentage Color Removal by Electrocoagulation**
Initial COD= 689 mg/l, Voltage= 5V, Current= 4A, Number of electrode=6, Electrodes are fully submerged

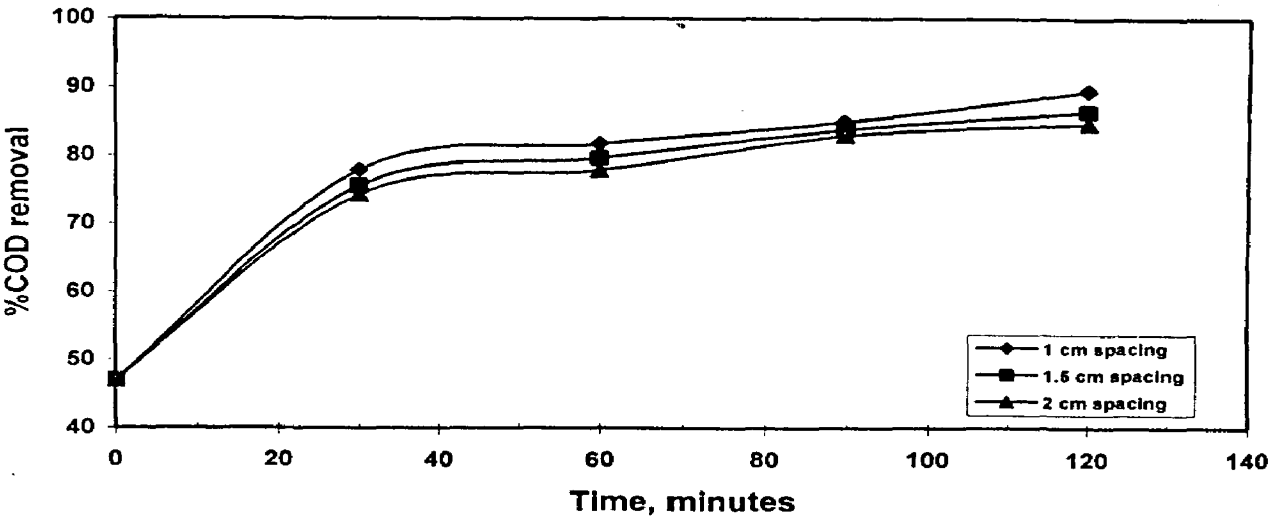


Fig. 7.33 : Effect of Inter-Electrode Spacing on Percentage COD Removal by Combination of Acidification and Electrocoagulation
Initial COD= 1300 mg/l, Voltage= 5V, Current= 4A, Number of electrode= 6, Electrodes are fully submerged

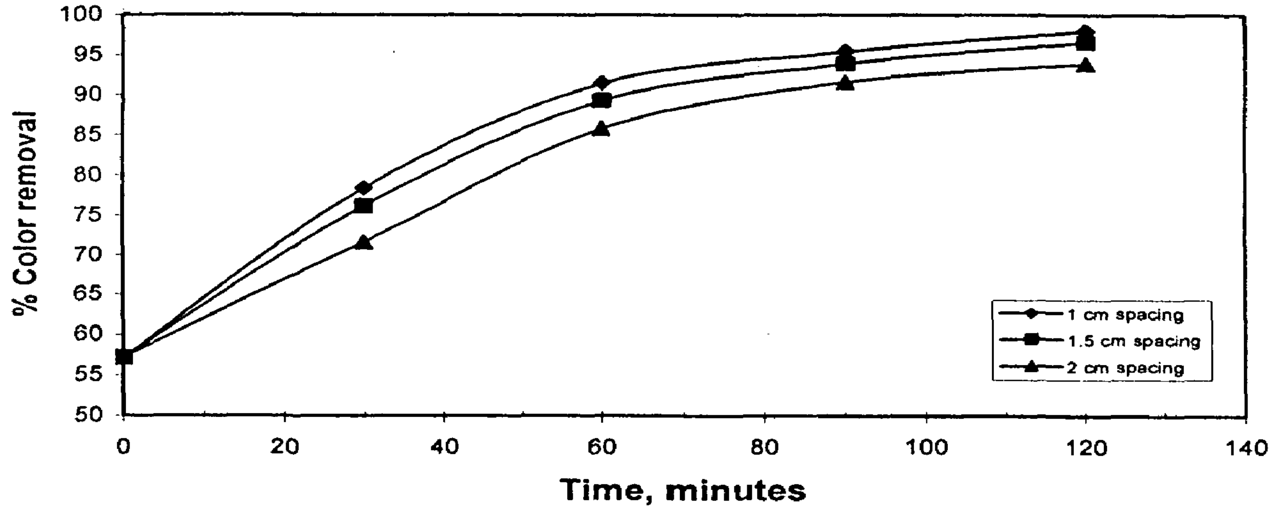


Fig. 7.34 : Effect of Inter-Electrode Spacing on Percentage Color Removal by Combination of Acidification and Electrocoagulation
Initial COD= 1300 mg/l, Voltage= 5V, Current= 4A, Number of electrode= 6, Electrodes are fully submerged

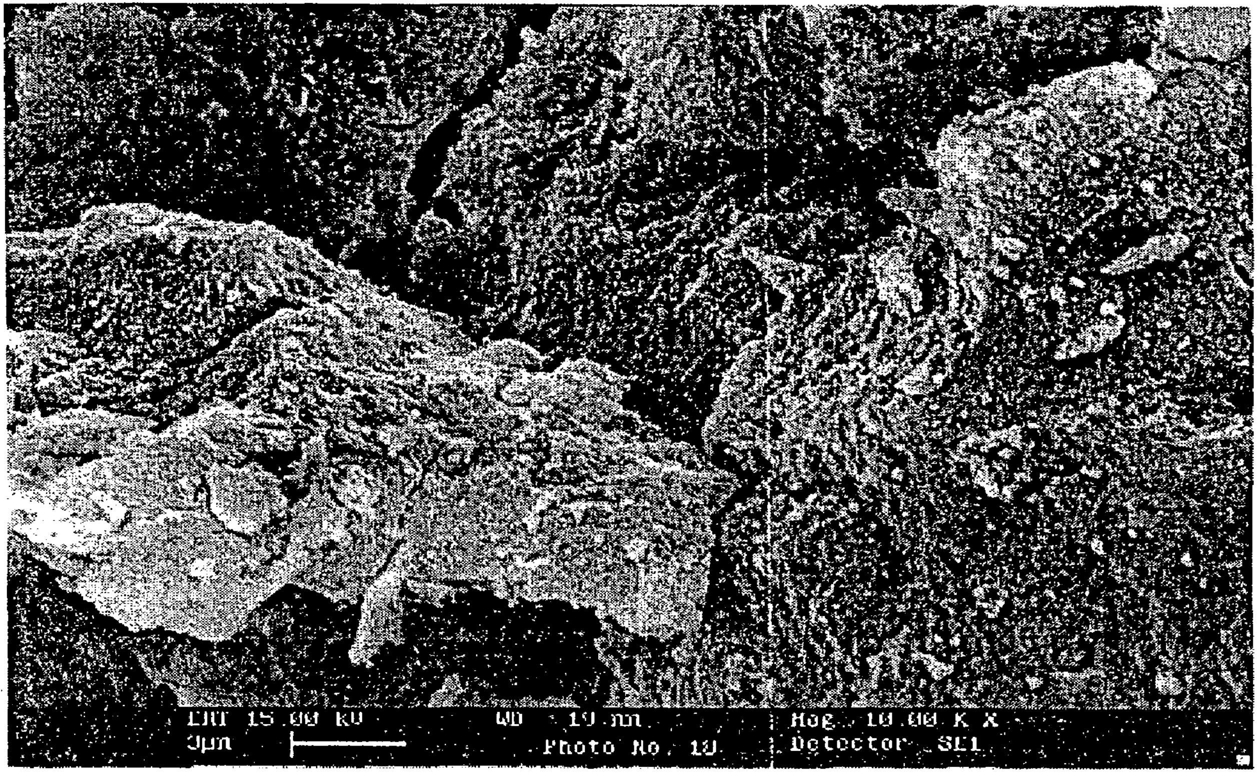


Fig. 7.35 : **Scanning Electron Micrograph of Sludge after Acidification at 1000 Times Magnification**

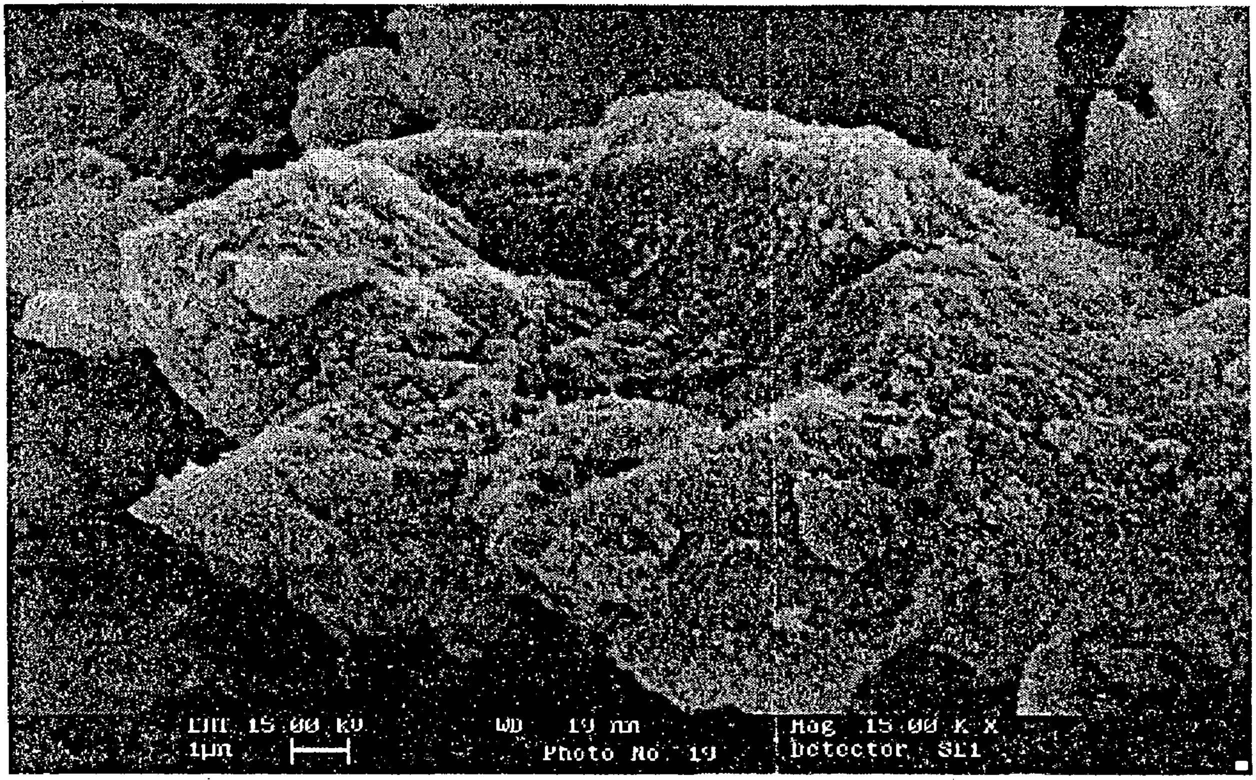


Fig. 7.36 : **Scanning Electron Micrograph of Sludge after Acidification at 1500 Times Magnification**

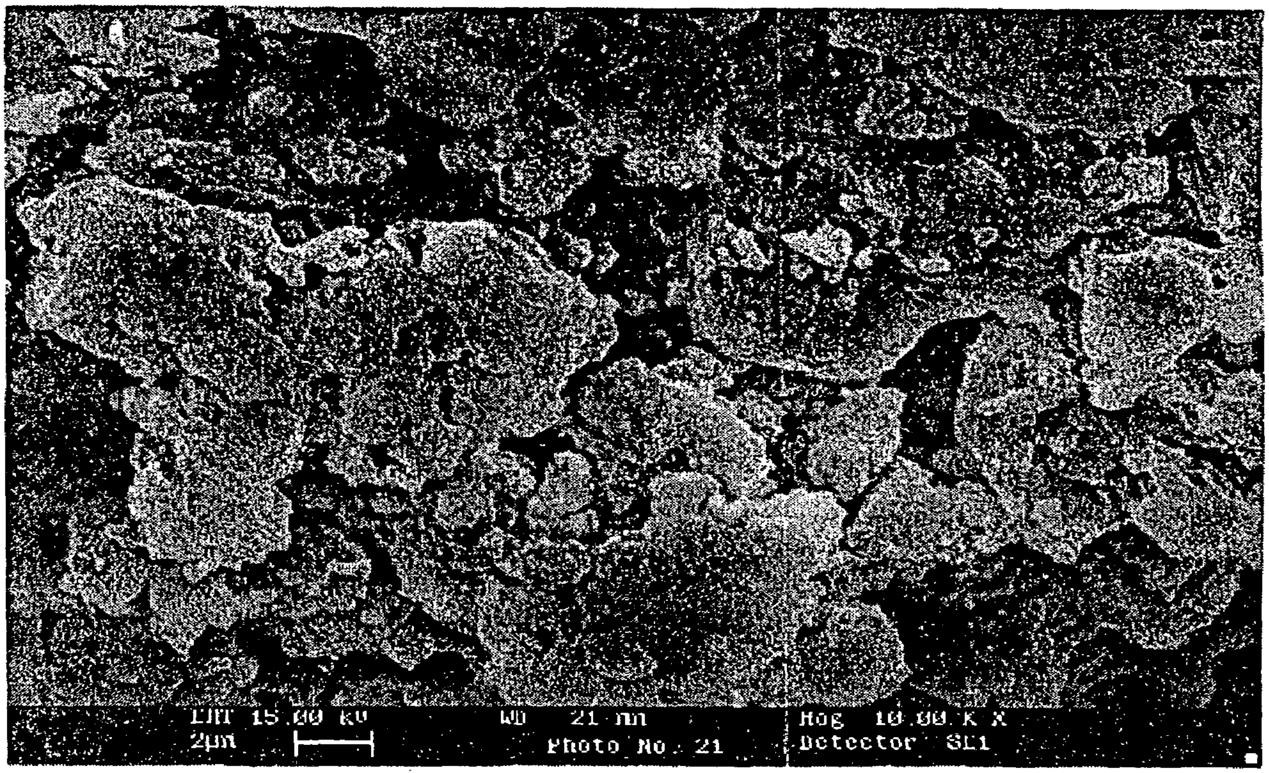


Fig. 7.37 : Scanning Electron Micrograph of Sludge after Electrocoagulation at 1000 Times Magnification

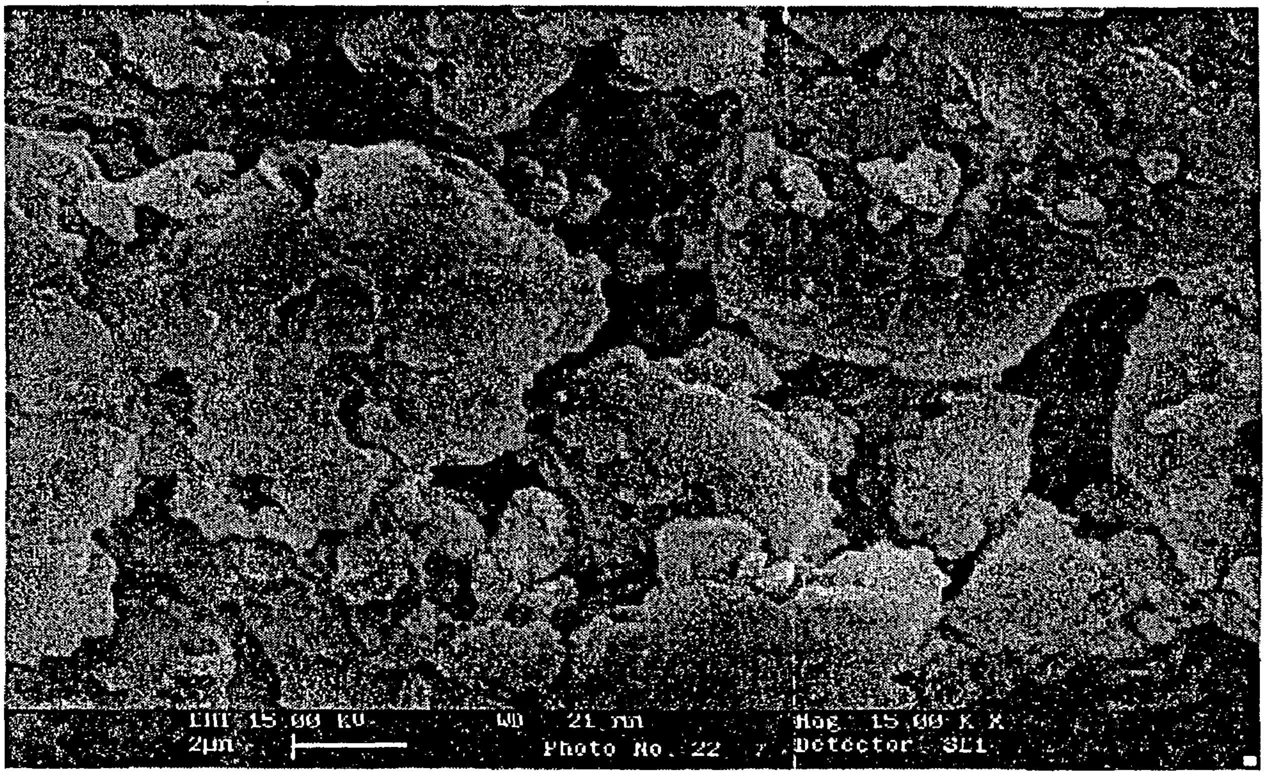


Fig. 7.38 : Scanning Electron Micrograph of Sludge after Electrocoagulation at 1500 Times Magnification

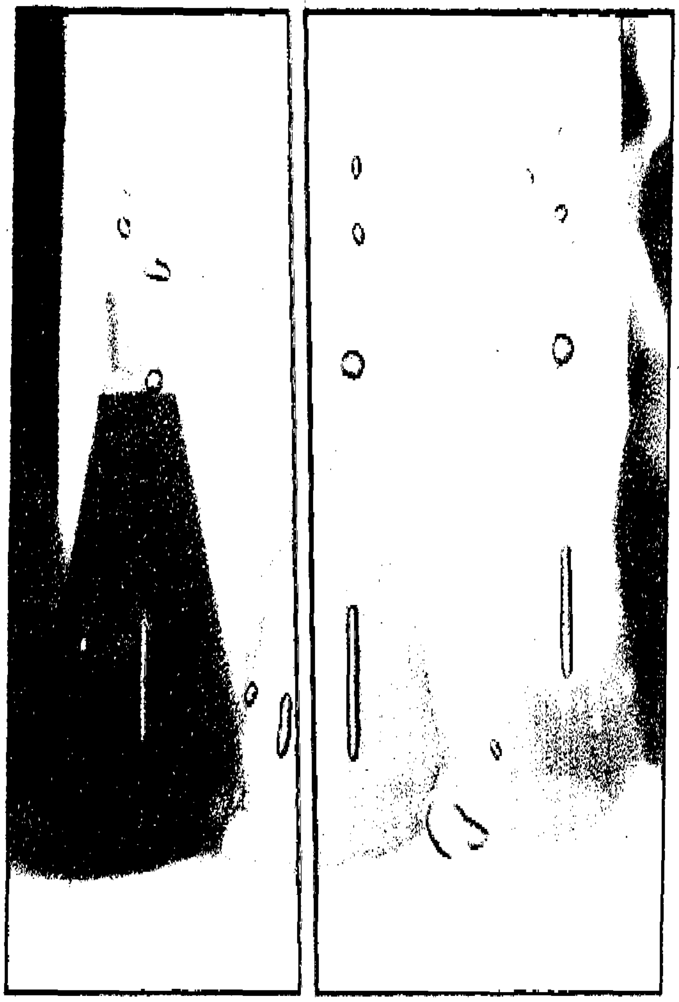


Fig. 7.41: Color comparison after two stage treatment of effluent by acidification and electrocoagulation

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

The following major conclusions can be drawn from the present work:

(1) Removal of COD and color by electrocoagulation increases as the pH of the effluent decreases.

(2) Percentage removal of COD and color increases with time till it attains equilibrium. Optimum time for it is 2 h.

(3) Removal of COD and color was found to increase with number of electrodes up to a certain number of electrodes, after that no appreciate increase in removal was observed. Optimum number of plates was found to be 6.

(4) Removal of COD and color was found to increase with increases in current density.

(5) Precipitation of the lignin from the effluents with sulfuric acid followed by electrocoagulation treatment considerably increases the COD removal efficiency.

(6) COD and color removal is maximum for Aluminum electrodes system when the plates are fully submerged.

(7) With the increase in inter-electrode spacing the percentage removal of COD and color from wastewater was observed to decrease.

8.2 RECOMMENDATIONS

(1) Many more metals like iron, stainless steel, copper, brass, titanium, can be used as electrodes. Various combinations of these electrodes could be studied for treatment of pulp and paper mill effluent.

(2) Many more combinations by varying the anode and cathode can be studied.

(3) Continuous study of electrocoagulation can be performed to see the effect of flow rate and concentration.

(4) Further pilot scale studies are required to evaluate the suitability of electrocoagulation with different type of electrodes system.

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APPENDIX A

EXPERIMENTAL DATA

Effect of pH on Removal of COD and Color for Al Electrode System

Initial COD: 1300 mg/l, Initial pH of the wastewater: 10.8

Number of Al Electrodes: 8, Electrode spacing: 1 cm

Voltage Applied: 5 V, Current applied: 1.2 A, Electrodes are fully submerged

Sample was taken after every 15 min and total 2 h of current passing and 1 h of settling, percentage removal was measured. pH was adjusted with the addition of the conc.H_2SO_4.

Table A1: Percentage COD and Color Removal by Electrocoagulation for Different pH

Time, min	pH=10.8		pH=7		pH=6		pH=3	
	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	21.54	29.52	17.14	40.00	19.08	45.45	33.96	47.58
60	31.15	36.98	28.76	55.19	34.69	57.27	43.40	64.68
90	39.62	40.85	39.62	58.44	47.96	60.61	55.01	76.13
120	42.62	43.27	48.86	61.04	53.57	63.64	67.92	81.94

Table A2: Percentage COD and Color Removal by Combination of Acidification and Electrocoagulation for Different pH

Time, min	pH=7		pH=6		pH=3	
	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal
0	19.23	6.72	24.62	8.79	47.00	57.16
30	33.08	44.03	39.00	50.25	65.00	77.54
60	42.46	58.20	50.77	61.03	70.00	84.87
90	51.23	61.24	60.77	64.07	76.15	89.77
120	58.69	63.65	65.00	66.83	83.00	92.26

Effect of Number of Electrodes on Removal of COD and Color for Al Electrode System

Initial COD: 1300 mg/l, Initial pH of the wastewater: 10.8

pH was adjusted to 3 and settle for 3 h and supernatant was taken for EC

Electrode spacing: 1 cm, Voltage Applied: 5 V, Current applied: 1.2 A

Electrodes are fully submerged

Sample was taken after every 15 min and total 2 h of current passing and 1 h of settling, percentage removal was measured. pH was adjusted with the addition of the conc.H_2SO_4.

Table A3: Percentage COD and Color Removal by Electrocoagulation for Different Number of Electrodes

Time, min	4 Al electrodes		6 Al electrodes		8 Al electrodes		12 Al electrodes	
	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	27.43	23.55	31.79	25.48	33.96	33.55	36.14	58.39
60	37.59	47.58	42.67	49.68	45.57	54.52	53.56	79.68
90	48.48	65.48	54.14	69.19	57.18	72.26	72.42	92.58
120	53.56	73.55	62.99	78.55	67.92	81.94	82.58	97.68

Table A4: Percentage COD and Color Removal by Combination of Acidification and Electrocoagulation for Different Number of Electrodes

Time, min	4 Al electrodes		6 Al electrodes		8 Al electrodes		12 Al electrodes	
	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal
0	47.00	57.16	47.00	57.16	47.00	57.16	47.00	57.16
30	61.54	67.25	63.85	68.08	65.00	71.53	66.15	82.17
60	66.92	77.54	69.62	78.44	71.15	80.51	75.38	91.29
90	72.69	85.21	75.69	86.80	77.31	88.11	85.38	96.82
120	75.38	88.67	80.38	90.81	83.00	92.26	90.77	99.00

Effect of current density on removal of COD and color for Al electrode system

Initial COD: 1300 mg/l, Initial pH of the wastewater: 10.8

pH was adjusted to 3 and settle for 3 h and supernatant was taken for EC

Number of Al Electrodes: 6, Electrode spacing: 1 cm

Voltage Applied: 5 V, Electrodes are fully submerged

Sample was taken after every 15 min and total 2 h of current passing and 1 h of settling, percentage removal was measured. pH was adjusted with the addition of the conc.H_2SO_4.

Table A5: Percentage COD and Color Removal by Electrocoagulation for Different Current Density (CD)

Time, min	CD= 79.36 A/m^2		CD=119.05 A/m^2		CD= 158.73 A/m^2		CD= 198.41 A/m^2	
	% COD removal	%color removal	% COD removal	%color removal	% COD removal	%color removal	% COD removal	%color removal
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	48.48	37.74	55.30	48.08	58.20	49.60	61.54	53.98
60	58.49	57.10	62.84	68.97	65.60	80.10	68.94	84.08
90	64.30	75.81	69.09	85.48	71.70	89.39	74.89	92.02
120	74.75	82.10	77.94	89.52	80.26	95.45	82.29	98.06

Table A6: Percentage COD and Color Removal by Combination of Acidification and Electrocoagulation for Different Current Density (CD)

Time, min	CD= 79.36 A/m^2		CD=119.05 A/m^2		CD= 158.73 A/m^2		CD= 198.41 A/m^2	
	%COD removal	%color removal	%COD removal	%color removal	%COD removal	%color removal	%COD removal	%color removal
0	47.00	57.16	47.00	57.16	47.00	57.16	47.00	57.16
30	72.69	73.33	76.31	77.76	77.85	78.41	79.62	80.29
60	78.00	81.62	80.31	86.71	81.77	91.47	83.54	93.18
90	81.08	89.64	83.62	93.78	85.00	95.45	86.69	96.58
120	86.62	92.33	88.31	95.51	89.54	98.05	90.62	99.17

Effect of Electrodes Submergence on Removal of COD and Color for Al Electrode System

Initial COD: 1300 mg/l, Initial pH of the wastewater: 10.8

pH was adjusted to 3 and settle for 3 h and supernatant was taken for EC

Number of Al Electrodes: 6, Electrode spacing: 1 cm

Voltage Applied: 5 V, Current applied: 4 A

Sample was taken after every 15 min and total 2 h of current passing and 1 h of settling, percentage removal was measured. pH was adjusted with the addition of the conc.H_2SO_4.

Table A7: Percentage COD and Color Removal by Electrocoagulation for Different Electrode Submergence

Time, min	25 % Submergence		50 % Submergence		75 % Submergence		100% Submergence	
	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	49.20	40.91	51.81	42.47	54.86	46.44	58.20	49.60
60	54.28	71.48	58.49	73.87	62.55	77.10	65.60	80.10
90	59.36	80.44	65.02	83.63	68.65	87.34	71.70	89.39
120	64.44	82.18	69.09	86.18	74.02	92.55	80.26	95.45

Table A8: Percentage COD and Color Removal by Combination of Acidification and Electrocoagulation for Different Electrode Submergence

Time, min	25 % Submergence		50 % Submergence		75 % Submergence		100 % Submergence	
	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal
0	47.00	57.16	47.00	57.16	47.00	57.16	47.00	57.16
30	73.08	74.69	74.46	75.35	76.08	77.05	77.85	78.41
60	75.77	87.78	78.00	88.81	80.15	90.19	81.77	91.47
90	78.46	91.62	81.46	92.99	83.38	94.58	85.00	95.45
120	81.15	92.37	83.62	94.08	86.23	96.81	89.54	98.05

Effect of Inter Electrode Spacing on Removal of COD and Color for Al Electrode System

Initial COD: 1300 mg/l, Initial pH of the wastewater: 10.8

pH was adjusted to 3 and settle for 3 h and supernatant was taken for EC

Number of Electrodes: 6, Electrodes are fully submerged

Voltage Applied: 5 V, Current applied: 4 A

Sample was taken after every 15 min and total 2 h of current passing and 1 h of settling, percentage removal was measured. pH was adjusted with the addition of the conc.H_2SO_4.

Table A9: Percentage COD and Color Removal by Electrocoagulation for Different Inter Electrode Spacing

Time, min	1 cm		1.5 cm		2 cm	
	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal
0	0.00	0.00	0.00	0.00	0.00	0.00
30	58.20	49.60	53.85	44.35	51.38	33.87
60	65.60	80.10	61.68	75.03	58.35	66.94
90	71.70	89.39	69.52	85.87	67.78	80.48
120	80.26	95.45	74.60	92.15	71.26	85.87

Table A10: Percentage COD and Color Removal by Combination of Acidification and Electrocoagulation for Different Inter Electrode Spacing

Time, min	1 cm		1.5 cm		2 cm	
	%COD removal	%Color removal	%COD removal	%Color removal	%COD removal	%Color removal
0	47.00	57.16	47.00	57.16	47.00	57.16
30	77.85	78.41	75.54	76.16	74.23	71.67
60	81.77	91.47	79.69	89.30	77.92	85.83
90	85.00	95.45	83.85	93.95	82.92	91.64
120	89.54	98.05	86.54	96.63	84.77	93.95