STUDIES ON REMOVAL OF COTTON BLUE DYE FROM AQUEOUS SOLUTION USING ELECTROCOAGULATION

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
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MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(with specialization in Industrial Pollution Abatement)

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the dissertation entitled **"STUDIES ON REMOVAL OF COTTON BLUE DYE FROM AQUEOUS SOLUTION 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 2006 to June 2007 under supervision of **Dr. I. D. Mall and Dr. Shishir Sinha**, 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.

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CERTIFICATE

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

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ABSTRACT

Dyes and Dye Intermediates industry is an important sector of the Indian Chemical Industry. The Indian companies together account for around 7.0% of the world production. Dyes and pigments are widely used in textile, leather, paper, plastic, food and other industries. Many dyes and pigments have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and also on humans. Various treatment processes used for the removal of dyes from the waste water include electro-coagulaton, adsorption, photochemical, coagulation and sedimentation, membrane separation, biological treatment, etc. EC process provides a simple, reliable and cost-effective method for the treatment of wastewater without any need for additional chemicals, and thus the secondary pollution. It also reduces the amount of sludge, which needs to be disposed.

In the present study, electro-coagulation using aluminum electrodes has been used for the removal of Cotton Blue dye from the aqueous solution. Batch studies were conducted to see the effects of various parameters like pH, inter electrode distance, applied voltage, number of electrodes, initial concentration of Cotton blue dye, and electrolysis time on the removal of Cotton Blue dye. The efficiency of the method tested was determined by measurement of color removal. For dye solutions with COD of approximately 42 mg/l and dye concentrations of 100 mg/l, high dye removal (97%, i.e., color falls from an initial value of 1400 to 22 Pt-Co units) was obtained when the pH ranged from 6 to 8, time of electrolysis was approximately 15 min, applied voltage was approximately 11 V, number of electrode was six, and inter-electrode distance was 0.5 cm. During the EC process under these conditions, COD reduction was found to be ~ 74 % and TOC removal was 61.4 %. Small difference between color diminution has been found with the progress of treatment. Percent removal decreases with increase in initial concentration of Cotton blue.

Optimized operational conditions were applied to real textile wastewater which led to satisfactory color removal (more than 95%) though electrolysis time and anode consumption is more in case of real textile waste water.

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Chapter 1

INTRODUCTION

Ever since primitive people could create, they have been endeavoring to add color to the world around them. They used natural matter to stain hides, decorate shells, and paint their story on the walls of ancient caves. Scientists have been able to date the black, white, yellow and reddish pigments made from ochre used by primitive man in cave paintings to over 15,000 BC. After the discovery of synthetic dye by Perkin, they have been widely used by mankind. However, along with the properties such as stronger colours, variety, consistency etc., comes the problem of water pollution.

Contamination due to pollution denies some 3.3 billion people access to clean water, and 2.5 billion people have no water sanitation services. In developing countries an estimated 90 per cent of wastewater is discharged without treatment into rivers and streams. Each year there are about 250 million cases of water-related diseases, with some 5-10 million deaths [http://www.fig.net/pub/figpub/pub23/figpub23.htm].

Growing population and raising standard of living of people are demanding of quality industrial products at phenomenal pace. Thus the industrial need of water is increasing day by day. Industrial effluents constitute a major source of polluted water and contain different kinds of toxic pollutants. With the quality of water becoming poor, availability of fresh water being scarce treatment of industrial wastewater is necessary to lower the concentration of toxic pollutants in wastewater to the level of permissible limits.

1.1 INDUSTRIAL WASTE WATER POLLUTION IN INDIA

As per Central Statistical Organization (CSO), there are about 32 lakhs industries in India and out of which 1,35,551 are registered manufacturing industries. As per the latest inventory of Central Pollution Control Board, there are about 8432 large and medium polluting industries in India [http://www.and.nic.in/page15.pdf]. In pace with the rise in industrial need of water, wastewater from industries is also going up continuously. The total wastewater generated from all major industrial sources is shown in Table1.1

Table 1.1. Wastewater generation by industries

S. No.	Industrial sector	Annual wastewater water discharge (million cubic meters) (%)	Annual consumption (million cubic meters)	Proportion of water consumed in industry
1.	Thermal power plants	27000.9	35157.4	87.87
2.	Engineering	1551.3	2019.9	5.05
3.	Pulp and paper	695.7	905.8	2.26
4.	Textiles	637.3	829.8	2.07
5.	Steel	396.8	516.6	1.29
6.	Sugar	149.7	194.9	0.49
7.	Fertilizer	56.4	73.5	0.18
8.	Others	241.3	314.2	0.78
	Total	30729.2	40012.0	100.0

Source: CPCB, 2002

1.2 DYES AND WATER POLLUTION

Dyes are defined as colored substances, also called a dyestuff, which imparts more or less permanent color to other materials and are used for staining and colouring. Dyes may be classified in various ways: according to color (blue, red, and so on); origin (natural – from vegetable and animal matter – or synthetic); chemical structure (the most precise); kinds of material to which they are applied (cloth, paper, leather, plastic, food, and biological specimens); and method of application. Many thousands of dyes have been prepared and because of vastly improved properties imparted upon the dyed materials quickly replaced the traditional natural dyes. However this also meant that the effluents containing them were harder to treat and hence another headache in ever growing problem of water pollution

1.2.1 Classification and Consumption Pattern of Dyes

Dyes are classified according to various systems. The detailed description of dyes is given in chapter 2. The most commonly used one is the one used by the US International Trade Commission. According to this system, there are different types of dyes, as detailed in the table given below.

Tablel.2. Classification of dyes and their applications

Group	Application
Acid	Wool, silk, paper, synthetic fibers, leather
Azoic	Printing Inks and Pigments
Basic	Silk, wool, cotton
Direct	Cotton, cellulosic and blended fibers
Disperse dyes	Synthetic fibers
Reactive	Cellulosic fiber and fabric
Mineral and pigments dyes	Cotton, cellulosic, blended fabric, paper
Sulphur	Cotton, cellulosic fiber
Vat dyes	Cotton, cellulosic and blended fiber

Source: *Best Management Practices for Pollution Prevention in the Textile Industry,* EPA, Office of Research and Development, 1995; Snowden- Swan, L.J. "Pollution Prevention in the Textile Industries," in *Industrial Pollution Prevention Handbook,* Freeman, H.M. (Ed.), McGraw-Hill, Inc., New York, 1995.

The Indian dye industry is valued at approximately $3 billion with an estimated export of about 1 billion. The industry is characterised by the co-existence of a small number of players in the organised sector (around 50 units) and a large number of small manufacturers (around 1,000 units) in the unorganised sector. The table below shows distribution and anticipated production data for past years. How ever according to latest data the production is estimated to be around 1,30,000 tonnes or about 7 % of the world production. India is now the second largest producer of dyes and dye intermediaries in Asia. There are around 750 varieties of dyes and dye intermediates produced in India [www.ficci.com/events/past-events/2006/past-events-2006.htm]. In spite of large production of dyes and their intermediates, the per capita consumption of India is very low (50 g) as compared to world average (400 g). The distribution of producing units is skewed towards with western region (Maharashtra and Gujarat) accounting for 90% mainly due to due to availability of raw materials and pre-dominance of textile industry in these states. In fact, nearly 80% of the total capacity is in the state of Gujarat, where there are nearly 750 units. [http://www.agriculture-industry-india.com/agricultural-commodities/dye.html].

Dyes are widely used by textiles, leather, paper, paints, plastics, printing, pharmaceutical, lubricant, cosmetic industries and food industry. In India 80% of the dyes manufactured is consumed by fabric & textile Industry. This links the dyestuff industry's fortunes to that of the textile industry.

Table1.3. Production capacities of different types of dyes

Product	**2003-2004**		**2004-2005**	
	Actual		**Actual Anticipated**	
	Installed capacity	**Production**	**Installed capacity**	**Production**
Azo Dyes	8.7	3.9	8.7	4.5
Acid Direct Dyes (Other than Azo)	0.2	0.0	0.2	0.0
Basic Dyes	0.5	0.1	0.5	0.0
Disperse Dyes	6.3	1.2	6.5	1.1
Fast Colour Bases	0.6	0.0	0.6	0.0
Ingrain Dyes	0.3	0.2	0.3	0.3
Oil Soluble Dyes(Solvent Dyes)	1.6	0.0	1.6	0.0
Optical Whitening Agents	1.1	0.3	1.1	0.3
Organic Pigment Colours	12.3	11.3	12.3	13.3
Pigment Emulsion	6.4	2.4	6.4	2.5
Reactive Dyes	6.2	2.3	6.2	2.7
Sulphur Dyes (Sulphur Black)	3.3	2.9	3.3	2.4
Vat Dyes	2.9	1.0	2.9	1.1
Solubilised Vat Dyes	0.1	0.0	0.1	0.0
Food Colours	0.1	0.0	0.1	0.0
Nepthols	3.5	0.5	3.6	0.5
Total	**54.1**	**26.1**	**54.4**	**28.7**

Source: www.gujexim.com/tradeleads_chem_dyes.htm

1.2.2 Health and Environmental Effects of Dye Bearing Effluents

Most of the dyes being used in different industries have not been evaluated for their impact on health and the environment. The synthetic dyes are resistant to degradation by conventional wastewater treatment plants and are released into environment untreated thus causing pollution of surface and ground waters in the areas of the world harboring such industries.

Human health

Dye bearing effluents contain significant level of organic contaminants, which are toxic as they create odour, bad taste, unsighty colour, foaming etc. Some of the dyes present in the wastewater are carcinogenic and harmful not only to human beings but also to plants and animals. In addition, some dyes are highly cytotoxic to mammalian cells and act as a tumor-enhancing agent. These dyes may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic effects on humans. Several textile and food dyes, and dye intermediates like benzidines, have been linked to carcinogenicity.

As per ETAD (Ecological and Toxicological Association of Dyes) risk paused by any chemical substance on human health is a function of toxicity and exposure. Humans are exposed to dyes through four different channels inhalation, dermal exposure, ingestion and eye contact. The health effects paused are mainly due to inhalation and ingestion.

- Inhalation: respiratory irritation with symptoms of coughing, running nose, or throat irritation. Certain dyes, especially reactive dyes, may cause allergic dermal or respiratory reactions. Symptoms of respiratory sensitization can occur including asthmatic-like responses such as: coughing, wheezing, tightness in the chest, shortness breath and loss of consciousness.
- Ingestion: Dyes may be absorbed through the respiratory tract or digestive tract causing health problems.

Table1.4. Dyes used in Industry and their possible effects

Dye	Possible Effect
Aniline blue	Bladder carcinogen
Auramine O	Bladder carcinogen and mutagen
Congo red	Highly toxic, mutagen and irritant
Fast green	Animal carcinogen
Indigo carmine	Mutagen
Malachite green	Systemic poison
Orange G	Mutagen
Uranyl nitrate	Radioactive and oxidising agent

Ecological Impact: The dyes, generally, have complex aromatic structures which provide them physico-chemical, thermal and optical stability i.e., they are stable to light, oxidizing agents and heat. Hence they offer considerable resistance to their biodegradation, causing aesthetic, acute and chronic toxicity problems in receiving waters thus, upsetting aquatic life. Moreover, the unused dyes and color released in effluent interferes with the transmission of light in the water bodies that receive the effluent, which in turn inhibits the photosynthesis activity of aquatic biota. Dyes accumulate in sediments at many sites, especially at locations of wastewater discharge, which has an impact on the ecological balance in the aquatic system. Ground water systems are also affected by these pollutants because of leaching from soil [Sharma et al., 1999].

The large number of dyes and high potential for toxicity of dyes and its component has made this class of compounds the most extensively reviewed and regulated under various pollution acts around the world.

1.3 DISCHARGE STANDARDS FOR INDUSTRIAL WASTE WATER

Standards for the discharge of wastewaters from various industries are directly linked to the wastewater regulations and the water pollution control policies in force in the country/state concerned. CPCB has set Minimal National Standards (MINAS), for the discharge of pollutants from various industries. MINAS for a particular industry is the effluent standard achievable by the industry by installing pollution control measures which are within the techno-economic capability of the industry and MINAS should not be violated under any circumstances. MINAS for some dye utilizing industries are tabulated.

Table1.5. MINAS for Dye and Dye Intermediate Industry

Parameter	Concentration not to exceed milligrams per liter (except for pH, temperature and bio-assay)
pH	6.0 – 9.0
Colour Hazen Unit	400.0
Suspended Solids	100.0
BOD (3 days at 27 °C)	100.0
Oil and Grease	10.0
Phenolics as C_6H_5OH	1.0
Cadmium as Cd	0.2
Copper as Cu	2.0
Manganese as Mn	2.0
Lead as Pb	0.1
Mercury as Hg	0.01
Nickel as Ni	2.0
Zinc as Zn	5.0
Total Chromium	2.0
Bio-assay test	90% survival in 96 hours.

Source: http://www.cpcb.nic.in/standard24.htm, EPA Notification
GSR 742(E) dt., 30th Aug.,1990

Table1.6. MINAS for Man-made fiber industry

Process	Parameter	Concentration not to exceed, mg/l (except for pH)
Synthetic	Suspended Solids	100
	BOD, 3 days at 27 °C	30
	pH	5.5 to 9.0
Semi-synthetic	pH	5.5-9.0
	Suspended Solids	100
	BOD, 3 days at 27 °C	30
	Zinc (as Zn)	5

Source: http://www.cpcb.nic.in/standard41.htm

Table1.7. MINAS for Cotton textile industries (composite and processing)

	Parameter	**Concentration not to exceed, milligram per liter (except for pH and bioassay)**
Common	pH	5.5. to 9.0
	Suspended solids	100
	BOD, 3 days at 27 °C	150
	Oil and grease	10
	Bio-assay test	90% survival of fish of after 96 hours in 100% effluent
Special	Total chromium (as Cr)	2
	Sulphide (as S)	2
	Phenolic compounds (as C_6H_5OH)	5

Source: http://www.cpcb.nic.in/standard41.htm

1.4 AIM AND OBJECTIVES

- The aim of the present work is testing the potential of electro-coagulation using aluminum electrodes as a treatment technique for the textile dyes in an aqueous medium, with Cotton blue (aniline blue) solutions as synthetic stimulant for waste.
- Study the effect of pH, inter electrode distance, number of electrodes, applied voltage, electrolysis time, and initial concentration on the removal of Cotton Blue from aqueous solution by batch process.
- Determination of the optimum operating range for each of the operating variables for maximum decolorization efficiency of azo dye.
- To comment on viability and potential of electro coagulation as a removal technique for the given case.

Chapter 2

LITERATURE REVIEW

Most of the synthetic dye wastes are toxic; harmful to human, animal and plant life. Textile industries consume large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products [Mishra and Tripathy, 1993; Banat et al., 1996]. The presence of very low concentrations of dyes in effluent is highly visible and undesirable [Nigam et al., 2000]. There are more than 100,000 commercially available dyes. Due to their chemical structure, dyes are resistant to fading on exposure to light, water and many chemicals. Many dyes are difficult to decolourise due to their complex structure and synthetic origin. Extensive work has been carried out on methods for treatment of dye bearing waste water.

2.1 DYES AND ITS CLASSIFICATION

A dye is a colored substance or an organic compound, which when applied in a solution to a fabric, imparts a color resistant to washing. All aromatic compounds absorb electromagnetic energy but only those that absorb light with wavelengths in the visible range (~350-700 nm) are colored. Dyes contain *chromophores*, delocalized electron systems with conjugated double bonds, and *auxochromes*, electron-withdrawing or electrondonating substituents that cause or intensify the colour of the chromophore by altering the overall energy of the electron system. Usual chromophores are -C=C-, -C=N-, -C=O, -N=N-, $-NO_2$ and quinoid rings, usual auxochromes are $-NH_3$, -COOH, $-SO_3H$ and –OH [http://www.ifc.org/ifcext/enviro.nsf/ AttachmentsByTitle/gui_dye_WB/$FILE/dye_PPAH.pdf].

Reactive Dyes: The dyes contain a reactive group, either a haloheterocycle or an activated double bond, that, when applied to a fibre in a weakly alkaline dye bath, forms a chemical bond with an hydroxyl group on the cellulose fibre dyed and cannot be removed by washing or boiling. The main feature of the dyestuff is its low affinity to cellulose; therefore large amounts of salt are required to force its deposition on the fabric. These dyes are soluble in water and are salted out of solution onto the fiber where they are made to react chemically within the fibers. They are mainly used for dyeing cellulosic fibres, such as cotton and rayon. Reactive dyes are used where bright dyeing with high light and wash fastness is required. Reactive dyeing is now the most important method for the coloration of cellulosic fibres.

Acid Dyes: Acid dyes are salts of sulphonic acids consisting very large molecules of linked aromatic rings. These dyes are applied to fibres such as silk, wool, nylon and modified acrylic fibres from neutral to acid dye baths. Attachment to the fibre is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fibre. Acid dyes are not substantive to cellulosic fibres.

Azo Dyes: These dyes are synthetic organic dyes that contain nitrogen as the azo group -N=N- as part of their molecular structures; more than half the commercial dyes belong to this class. They are insoluble dyes that are not applied directly as dyes, but are absorbed on the surface of the substance to be dyed. Azo dyes are used for cotton, silk and rayon. Azo dyes became the most important commercial colorants because of their wide colour range, good fastness properties, and tinctorial strength (colour density), which is twice that of the anthraquinones.

Basic Dyes: Basic dyes are water soluble cationic dyes which are mainly applied to acrylic fibres but find some use for wool, and silk. Usually acetic acid is added to the dye bath to help the take up of the dye onto the fibre. A mordant, usually a metallic salt is used to increase the affinity of the fabric for the dye. Basic dyes include the most brilliant of all the synthetic dyes known and are used to produce bright and deep shades with good light and wash. Basic dyes are also used in the coloration of paper.

P;0

Sulphur Dyes: These dyes are sulfur-containing, complex synthetic organic dyes to cellulose, where they become substantive to the fibre. On exposure to air, the dyes in the fibre are oxidized back to their original insoluble form. They are fast to washing, persipiration, and light.

Disperse Dyes: Originally developed for the dyeing of cellulose acetate. They are substantially water insoluble. They can also be used to dye nylon, triacetate, polyester and acrylic fibres. With the change in the product profile of the textile industry from the high-cost cotton textiles to the highly durable and versatile synthetic fibres, the consumption pattern of dyes has also been changing. Polyesters are projected to account for a large part of dye consumption in the country. Accordingly, disperse dyes, which find application in olyesters, are projected to grow faster.

Natural Dyes: They can be broken down into two categories: substantive and adjective. Substantive, or direct dyes, become chemically fixed to the fiber without the aid of any other chemicals or additives, such as indigo or certain lichens. Adjective dyes, or mordant dyes, require some sort of substance, (usually a metal salt) to prevent the color from washing or light-bleaching out. Most natural dyes are adjective dyes, and do require the application of a mordant (the metal salt) solution to the fibers at some point in the dyeing process.

Direct Dyes: These are also called Substantive Dye, any of a class of coloured, water-soluble compounds that have an affinity for fibre and are taken up directly, such as the benzidine derivatives. Direct dyes are usually cheap and easily applied, and they can yield bright colours. Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

Mordant Dyes: As the name suggests these dyes require a mordant. This improves the fastness of the dye on the fibre such as water, light and perspiration fastness. The most important mordant dyes are the synthetic mordant dyes (chrome dyes) used for wool, these comprise some 30% of dyes used for wool and are especially useful for black and navy shades. The mordant used is potassium dichromate applied as an after-treatment.

2.2 SOURCES OF TEXTILE DYE BEARING WASTE WATER

Dyes are widely used by textiles, leather, paper, paints, plastics, printing, pharmaceutical, lubricant, cosmetic industries and food industry. The largest waste stream from most textile mills comes from processes involved in washing, bleaching, and dyeing is wastewater. Dyeing and finishing are the two important processes generally applied in most of the textile manufacturing industries. These two processes generate considerable amount of wastewater, which may contain strong color, suspended particles, high pH and high chemical oxygen demand (COD) concentration. The textile industry utilizes about 10,000 dyes and pigments. In textile industries, because of the low efficiency (60–90%) of dye fixing on textile fibers, substantial amounts of unfixed dyes are released in wastewaters. Wastewater generation from a typical dyeing facility is estimated at 3800 to 7500 m^3 per day [http://www.p2pays.org/ref/11/10489/sectors73ak.html]. The typical sources and quantum of wastewater generated are given in the following table.

Table 2.1. Sources and quantum of wastewater generated in a typical Textile industry

S. No	Type of Operation	Spent Liquor (lit/kg of yarn)	Wash Water (lit/kg of yarn)	Total (lit/kg of yarn)
1.	Scouring	10-15	30-40	40-55
2.	Bleaching	20-25	40-50	60-75
3.	Dyeing	10-15	100-150	110-165

Source: http://www.wittsenvis.org/news_6_apr03.htm

2.3 TREATMENT METHODS OF DYE BEARING WASTE WATER

The dyestuff industry is one of the heavily polluting industries. There are a large number of dyes and their high potential for toxicity have made this class of compounds the most extensively reviewed and regulated under various pollution acts around the world. The discharge of dye wastewater into the environment causes various extensive pollution problems as already discussed. Hence the ubiquitous colour needs to be regulated. But removing the colour from effluents is extremely difficult. There is no universally applicable technique for treatment of dye bearing wastewaters and hence it is on case by case basis the techniques are selected.

Research and development, therefore focuses on sector-specific methods and technologies to remove colour and similar contaminants from different kinds of waste streams. Depending on the quantum, concentration, toxicity, and presence of non biodegradable organics in the industrial wastewater, its treatment may consist of any one or more of the following processes:

2.3.1 Chemical Processes

These enhance the degradation of volatile organic compounds present at low concentrations in contaminated media. These process include Oxidative processes, H_2O_2-Fe (II) salts (Fentons reagent), Ozonation, Photochemical, Sodium hypochloride (NaOCl), electrochemical destruction.

Ozonation

Widely used in the water treatment, ozone is now used (either alone or in combination with other treatments, such as O_3-UV or O_3-H_2O_2) in the treatment of industrial effluents [C. Allegre et al., 2006]. The combination of activated carbon with ozone enhanced the decolourization of the solutions and especially the mineralization of the organic matter. Activated carbon acts both as an adsorbent and as a catalyst in the reaction of ozonation [Faria et al., 2005]. The major drawbacks with ozonation is cost, continuous ozonation is required due to its short half-life.

Photochemical

Heterogeneous photo catalysis has been considered as a cost effective alternative for the purification of dye containing wastewater [Aleboyeh et al., 2003]. Indeed recent studies have demonstrated that photo catalysis can be used to mineralize organic compounds or degrade dyes using TiO_2 under UV irradiation. Moreover, photo catalysis does not require expensive oxidants and can be carried out at mild temperature and pressure [EPA Hand Book, Advanced Photochemical Oxidation Processes, Dec 1998].

Electrochemical destruction

The organic and toxic pollutants present in treated wastewaters such as dyes and phenols are usually destroyed by a direct anodic process or by an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone, etc. There is little or no consumption of chemicals and no sludge build up [Oeguetveren et al., 1992]. Relatively high flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to the price of chemicals.

2.3.2 Physical Treatment Methods

Coagulation-flocculation

Surfactants and dyes with high molecular weights are successfully removed by the coagulation/flocculation processes followed by sedimentation, flotation and filtration, respectively. The major disadvantage of coagulation/flocculation processes is the production of sludge which results in high disposal costs. However, amount of sludge could be minimized if only a low volume of the highly coloured dye bath could be eliminated by chemical treatment directly after the dyeing process [Golob et al. 2005].

Ion-Exchange

Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cation and anion dyes can be removed from dye-containing effluent this way. Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes. But this method is not economical as far as the cost is concerned [Slokar and Le Marechal, 1998].

Adsorption

Adsorption is a simple and economical method for wastewater treatment. Decolourization is a result of two mechanisms: adsorption and ion exchange and is influenced by many physio-chemical factors, such as, dye/ sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time. It has been used for removal of heavy metals, non-biodegradable organic compounds like phenols, toxic substances, dyes etc taste and odour control in water and wastewater treatment.

Membrane Processes

The increasing cost of water and its wasteful consumption have now induced a treatment process which is integrated in in-plant water circuits rather than as a subsequent treatment [C. Allegre et al., 2006]. Processes using membranes provide very interesting possibilities of separating hydrolyzed dyestuffs and dyeing auxiliaries, thus simultaneously reducing coloration and the BOD/COD of the wastewater. In the current studies, it is difficult to recommend a particular membrane process (MF, UF, NF and RO), and the choice is guided by the desired quality of the permeation results. These include

- Reverse osmosis
- Nanofiltration
- Ultrafiltration (UF)
- Microfiltration (MF)

2.3.3 Biological Treatment Methods

Biological treatments reproduce, artificially or otherwise, the phenomena of self-purification that exist in nature. Self purification comprises the whole process by which an aquatic environment achieves the re-establishment of its original quality after pollution. Biological treatments differ according to the presence or absence of oxygen. Activated sludge process is the most commonly used treatment process. As a result of the low biodegradability of most of the dyes and chemicals used in the textile industry, their biological treatment by activated sludge does not always meet with great success: in fact most of these dyes resist aerobic biological treatment.

The addition of adsorbents, such as bentonite or powdered activated carbon to biological treatment systems is necessary in order to obtain good elimination of non-biodegradable or microorganism-toxic organic substances produced by the textile industry, particularly by dye houses [Pala et al., 2002], thus reducing the harmful effect on microorganisms. Other methods consist in combining oxidative chemical treatments following the biological treatment including the possibility of using organic flocculants [Pala et al., 2002]. The removal of colour by using biological treatment is widely used. The use of wood rotting fungus [Zhang et al., 1999], Bjerkandera sp. Strain BOL 13 [Axelsson et al., 2006] has been used for effective colour removal. Other fungi such as, Hirschioporus larincinus, Inonotus hispidus, Phlebia tremellosa and Coriolus versicolor have also been shown to decolorize dye-containing effluent.

Table 2.2. Techniques, Principles and References

Technique	Principle	Reference studies
Adsorption	Surface adherence. Decolourization is a result of two mechanisms: adsorption and ion exchange and is influenced by many physio-chemical factors, such as, dye/ sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time	Mall et al. [2005], Chakraborty et al. [2005], Kasgoz et al. [2005], Mall et al. [2006], Orfio et al. [2006], Chu and Chen [2002], Liversidge et al. [1997], Gupta and Shukla [1992], Mckay et al. [1980] etc
Biological Processes	Self purification, use of biological organisms	Daneshvar et al.[2006], Chen et al.[2005], Gill et al.[2002], Axelsson et al. [2006] etc
Chemical Processes	Degradation of compounds present at low concentrations in contaminated media by chemical reaction	Lucas et al. [2007], Raghu and Basha [2007], Allegre et al. [2006] etc
Electrocoagulation	Electrocoagulation involves the generation of coagulants in situ by dissolving electrically metal ions from metal electrodes. The metal ions generation takes place at the anode and hydrogen gas is released from the cathode. The hydrogen gas would also help to float the flocculated particles out of the water.	Oeguetveren et al.[1992], Do and Chen [1994], Silva & Filho [2001], Szpyrkowicz et al. [2001], Kim et al. [2002], Can et al. [2003], Alinsafi et al. [2004], Bayramoglu et al. [2003], Mollah et al. [2004], Pathak et al. [2004], Kobya et al. [2005], Kashefialasl et al. [2005], Golder et al. [2005], Vaghela et al. [2005], Ghalwa et al. [2005], Daneshvar et al. [2002, 2004, 2006], Chrysafopoulou et al. [2006], S. Mahesh et al. [2006], Aleboyeh et al. [2007] etc
Membrane Processes	Selective permeability, filteration	Qin et al. [2007], Allegre et al. [2006], Mozia et al. [2005], Machenbach [1998] etc
Photochemical	This method degrades dye molecules to CO_2 and H_2O by UV treatment in the presence of H_2O_2	Aleboyeh et al. [2003], Colonna et al. [1999], Slokar and Le Marechal [1997] etc

2.4 SELECTION OF METHODOLOGY

A wide range of techniques and methods exist for treatment of dye bearing waste water. There are *Physical processes,* are used to substantially remove floating and settleable solids in wastewater. This process include screening, sedimentation, adsorption, membrane filtration, ion exchange, Irradiation, or *Chemical Processes,* which enhance the degradation of volatile organic compounds present at low concentrations in contaminated media. *Biological treatment,* in which bacteria break down the organic parts of wastewaters; usually accomplished by bringing the wastewater and bacteria together in trickling filters, aerobic, anaerobic or in the activated sludge process. A number of membrane based processes also exist.

As there is a wide range in pH and dyes are highly coloured materials, which are difficult to decompose biologically, conventional Physico-chemical and biological treatment processes are not effective in removing dyes from wastewaters. Moreover all these processes are costly and cannot be used by small industries to treat the wide range of dye wastewater.

However after a brief review of available literature and consultation with guide we have decided to test the effectiveness of electro coagulation on treatment of textile dye bearing waste waters with Cotton blue, CAS 28631-66-5 which is a azo dye extensively used in textile industry, as the contaminant. The EC technology offers an alternative to the use of metal salts or polymers and poly-electrolyte addition for breaking stable emulsions and suspensions. The technology removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueoues media by introducing highly charged polymeric metal hydroxide species. These species neutralize the electrostatic charges on suspended solids to facilitate agglomeration or coagulation and resultant separation from the aqueous phase.

EC is a technique with large potential as seen from the literature review presented in and also one of the lesser explored one. It has already proved to be an efficient technique in a wide variety of other processes of metal removal and wastewater treatment. EC process provides a simple, reliable and cost-effective method for the treatment of wastewater without any need for additional chemicals, and thus the secondary pollution

Electro-coagulation would subsequently generate less solid waste, thus saving on disposal costs. The EC process also has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation. Electro coagulation thus deserves a thorough study as a technique for treatment of textile reactive dye bearing waste water.

Table 2.3. Advantages and disadvantages of the current methods of dye removal from industrial effluents

Processes	Advantages	Disadvantages
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of dyes High Costs
Coagulation–flocculation	Elimination of insoluble dyes	Production of sludges High Costs
Adsorption on activated carbon	Suspended solids and organic substances well reduced	Blocking filter High Cost of activated carbon
Ozone treatment	Good decolorization	No reduction of the COD Additional costs
Electrochemical processes	Capacity of adaptation to different volumes and pollution loads	Sludges/Flocs
Reverse osmosis	Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure Membrane fouling problem
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts. Treatment of high concentrations	Membrane costs/ maintenance

2.5 LITERATURE REVIEW

The most popular and researched technique at present is adsorption. Excellent research literature on textile dye treatment is available from Mall et al. [2005] on Congo red, Chakraborty et al. [2005] on reactive red, Kasgoz et al. [2005] who has worked on indigo carmine, Mall et al. [2006] on orange G, Orfio et al. [2006] on rifafax red, Vadiyelan et al. [2005] on methylene blue, Chu and Chen [2002] on basic blue3, Liversidge et al. [1997] on basic blue 41, Gupta and Shukla [1992] on omega chrome red, Mckay et al. [1980] on reactive red etc. A wide range of adsorbents exist which include Activated Carbon, BFA, RHA, Peat, etc.

A lot of literature has already been accumulated on chemical processes. Most recently Lucas et al. [2007] has presented his work on degradation of azo dye using a hybrid chemical biological method utilizing fenton's reagent yeast. Raghu and Basha [2007] has worked on electrochemical oxidation, Allegre et al. [2006] on chemical assisted photo degradation etc.

Similarly biological processes have been studied by Daneshvar et al. [2006] who tested microalgae on malchite green, Chen et al. [2004], Gill et al. [2002] on copper complexed dyes etc.

Membrane processes are also well researched. A number of researches have like Qin et al. [2007], Allegre et al. [2006] on treatment and recycling of reactive dye bearing effluents, sungpet 2004 on treatment of rinsing effluents, Calabro on membrane distillation 1991 etc.

However though membrane filtration methods have the ability to clarify, concentrate and, most importantly, to separate pollutants continuously from effluent. The concentrated residue left after separation poses disposal problems, and high capital cost and the possibility of clogging, and membrane replacement is its disadvantages.

Electro coagulation is fast catching the eye of researchers as an effective alternate technique for waste water treatment. When reactions are driven or forced, the elements or compounds will approach their 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 out and can easily be removed by a number of secondary separation techniques.

Electro coagulation systems have been in existence since **Dieterich**, patented one in 1906, how ever only recently have they aroused interest for treatment of textile dye bearing wastes using a variety of anode and cathode geometries, including plates, balls, fluidized bed spheres, wire mesh, rods, and tubes. It is increasing being suggested for separation of solids from the water molecules and treatment of heavy metals, virus, bacteria, pesticides, arsenic, MTBE, cyanide, BOD, TDS, and TSS along with treatment of Municipal, Industrial, wastewater contaminated with sewage treatment, dairy, plating shops, contaminated soil, steam cleaner and car wash water, mining, laundries, and textile dyes. Recently a lot of work is being done on treatment of dye bearing waste water from textile industry using this method.

Oeguetveren et al. [1992] made an attempt to remove a dye such as Acilan Blau using electrochemical method. Effects of several factors on the removal rate were examined such as pH, presence of supporting electrolyte, duration of electrolysis, initial dye concentration and applied potential. Removal rate of 100% was practically achieved in a very short time with synthetic solutions. Additionally, samples of waste water taken from the operating line of a local textile plant have also been treated in the reactor. Complete removal of the dyes (98-100%) from these solutions have been achieved with a little increase in time.

Do and Chen [1993] studied effects of various parameters during decolurization treatment of textile waste waters. In the electrocoagulation of Drimarene Discharge X-3LG ® (R12S) and Samaron Yellow 4 the effects of sacrificial anodes, initial pH, rate of stirring and concentrations of dyes on the fraction of decolourization were tested. The experimental results revealed that the colour of dyes in the aqueous phase was effectively removed when iron and aluminium were used as sacrificial anodes and the concentration of the dyes was less than 100p.p.m. When the concentration of R12S exceeded 300 p.p.m, iron was a more suitable sacrificial anode for electrocoagulation of R12S than aluminium. For the electrocoagulation of D05H in aqueous solution aluminium as a sacrificial anode was superior to iron when the concentration of D05H exceeded 300p.p.m. Using iron as sacrificial anode, the residual concentration fraction of R12S was decreased below 10% when the initial concentration of R12S and charge passed were 500p.p.m. and 120C, respectively. The decolourization fraction of D05H was 99% when aluminium was used as sacrificial anode.

Silva and Filho [2001] investigated the application of electrolysis technology as an alternative for removal of color from textile wastewater. The study included a series of experiments with aqueous solutions of two commonly used sulphur dyes: Brown Sodyesul 2GBB ECO and Blue Sodyesul 7RB ECO. The experimental program involved experiments of chemical coagulation and electrolytic treatment to compare the performance. In the experiments of electrolytic treatment using steel electrodes, an investigation was carried out on the effects of parameters such as applied potential, initial pH and conductivity on the efficiency of colour removal. The experimental results are assessed in terms of the abatement of colour as measured in absorbance values. These measurements were used to determine the percent efficiency of the process. Colour abatement of at least 99% was achieved in a contact time of 10 minutes with an applied potential of 5.0 V. The electrolytic process proved to be an effective route for the removal of colour from wastewaters. Overall, the experimental results suggest the main removal mechanism is the electrocoagulation of the dye.

Szpyrkowicz et al. [2001] describes the removal of colour from textile wastewater bearing a mixture of three disperse dyes. The experiments were carried out in a reactor equipped with an Al sacrificial anode (100 cm^2) and a stainless steel cathode of the same dimensions. Decolorisation occurred as a result of destabilisation of colloids due to an effect of an electric field generated between the electrodes (polarisation coagulation) and the reactions with coagulating compounds, formed in situ during anode oxidation (volumetric coagulation), followed by a subsequent flotation of agglomerates of the particles. During the study the following parameters were varied: initial pH of the solution, current density (between 100 and 300 A m^{-2}) and an initial concentration of the dyes. The best results of elimination of colour, equal to 99%, were obtained during 5 minutes of treatment under the conditions of pH of 9.

Kim et al. [2002] studied the color removal of Reactive Blue 49, Reactive yellow 84, Disperse blue 106 and Disperse yellow 54 with Al, Fe and stainless steel electrode in a continuous mode with flow rate as $100 \mathrm{ml min}^{-1}$. Effect of anode material on EC of dyes was studied at a current density of $4.45\ \mathrm{mAcm}^{-2}$, seven pairs of electrode, with 1 cm of electrode gap and $1000\ \mathrm{mgL}^{-1}$ of NaCl was added to increase the conductivity. The removal of color found for dye RB49 was greater than75%, RY84 was greater than 90%, DB106 was greater than 95% and for DY54 was greater than 98%. Dye removal was more efficiently achieved by Al electrodes than those of SUS or Fe and was not significantly affected by initial pH as long as pH was maintained between 4 and 10.

Fernandes et al. [2004] has worked on Electrochemical degradation of C. I. Acid Orange 7 (AO7) using boron doped diamond electrode (BDD). Electrochemical experiments were conducted at 25 °C in a conventional three-electrode cell, with a working volume of 0.25 L. A boron doped diamond electrode was used as anode and a copper foil as cathode. Results have shown an almost complete colour removal and COD removal, higher than 90%.

Bayramoglu et al. [2003] have worked on removal of reactive textile dye Remazol Red RB 133 from an aqueous medium by the electrocoagulation method using aluminum electrodes. Results showed that 88% decolorization efficiency may be obtained for the current density of approximately $10\ \mathrm{mA/cm}^2$ in 10 min and at pH 6. The decolorization efficiency for Al electrode falls in a linear fashion from 100 to 70% with increase in concentration of the dye from 100 to 1000 mg/l. Study also showed that the initial pH of the dye solution and the quantity of electricity consumed are important process variables that affect the process decolorization efficiency, as well as the process economics via variable cost items such as electrical energy and electrode material consumption.

Bharatimohan and Prabhu [2003] have carried out investigations on effluent treatment for textile pretreatment waste water using electrocoagulation method has been studied. Treated water was reused. It showed better performance in textile processing as well as in effluent character up to two recyclings.

Butnaru et al. [2003] discuss the possibility to treat wastewater from cellulose dyeing with direct dyes by electrocoagulation. Four direct dyes are analyzed, at different concentrations. COD decrease and color of the residual solution are investigated, as well as the volume of the sludge produced in the process. Optimum treatment parameters are determined for the electro-coagulation process.

Pathak et al. [2004] have successfully worked on EC treatment of orange II dye solution in a continuous flow cell by using sacrificial iron electrodes. The cell contained five parallel iron electrodes, which form four parallel cells. The internal volume of the cell is approximately 450 ml. Inter electrode distance was 0.6 cm and experiments were run at 25 °C. This study showed the 99% removal of the dye from the waste stream under the optimum conditions. The optimum conditions were; current = 4.0A (42 V); initial pH = 7.3; flow rate = 350 mL/min; and dye concentration = 10 ppm

Sanroman et al. [2004] have worked on Electrochemical decolourisation of structurally different dyes (bromophenol blue, indigo, poly R-478, phenol red, methyl orange, fuchsin, methyl green and crystal violet). This study showed that the electrochemical process allowed a colour removal of all dyes studied, although the decolourisation rate largely depended on the chemical structure of the different dyes. Nearly complete decolourisation was achieved in 30 min for bromophenol blue followed by methyl orange (95% in 30 min) and methyl green (90% in 60 min), whereas phenol red was hardly decolourised (30% in 60 min). In mixtures of two dyes, the decolourisation rate became similar for both dyes.

Alinsafi et al. [2005] worked with Al electrode for the removal of Reactive Blue dye with an electrode spacing of 2 cm and optimum current density of 12mAcm^{-2}, and operating time of 105min. it was found that color removal was greater than 90%.

Kobya et al. [2005] have worked on electrocoagulation of levafix orange textile dye solution by using aluminum sacrificial anode. And inter electrode distance was 1.1cm. It was found that almost complete removal of pollutants (99.9%) was obtained with typical operating conditions; 100 A/m^2 current density, 15 min operating time and initial pH 3. On the other hand, 95% decolorization efficiency may be obtained for the same current density in 12 min and at pH 6.4. The corresponding electrode and energy consumptions during the electrolysis were found to be 1.8 kg Al/kg dye and 35 kWh/kg dye. The decolorization efficiency for Al electrode falls in a linear fashion from 99.6 to 88% with increase in concentration of the dye from 100 to 500 mg/l

Kashefialasl et al. [2005] have studied the batch removal of the reactive textile dye Colored Index (C. I.). Acid yellow 36 from an aqueous medium by the electrocoagulation method using iron electrodes. The effects of electrolyte concentration, initial pH, current density, electrode area, interelectrode distance, dye concentration, and treatment time on the decolorization efficiency have been investigated. The results showed that when the initial concentration of the dye was 50 ppm, the dye was effectively removed (83%) at pH ranging from 7 to 9, time of electrolysis of approximately 6 min, current density of approximately 127.8 A/m^2, temperature of approximately 298 °K, and interelectrode distance of 2.5 cm. It was also found that the color removal percent with increasing of dye concentration decrease.

Ghalwa et al. [2005] have worked on electrochemical degradation of Acid Green dye (C.I. 61570) in aqueous wastewater dyestuff solutions using a lead oxide coated Titanium electrode. results of the electrocatalytic oxidation process of the dyestuff solutions were expressed in terms of the remaining dye concentration and chemical oxygen demand (COD) values. Electrolytic cell volume was kept 150 cm^3 and distance between electrode was 3 cm. The optimum operating conditions of the treatment process were a current density of 15 mA/cm^2 a temperature of 30 °C, an initial dye load concentration of 100 mg/l, and an electrolysis time of 10 min. This study concluded that the prepared PbO_2/Ti electrode has a high efficiency in the removal of acid green dye from their aqueous solutions, at low current densities, short electrolysis times, and mild temperatures.

Daneshvar et al. [2002] has studied decolorization of orange II by electrocoagulation method. EC of dye-containing aqueous solutions were carried out in the beakers (250 ml). The results showed that the orange II was effectively removed at initial pH of 7.5- 8.5. When the stirring rate exceeded 100 rpm, the removal efficiency decreased. The results also indicated that the removal efficiency of orange II and COD of the sample were raised to > 98 and > 84%, respectively. When iron was used as sacrificial anode and the initial concentration of orange II was about 50 ppm, the optimum current density, stirring rate, initial concentration, distance between the electrodes, were 34.62 A/m^2, 100rpm, (50-200 ppm), 2 cm, respectively.

Also **Daneshvar et al. [2004]** have studied electrocoagulation of Acid Red 14 dye. The EC unit consisted of an 0.5 L electrochemical reactor with iron anode and steel cathode. It was found that 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/m^2, 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%. The experimental results also showed that an EC cell with several electrodes was more effective than a simple electrochemical cell in color removal.

Again **Daneshvar et al. [2006]** worked on electrocoagulation for the removal of color from solutions containing C. I. Basic Red 46 (BR46) and C. I. Basic Blue 3 (BB3). The study shows that an increase in the current density up to 60–80Am^{-2} enhanced the color removal efficiency, the electrolysis time was 5 min and the range of pH was determined between 5.5 and 8.5 for two mentioned dye solutions. It was found that for, the initial concentration of dye in solutions should not be higher than 80 mgl^{-1} in order to achieve a high color removal percentage. The optimum conductivity was found to be 8$mScm^{-1}$, which was adjusted using proper amount of NaCl with the dye concentration of 50 mgl^{-1}.

Modirshahla et al. [2006] has investigated the effect of different electrode connections on the removal efficiency of Tartrazine from aqueous solutions by electrocoagulation. In this work it was shown that the EC treatment achieves a fast and effective removal of Tartrazine. For 250 ml dye solution with COD of approximately 30 mg/l, dye concentration of 40 mg/l, color and COD elimination of 100% and 90% were obtained, respectively, when the pH was about 5.78, time of electrolysis was approximately 6 min, current density was approximately 120 A/m^2, iron anode and aluminium cathode and interelectrode distance was 1.5 cm. Electrocoagulation with

Fe/Al (anode/cathode) was more effective for the treatment process than Fe/Fe electrode pair.

In the study by **Chrysafopoulou et al. [2006]** an electrolytic pilot scale unit was manufactured for the tertiary treatment of biologically processed wastewater aiming at its reuse for groundwater recharge or for agricultural purposes. The integrated pilot unit consisted of two compartments, the electrolytic cell (reactor) and the unit of flotation and precipitation of the coagulated colloid particles. The anode of the cell was a DSA type electrode with iridium and platinum oxide mixture deposited on a titanium substrate; Stainless Steel 316 was used for the cathode. The unit has been operating at the Wastewater Treatment Plant (WWTP) of the Herakleion Industrial Park (Crete, Greece). The results obtained from the operation of the unit for the tertiary treatment of industrial wastewater are very encouraging. Complete discolouration and disinfection of the wastewater as well as essentially the complete removal of suspended solids.

Aleboyeh et al. [2007] studied The decolorization of C.I. Acid Red 14 (AR14) azo dye by EC process in a batch reactor. Response surface. methodology (RSM) was applied to evaluate the simple and combined effects of the three main independent parameters, current density, time of electrolysis and initial pH of the dye solution on the color removal efficiency and optimising the operating conditions of the treatment process. Analysis of variance (ANOVA) showed a high coefficient of determination value ($R^2 = 0.928$) and satisfactory prediction second-order regression model was derived. Maximum color removal efficiency was predicted and experimentally validated. The optimum current density, time of electrolysis and initial pH of the dye solution were found to be $102 \mathrm{Am}^{-2}$, 4.47 min and 7.27, respectively. Under optimal value of process parameters, high removal (>91%) was obtained for Acid Red 14. Graphical response surface and contour plots were used to locate the optimum point.

As seen from the review systems using a variety of anode and cathode geometries exist. A brief summary of recent work using different setups is given below.

Table 2.4. Brief summary of parameters of recent work on electro coagulation of dye bearing wastes

Reference	Process Batch-B Cont.-C	Dye	Electrode	Area (A)/ Volume (V)	Current Density	Time (min)	Inter-electrode distance (cm)	Conc range (ppm)	pH range	Temp. (°C)	%age color removal
Oeguetveren et al. 1992	B	Acilan Blau				8- 10					> 99
J.S. Do et al.1994	B	Reactive Disperse	Fe(II),Al	A-5cm^2 V-200ml	20 mA/cm^2	15	1.5	100	7	28	R12S>90 D05H>95
Silva and Filho 2001	B	Brown Sodyesul 2GBB	Steel			10		100-500			99
Szpyrkowicz et al. 2001	B	Dye Mixture	Anode-Al Cathode-Steel	Area-100 cm^2	100-300 A/m^2	5			9		99
Tak-Hyun Kim et al.,2002	C	Reactive Blue 49, Reactive yellow 84, Disperse blue 106, Disperse yellow 54	Al, Fe, stainless steel (SUS 304)	A-80 cm^2 V-1.65L	4.45 mA/cm^2	Flow rate-100 ml/min	1	500	4-10		RB49 > 75 RY84 > 90 DB106 > 95 DY54 > 98
M.Bayramoglu et al. 2003	B	Remazol Red RB 133	Al	A-78cm^2 V- 250ml	10 mA/cm^2 V-30V	10	1.1	100-1000	6	25	100-70
Pathak et al., 2004	C	Orange II	Fe	450 ml	159.5 A/m2	Flow rate-350 mL/min.	0.6	< 50	6-8	25	99
A. Alinsafi et al. 2005	C	Reactive blue	Al	V-100ml	12 mA/cm^2	105	2	50	10	-	> 90
M. Kobya et al. 2005	B	Levafix orange	Al	A-78cm^2	100 A/m^2 V-30V	12	1.1	100-500	6.4	25	99.6-88

Table 2.4 (Contd.)

Reference	Process Batch-B Cont.-C	Dye	Electrode	Area (A)/ Volume (V)	Current Density	Time (min)	Inter-electrode distance (cm)	Conc range (ppm)	pH range	Temp. (°C)	%age color removal
M. Kashefialasl et al. 2005	B	C.I.Acid Yellow 36	Fe	250 ml	127.8 A/m^2	6	2.5	50	7-9	28	83
Golder et al. 2005	B	Methylene blue Eosin yellowish	MS	100 ml	16.1 mA/cm^2	5 15	1.2	200	6.8	27	97
Ghalwa et al. 2005	B	C.I.Acid Green 61570	Lead oxide coated titanium	150 ml	15mA/cm^2	10	3.0	100	1.5-4.0	30	> 90
Modirshah-la et al. 2006	B	Tartrazine	Anode-Fe Cathode-Al	250 ml	120 A/m^2	6	1.5	40	5.78	28	100
Chrysafopou lou et al. 2006		Pilot Plant for waste	Ir-Pt on Titanium/ss 316								99
Daneshvar et al. 2002	B	Orange II	Fe	A-0.0106 m^2 V -250 ml	34.62 A/m^2	5	2	< 200	7.5-8.5	25	> 98
Daneshvar et al. 2004	B	Azo dye-Acid Red 14	Anode- Fe (ST 37-2) Cathode-steel (grade 304)	V - 0.5 L	80 A/m^2	4	1	< 150	6-9	27	93
Daneshvar et al. 2006	B	C. I. Basic Red 46 C. I. Basic Blue 3	Anode -Fe (ST 37-2) Cathode-steel (grade 304)	V – 250 ml	60–80 A/m^2	5	1.5	< 80	5.5 - 8.5		BR46 > 90 BB3 > 98
S. Mahesh et al. 2006	B	Paper mill waste water (black liquor)	Fe	V - 2 L	55.56 A/m^2	60			7.08	31	90
Aleboyeh et al 2007	B	Acid Red 14	Al		102 A/m^2	4.47		100-1000	7.27		> 91%

Conclusions from literature review

- There are many processes to remove dyes from colored effluents such as adsorption, precipitation, chemical degradation, photodegradation, biodegradation, chemical coagulation and electrocoagulation .
- Adsorption processes are very time-consuming and costly with low efficiency.
- Chemical degradation by oxidative agents such as chlorine is the most important and effective methods, but it produces some very toxic products such as organochlorine compounds.
- Photo oxidation by UV/H_2O_2 or UV/TiO_2 needs additional chemicals, and therefore causes a secondary pollution.
- Although biodegradation process is cheaper than other methods, it is less effective because of the toxicity of dyes that has an inhibiting effect on the bacterial development.
- Biological activity, in liquid state fermentations, is incapable of removing dyes from effluent on a continuous basis. This is due to the time period of a few days required for decolourisation-fermentation processes.
- Physical and chemical methods of dye removal are effective only if the effluent volume is small. This limits the use of physio-chemical methods, such as membrane filtration to small-scale in situ removal.
- A limiting factor of removal methods is cost. This is true even in lab-scale studies, and methods, therefore, are unable to be used by large-scale industry.
- Electrocoagulation is an electrochemical wastewater treatment technology that is currently experiencing both increased popularity and considerable technical improvements. Electrocoagulation has already proven very effective in the removal of contaminants from water.
- EC systems use a using a variety of anode and cathode geometries, including plates, balls, fluidized bed spheres, wire mesh, rods, and tubes.

- EC process would eliminate adding expensive chemicals to the wastewater and would subsequently generate less solid waste, thus saving on disposal costs.
- The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
- EC process provides a simple, reliable and cost-effective method for the treatment of wastewater without any need for additional chemicals, and thus the secondary pollution.

Chapter 3

ELECTROCOAGULATION FUNDAMENTALS

EC technique uses a direct current source between metal electrodes immersed in polluted water. The electrical current causes the dissolution of metal plates including iron or aluminum into wastewater. The metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [Daneshwar et al., 2006].

Compared with traditional flocculation and coagulation, electro-coagulation has, in theory, the advantage of removing small colloidal particles; they have a larger probability of being coagulated because of the electric field that sets them in motion. Addition of excessive amount of coagulants can be avoided, due to their direct generation by electro-oxidation of a sacrificial anode [Alinsafi et al., 2005].

The EC process is characterized by a fast rate of pollutant removal, compact size of the equipment, simplicity in operation, energy efficiency, and low operating and equipment costs [N. Daneshvar et al., 2004]. The EC is a simple and efficient method for the treatment of water and many kinds of wastewater. It has been tested successfully for the treatment of various effluents such as wastewater containing food and protein wastes, textile wastewater, aqueous suspensions containing ultrafine particles, fluoride-containing water, restaurant wastewater, textile dye solutions, and smelter wastewater containing harmful arsenic.

3.1 MECHANISM OF EC

Generally, three main processes occur during EC process:

(a) electrolytic reactions at electrode surfaces;

(b) formation of coagulants in the aqueous phase;

(c) adsorption of soluble or colloidal pollutants on coagulants and removal by sedimentation or flotation.

The most widely used electrode materials in EC process are aluminum and iron. In the case of aluminum, main reactions at electrodes are as:

Anode: $Al_{(s)} \rightarrow Al^{3+} + 3e^-$ (1)

Cathode: $3H_2O + 3e^- \rightarrow 3/2\ H_2(g) + 3OH^-$ (2)

The destabilized particles then aggregate to form flocs. In the meantime, the tiny hydrogen bubbles produced at the cathode induce the floatation of most flocs, helping to effectively separate particles from wastewater.

$Al(aq)^{3+}$ and OH^- ions generated by electrode reactions (1) and (2) react to form various monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, and $Al(OH)_4^-$ and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$, which transform finally into $Al(OH)_3$ according to complex precipitation kinetics.

Formation rates of the different species play an important role in the decolorization process. Several interaction mechanisms are possible between dye molecules and hydrolysis products, and the rates of these depend on the pH of the medium and types of ions present. Two major interaction mechanisms have been considered in recent years: precipitation and adsorption, each one being proposed for a separate pH range. Flocculation in the low pH range is explained as precipitation, while that in the higher pH range (>6.5) is explained as adsorption [O. T. Can et al., 2003].

Precipitation:

dye + monomeric Al → [dye monomeric Al](s), pH 4.0-5.0 (3)

dye + polymeric Al → [dye polymeric Al] (s), pH 5.0-6.0 (4)

Adsorption:

dye + $Al(OH)_3(s)$ → [particle] (5)

[dye polymeric Al] (s) + $Al(OH)_3(s)$ → [particle] (6)

Freshly formed amorphous $Al(OH)_3$ "sweep flocs" have large surface areas, which is beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. These flocs polymerize as

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \quad (7)$$

and they are removed easily from the aqueous medium by sedimentation and by H_2 flotation.

When iron is used as anodes, upon oxidation in an electrolytic system, it produces iron hydroxide, Fe(OH)*n* where $n = 2$ or 3. Two mechanisms for the production of the metal hydroxide have been proposed [N. Daneshvar et al., 2005]:

(a) Mechanism 1:

- Anode: $4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^-$

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

- Cathode: $8H^+(aq) + 8e^- \rightarrow 4H_2(g)$
- Overall: $4Fe(s) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 4H_2(g)$

(b) Mechanism 2:

- Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

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

- Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
- Overall: $Fe(s) + 2H_2O(l) \rightarrow Fe(OH)_2(s) + H_2(g)$

The insoluble metal hydroxides of iron can remove dye molecules by surface complexation or electrostatic attraction. In surface complexation, it is assumed that the pollutant can act as a ligand to bind a hydrous iron moiety with precipitation and adsorption mechanisms [N. Daneshvar et al., 2006]:

Precipitation:

dye + monomeric Fe → [dye monomeric Fe](s)
dye + polymeric Fe → [dye polymeric Fe](s)

Adsorption:

dye + $Fe(OH)_n(s)$ → [Sludge]
[dye polymeric Fe](s) + $Fe(OH)_n(s)$ → [Sludge]

In electrostatic attraction, the hydroxided iron oxide particles contain of apparent positive and negative charge, which attract the oppositely charge polluting species and remove them from solution.

Thus the EC process has successfully been used for the treatment of wastewaters including electroplating wastewater, laundry wastewater, latex particles and textile wastewaters. Meanwhile, EC process has been widely used to decolorize various structurally different dye containing solutions such as disperse, reactive and acidic dyes.

3.2 ELECTROCOAGULATION PRACTICES

EC systems are run either on batch or on continuous basis. Following text gives a brief account of both types of systems as in practice.

3.2.1 Batch Electrocoagulation System

In a batch EC process, electrocoagulation of dye solution is carried out in a reactor with a magnetic stirrer to agitate the solution. The electrodes are placed inside a glass reactor and connected to a digital power supply. In each run, fixed volume of dye solution is decanted into the electrolytic cell and the run is started. Samples were withdrawn at appropriate time intervals. And then filtered and analyzed for the residual dye concentration using double beam UV/VIS spectrophotometer.

Batch reactor applications typically operate with a fixed wastewater volume per treatment cycle but suffer from the perceived disadvantage (from a design and operational standpoint) that conditions within the reactor change with time.

3.2.2 Continuous Electrocoagulation System

Electrocoagulation of dye-containing solution was carried out in a flow-through EC apparatus consisting of a flow-through cell, the electrode assembly, the feed pump and the DC power supply unit. At the beginning of a run, the dye solution of desired concentration is pumped through the cell at a predetermined flow rate and after the treatment of desired volume of dye solution, the EC run is stopped. Concentration of the dyestuff in the treated sample is analyzed using the UV-Vis spectrophotometer.

Continuous EC systems are capable of treating large volumes of waste wasters. Flow regime should be laminar because it favours the growth of large flocs that are easier to remove. A key advantage for such reactor systems is that their coagulant requirements are essentially fixed, a major advantage in terms of both design and operation [Holt et al., 2005].

In a continuous stirred tank reactor, the concentration of materials in the feed stream was immediately lowered to the concentration in the tank and effluent. Therefore, the overall rate of reaction, and consequently the conversion of the reactant to product, will be less than that for a plug flow tubular reactor (PFTR), where no such lowering of concentration upon entering the reactor occurs. If the gap between the electrodes is closer, and the ratio of length/width is much larger than 1, it is able to be considered that there is no mixing of the fluid in a longitudinal direction. Therefore, reactor can be considered a PFTR [Kim et al., 2002].

3.3 FACTORS CONTROLLING ELECTROCOAGULATION

Decolorization of dye solution by EC process is influenced by a number of factors such as:

1. pH
2. Initial concentration
3. Electrolysis time
4. Current density
5. Electrode material
6. Inter electrode distance
7. Number of electrodes

3.3.1 pH

pH is an important parameter influencing the performance of the EC process. The effect of pH on the process performance is explained as follows: the dominant aluminum species are different according to the solution pH; Al^{3+} and $Al(OH)^{2+}$ are dominant in pH 2–3, and with pH between 4 and 9, various polymeric species such as $Al_{13}O_4(OH)_{24}{}^{7+}$ are formed and precipitated as $Al(OH)_3(s)$. For initial pH values between 4 and 9, the solution pH stabilizes very quickly at nearly constant value around

9 due to the buffering capacity of complex nature of aqua Al^{3+}/ $Al(OH)_3$ system. When initial pH is higher than 9, the monomeric anion, $Al(OH)^{4-}$ is formed at the expense of amphoteric $Al(OH)_3(s)$ which causes a slight decrease in final pH by consuming OH^- ions. Moreover, as $Al(OH)^{4-}$ does not exhibit any decolorization capacity, a decrease is noted also in the removal efficiency above pH 9. In conclusion, higher decolorization efficiency is obtained in acidic to neutral mediums, as the majority of aluminum complexes and the precipitates responsible for adsorptive decolorization are optimally formed in pH range 4–9.

3.3.2 Initial Concentration

Percent removal decreases with the increase in the initial concentration of the dye. This could be due to the presence of intermediate products produced during the electrolysis process at higher concentrations, which then could compete for the active sites on the electrode, or these intermediate products may be insoluble in water and would block the electrode's active sites. On the other hand one of the most important pathways of color removal by EC process is adsorption onto metallic hydroxide flocs and the adsorption capacity of flocs is limited.

3.3.3 Electrolysis Time

The color removal efficiency depends directly on the concentration of ions produced by the electrodes. When the electrolysis period increases, an increase occurs in the concentration of ions and their hydroxide flocs. Therefore, percent removal increases with increase in time of electrolysis.

3.3.4 Current Density

In all EC processes, current density is the most important parameter for controlling the reaction rate within the reactor. When the current density increases, the efficiency of ion production on the anode and cathode increases. Therefore, there is an increase in floc production in the solution and hence an improvement in the efficiency of color removal. Moreover, bubble generation rate increases, and the bubble size decreases with increasing current density, which are both beneficial for high pollutant removal efficiency by H_2 flotation.

3.3.5 Electrode Material

The electrode material impacts markedly on the performance of the EC reactor. The anode material determines the cation introduced into solution. Several researchers have studied the choice of electrode material with a variety of theories as to the preference of a particular material. The most common electrodes are aluminium or iron plates.

Do and Chen [1994] compare the performance of iron and aluminium electrodes for removing colour from dye-containing solutions. Their conclusion was that the optimal EC conditions varied with the choice of iron or aluminium electrodes, which in turn is determined by some factors such as initial pollutant concentration, pollutant type. Kim et al. [2002] has also shown that dye removal was more efficiently achieved by Al electrodes than those of SUS or Fe.

3.3.6 Inter Electrode Distance

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

3.3.7 Number of Electrodes

There is direct relation between removal efficiency and total no. of electrodes. So when the number of electrodes increase, the distribution of the coagulation agents density is more effective. This can produce the related coagulation and completes the removal of samples.

3.4 ADVANTAGES OF EC

- EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running.
- The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.

- Sludge formed by EC 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.
- The EC 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
- EC 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.
- 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.
- The electrolytic processes in the EC cell are controlled electrically and with no moving parts, thus requiring less maintenance.
- The EC 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.
- Flocs formed by EC are similar to chemical flocs, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.

3.5 DISADVANTAGES OF EC

- The sacrificial electrodes are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.
- The use of electricity in many places may be expensive.
- An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit.
- High conductivity of the wastewater suspension is required.

Chapter 4

MATERIAL AND METHODS

In the present study, aluminum electrodes have been utilized for the treatment of Cotton Blue bearing aqueous solution by electrocoagulation. Experimental details of the study have been presented in this chapter. These details include characterization of electrodes, residues from a dye-loaded sample and batch EC studies using aluminum electrode.

4.1 COTTON BLUE: PROPERTIES, USES AND HEALTH EFFECTS

Cotton Blue dye was obtained from Chemport India Pvt. Limited with a molecular structure as shown in Figure 4.1. The characteristics of Cotton Blue dye are summarized in Table 4.1. Cotton Blue is a mixture of methyl blue and water blue. It may also be either one of them. Cotton blue is a synthetic coal tar dye, is used in textile industry for dyeing of clothes (blue jeans) and other blue denim. Cotton Blue is widely used as a counter stain, collagen stain, connective tissue stain, and in bacteriological media. Cotton blue has limited use as an indicator in analytical chemistry. Synthetic wastewater solutions of dye of desired concentrations (50–1000 mg/l) were prepared by dissolving in distilled water.

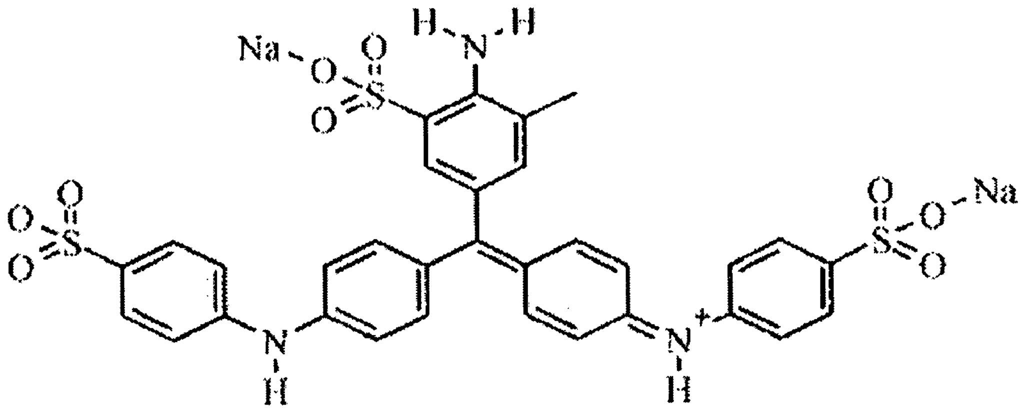


Fig. 4.1 Molecular structure of Cotton Blue

Table 4.1. Properties and health effects of Cotton Blue

Chemical Name	Aniline Blue WS
Colour Index	42755
Chemical Formula	$C_{32}H_{25}N_3Na_2O_9S_3$
Molecular Weight	737.74
Class	Triarylmethane
Appearance	Dark Purple Solid
Odor	Odorless.
Solubility aqueous	Soluble
Absorption maximum	607-610
Vapor Pressure	14 mm Hg water
Boiling Point	~ 100 °C
Stability	Stable. Incompatible with strong oxidizing agents
Hazardous Decomposition Products	Burning may produce carbon oxides (CO, CO_2), nitrogen oxides (NO_x), sulfur oxides.
Potential Health Effects	There is limited data available on the effects of this dye on humans.
Inhalation	May cause irritation to the respiratory tract. Symptoms may include coughing and shortness of breath
Ingestion	Causes irritation to the gastrointestinal tract. Symptoms may include nausea, vomiting and diarrhea
Skin Contact	May cause irritation with redness and pain
Eye Contact	May cause irritation, redness and pain. This product contains an anionic dye. Similar dyes have not caused injury to the cornea or conjunctiva in documented exposure cases with human or rabbit eyes.
Chronic Exposure	Chronic exposure may cause skin effects. Lengthy exposures may affect the ability of blood to carry oxygen (methemoglobinemia), resulting in bluish discoloration of lips and tongue (cyanosis).
LD_{50} / LC_{50}	Not available

4.1.1 Analytical Measurement

The determination of the concentration of Cotton Blue was done by finding out the absorbance characteristic wavelength using UV/VIS spectrophotometer (HACH Co., Model DR/5000). A standard solution of dye was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) was determined from this plot. The λ_{max} for Cotton Blue was found to be 600 nm. Calibration curve was plotted between the absorbance and the concentration of dye solution. The linearity of calibration curve (Fig. 4.2) indicated the applicability of the Lambert-Beer's Law.

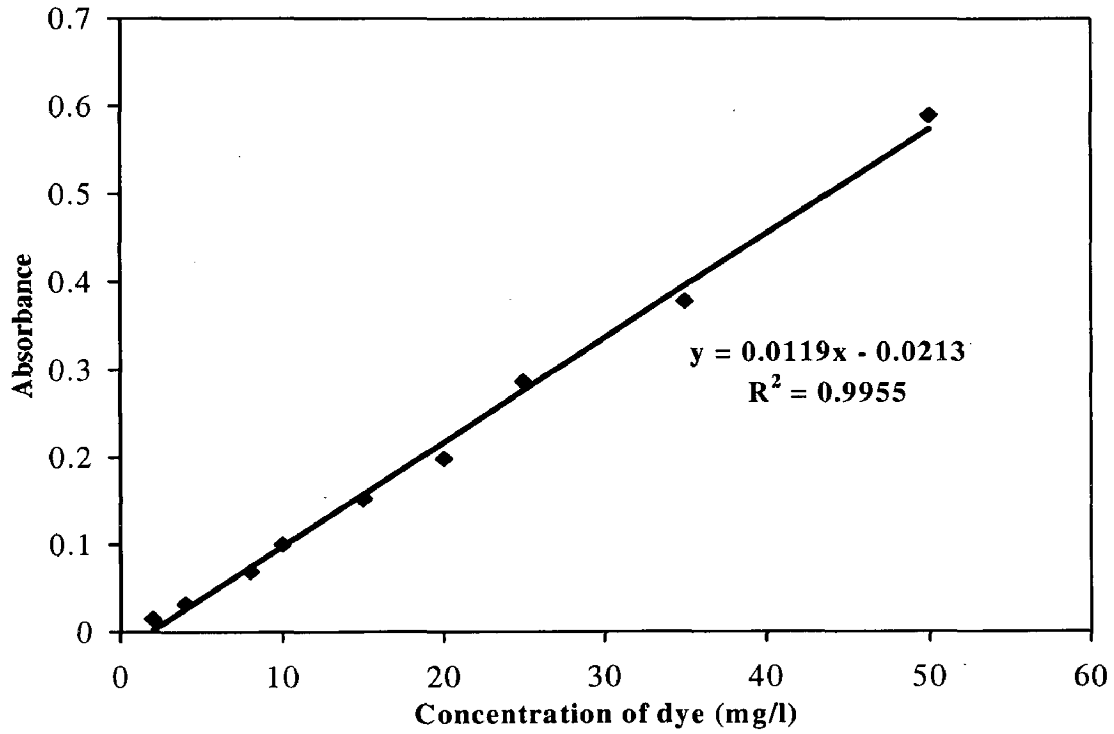


Fig. 4.2 Calibration Graph of Cotton Blue

4.2 EXPERIMENTAL PROGRAMME

4.2.1 Experimental Apparatus

The lab-scale batch experimental setup used for the electrochemical degradation studies is shown in Fig 4.3. Experiments were carried out in a 1.5-L (10.8cm x 10.8cm x 13cm) rectangular reactor made up of Perspex glass. Al plates of thickness 1 mm were used as electrodes. Dimensions of electrodes were 8cm x 8cm and the spacing between two electrodes in EC cell was 0.5 cm. The total effective surface area of each electrode was 64 cm^2 and there was a 5 cm distance between the bottom of the electrodes and the bottom of the cell, which allowed easy stirring. Magnetic stirrers were used to agitate the solution. The stirrer was employed in the electrochemical cell to maintain an unchanged composition. The electrodes were then connected to a digital DC power supply (Range: 0-20 V, 0-5 A).

4.2.2 Experimental Procedure

All of the runs are performed at room temperature and at a constant magnetic stirring speed. The experiments were performed on dye solutions of known concentration C_0 and pH_0. The pH of the solutions was measured by pH meter (SENSOdirect pH-24, Aqualytic, Germany) and adjusted by adding NaOH or H_2SO_4 solutions. At the beginning of a run, 1.5L solution of the desired concentration of the dye was fed into the reactor and the run was started. Samples were withdrawn at appropriate time intervals. And then filtered and analyzed for the residual dye concentration using double beam UV/VIS spectrophotometer. At the end of the run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried, and reweighed.

4.2.3 Analytical Method

A UV-Vis spectrophotometer (HACH, DR/5000) was employed to measure the maximum wavelength (λmax = 600nm), which was used to measure the concentration of the dye. The equation used to calculate the color removal efficiency in the treatment experiments was:

$$\mathrm{CR}(\%) = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C were the initial and final concentrations of the dye in solution (mg/l), respectively. True color of Cotton blue dye solution and real textile waste water was measured by adapting Colorimetric Platinum Cobalt method using a HI 93727 colorimeter (Range: 0-500 PCU). Calibration curve was plotted between the Platinum

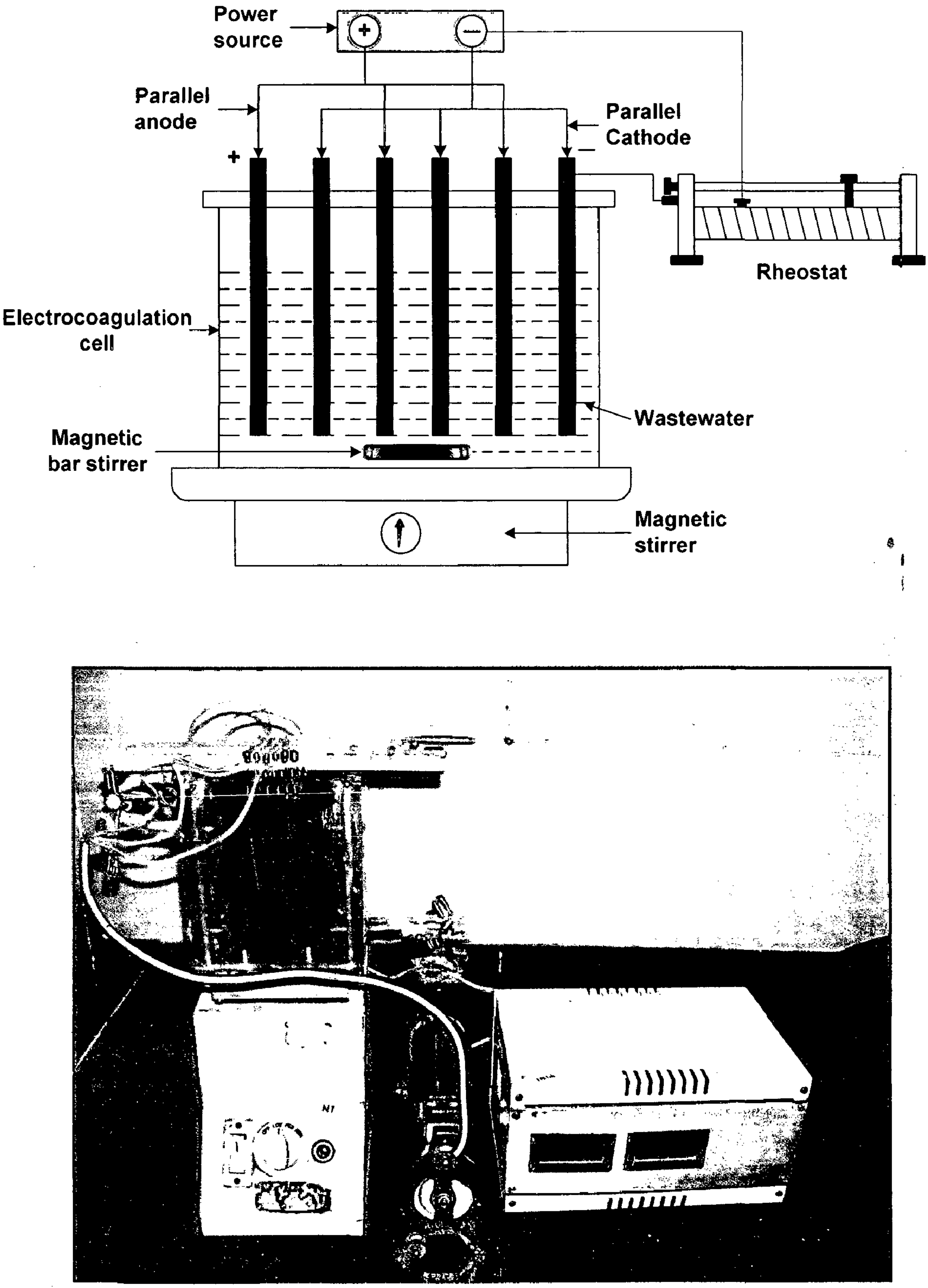


Fig. 4.3 Schematic diagram of experimental setup of the EC cell

Cobalt Units (PCU) and the concentration of dye solution. Fig. 4.4 shows the calibration curve of Cotton blue dye for true color.

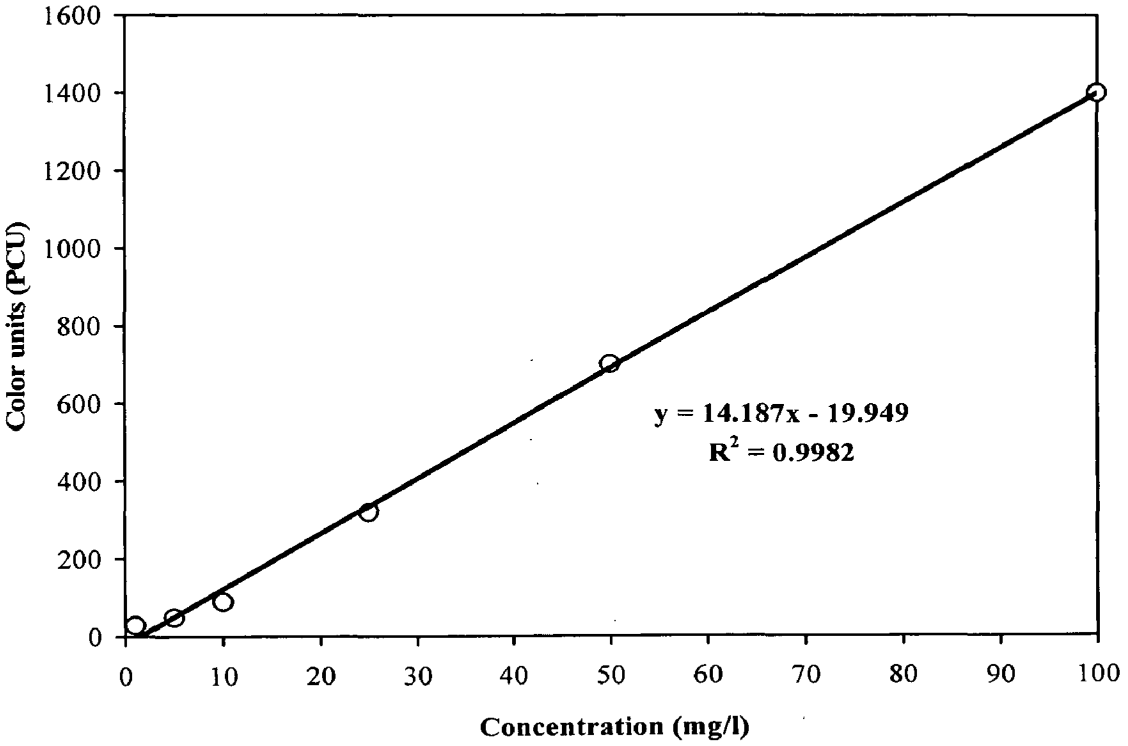


Fig. 4.4 Calibration Graph of Cotton Blue for color

4.3 CHARACTERIZATION OF ELECTRODES AND RESIDUES

4.3.1 Scanning Electron Micrograph (SEM)

SEM analysis of aluminum electrodes were carried out before and after the EC treatment of Cotton Blue from aquous solution by using LEO 435 VP Scanning electron microscope.

4.3.2 X-Ray Diffractometer (XRD)

The XRD analysis of the residues were carried out with a Bruker AXS D8 ADVANCE diffractometer operating with Cu Kα radiation source filtered with a graphitic monochromator ($\lambda = 1.5406$). The samples were crushed to a fine powder and pressed into a sample holder. The XRD scans were recorded from $2\theta = 5°$ to $100°$ using a step size of 0.05° and a count time of 3 s.

4.3.3 Thermo Gravimetric Analysis (TGA)

The TGA analysis of the residues were carried out by using Perkin Elemer (Pyris Diamond) Thermogravimetric Analyser. Thermogravimetric analysis involves heating a sample in an inert or oxidising atmosphere and measuring the weight. The weight change over specific temperature ranges provides indications of the composition of the sample and thermal stability. TGA scans were recorded from 25°C to 1000°C using a scan rate of 10°C/min in the atmosphere of Nitrogen and Air.

Chapter 5

RESULTS AND DISCUSSIONS

The detailed discussion on the results of the experiments conducted is given in this chapter. These results include:

- Batch electro-coagulation studies
- Characterization of electrodes and residues

5.1 BATCH STUDY

In order to study the effect of different parameters the batch operations were performed. Batch EC experiments were carried out in 1.5L electrolytic cell for the removal of Cotton Blue (CB) from synthetic solutions of known concentrations by using aluminum electrodes. The effect of various operating parameters, viz. initial concentration (C_0), electrode number (N), inter electrode distance (g), applied voltage (V), electrolysis time(t), and initial pH (pH_0) were studied and presented here.

5.1.1 Effect of the Initial pH (pH_0)

pH is an important parameter that influence the performance of the EC process. To examine the effect of pH_0, the dye solution was adjusted to the different pH_0 ranging from 3 to 11 by adding 0.1 N NaOH or 0.1 N H_2SO_4 solution. Original pH of the dye solution in distilled water was 5.95. The CB removal efficiency with pH_0 is shown in Fig 5.1. It can be seen that the removal at original pH is about 85.4 %. The results reveal that when pH_0 of the dye solutions was in the range 5.95 - 8.0, there was maximum color removal efficiency. For $pH_0 < 5.95$, the proton in the solution get reduced to H_2, and thus, the proportion of hydroxide ion produced is less and consequently there is less CB removal efficiency. When pH_0 of the dye solution was increased from 5.95 to 8.0, there was slight increase in efficiency. As the pH_0 was further increased from 8.0, slight decrease in removal efficiency is seen. At $pH_0 > 8$, the amount of hydroxide ions in solution increase. Consequently, some of the hydroxide ions are probably oxidized at the anode. This action prevents the

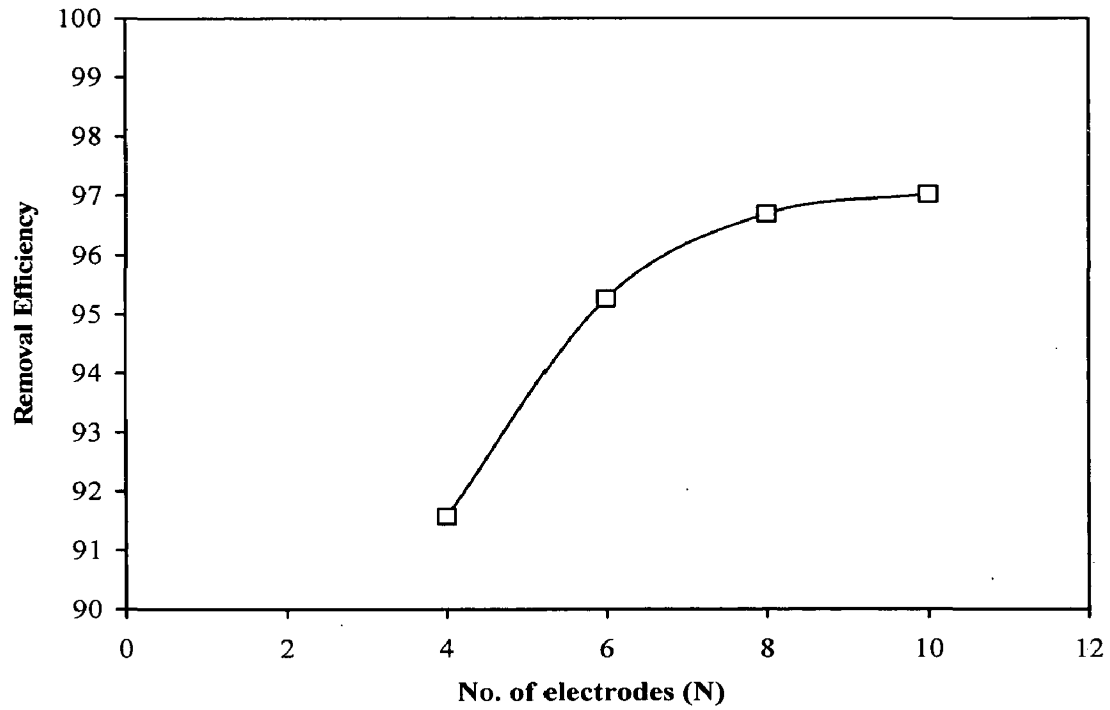


Fig. 5.3 Effect of number of electrodes on the CB removal efficiency from aqueous solution. C_0 = 100 mg/l, t = 5 min, and g = 0.5 cm.

5.1.4 Effect of Electrolysis Time (t)

During electrolysis, the positive electrode undergoes anodic reactions while cathodic reactions occur on the negative electrode. The released ions neutralize the particle charges, and thereby initiate coagulation. The color-removal efficiency depends directly on the concentration of ions produced by the electrodes. When the electrolysis period increases, an increase occurs in concentration of ions and their hydroxide flocs. Consequently, an increase in the electrolysis time (t) increases the dye removal efficiency [Daneshwar et al., 2004].

Accordingly, as shown in Fig. 5.4, an increase in t from 3 to 30 min increases the removal efficiency from 69.5% (413 Pt-Co units) to 98% (8 Pt-Co units). Decolorization efficiency remains constant above 15 min. Therefore for a solution having C_0 = 100 mg/l (1400 PCU), the optimum time of electrolysis was 15 min.

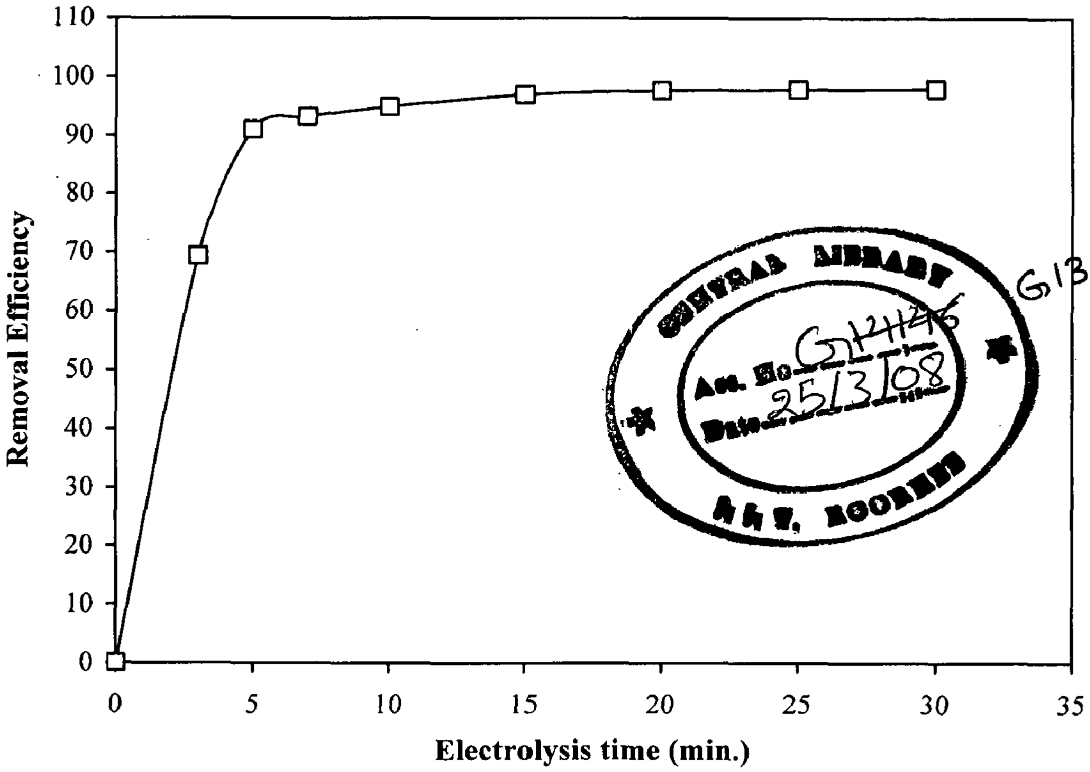


Fig. 5.4 Effect of electrolysis time on the CB removal efficiency from aqueous solution. C_0 = 100 mg/l, g = 0.5 cm, t = 30 min, V = 11V, and N = 6.

5.1.5 Effect of Applied Voltage (V)

The effect of voltage on the removal efficiency of dye is shown in Fig. 5.5. The color removal efficiency increases upto 97% with a voltage of 11 V for 15 min treatment, i.e., from an initial value of 1400 to 22 platinum-cobalt units (PCU) and then it remained almost constant for higher voltages. As the voltage increases, the efficiency of ion production on the anode and cathode increases, therefore, there is an increase in floc production in the solution and hence an improvement in the efficiency of color removal. For a solution with a dye concentration of 100 mg/l, the optimum voltage was 11 V. [Modirshahla et al., 2006].

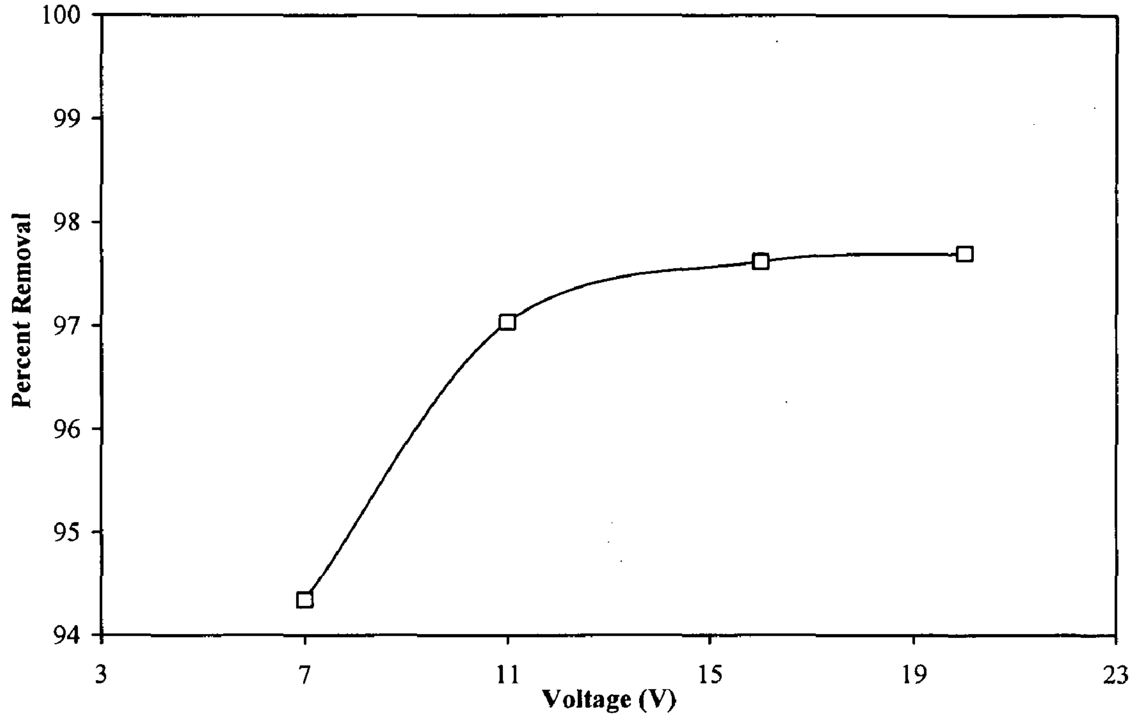


Fig. 5.5 Effect of applied voltage on the CB removal efficiency from aqueous solution. $C_0 = 100$ mg/l, t = 15 min, g = 0.5 cm, and N = 6.

5.1.6 Effect of the Initial Dye Concentration (C_0)

As shown in Fig. 5.6, the removal efficiency decreases with the increase in the initial concentration of the dye. The decolorization efficiency falls from 97% (i.e., from an initial value of 1400 to 22 PCU) to 89% (i.e., from an initial value of 18800 to 2060 PCU) with increase in concentration of the CB dye from 100 to 1000 mg/l. However, between 100 and 500 mg/l of dyestuff initial concentration, the decrease in the dye removal efficiency is insignificant. This may be due to the fact that the required amounts of coagulant produced electrochemically is sufficient to remove maximum amount of dye in this concentration range. However, with further increase in C_0 from 500 to 1000 mg/l, a decrease in CB removal efficiency is seen in Fig. 5.6. This may be due to the insufficient production of hydroxides. Also at higher C_0, intermediate product formed block the electrode active sites, and thus, decrease the removal efficiency. It is quite clear that under the present experimental conditions, the lower is the dye concentration the better is the removal efficiency. [Kobya et al., 2006].

As shown in Fig. 5.7, the dye solution with different initial concentrations (C_0 = 100, 300, 500 mg/l) was treated by EC at optimized conditions. It can be seen that the residual fraction of dye effectively reduced to less than 4.0% when the initial concentration of dye was in the range 100-500 mg/l and the electrolysis period exceeded 15 min. When the initial concentration of dye was 100 mg/l, the residual concentration was decreased to 3mg/l in 15 min. Increasing the initial concentration of dye required increased electrolysis time for electro-coagulation of dye. [Do and Chen, 1994]

5.1.7 Effect of Initial Dye Concentration on Anode Consumption

The effect of initial dye concentration on anode consumption of dye is shown in Fig. 5.8. Anode consumption increases from 0.092 gm to 0.144 gm with increase in C_0 from 100 mg/l to 1000 mg/l for 30 min treatment. The anode consumption was not affected much by the initial dyestuff concentration. Despite the increase in the C_0, the anode consumption did not change significantly.

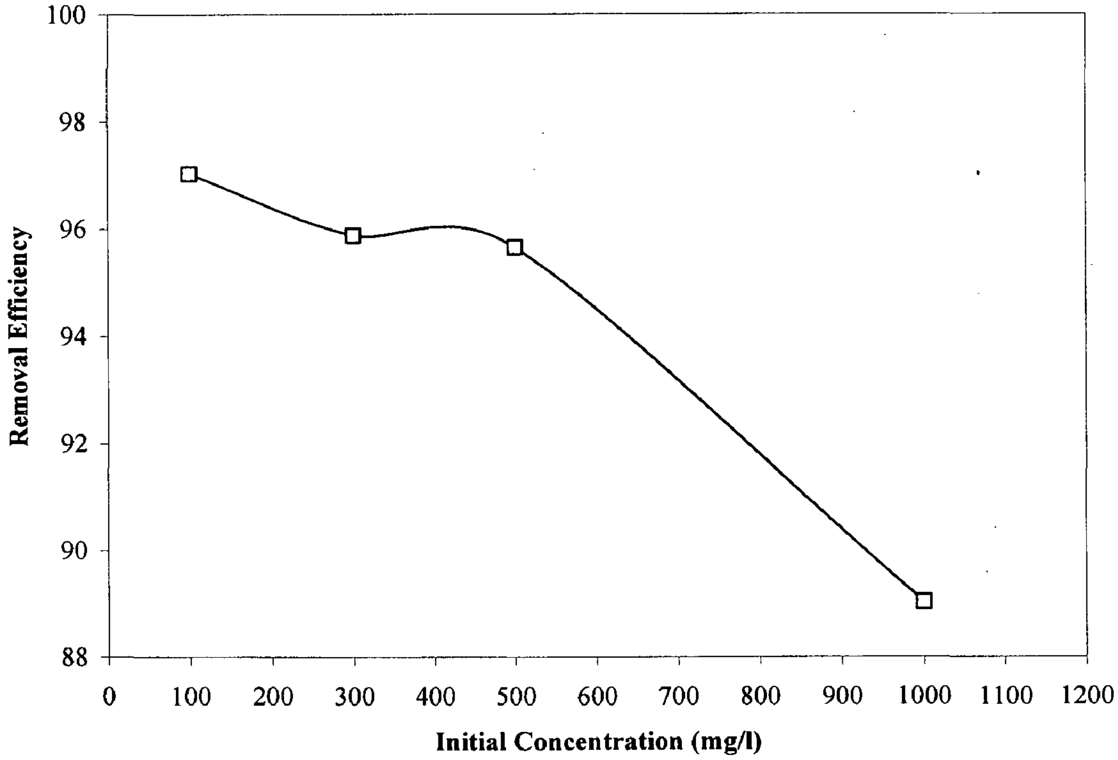


Fig. 5.6 Effect of initial concentration on the CB removal efficiency from aqueous solution. t =15 min, g = 0.5 cm, V = 11V, and N = 6.

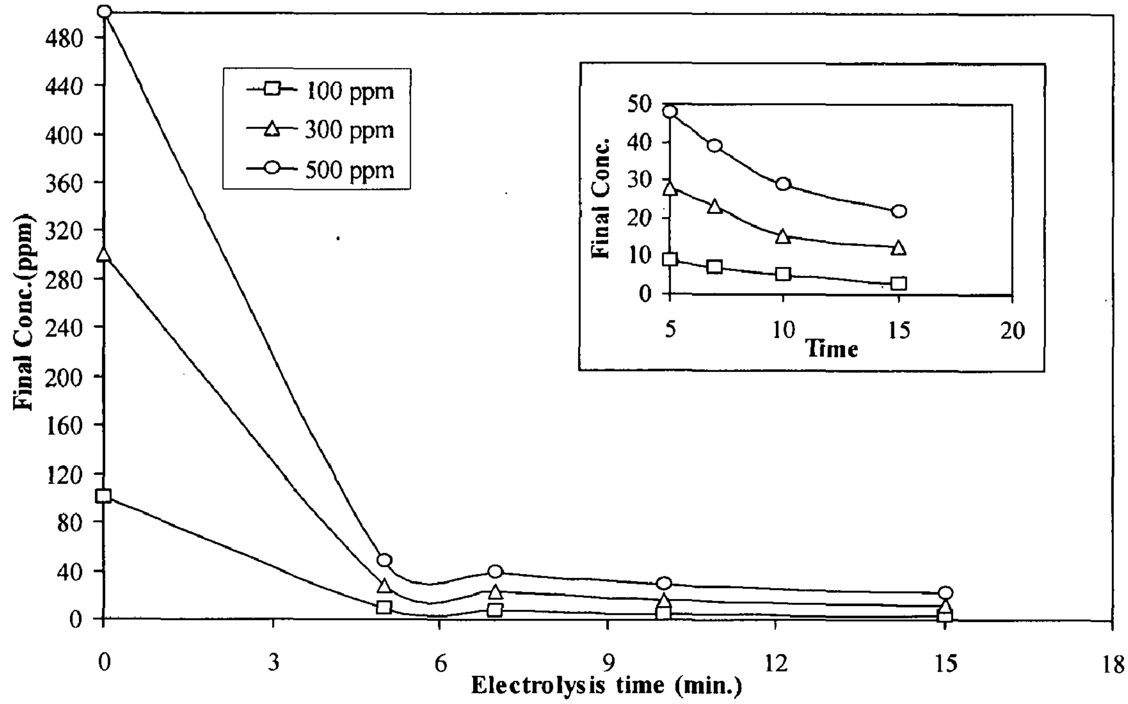


Fig. 5.7 **Effect of electrolysis time on the CB removal efficiency from aqueous solution. C_0 = 100, 300, 500 mg/l, g = 0.5 cm, t = 15 min, V = 11V, and N = 6.**

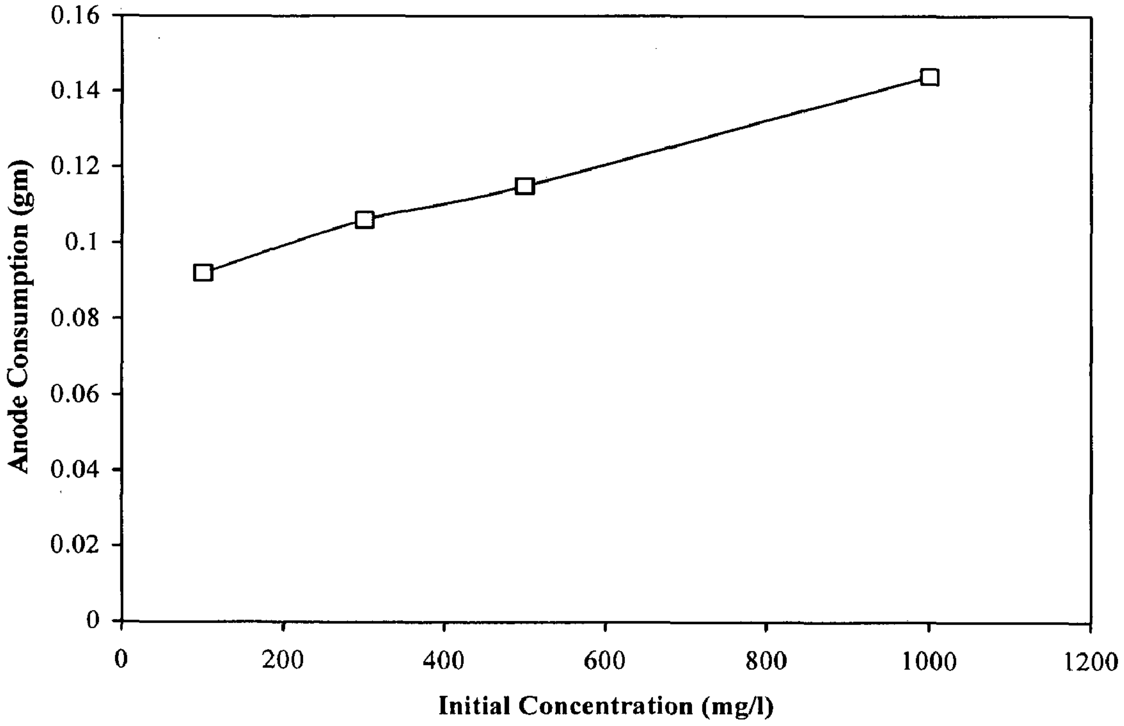


Fig. 5.8 **Effect of initial concentration on the anode consumption. t = 30 min, g = 0.5 cm, V = 11 V, and N = 6.**

5.1.8 Batch Study using Tap water

Figs. 5.9 - 5.10 show the influence of electrolysis time on the removal of dye when dye solutions of different concentrations are prepared in tap water. Fig. 5.9 shows almost equal removal efficiency (87.6% for 100 mg/l and 86.2% for 500 mg/l) for 5 min electrolysis time (t). However, further increase in t shows a slight increase (~ 2 %) in removal efficiency for $C_0 = 500$ mg/l whereas it is 10 % for $C_0 = 100$ mg/l. That means removal efficiency decreases with the increase in concentration. Accordingly, as shown in Fig. 5.10, color decreases from 1400 platinum-cobalt units to 20 PCU (98.6%) for 100 mg/l solution and from 7073 to 490 PCU (93.1%) for 500 mg/l CB dye solution for 15 min treatment. Residual color remains almost constant for t > 15 min for both the concentrations.

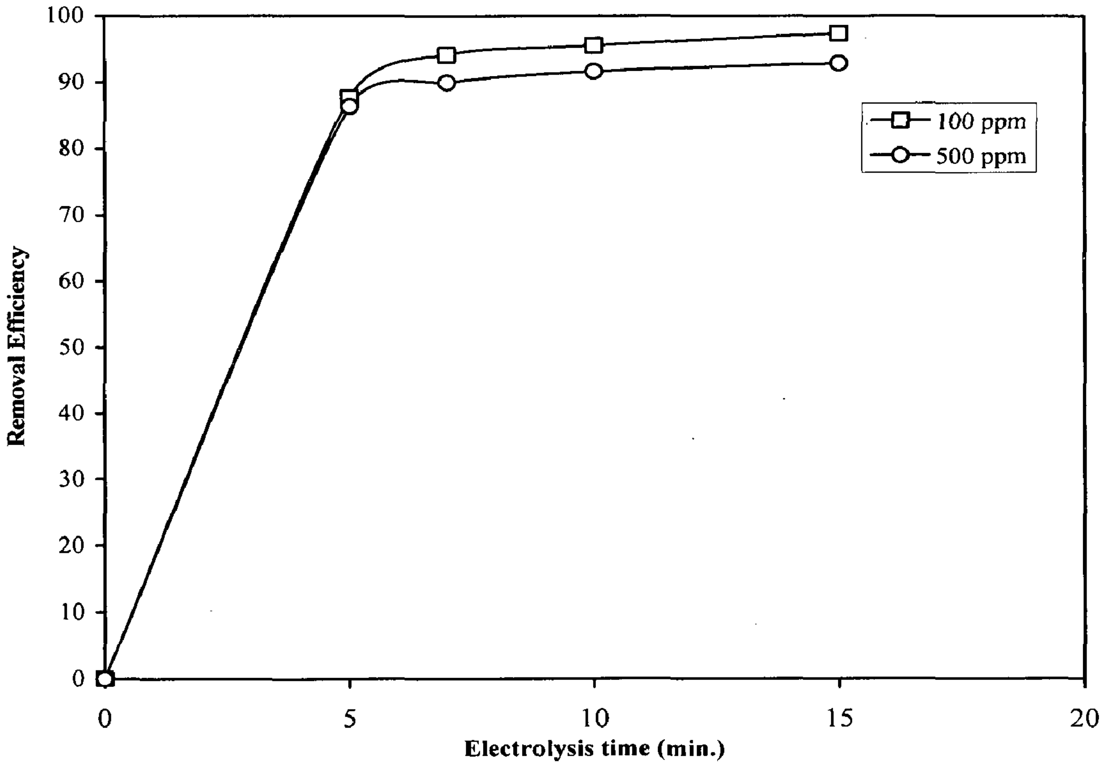


Fig. 5.9 **Effect of electrolysis time on CB removal when dye solution of different concentrations are prepared in tap water.**

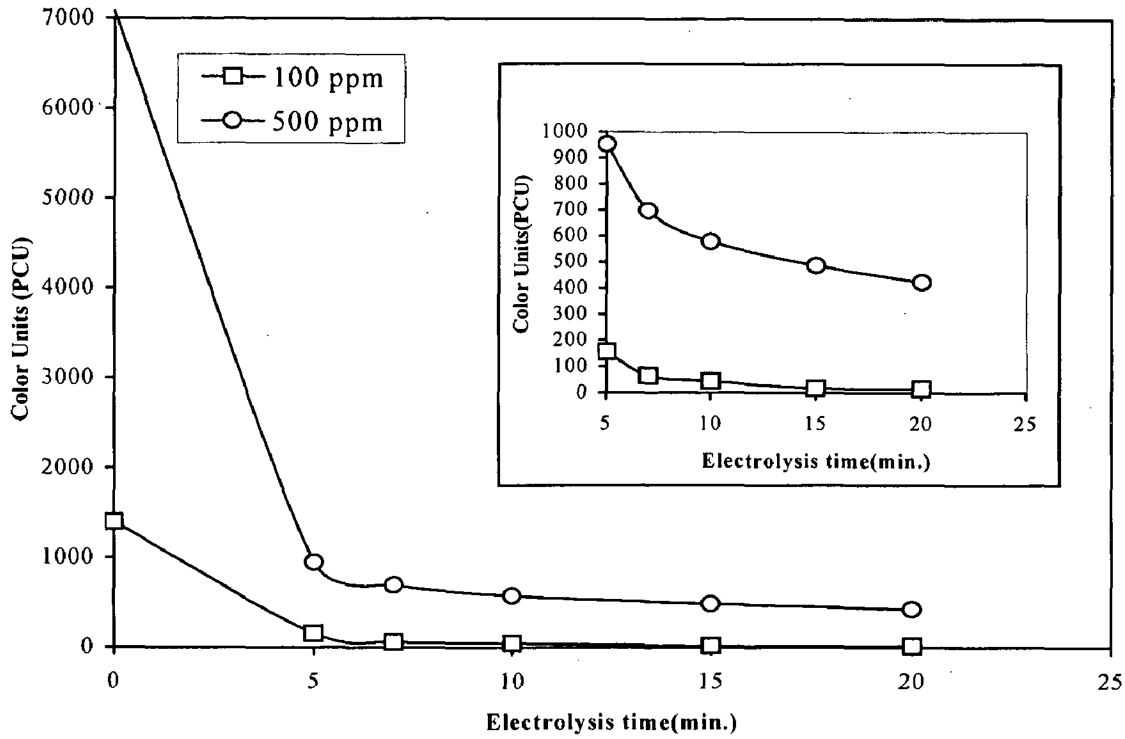


Fig. 5.10 Variation in color (Pt-Co Units) of dye solution of different concentrations with time in tap water.

5.1.9 Comparison Between Tap and Distilled Water Results

Figs. 5.11-5.12 compare the results of decolorization of 100 mg/l dye solution prepared in tap and distilled water. Fig. 5.11 shows that decolorization efficiency is initially more in case of distilled water upto 5 min treatment but after that color removal percent increases more in tap water and then it remains almost equal in both the cases for 15 min of treatment. As seen from Fig. 5.12, Platinum-cobalt units show a fall from an initial value of 1400 to 156 (88.9%) and 107 (92.4%) PCU for tap and distilled water respectively for 5 min treatment. It also shows that PCU decreases gradually in case of distilled water and decreases rapidly in case of tap water. Therefore, it has been seen from Figs. 5.11-5.12 that the results are almost similar in tap and distilled water after 15 min treatment.

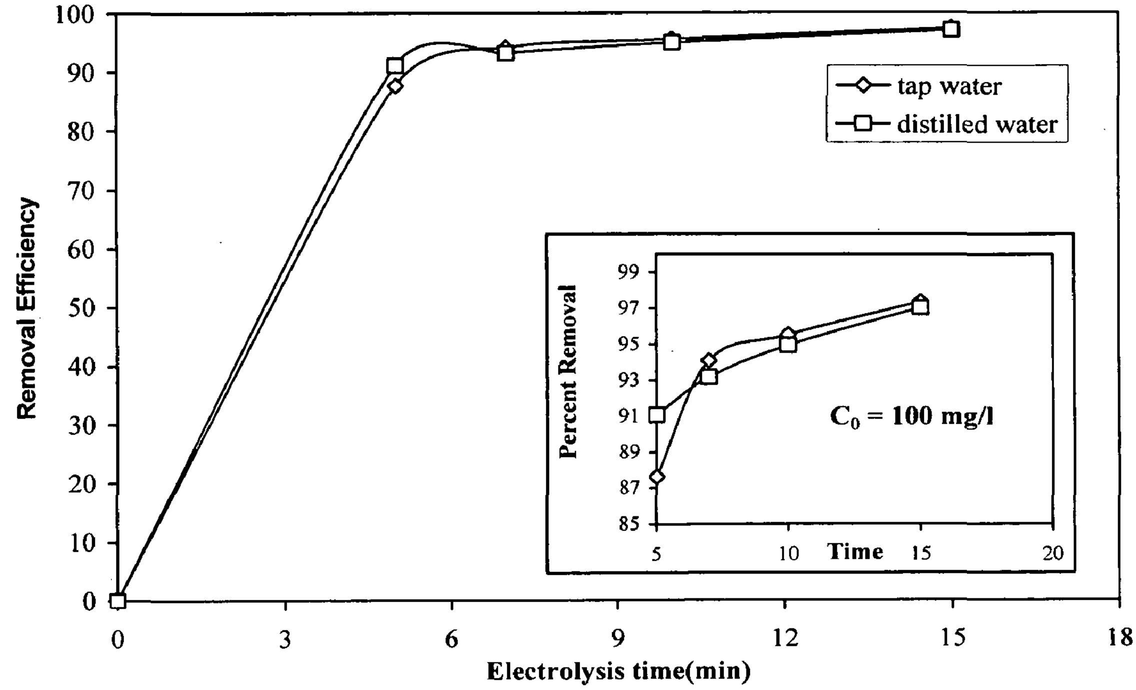


Fig. 5.11 Effect of electrolysis time on the removal efficiency of 100 mg/l dye solution in tap and distilled water.

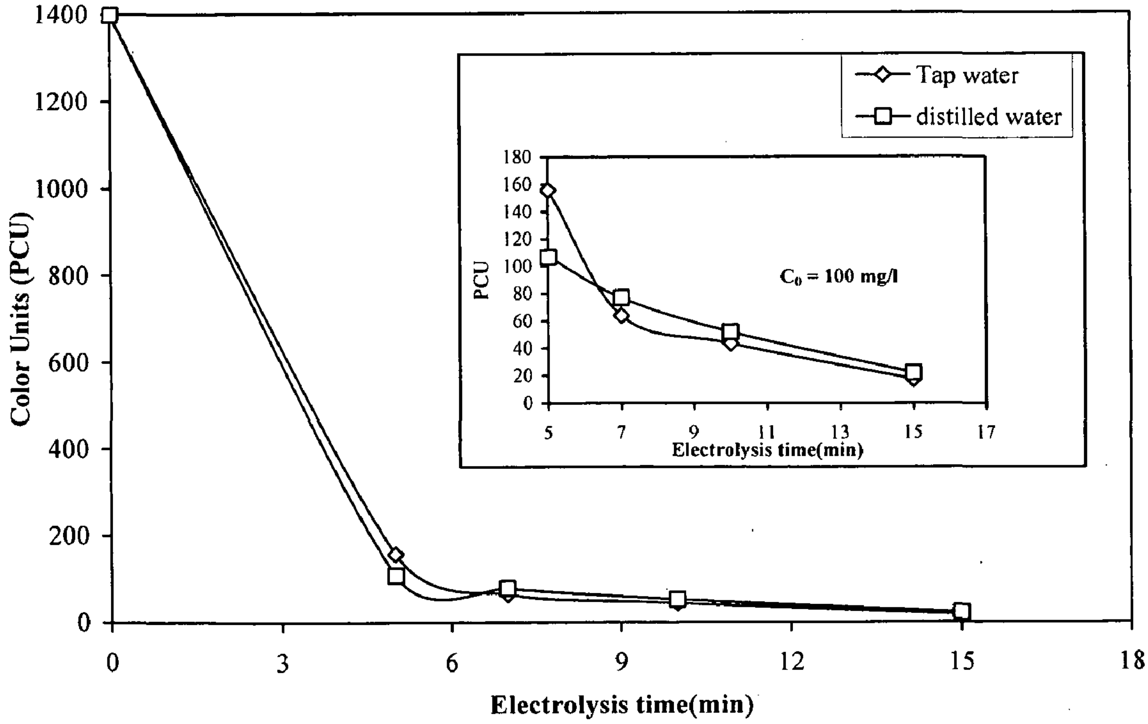


Fig. 5.12 Variation in color (Pt-Co Units) of 100 mg/l dye solution with time in tap and distilled water.

5.1.10 Real Textile Waste Water Results

Two real textile waste water samples, one from textile industry's dyeing section, Ghaziabad (real waste I) and other from Roorkee (real waste II), were also tested at optimized operational conditions based on experiments done. They led to satisfactory decolorization though the electrolysis time for removal is more than that for the synthetically prepared waste. The results are shown in Figs. (5.13-5.14). The decolorization efficiency of real waste I was found to be 97% at 60 min electrolysis time, i.e., from an initial value 6000 to 180 platinum-cobalt units and decolorization efficiency of real waste II was found to be 95.9% at 30 min electrolysis time, i.e., from an initial value 6800 to 280 platinum-cobalt units. Anode consumption was 1.365 gm and 0.505 gm for real waste I and II respectively. The real textile waste water contains large amounts of substances such as sizing agents, surfactants, volatile organic compounds, salts etc. These interfere with EC process and thus electrolysis time and anode consumption is much higher for real textile waste water.

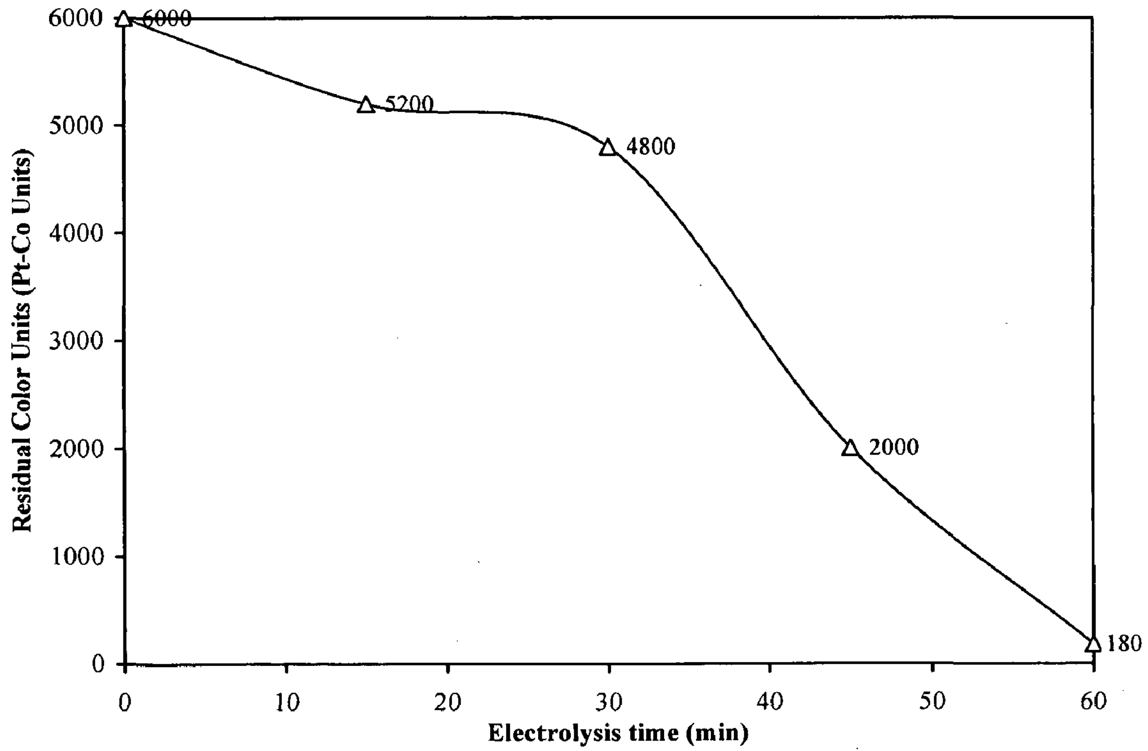


Fig. 5.13 Variation in Color units (Pt-Co Units) with electrolysis time for real waste I at optimized conditions: V = 11V, g = 0.5 cm, N = 6 and t = 60 min.

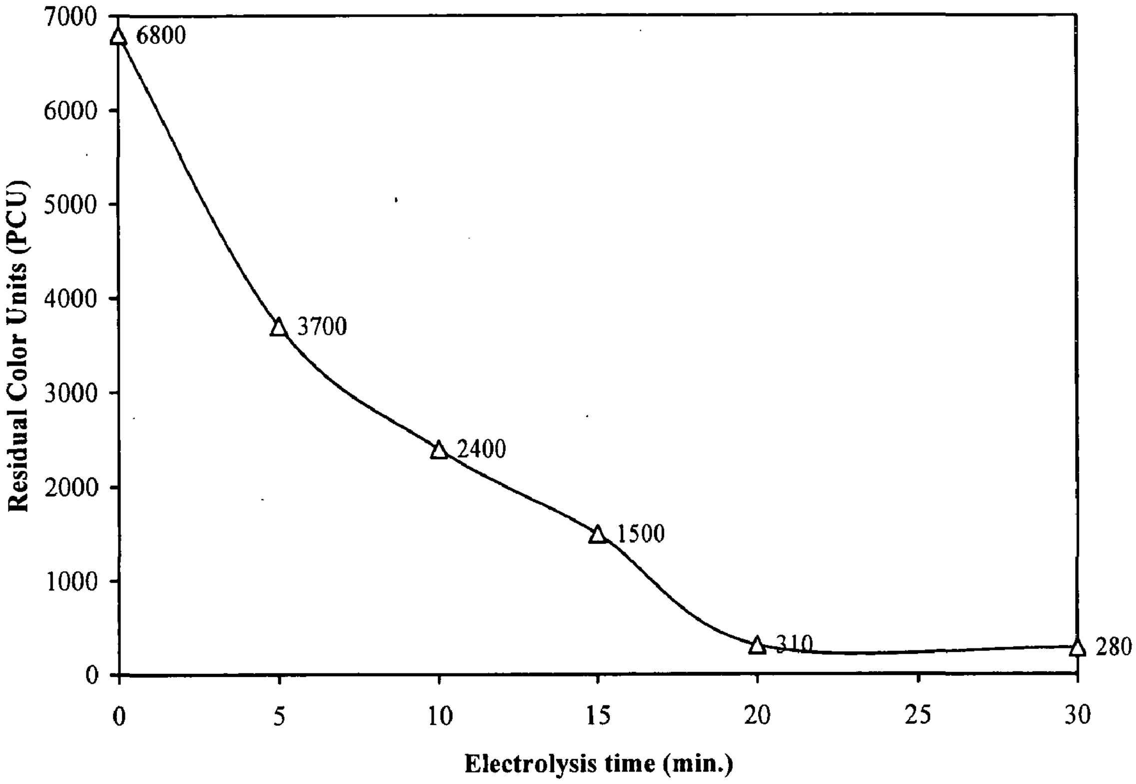


Fig. 5.14 Variation in Color units (Pt-Co Units) with electrolysis time for real waste II at optimized conditions: V = 11V, g = 0.5 cm, N = 6 and t = 30 min.

5.1.11 Characteristics of Treated Effluent

Characteristics parameters of CB dye solution is shown in Table 5.1. CB dye solution of C_0 = 100 mg/l is being treated by using EC process at optimized conditions (inter-electrode distance of 0.5 cm, applied voltage of 11 V, pH ranging from 6 to 8, electrolysis time of 15 min). Fig. 5.15 shows the original and residual (after EC treatment) color of CB dye solution of C_0 = 100mg/l. The table given below presents the original and residual values of characteristics parameters. COD removal of 74 % (i.e., from an initial value of 42 to 11 mg/l) is accompanied with ~98% of color removal (i.e., from an initial value of 1400 to 22 platinum-cobalt units). TOC reduction is found to be 61.4 %. In 15 min electrolysis time, the pH level changes from its initial value of 5.95 to 8.82 for C_0 = 100 mg/l.

Table 5.1. Original and Reduced levels of Characteristics Parameters of Cotton Blue for EC process at optimized conditions

Parameters	**Original Value (before EC treatment)**	**Reduced Value (after EC treatment)**
Chemical Oxygen Demand COD (mg/l)	42	11
Total Organic Carbon TOC (mg/l)	145	56
Color (Pt-Co units)	1400	22
Conductivity (mMhos)	0.055	0.036
pH	5.95	8.82

Optimized conditions: C_0 = 100 mg/l, electrolysis time (t) = 15 min, applied voltage (V) = 11 V, inter-electrode distance (g) = 0.5 cm, number of electrodes (N) = 6.

5.2 CHARACTERIZATION OF ELECTRODES AND ELECTRODE BY-PRODUCT

For structural and morphological characteristics of electrodes, scanning electron micrograph (SEM) analysis and X-ray diffraction were carried out. Thermogravimetric analysis (TGA) of the residues were carried out to check the thermal stability.

5.2.1 SEM Analysis of Electrodes

SEM images of aluminium electrodes before and after EC were obtained to compare the surface texture. Fig. 5.16(a) shows the original aluminium plate surface prior to its use in EC experiments. The surface of the electrode is uniform except few dents on the surface. Fig. 5.16(b) shows the SEM of the same electrode after several cycles of its use in Electrocoagulation experiments. The electrode surface is now found to be rough, with a number of dents of about 10- 100 μm in width and depth. These dents are formed around the nucleus of the active sites where the electrode dissolution occurs producing aluminium hydroxides. The formation of a large number of dents may

Fig. 5.15 Original and reduced Color of CB dye solution of $C_0 = 100$ mg/l by using EC process

be attributed to the anode material consumption at active sites due to the generation of oxygen at its surface. Fig. 5.17 shows a magnified view of one such dent on the electrode surface before and after EC experiments. It may be seen that the dents in the electrode entrap degradation byproducts such as micro-flocs and sludge particles. Thus, the active surface in the dent is blocked for further participation in the removal of dye. Adsorbed species from the solution onto the active sites of the dents and onto the micro-flocs and the sludge particles also show higher resistance to degradation [Mahesh et al., 2006].

5.2.2 XRD Analysis of Electrode By-product

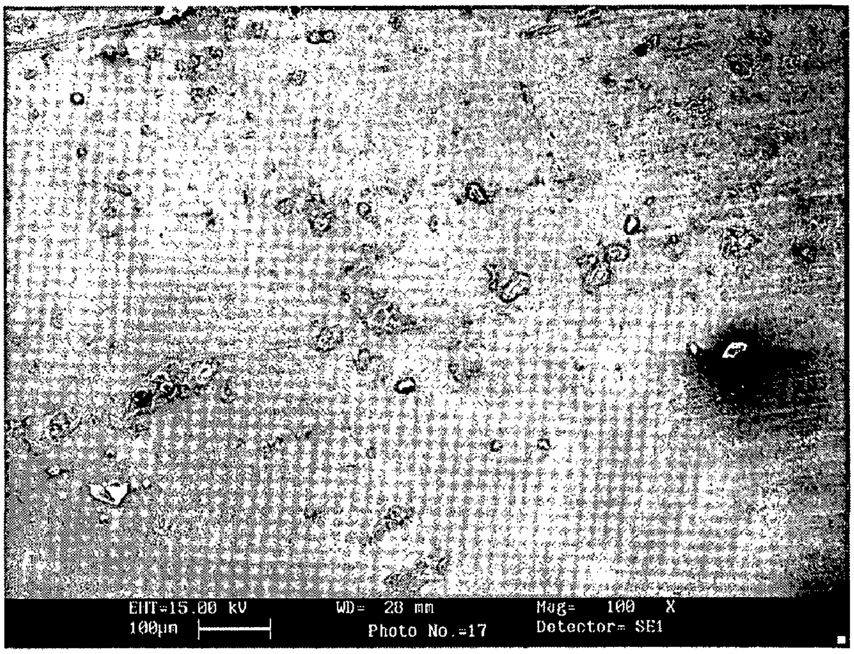
X-ray diffraction (XRD) analysis of EC residues were carried out to determine the constituent of residues. It is observed that Corundum [α-Al_2O_3], Aluminum oxide [γ-Al_2O_3], Diaspore ($Al_2O_3.H_2O$), Wavellite [$Al_3(PO_4)_2(OH)_3.5H_2O$], Clinochlore [$(Mg,Fe^{+2})_5Al(Si_3Al)O,(OH)_8$ are the major components present in the residue.

5.2.3 TGA Analysis of Electrode By-product

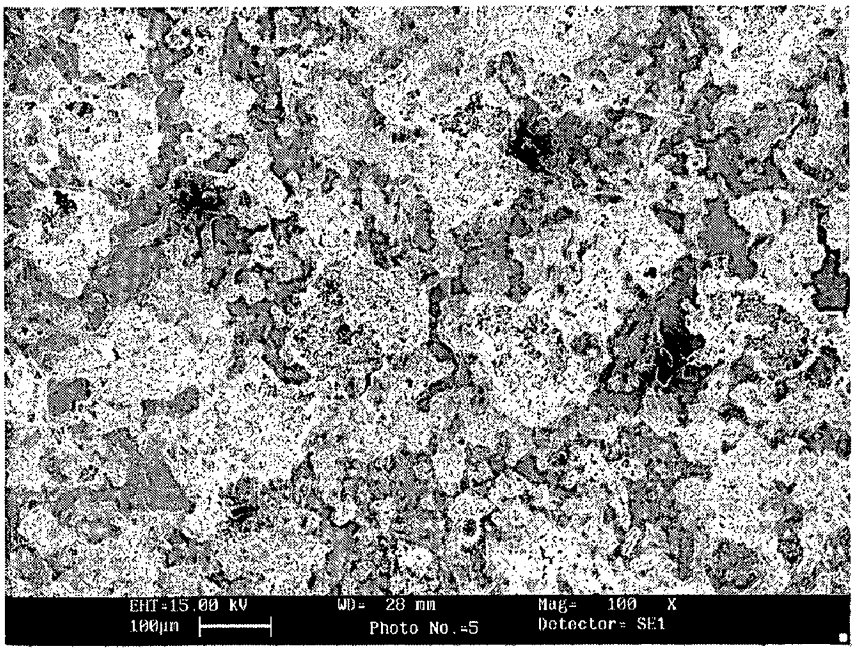
The residues pose problems to their disposal and management. The recent trend emphasizes on utilizing them for some beneficial purpose and rendering them innocuous and benign to the environment. The use of EC for the treatment of various wastewaters generates large volumes of solid residue. These solid residues have great potential for energy recovery. The dried residues can be used directly or by making fire-briquettes in the furnace combustors/incinerators to recover energy value.

The principal experimental variables which could affect the thermal degradation characteristics in air and nitrogen flow are the pressure, the gas (purge gas) flow rate, the heating rate, the weight of sample and the sample size fraction. In the present study, the operating pressure was kept slightly positive, the purge gas (air or nitrogen) flow rate was maintained at 200 ml/min and the heating rate was maintained at 10 °C/min.

The thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and differential thermal gravimetery (DTG) curves of the residues in oxidizing and inert atmosphere at the heating rate of 10 °C/min is shown in Fig. 5.19 and 5.20, respectively. The TG traces for the residues (Fig. 5.19) in oxidizing atmosphere shows that the loss of moisture and the evolution of some light weight molecules including water take place (10 % weight loss) from 25 °C to 100 °C. Higher temperature drying (from 100 °C to 400 °C) occurs due to loss of the surface tension bound water of the particles. The rate of weight loss was found to increase between ~400 °C to ~570 °C (~40 % weight loss) and ~4 % weight loss between ~600 °C to 1000 °C. In the last temperature range, residues oxidize and lose their weight gradually. The strong exothermic peak centered between 400-600 °C is due to the oxidative degradation of the sample. This broad peak as that observed from the first derivative loss curve (dTG) may be due to the combustion of carbon species. At higher temperatures (third zone), the samples present a gradual weight loss up to 1000 °C. This weight loss has been reported to be associated in part with the evolution of CO_2 and CO. Thermal degradation characteristics in flowing nitrogen atmosphere shows moisture removal of about 10% upto 100 °C as in the air atmosphere followed by removal of light volatiles upto 1000 °C. Only fixed carbons are left after 1000 °C and they are about 48% of the original sample weight. This shows that the EC generated residues has high potential to be very good heating fuel.

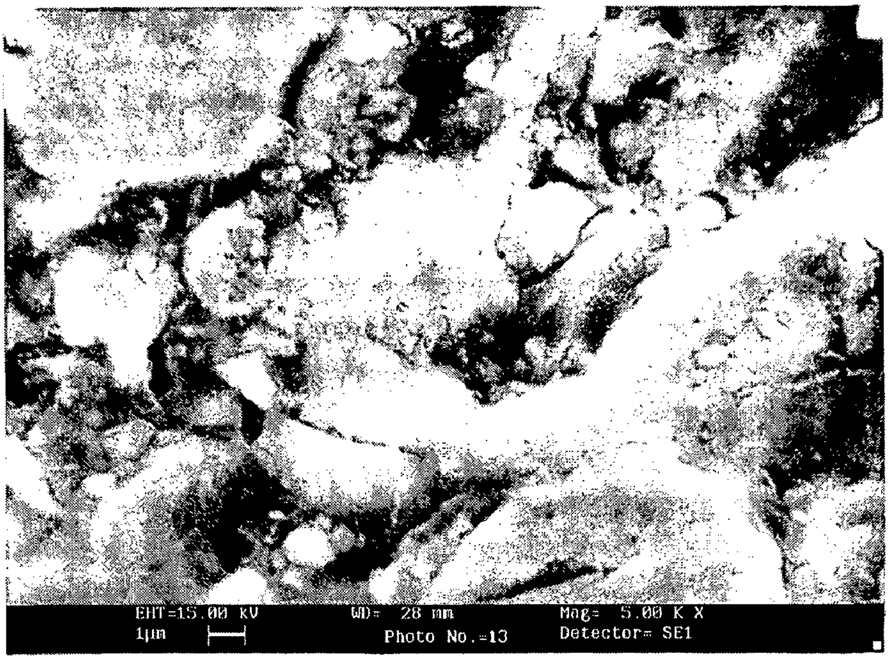


(a) Unused electrode

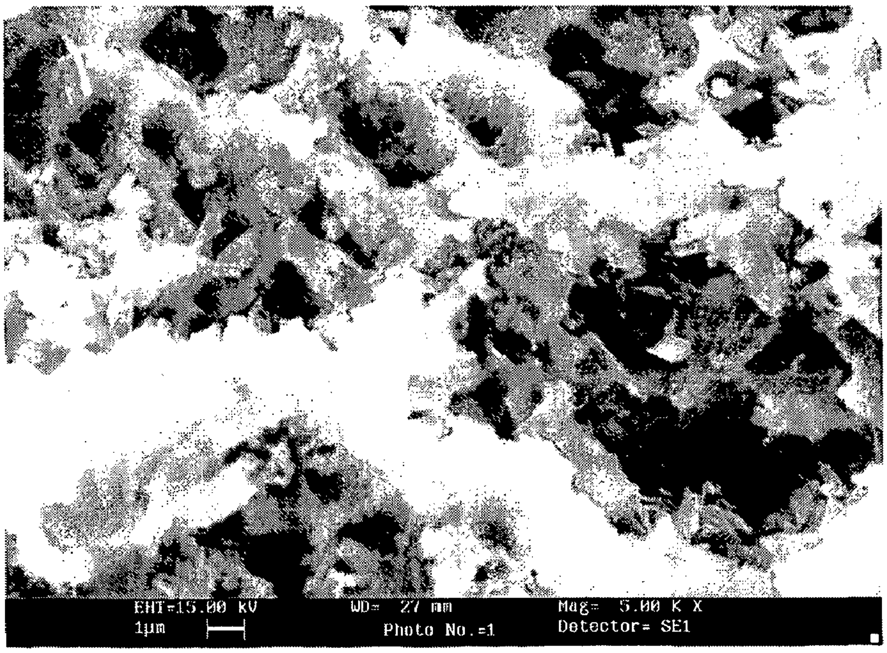


(b) Used electrode

Fig. 5.16 Scanning electron micrograph of aluminum electrode before and after electrocoagulation at 100 X magnification



(a) Unused electrode



(b) Used electrode

Fig. 5.17 Scanning electron micrograph of aluminum electrode before and after electrocoagulation at 5000 X magnification

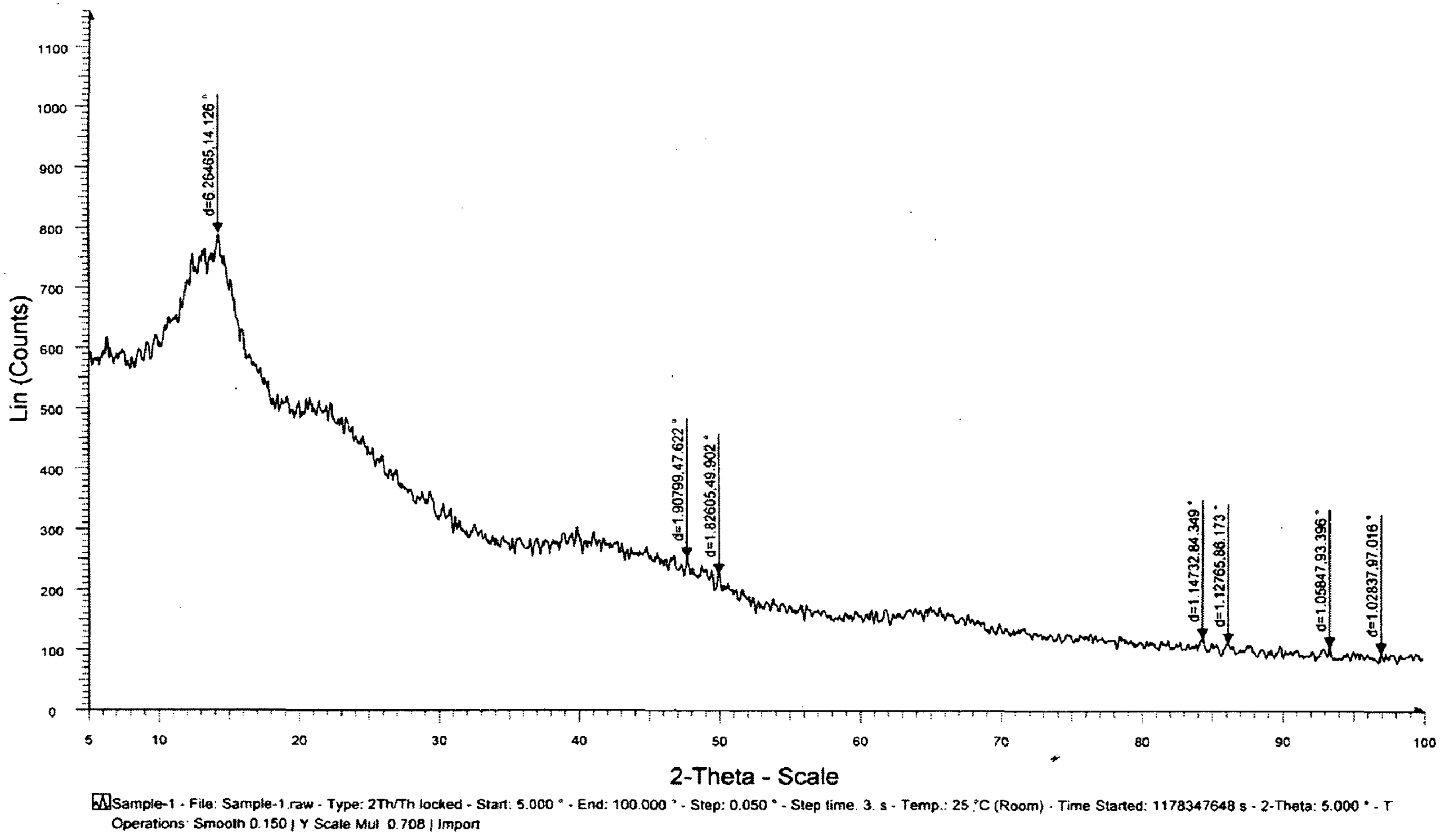


Fig. 5.18 X-ray diffraction analysis of Al-Al electrode by-product

Institute Instrumentation Centre, IITR, Roorkee.

Sample Name: 1
Data Name: Renu-2
Measurement Date: 5/4/2007
Sample Weight: 11.33 mg
Reference Weight: 10 mg
Reference Name: Alumina Powder

Temperature Program:

	Cel	Cel	Cel/min	min	s
1*	25	1000	10	0	0.5

Instrument: Perkin Elmer (Pyris Diamond)
Operator: A.K.Saini
Pan: Alumina
Atmosphare: Air (200 ml/min)

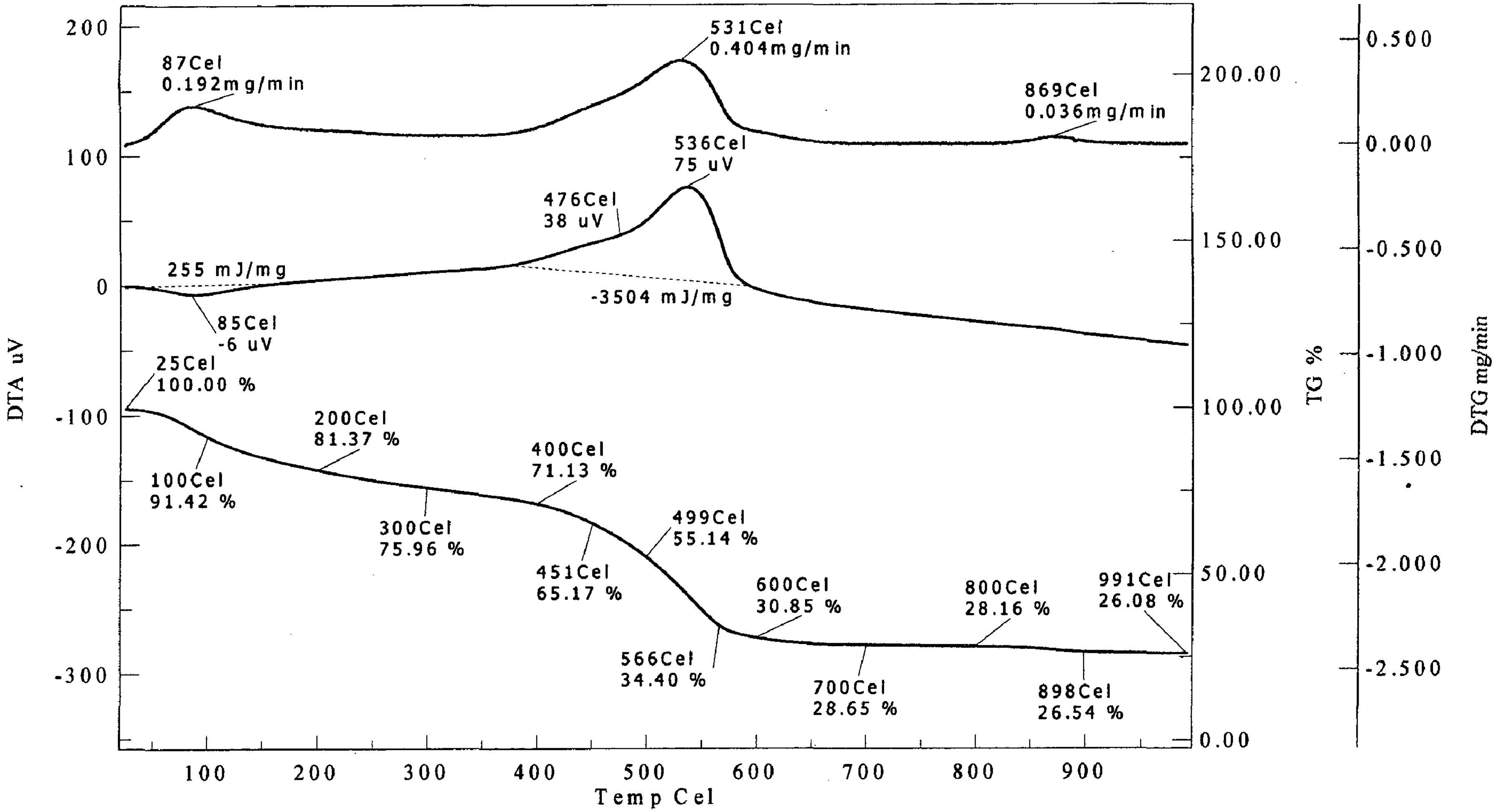


Fig. 5.19 Thermal degradation analysis of Al-Al electrode by-product flowing through air

Institute Instrumentation Centre, IITR, Roorkee.

Sample Name:	1					Instrument:	Perkin Elmer (Pyris Diamond)
Data Name:	Renu-1	Temperature Program:				Operator:	A.K.Saini
Measurement Date:	5/3/2007	Cel Cel	Cel/min	min	s	Pan:	Alumina
Sample Weight:	10.29 mg	1* 26 1000	10	0	0.5	Atmosphare:	Nitrogen (200 ml/min)
Reference Weight:	10 mg						
Reference Name:	Alumina Powder						

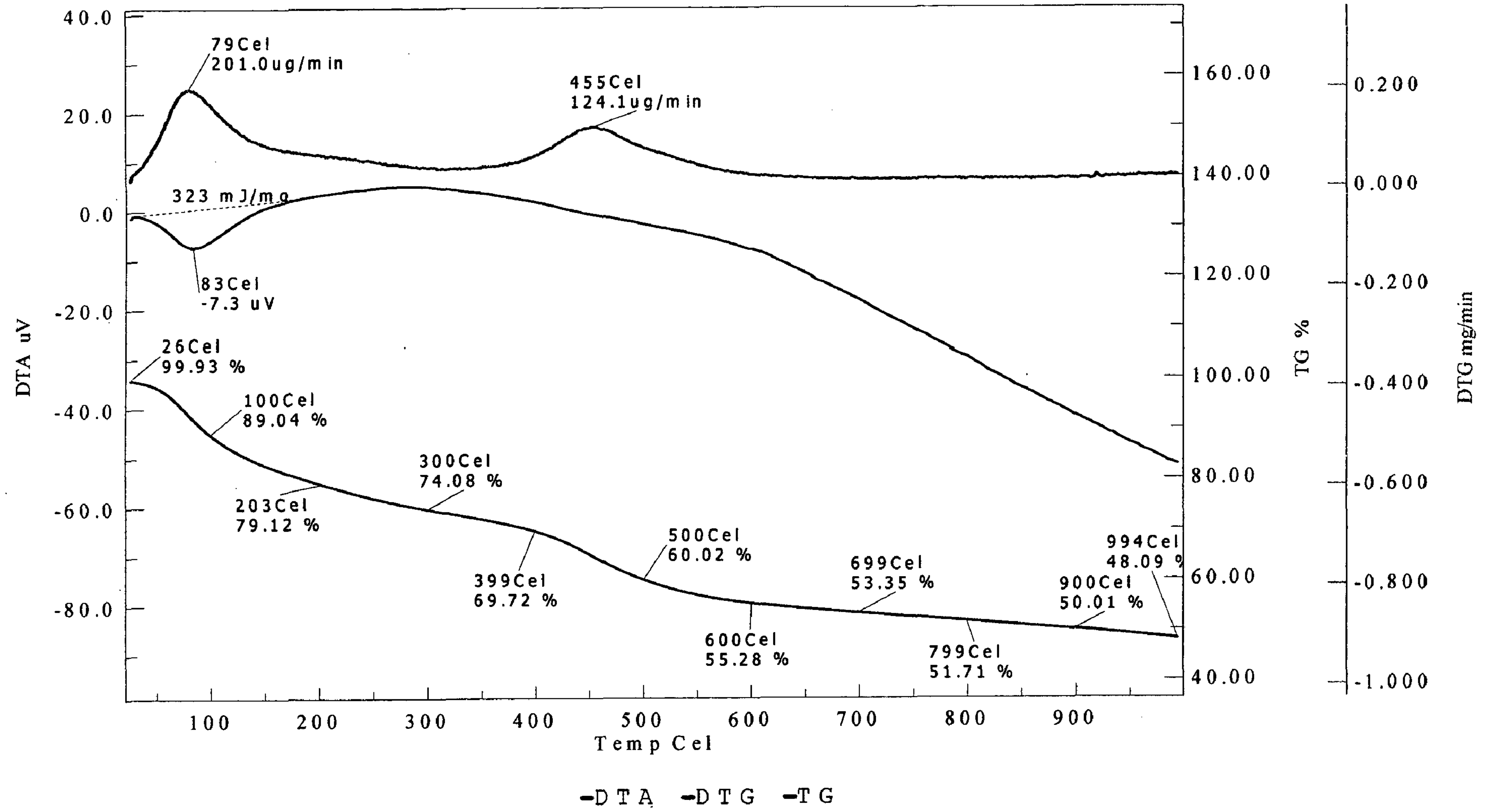


Fig. 5.20 Thermal degradation analysis of Al-Al electrode by-product flowing through nitrogen.

Chapter-6

CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSIONS

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

1. Effect of pH on percent removal of Cotton blue shows that this dye solution decolorized more efficiently when the initial pH values of the solution ranged from 6.0 to 8.0.
2. The effect of inter electrode distance on removal of CB from synthetic dye solution shows that percent removal of dye solution decreases with the increase in electrode gap but it does not have a significant effect on the dye removal efficiency.
3. Effect of electrolysis time on removal of CB shows that percent removal of dye increases with the increase in time of treatment. However, the difference of the magnitude of increase in efficiency is decreasing. And increasing the initial concentration of dye required increased electrolysis time for EC of dye.
4. Percent removal of CB increases with the increase in voltage up to a certain limit and then remains almost constant.
5. Effect of initial concentration of dye on percent removal by EC using aluminum electrodes shows that for any electrolysis time the percent removal decreases with increase in initial concentration of CB. An increase in initial dyestuff concentration does not result in a significant increase in electrode consumption.
6. Results has shown that EC using aluminum electrodes achieves a fast and effective reduction (more than 97%, i.e., color falls from an initial value of 1400 to 22 PCU) of synthetic dye solution of CB. Small difference between color diminution has been found with the progress of treatment.
7. At 15 min of electrolysis time and voltage of 11 V, a COD removal of 74 % is accompanied with ~98% of color removal. TOC reduction is found to be 61.4 %.

8. The SEM images showed the changes in the anode plate structure with small dents formed after repeated EC cycles. The EC treatment efficiency shows deterioration because of the formation of dents on the anode surface with prolonged use of the EC reactor.
9. Thermal analysis of electrode by-product showed that oxidative degradation of the sample takes place roughly between 400 °C – 600 °C, leaving a residue which is 30 % of the original weight. These dried residues can be used directly or by making fire-briquettes in the furnace combustors/incinerators to recover energy value.
10. Optimized operational conditions were applied to real textile waste water which led to satisfactory color removal though electrolysis time and anode consumption is more in case of real textile waste water.
11. EC requires simple equipments. It is cost-effective, and easily operable. Since practically no chemical addition is required in this process, it brings minimum chance of secondary pollution. It produces minimal sludge. Therefore, it can be used as a potentially viable and inexpensive tool for electrocoagulation of textile dyes.

6.2 RECOMMENDATIONS

1. An impermeable oxide film may be formed on the cathode that may interfere with the performance of the EC cell. However, changing polarity may help reduce this interference.
2. Periodically mechanical cleaning of the electrodes is required to control the passivation of electrodes.
3. Since it is seen that removal efficiency is high in case of lower concentrations, EC process should primarily be used as a secondary treatment technique which eliminates use of any tertiary treatment method required with other methods.
4. Based on results it is seen that EC process has great potential for dye bearing waste water treatment and its effects on other contaminants should also be tested.
5. If found successful with other contaminants development of a portable prototype for water treatment needs to be worked upon with a view of using it all across for water treatment in industries as well as homes.

APPENDIX: Observation Tables

Table 1. Characteristics of the EC cell

Electrodes	
material (anode and cathode)	aluminum
shape	rectangular plate
size	8 cm – 8 cm
thickness (mm)	1
plate arrangement	parallel
effective electrode surface area (cm^2)	64
Reactor Characteristics	
make	Perspex
reactor type	batch mode
dimensions (cm)	10.8 cm — 10.8 cm — 13.0 cm
volume (dm^3)	1.5
electrode gap (mm)	5
stirring mechanism	magnetic bar
Power Supply	direct current (DC)
voltage range (V)	0-20
current range (A)	0-5

Table 2. Standard Graph of Cotton Blue dye

Concentration (mg/l)	Absorbance
2	0.015
4	0.032
8	0.069
10	0.100
15	0.152
20	0.198
25	0.286
35	0.377
50	0.589

Table 3. Standard Graph of Cotton Blue dye for Color in Pt-Co units

Concentration (mg/l)	Color Units (Pt-Co units)
1	30
5	50
10	90
25	320
50	700
100	1400
500	10200
1000	18800

Table4. Effect of electrode gap on CB removal efficiency from aqueous solution. $C_0 = 100$ mg/l, pH = 6, and N = 6.

g = 0.5 cm

Time(min)	Absorbance	Concentration	% Removal	Color Units (PCU)
5	0.028	4.142857	95.85714	38.82571
7	0.026	3.97479	96.02521	36.44134
10	0.02	3.470588	96.52941	29.28824
15	0.014	2.966387	97.03361	22.13513
20	0.009	2.546218	97.45378	16.1742
25	0.006	2.294118	97.70588	12.59765
30	0.004	2.12605	97.87395	10.21328

g = 0.8 cm

Time(min)	Absorbance	Concentration	% Removal	Color Units (PCU)
5	0.037	4.89916	95.10084	49.55538
7	0.031	4.394958	95.60504	42.40227
10	0.025	3.890756	96.10924	35.24916
15	0.015	3.05042	96.94958	23.32731
20	0.009	2.546218	97.45378	16.1742
25	0.006	2.294118	97.70588	12.59765
30	0.004	2.12605	97.87395	10.21328

g = 1 cm

Time(min)	Absorbance	Concentration	% Removal	Color Units (PCU)
5	0.042	5.319328	94.68067	55.5163
7	0.036	4.815126	95.18487	48.36319
10	0.023	3.722689	96.27731	32.86479
15	0.011	2.714286	97.28571	18.55857
20	0.008	2.462185	97.53782	14.98202
25	0.006	2.294118	97.70588	12.59765
30	0.004	2.12605	97.87395	10.21328

g =1.3 cm

Time(min)	Absorbance	Concentration	% Removal	Color Units (PCU)
5	0.044	5.487395	94.51261	57.90067
7	0.037	4.89916	95.10084	49.55538
10	0.02	3.470588	96.52941	29.28824
15	0.012	2.798319	97.20168	19.75076
20	0.006	2.294118	97.70588	12.59765
25	0.003	2.042017	97.95798	9.021092
30	0.004	2.12605	97.87395	10.21328

Table5. Effect of number of electrodes on the CB removal efficiency from aqueous solution. $C_0 = 100$ mg/l, pH = 6, and g = 0.5 cm.

N = 4				
Time (min)	**Absorbance**	**Concentration**	**% Removal**	**Color Units (PCU)**
5	0.079	8.428571	91.57143	99.62714
7	0.068	7.504202	92.49580	86.51311
10	0.035	4.731092	95.26891	47.17101
15	0.011	2.714286	97.28571	18.55857
20	0.002	1.957983	98.04202	7.828908
25	0.001	1.87395	98.12605	6.636723
N = 6				
Time(min)	**Absorbance**	**Concentration**	**% Removal**	**Color Units (PCU)**
5	0.035	4.731092	95.26891	47.17101
7	0.022	3.638655	96.36134	31.67261
10	0.009	2.546218	97.45378	16.1742
15	0.006	2.294118	97.70588	12.59765
20	0.004	2.12605	97.87395	10.21328
25	0.002	1.957983	98.04202	7.828908
N = 8				
Time(min)	**Absorbance**	**Concentration**	**% Removal**	**Color Units (PCU)**
5	0.018	3.302521	96.69748	26.90387
7	0.008	2.462185	97.53782	14.98202
10	0.004	2.12605	97.87395	10.21328
15	0.003	2.042017	97.95798	9.021092
20	0.002	1.957983	98.04202	7.828908
25	0.001	1.87395	98.12605	6.636723
N =10				
Time(min)	**Absorbance**	**Concentration**	**% Removal**	**Color Units (PCU)**
5	0.014	2.966387	97.03361	22.13513
7	0.006	2.294118	97.70588	12.59765
10	0	1.789916	98.21008	5.444538

Table6. Effect of applied voltage on the CB removal efficiency from aqueous solution. $C_0 = 100$ mg/l, g = 0.5 cm, and N = 6.

Voltage = 6 V				
Time (min)	**Absorbance**	**Concentration**	**% Removal**	**Color units (PCU)**
0		100	0	1398.751
5	0.106	10.69748	89.30252	131.8161
7	0.094	9.689076	90.31092	117.5099
10	0.072	7.840336	92.15966	91.28185
15	0.046	5.655462	94.34454	60.28504
20	0.025	3.890756	96.10924	35.24916
Voltage = 11 V				
Time (min)	**Absorbance**	**Concentration**	**% Removal**	**Color units (PCU)**
0		100	0	1398.751
5	0.085	8.932773	91.06723	106.7803
7	0.06	6.831933	93.16807	76.97563
10	0.039	5.067227	94.93277	51.93975
15	0.014	2.966387	97.03361	22.13513
20	0.006	2.294118	97.70588	12.59765
Voltage = 16 V				
Time (min)	**Absorbance**	**Concentration**	**% Removal**	**Color units (PCU)**
0		100	0	1398.751
5	0.072	7.840336	92.15966	91.28185
7	0.052	6.159664	93.84034	67.43815
10	0.009	2.546218	97.45378	16.1742
15	0.007	2.378151	97.62185	13.78983
20	0.004	2.12605	97.87395	10.21328
Voltage = 20 V				
Time (min)	**Absorbance**	**Concentration**	**% Removal**	**Color units (PCU)**
0		100	0	1398.751
5	0.064	7.168067	92.83193	81.74437
7	0.04	5.151261	94.84874	53.13193
10	0.01	2.630252	97.36975	17.36639
15	0.006	2.294118	97.70588	12.59765
20	0.003	2.042017	97.95798	9.021092

Table7. Effect of initial concentration on the CB removal efficiency from aqueous solution. $C_0 = 100, 300, 500$ mg/l, g = 0.5 cm, V = 11V, and N = 6.

$C_0 = 100$ mg/l				
Time (min)	**Absorbance**	**Concentration**	**% Removal**	**Color Units (PCU)**
0		100	0	1398.751
5	0.085	8.932773	91.06723	106.7803
7	0.06	6.831933	93.16807	76.97563
10	0.039	5.067227	94.93277	51.93975
15	0.014	2.966387	97.03361	22.13513
20	0.006	2.294118	97.70588	12.59765
25	0.004	2.12605	97.87395	10.21328
30	0.002	1.957983	98.04202	7.828908
$C_0 = 300$ mg/l				
Time (min)	**Absorbance**	**Concentration**	**% Removal**	**Color Units (PCU)**
0		300	0	4236.151
5	0.308	27.67227	90.77591	372.6375
7	0.252	22.96639	92.34454	305.8751
10	0.162	15.40336	94.86555	198.5785
15	0.126	12.37815	95.87395	155.6598
20	0.1	10.19328	96.60224	124.663
25	0.085	8.932773	97.02241	106.7803
30	0.074	8.008403	97.33053	93.66622
$C_0 = 500$ mg/l				
Time (min)	**Absorbance**	**Concentration**	**% Removal**	**Color Units (PCU)**
0		500	0	7073.551
5	0.544	47.5042	90.49916	653.9931
7	0.439	38.68067	92.26387	528.8137
10	0.319	28.59664	94.28067	385.7515
15	0.238	21.78992	95.64202	289.1845
20	0.187	17.5042	96.49916	228.3831
25	0.148	14.22689	97.15462	181.8879
30	0.14	13.55462	97.28908	172.3504

Table8. Effect of initial pH on the CB removal efficiency from aqueous solution. $C_0 = 100$ mg/l, N = 6, and g = 1 cm.

pH = 3			
Time (min)	**Absorbance**	**Concentration**	**% Removal**
5	0.611	69.2437	30.7563
7	0.526	45.99160	54.0084
10	0.268	24.31092	75.68908
13	0.096	9.857143	90.14286
15	0.015	3.050420	96.94958
20	0.012	2.798319	97.20168
pH = 5			
Time (min)	**Absorbance**	**Concentration**	**% Removal**
5	0.368	32.71429	67.28571
7	0.339	30.27731	69.72269
10	0.273	24.73109	75.26891
13	0.067	7.420168	92.57983
15	0.012	2.798319	97.20168
20	0.117	11.62185	88.37815
pH = 8			
Time (min)	**Absorbance**	**Concentration**	**% Removal**
5	0.097	9.941176	90.05882
7	0.067	7.420168	92.57983
10	0.035	4.731092	95.26891
13	0.007	2.378151	97.62185
15	0.002	1.957983	98.04202
20	0.001	1.873950	98.12605
pH = 11			
Time (min)	**Absorbance**	**Concentration**	**% Removal**
5	0.097	12.12605	87.87395
7	0.053	9.941176	90.05882
10	0.067	7.420168	92.57983
13	0.004	2.126050	97.87395
15	0.002	1.957983	98.04202
20	0.001	1.873950	98.12605

Table9. Effect of initial concentration on the anode consumption. t = 30 min, g = 0.5 cm, V = 11 V, and N = 6.

Concentration	W_i(gm)	W_f(gm)	Net consumed
100	65.88	65.788	0.092
300	65.788	65.682	0.106
500	65.682	65.567	0.115
1000	65.567	65.423	0.144

Table10. Real waste water results

Real Waste I	
Time(min)	**Color Units (PCU)**
0	6000
15	5200
30	4800
45	2000
60	180
Anode consumption = 1.365 gm	
Real Waste II	
Time (min)	**Color Units (PCU)**
0	6800
5	3700
10	2400
15	1500
20	310
30	280
Anode consumption = 0.505 gm	

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