STUDIES ON TREATMENT OF TEXTILE INDUSTRY WASTEWATER

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Chemical Engineering

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ABSTRACT

The removal of COD and Dye from synthetic textile wastewater (STW) by electrochemical treatment (ECT) using Aluminum (Al) electrode material followed by adsorption with activated carbon was investigated in this study. STW was prepared by dissolving commercial grade reactive black dye with other chemicals as listed in table 4.1, in distilled water (DW). The prepared STW showed 3148 mg/l of COD and 200 mg/l of dye concentration

Three factors and five level full factorial central composite (CC) design, based on response surface methodology (RSM) were used for experimental design and analysis of data.Three operational parameters, namely *J*: 14.17–308.64 mA/cm2; *t*: 30–180 min and *pH*: 4–10, have been taken as input parameters and percentage COD removal (*Y1*), percentage Dye removal (*Y2*), and specific energy consumed (KWh per litre of effluent treated) (*Y3*) have been taken as a responses of the system.

Multi-response processes optimization by desirability function approach was used to optimize the ECT of STW which maximize the Y_1 and Y_2 simultaneously minimize Y_3. The optimum values of operational parameters were found to be J 14.17 mA/cm^2, t 102 min, and pH 6.25. Optimum Y_1, Y_2 andY_3 were found to be 63.41%, 90.93% and 0.0035 kWh/kg effluent treated. First order kinetics fitted the kinetic data for COD removal and dye removal. Kinetic constant for dye removal and COD removal at 30°C was 0.0205 min^{-1} and 0.0097 min^{-1} and at 50°C was 0.037 min^{-1} and 0.011 min^{-1}, respectively, which indicated removal increases with increase in temperature. Aluminium balance showed that aluminium in treated STW, sludge and scum was 25.16 mg/l, 0.50778g and 0.06006 g, respectively.

Electrochemically treated STW COD content was found to be 1152 mg/l and this was further treated by adsorption process with activated carbon to meet the discharge standard. Optimum condition for the adsorptive treatment of STW was found to be: initial pH ≈ 3.0, adsorbent dose of 35 g/l and contact time ≈22 h giving 88.28% COD removal (135mg/l of residual COD). Langmuir isotherm was found to fit the equilibrium data by showing R^2=0.95. Value of Langmuir isotherm parameters K_L and q_m were found to be 0.00004 l/mg and 4509.02 mg/g, respectively. A high q_m value indicates a higher affinity of adsorbate to adsorbent.

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NOMENCLATURE

ABBREVIATIONS

BCM	Billion Cubic Meters
AC	Activated carbon
EC	Electro coagulation
EO	Electro oxidation
ACA	Activated carbon adsorption
GAC	Granular activate carbon
ECT	Electrochemical treatment
CC	Chemical coagulation
FTIR	Fourier transform infrared spectroscopy
SS	Suspended Solids
MINAS	Minimal National Standards
STW	Synthetic textile wastewater
RB	Reactive Black
COD	Chemical oxygen demand
BOD	Biochemical oxygen demand
TDS	Total dissolved solid
DO	Dissolved oxygen
FAS	Ferrous ammonium sulphate
AOP	Advance oxidation process

CHAPTER- 1

INTRODUCTION

1.1 GENERAL

Water is one of the most essential elements on earth. Oceans containing salt covered 97% of the water. Remaining 3%, two thirds of remaining 3% is in the form of ice and snow leaving only about 1% of the total water as fresh water. Ground water contains for about 98% of this fresh water and the surface water is only about 2%. Thus of the total amount of water present on Earth, only about 0.02% is available in the lakes and streams. The requirement of fresh water for industrial use will increase from 30 BCM (Billion Cubic Meters) to 120 BCM by 2025 AD (Babu, 2007). A rapid industrialization has lead to the industrial effluents and sewage, resulting in water pollution which leads to water crisis in India and all over the world.

Rrapid development has improved the standard of living and quality of life for millions of peoples the world over. This development has come at the cost of a thirty-fold increase in the use of fossil fuels and a fifty-fold increase in industrial production over the 2 past centuries. As a result, significant amounts of existing natural resources have been consumed by industry, leaving the earth depleted for future generations. Much of the waste produced from these activities is directly discharged into natural water bodies (Visvanathan et al., 2006). One of the major challenges facing mankind today is to provide clean water around the world. The total wastewater generated from major industries is shown in Table1.1 and needs serious efforts for its treatment.

1.2 TEXTILE INDUSTRIES

Among many engineering disciplines textile engineering has a direct connection with environmental aspects. The textile industry is a group of related industries which uses a variety of natural (cotton, wool, etc.) and/or synthetic fibres to produce fabric.

Traditionally, the textile industry is very energy, water, and chemical-intensive. About 60% of the energy is used by dyeing and finishing operations. Environmental problems associated with the textile industry are typically those associated with water pollution. Textile industry plays an important role in the economy of the country. Out of

various activities in textile industry, chemical processing contributes about 70% of pollution. Natural impurities extracted from the fibre being processed along with the chemicals used for processing are the two main sources of pollution. Effluents are generally hot, alkaline, strong smelling and colored by chemicals used in dyeing processes. Some of the chemicals discharged are toxic. Other environmental issues now considered equally important and relevant to the textile industry include air emissions, notably Volatile Organic Compounds (VOC).

The textile industries in Tamilnadu, Mumbai, Surat, Ahmedabad, Ludhiana, Panipat, Coimbatore, and Kanpur, Tirpur in Tamilnadu are the main center of textile industry in India. Two Western States Maharashtra and Gujarat account for over 90% of dyestuff production in the country. Gujarat alone produces 80% or so. Within India, the major players in the pigments industry are Color Chem. and Sudarshan Chemicals while in the dyestuff industry companies such as are Atul, Clariant India, Dystar, Ciba Specialties and IDI are important players. [http://myiris.com/shares/sectors/sectorReport.php?secode+DYESTUFF&peercode=AII&fname=./data/dyestuff/dyestuff.htm].

The textile industry is very water demanding. Water is used for cleaning the raw material and for many flushing steps during the whole production (Fig.1.). To produce one tonne of cloth 200-250m^3 of water is required (CPCB, 2005). Textile industries generate large volumes of wastewaters polluted with dyes. Due to dyes high molecular weighs, their complex structures, and especially their high solubility in water, they persist once discharged into a natural environment. Thus, their removal from industrial effluents is also a subject of the major importance from the environmental point of view. (Pablocan Izares et.al, 2006). The textile industries can be divided into drying processes and wet processing from a standpoint of water usage. The drying process uses a small amount of water and contributes an insignificant load to wastewater generation. On the other hand, the wet processing involves many operations such as preparation, dyeing, printing and finishing which consume large quantities of water and is, therefore, the major source of textile industry wastewater. (Charoenlarp et.al, 2009) The pollution induced by dyestuff losses and discharge during dying and finishing processes in the textile industry has been a serious environmental problem for years; dyes in the

wastewater undergo chemical as well as biological changes, consume dissolved oxygen from the stream, and destroy aquatic life because of their toxicity. It is therefore necessary to treat textile effluents prior to their discharge into the receiving water (O. T. Can et.al, 2003).

Table 1.1 Waste water 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

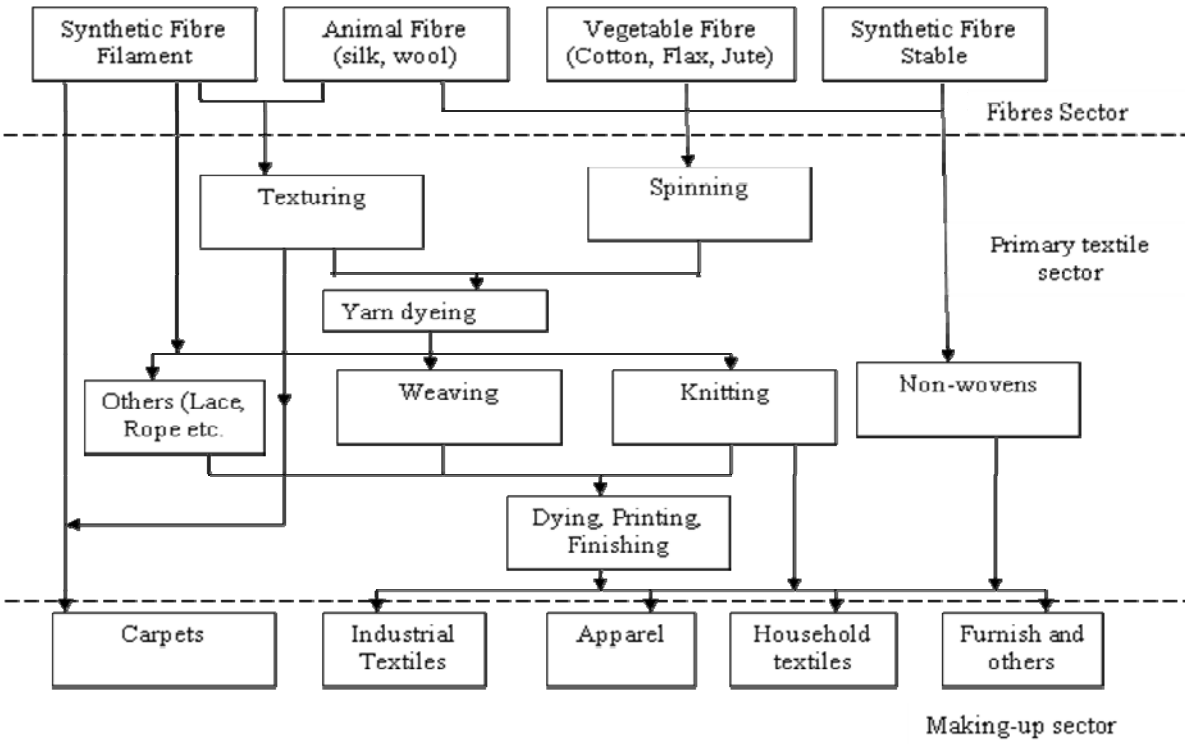


Fig. 1.1 Process flowsheet of textile industry

Source: http://www.p2pays.org/ref/11/10489/sectors71.html

1.3 HEALTH AND ECOLOGICAL EFFECT

The textile wastewaters are highly toxic in nature as they contain large varieties of dyes such as azoic, indigo, and aniline used in various processes. Wastewater also contains bleaching agents, salts, acids, alkalis, and heavy metals. The health effects caused are mainly due to inhalation and ingestion. 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 immediately or after a delay of several hours and include asthmatic-like responses such as: coughing, wheezing, tightness in the chest, shortness breath and loss of consciousness. Dyes may be absorbed through the respiratory tract or digestive tract causing health problems.

The dyes do not degrade in exposure of light, oxidizing agents and heat causing considerable resistance to their biodegradation. Therefore, causing aesthetic, acute and chronic toxicity problems in receiving waters thus, and upsetting aquatic life.

Other than this, dyes released in effluent interferes with the transmission of light in the water bodies, which in turn inhibits the photosynthesis activity.

Ground water systems are also affected by these pollutants because of leaching from soil. These dyes may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic effects on humans.

1.4 TYPES AND STRUCTURE OF DYES

Dyes stuff are produced over 700,000 tons annually estimated from more than 100,000 commercially available dyes (Lee et al., 2006) and applied in many different industries, including the textiles, paper, cosmetic, leather, food and pharmaceutical industries. Dyes are soluble at some stage of the application process, whereas pigments in general retain essentially their particulate or crystalline form during application. A dye is used to impart color to materials of which it becomes an integral part.

Dyes are classified in three broad categories:

(a) Anionic: direct, acid and reactive dyes;

(b) Cationic: all basic dyes and

(c) Nonionic: dispersed dyes.

Mostly, correlation of chemical structure with color has been accomplished in the synthesis of dye using a chromogen–chromophore with auxochrome. Chromogen is the aromatic structure containing benzene, naphthalene, or anthracene rings. A chromophore group is a color giver and is represented by the following radicals, which form a basis for the chemical classification of dyes when coupled with the chromogen: azo (-N=N-); carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (>C=NH or -CH=N-); nitroso (-NO or N-OH); nitro (-NO2 or =NO-OH); and sulfur (>C=S, and other carbon-sulfur groups). The chromogen–chromophore structure is often not sufficient to impart solubility and cause adherence of dye to fiber. The auxochrome or bonding affinity groups are amine, hydroxyl, carboxyl, and sulfonic radicals or their derivatives (MIGA, 2006).

. 1.5 WASTEWATER CHARACTERSTICS AND DISCHARGE STANDARD

Textile industry is water intensive and utilizes wide variety of chemicals and dyes. Effluent being discharged from the textile industries into the sewage systems or neighboring water receiving bodies is presently a cause for major environmental and health concerns. The main liquid effluents generated from rinsing, bleaching, washing operation. Mostly, wastewaters from manufacturing units are highly variable in composition that wastewater contain a large number of different compounds, intermediate products, and even the dyes themselves. Waste water discharged from the textile industry is solution of complex chemical with high color value. The color in the effluent is mainly due to unfixed dye. The concentration of unused dyes in the effluent depends upon the nature of dyes and dyeing process underway at the time. It is considered as a more dangerous source of environmental problem. High chemical oxygen demands (COD), biochemical oxygen demands (BOD), suspended solids and intense color due to dye intermediates or residues and auxiliary chemicals are normal their wastewaters characterize from the dye production process. Typical characteristics of textile effluent are given in Table 1.2.

Table 1.2 Typical characteristics of textile effluent

Parameters	Values
pH	6.0-10.0
Temperature	35-45˚C
Biochemical Oygen Demand (mg/l)	100-4,000
Chemical Oxygen Demand (mg/l)	250-10,000
Total Suspended Solids (mg/l)	100-5000
Total Dissolved Solids (mg/l)	1,800-6,000
Chlorides (mg/l)	1,000-6,000
Total Alkanity (mg/l)	500-800
Sodium (mg/l)	600-2,175
Total Kjeldahl Nitrogen (mg/l)	70-80

Wastewater discharge regulatory bodies sets the discharge standards for the wastewaters and pollution control policies. 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 in Table 1.3, 1.4 and 1.5. General standards for discharge of environmental pollutants set by CPCB, India has also been tabulated in Table 1.6.

Table 1.3 MINAS for cotton textile industries (composite and processing)

Parameter	**Concentration not to exceed, milligram per liter (except for pH and bioassay)**
pH	5.5. to 9.0
Suspended solids	100
BOD, 3 days at 27^{o}C	150
Oil and grease	10
Bio-assay test	90% survival of fish of after 96 hours in 100% effluent
Total chromium (as Cr)	2
Sulphide (as S)	2
Phenolic compounds (as C6H5OH)	5

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

Table 1.4 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 ^{o}C	30
	pH	5.5 to 9.0
Semi-synthetic	pH	5.5-9.0
	Suspended Solids	100
	BOD, 3 days at 27 ^{o}C	30
	Zinc (as Zn)	5

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

Table 1.5 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 ^{o}C)	100.0
Oil and Grease	10.0
Phenolics as C6H5OH	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

Table 1.6. General standards for discharge of environmental pollutants.

Parameter (mg/l)	Inland surface water	Public sewers	Land for irrigation	Marine/coastal areas
Suspended solids,	100	600	200	(a) For process wastewater (b) For cooling water effluent 10 per cent above total suspended matter of influent.
Particle size of suspended solids	shall pass 850 micron IS Sieve	-	-	(a) Floatable solids, solids max. 3 mm (b) Settleable solids, max 856 microns
pH value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
Temperature	shall not exceed 5°C above the receiving water temperature			shall not exceed 5°C above the receiving water temperature
Oil and grease, max	10	20	10	20
Total residual chlorine	1.0	-	-	1.0
Ammonical nitrogen (as N)	50	50	-	50
Total kjeldhal nitrogen (as N)	100	-	-	100
Free ammonia (as NH_3)	5.0	-	-	5.0
BOD (3 d)	30	350	100	100
COD	250	-	-	250
Arsenic (as As)	0.2	0.2	0.2	0.2
Mercury (as Hg)	0.01	0.01	-	0.01
Lead (as Pb)	0.1	1.0	-	2.0

Parameter (mg/l)	Inland surface water	Public sewers	Land for irrigation	Marine/coastal areas
Cadmium (as Cd)	2.0	1.0	-	2.0
Hexavalent chro-mium (as Cr^{+6})	0.1	2.0	-	1.0
Total chromium (as Cr)	2.0	2.0	-	2.0
Copper (as Cu)	3.0	3.0	-	3.0
Zinc (as Zn)	5.0	15	-	15
Selenium (as Se)	0.05	0.05	-	0.05
Nickel (as Ni)	3.0	3.0	-	5.0
Cyanide (as CN)	0.2	2.0	0.2	0.2
Fluoride (as F)	2.0	15	-	15
Dissolved phosphates (as P)	5.0	-	-	-
Sulphide (as S)	2.0	-	-	5.0
Phenolic compounds (as C_6H_5OH)	1.0	5.0	-	5.0
Radioactive materials:				
(a) Alpha emitters micro curie mg/l	10 -7	10 -7	10 -8	10 -7
(b) Beta emitters micro curie mg/l	10 -6	10 -6	10 -7	10 -6
Bio-assay test	90% survival of fish after 96 h in 100% effluent	90% survival of fish after 96 h in 100% effluent	90% survival of fish after 96 h in 100% effluent	90% survival of fish after 96 h in 100% effluent
Manganese	2	2	-	2
Iron (as Fe)	3	3	-	3
Vanadium (as V)	0.2	0.2	-	0.2
Nitrate Nitrogen	10	-	-	20

1.5 TREATMENT METHODS

Several biological and physico-chemical methods have been investigated for removal of COD, color and other contaminants from textile wastewater.

- ❖ Biological treatment method
  - Aerobic biological treatment
  - Anaerobic biological treatment

Biological treatment method for textile wastewater treatment reveled poor degradation due to presence of high molecular weight, complex structures, and high solubility of dyes (Georgiou et al., 2002; Izares et al., 2006), and require further treatment. Sometimes, pretreatment is done to remove dyes from wastewater to increase biodegradability before biological treatment.

Various physico-chemical techniques are also available for the treatment of textile wastewater.

- ❖ Physico-chemical techniques
  - Chemical coagulation
  - Electrochemical treatment (ECT),
  - Adsorption,
  - Membrane filtration,
  - Advanced oxidation processes

Most of these treatment methods have revealed either limited success and/or high consumption of energy. The coagulation process generates massive volume of hazardous sludge and poses a problem of sludge disposal, and treated wastewaters is contaminated by added coagulants and contribute secondary pollution. Membranes are costly and has drawback of the potential membrane fouling (Robinson et al., 2000). Whereas, adsorption processes are very time consuming and costly with low efficiency. Among various physico-chemical methods, EC treatment offers high removal efficiencies in comparatively compact reactors with simple equipments for control and operation of the process (Guven et al., 2009).

1.6 OBJECTIVES

The objectives of the present study are as follows:

1. To study the effects of operational parameters such as initial pH, current density, and electrolysis time on the COD and Dye removal and energy consumption for electrochemical treatment of textile wastewater with aluminum electrodes, utilizing full factorial central composite design based on response surface methodology.
2. To optimize operational parameters in view of maximizing the COD and Dye removal and simultaneously minimizing the energy consumption for the electrochemical treatment of textile wastewater.
3. To carry out physico-chemical analysis residues (scum and sludge).
4. To carry out aluminum mass balance in view of disposal of treated effluent.
5. To carry out adsorptive treatment of electrochemically treated textile wastewater with aluminum electrode.

CHAPTER- 2

LITERATURE REVIEW

Textile industry being one of the most complicated industries uses a number of dyes, chemicals and other materials to contribute desired quality to the fabrics. Therefore, generated wastewater from these industries bears very high values of contaminants. Most important conventional technologies for treatment of these wastewater including physico-chemical (commonly used physico-chemical treatment processes are filtration, air stripping, ion-exchange, chemical precipitation, chemical oxidation, carbon adsorption, ultra filtration, reverse osmosis, electro dialysis, volatilization and gas stripping) and chemical methods (ozonation and oxidation with hypochlorite ion, as well as advanced oxidation processes (AOPs) such as Fenton's reagent and photo catalytic systemsinvolvingTiO2/UV, H2O2/UVand O3/UV,) microbiological treatments and enzymatic decomposition (activated sludge processes, mixed cultures with aerobic and anaerobic decomposition and pure cultures with white-rot fungus and bacteria).

In recent times, there has been some interest is renewed in textile wastewater treatment plants based on electro-chemical treatment and adsorption technology for treatment of wastewater parameters like chemical oxygen demand, Dye removal, TDS etc. for which the alternative technologies are not feasible.

In this chapter, review of literature on the electrochemical treatment technology followed by adsorption for wastewater treatment is presented.

Zhian et al., (2011) studied on the removal of Acid Red 88(AR88) dye from aqueous solution by electro coagulation method and reported EC is cheaper and more efficient for dye removal in comparison with other water treatment processes. Electro coagulation of solution with an iron anode and aluminum cathode in pH of about 6-7, current density of 100 A/m^2, temperature of 298 K and electrode 1.5 centimeter apart and 6 minutes electrolysis time 96% dye is removed.

Tezcan et al., (2011) studied the electro coagulation process with semi-continuous and continuous flow regimes for the treatment of textile wastewater using iron electrodes to investigate the effects on COD and dyestuff removal efficiencies. With increasing feed flow rates from 240 to 930 ml/min at semi-continuous flow regime, the final COD concentrations were also increased from 97 to 226 mg/liter with a removal efficiencies of 95- 88% respectively. The absorbance of the dye was reduced by over 93% at all experiments.

Liang et al., (2011) studied the treatment of C. I. Reactive Yellow M-3RE in an aqueous solution by the electro coagulation (EC) method using iron anodes. The experimental results exposed that the color of C. I. Reactive Yellow M-3RE in aqueous phase was effectively removed (40.9%).

Phalakornkule et al., (2010) studied the electro coagulation of blue reactive, red disperse and mixed dyes with different material of electrodes. For a given current density, iron was superior to aluminum in treating both the reactive dye and the disperse dye. With an initial dye concentration of 100 ppm, the energy cost in achieving was on the order of 1 kWh per cubic meter and 95% color removal for both dyes.

Merzouk et al., (2010) studied the treatment of a synthetic wastewater in the batch electro coagulation (EC) by varying the various operating parameters, Textile wastewater was operated at various current densities ranging from 11.55 to 91.5 mA/cm^2 and various electrode gaps (1, 2 and 3 cm).They reported that the optimal operating parameters 10 minute treatment time with 1cm distance between electrode was apply on a textile wastewater and showed a high removal efficiency for the following variables: suspended solid 85.5%, turbidity 76.2%, biological oxygen demand (BOD) 88.9%, chemical oxygen demand (COD) 79.7%, and color over 93%.

Chithra et al., (2010) studied the modeling electro coagulation through adsorption kinetics. Aluminum and mild steel anodes were used to treat Acid Blue 113 dye effluent for COD removal by electro-coagulation. They reported that the electro coagulation of textile effluent follows pseudo second order kinetics. The electro-coagulation was modeled using adsorption isotherm and it has been observed that Langmuir isotherm models match satisfactorily with the experimental results.

Sengil et al. (2009) studied the effect of various operational parameters on decolorization of the reactive dye using iron sacrificial anode. The color removal efficiency for reactive black 5 dye (RB5) was 98.8% when iron was used as a sacrificial anode in 5 minute under the optimized conditions.

Khataee et al., (2009) studied the effect of operational parameters on decolorization of Acid Blue 9 solution via electro coagulation process and reported that for a solution of 20 mg/l dye, almost 98% color were removed in 8 minute when the pH was about 6 and the current density was approximately $25A/m^2$.

Bhaskar et al. (2009) studied the electro coagulation and electro oxidation techniques for purification of textile wastewater using mild steel as anode. They reported that suspended solids removed to the extent of 97% and COD removal was 54% by electro coagulation. The

effluent after electro-coagulation was further subjected to electro oxidation using two different materials viz. graphite and $RuO_2/IrO_2/TaO_2$ coated titanium as anodes and reported that COD removal was 90– 93% using graphite and 54% using $RuO_2/IrO_2/TaO_2$ coated titanium.

Ntuli et al., (2009) studied the physico-chemical characters of effluent from textile wet finishing operations in terms of its organic and inorganic pollutant loading and amenability to biodegradation. They reported that the effluent was highly turbid and colored, with average organic and inorganic loadings of 1766 kg $COD.day^{-1}$ and 964 kg $TDS.day^{-1}$ respectively and also TDS and SS levels of the effluent were 5849 mg/L, 3193 mg/L and 521 mg/L respectively.

Alaton et al., (2008) studied the electro coagulation of simulated Acid Dye bath effluent with aluminum (Al) and stainless steel electrodes. They reported that electro-coagulation of an Acid Dye bath was almost up to completion (100% for EC with Stainless Steel electrodes) color and partial COD removal could be achieved by using Al as well as Stainless Steel electrodes once working conditions were optimized. The study also revealed that electro coagulation with Stainless Steel electrodes was more attractive both in terms of treatment performance as well as electrical energy and sludge handling costs. The electrical energy requirement and sludge production rate were 17 kWh/ (m^3 wastewater) and 8200 g/ (m^3 wastewater) with Al electrodes, instead of 8 kWh/(m^3 wastewater) and 700g/(m^3 wastewater) with Stainless Steel electrodes.

Karuppiah et al., (2008) carried out the treatment of wastewater from synthetic textile industry by using the electro coagulation method. Mild steel and aluminum electrodes were kept as anodes; and aluminum was found to be more effective for the removal of suspended solids. Using aluminum as anode, the chemical oxygen demand (COD), and suspended solid was removed 67%, 99% respectively within 5 min.

Ghosh et al., (2008) studied the decolorization of Crystal Violet Solution by Electro coagulation. The results showed that the removal efficiency was enhanced with the increase in current density from 362.5 to 1112.5 A/m^2. It was found that the when electrolysis was carried out for 1 hr, the removal of 99.75% dye and 99% COD reduction took place. The dye solution was decolorized more efficiently when the initial pH values of the solution was greater than 8.5. Dye removal efficiency was decreased when the initial dye concentrations were more than 100 mg/L. Operating costs for the treatment of crystal violet dye using EC were evaluated for 100% removal of different initial dye concentrations with desired operating condition. Operating time and current density exhibit similar effects on the process performances and the operating cost.

Korbahti et al., (2008) studied the electrochemical treatment of simulated industrial textile wastewater by using iron electrodes in the presence of NaCl electrolyte in a batch

electrochemical reactor. They found that the highest removal for COD, color and turbidity were achieved as 93.9%, 99.5%, and 82.9%, repetitively. They optimized the reaction condition with 30°C as reaction temperature, 8V as applied potential (35.5 mA/cm2 current density) at 100% load and 25 g/liter electrolyte concentration within 183 min of reaction time. Under these conditions, COD, turbidity and color removals were predicted as 66.7%, 72.6% and 100%, respectively.

Kobya et al., (2006) studied the treatment of Levafix Orange textile dye solution by electro coagulation. The process performance was analyzed in terms of decolorization efficiency and the important cost-related parameters such as electrode and energy consumptions. 95% decolorization efficiency was obtained at suitable operating conditions; current density 100 A/m^2, operating time 12 min and initial pH 6.4. The corresponding electrode and energy consumption during the electrolysis were found to be 1.8 kg Al/kg dye and 35 kWh/kg dyes.

Kashefialasl et al., (2006) studied the treatment of dye solution by Acid Yellow 36 from electro coagulation by using iron electrodes. The increase of current density up to 127.8 A/m^2 enhanced the color removal efficiency. Results showed that the electrolysis time= 6 min and pH = 8 were optimum. It was also found that the % color removal decreses with increase in dye concentration. The optimum amount of electrolyte (NaCl) was found to be 8 g/l when the dye concentration was 50 mg/l.

Bayramoglu et al., (2006) studied the treatment of the textile wastewater by electro coagulation, Aluminum and iron electrode materials were used as sacrificial electrode in parallel and serial connection modes. The results showed that monopolar-parallel mode (MP-P) was the most cost-effective for Fe and Al electrodes. These electrodes showed similar results in removal efficiency of COD and turbidity, but Fe electrode was preferred due to its low cost. pH 7 for Fe electrode and pH 5 for Al electrode were found suitable in terms of removal efficiency of COD and turbidity from textile wastewater. $30Am^{-2}$ of current density and 15 min of operating time were found to be sufficient for Fe and Al electrodes. The highest electrode consumption is obtained with bipolar series mode (BP-S); approximately 0.27 kgm^{-3} for Fe electrode and between 0.18–0.23 kgm^{-3} for Al electrode. Mono polar parallel (MP-P) mode shows the lowest electrode consumption for both electrode materials; 0.12 kgm^{-3} for Al electrode and 0.16 kgm^{-3} for Fe electrode..

Alinsafi et al., (2005) studied the treatment of blue reactive dye solution with Electro-coagulation. The results were optimized by experimental design and surface response analysis in terms of color removal and chemical oxygen demand (COD) decrease. The efficiency of the

process is influenced strongly by the current and the time of the reaction. Optimal electrolysis time and current density were determined 90-95% decolorization and 30-36% COD removal.

Golder et al., (2005) studied the electro coagulation of aqueous dye solutions of two different industrial dyes (Methylene Blue and Eosin Yellowish) in presence of NaCl as electrolyte. Electro coagulation time up to 5 and 15 min was found to be sufficient for decolorization of aqueous dye solutions of Methylene Blue and Eosin Yellowish with mild steel electrodes. Both the dyes almost followed first-order kinetics. During electro processing of 200 mg/l solutions of MB or EY with mild steel electrodes, about 0.22 and 0.3 kg/m^3 sludge generation was observed with corresponding 87 and 78% COD removal. It was also noted that 1.5 KWh/m^3 power consumption reduced COD by 89 and 74% reduction for MB and EY, respectively.

Mollah et al., (2004) studied the treatment of Orange II azo-dye by electro coagulation technique in a continuous flow cell using sacrificial iron electrodes. The treatment of Orange II dye in a flow-through EC cell described in the present experiment can effectively remove 99% of the dye from the waste stream under optimum conditions. The residue from a blank run (pH = 7.3) and a dye added run (pH = 8.5) were collected by vacuum filtration and analyzed by XRD after drying in vacuum desiccators. The X-Ray diffraction data indicated the presence of mainly maghemite (Fe_2O_3) and magnetite (Fe_3O_4) in the residue.

Daneshvar et al., (2004) investigated the variables that influence the efficiency of decolorization of a solution containing an azo dye (Acid Red 14) by electro coagulation in order to compare the efficiency of different electrode connections for color removal. 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. The time of electrolysis was approximately 4 min, current density was around 80 A/m^2, the temperature was 300 K, and inter electrode distance was 1 cm. Under these conditions, the COD decreased by more than 85%. EC cell with monopolar electrodes showed higher color removal efficiency than an EC cell with bipolar electrodes.

Kobya et al., (2003) study the treatment of textile wastewaters by electro coagulation using iron and aluminum electrodes. The result showed that, in acidic medium, pH < 6, COD and turbidity removal efficiencies of aluminum are higher than those of iron, while in neutral and alkaline medium iron is preferable. High conductivity favors high process performances. On the other hand, for the same turbidity or COD removal efficiencies, iron requires a current density of 80–100 A/m^2, while aluminum requires 150 A/m^2 for a operating times of 10 min.

The energy consumption kWh per kg COD removed is lower with iron, while the electrode consumption per kg COD removed is lower generally with aluminum.

Can et al., (2003) studied the decolorization of Remazol Red 133 solutions by electro-coagulation using aluminum electrodes. Samples of dye solutions were analyzed using a Shimadzu model UV-160 double-beam spectrophotometer at ìmax (518 nm of Remazol Red RB 133). The decolorization efficiency increases rapidly up to 92.50% with a current density of 15 mA/ cm^2, and then it remains almost constant for higher current densities. The stirring rate was varied between 100 and 500 rpm, the decolorization efficiency shows a maximum for 200 rpm and then it decreases smoothly. The effect of conductivity was investigated between 250 and 4000 ίS/cm by using NaCl as the supporting electrolyte. The decolorization efficiency decreases steadily as the conductivity increases. The decolorization efficiency decreases when the dye concentration is increases.

Daneshvar et al., (2002) studied the decolorization of Orange II by use of iron as sacrificial anode in EC. They reported that at initial pH of 7.5 to/8.5 the orange II was effectively removed and 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 at optimized condition.

Kim et al., (2002) studied the effect on decolorization by continuous electro coagulation by varying operating parameters. They reported the dye removal decreases slowly from 4 to 9 but rapidly from 10-12 and the effect of lower current density was not significant but as the current density increases from 2 to 4.5 mA/cm^2, the dye removal ratio and reaction rate were proportionally increased from 98.0%, 0.26 $minute^{-1}$ to 99.4%, 0.34 $minute^{-1}$ respectively. With increasing the number of electrode from four to seven pairs, the dye removal increased from 87% to 98.3%. As the distance between electrode and dye concentration were increased the dye removal ratio decreased at optimal flow rate of 150 mg/liter.

Bangash et al., (2011) studied the dyes removal through activated charcoal (prepared from Bombax Cieba Tree) from aqueous solution using. They reported that the effect of high temperature on the kinetics of the adsorption is high in the initial 10 minutes (due to extra cellular binding,) and then continued slowly (due to sorption phase likely resulted from intracellular binding). The adsorption process follows first order kinetics. The values of rate constant were found to increase with the rise in temperature, which shows endothermic nature of the adsorption process.

Geethakarthi et al., (2011) studied the kinetic and equilibrium studies on adsorption of reactive dyes (Reactive Red 31 and Reactive Red 2) from aqueous solutions by activated carbon (particle size 600 μm) developed from preliminary tannery sludge developed. The initial dye

concentration was varied from 10 - 60 mg/liter, pH from 2 - 11, agitation speed from 100-140 rpm, adsorbent dosage from 0.5 g to 2.5 g and temperature from 30 ^{o}C -50 ^{o}C . With increasing pH the dye removal capacity of the reactive red dyes decreases. Batch kinetic data investigations on the removal of reactive dyes using tannery sludge activated carbon was suggested that the Pseudo second order adsorption mechanism was predominant for the sorption of the reactive dyes onto the tannery sludge based carbon. The adsorption data fitted well with Langmuir model than the Freundlich model.

Guendy et al., (2010) studied the coagulation and adsorption techniques for the treatment and reuse of wastewater in the textile industry. The use of combined processes has been suggested recently to overcome the disadvantage of individual unit processes. Coagulation and activated carbon adsorption techniques provides alternative medium for removing color at a much lower cost as compared with activated carbon adsorption only. Aluminum sulfate (Alum) and ferric chloride used as coagulants and granular activated carbon as an adsorbent. The results reveal that the application of coagulation before adsorption is most effective in removing dye almost 71- 97.7% using alum at pH 6- 8 and 53.7- 98.9% using FeCl3 at pH 4- 6 at a lower dose of both coagulants 70- 110 ppm., and 20- 90 ppm dye concentration. Dye removal by adsorption increased from 75- 90% by decreasing its initial concentration from 50 to 10 ppm for 2.5 gm granular activated carbon, from 80- 95% for 5 gm granular activated carbon at pH 8 and equilibrium time of shaking 120 min. at room temperature. The equilibrium data fitted very well to Freundlich Isotherm.

Patel et al., (2010) studied the adsorption and coagulation for the treatment of complex textile wastewater. Adsorbent dose plays an important role for removal because more active sites are available. The highest percentage removal of COD, BOD and color was found to be 87.6, 81.0 and 89.9% respectively using dosage of 9.0 g/liter at temperature of 300 K with agitator speed of 400 rpm for 60 minute. Also, the data were analyzed using Freundlich and Langmuir isotherm, in which Langmuir isotherm is more applicable than Freundlich isotherm.

Chaudhuri et al 2009 studied that removal of Remazol Red F-3B and Remazol Blue from aqueous solution by adsorption on coconut coir activated carbon and reported that the equilibrium adsorption was attained in 3 hrs when the solution have acidic pH range 1-3. Adsorption capacity of the activated carbon for the dyes was evaluated by batch equilibrium test and compared with that of a commercial activated carbon. According to Langmuir and Freundlich adsorption isotherms, the coconut coir activated carbon showed higher capacity for adsorption of Remazol Red F-3B than that of the commercial activated carbon.

Vijayaraghavan et al., (2009) studied the treatment of complex Remazol dye effluent (Reactive Black 5, Reactive Orange 16 , Remazol Brilliant Blue R and Remazol Brilliant Violet 5R) using sawdust- and coal-based activated carbons and they revealed that the pore diameter of the activated carbon played an important role in dye adsorption and in the pH range of 2–10.7 had no significant effect on the adsorption capacity. According to the Langmuir model, the maximum uptakes of coal based adsorbent were slightly lower than saw dust adsorbent. They also reported that saw dust adsorbent exhibited a decolorization efficiency of 100% under unadjusted pH conditions at 10.7, compared to that of 52% for coal based adsorbent.

Y.C. Sharma et al., (2009) studied the removal of malachite green from aqueous solutions and wastewaters by activated carbon developed from rice husk (an agricultural waste product). They reported that removal increased from 93.75 to 94.91% by decreasing the initial concentration from 100 to 60 mg/L in equilibrium time of 40 min. The process of removal follows first order kinetics and the data fitted well in Langmuir and Freundlich adsorption isotherm equations.

R. kant et al., (2009) studied that adsorption of dye Green B from a textile industry effluent using two different samples of activated carbon by static batch method and continuous process. They reported that percentage removal of dye decreased with increase in the initial concentration. In a static batch process, as the concentration of dye increases, the dye removal was found to decreases to almost half the initial value. Adsorption was higher in static batch reactor as compare to continuous process. In continuous process adsorption was higher at slower flow rate as compare to faster flow rate. Adsorption follows both the Langmuir and Freundlich isotherm. More amount of dye was absorbed on carbon sample C1 as compare to C2.

Sivakumar et al., (2009) studied the adsorption of Basic Red 29 by a non conventional activated carbon prepared from euphorbia antiquorum l wood. They reported that the uptake of dye increases with increase in initial dye concentration and temperature. The pseudo second-order kinetic model describes the adsorption much better than pseudo first-order mode. Langmuir model is more appropriate to explain the nature of adsorption with high correlation coefficient.

N.K.Amin (2008) studied the removal of Reactive Orange dye from aqueous solutions by adsorption on activated carbons prepared from sugarcane bagasse pith (main waste from sugarcane industry). The percentage removal of the dye was found to decrease with the increase in initial dye concentration and increase with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose and

conglomeration of the adsorbent. The percentage removal of dye by activated carbons was rapid in the beginning but it gradually decreased with time until it reached equilibrium. The Langmuir and Freundlich adsorption isotherm models were used. Pseudo second order model was found to best fit for the adsorption of reactive orange onto bagasse pith.

Al-Degs et al., (2007) studied the adsorption behavior of C.I. Reactive Blue 2, C.I. Reactive Red 4, and C.I. Reactive Yellow 2 from aqueous solution onto activated carbon. Activated carbon with a large surface area (820 m^2/g) and a modest surface charge density (0.54 group/nm^2) was shown to be effective in removing anionic reactive dyes from solution. They found that at pH 7.0 and 298 K, the maximum adsorption values as described using the Langmuir equilibrium isotherm model were 0.27, 0.24, and 0.11 mmol/g for C.I. Reactive Blue 2, C.I. Reactive Yellow 2 and C.I. Reactive Red 4 dyes, respectively. The adsorption capacity of the dyes on activated carbon increased in acidic solutions, but decreased in basic solutions. The adsorption capacity of the dyes increased when increasing the ionic strength of solution, this was attributed to dye aggregation in solution.

Iqbal et al., (2006) studied the adsorption behavior of dyes (bromophenol blue, alizarine red-S, methyl blue, methylene blue, eriochrome black-T, malachite green, phenol red and methyl violet) on activated charcoal. It was noted that adsorption of all the dyes on activated charcoal decreases with an increase in the pH and the temperature. Adsorption data was fitted to Freundlich, BET and Langmuir isotherms. The BET isotherm was not obeyed by all the dyes, suggesting that the adsorption on activated charcoal is chemisorption's. The adsorption also decreased with the pH except in case of methylene blue and malachite green.

Annadurai et al., (2002) used the cellulose-based wastes such as banana and orange peels for adsorption of dyes from aqueous solutions. The adsorption capacities for both peels decreased in the order methyl orange > methylene blue > Rhodamine B > Congo red > methyl violet > amido black 10B. In case of banana peel; when the pH is increased the amount of adsorption observed maximum at pH 6-7 but decreases when pH is increased further. In the case of orange peel the amount of dye adsorbed reaches at pH > 7. The amount of dye adsorption increases with time and it remains constant after 65 min. The Freundlich equation showed a somewhat better fit than the Langmuir equation for adsorption of dyes using banana peel, but exactly reversed using orange peels.

Table2.1. ECT and Adsorptive treatment reported by various authors

S.No	Waste Type	Technology Used	Electrode/Adsorbent Used	% Removal	References
1	Acid red dye	ECT	Iron, Aluminum, Graphite	Dye 95-98	Zhian et al., (2011)
2	Textile wastewater	EC and EO	MS used as anode, graphite and RuO2/IrO2/TaO2 coated titanium as anodes	SS-97%, 536-246ppm COD	Bhaskar et al. (2009)
3	Methylene blue (MB) and Eosin yellowish (EY)	ECT	MS Electrode	87% COD of MB and 78% of EY	Golder et al., (2005)
4	Textile wastewater	Fluidized bio film-CC-ECT	anodes were of titanium coated with RuO2, while SS were used as cathodes, and coagulants $Al_2(SO4)_3$, $FeCl_3.6H_2O$, FeSO4 .7H2O,	COD 95% and Dye 98%	Kim et al., (2002)
5	Dairy wastewater	ECT	Aluminum	COD 68.08%, TS 54.3% and turbidity 99.8%	Kushwaha et al., (2010)
6	Synthetic textile wastewater	EC T	Graphite as anode and SS as cathode	COD 43%,Color 75 %	Miled et al., (2010)
7	Cotton Blue Dye	EC T	Aluminum	Color 97%	Alhawat et al., (2008)

8	Reactive Black 5	ECT	Iron	Color 98.8%,	Sengil et al., (2009)
10	Levafix orange dye	ECT	Aluminum	Color 95%,	Kobya et al.,(2006)
13	Reactive Black5, Reactive Orange 16, Remazol Brilliant Blue R, Remazol Brilliant Violet 5R	Adsorption	Saw dust and Coal dust	Coal Dust based adsorbent showed high adsorption capacity than saw dust.	Vijyaraghavan et al.,(2009)
16	Basic Red 29	Adsorption	AC(EUPHORBIA ANTIQUORUM L)	Adsorption of dye increased from 47.62 mg/g to 139.13 mg/g	Shivakumar et al.,(2009)
17	Industrial Wastewater	Adsorption with	animal horn carbon (AHC)and commercial activated carbon(CAC)	COD=95.6%(AHC),96.34% (CAC)	Aluyor et al., (2008)

CHAPTER-3

THEORY

3.0 GENERAL

In electrochemical treatment (ECT) method of treating polluted water whereby sacrificial anodes corrode to release active coagulant precursors (usually aluminum or iron cations) into solution. Accompanying electrolytic reactions develop gas (usually as hydrogen bubbles) at the cathode. Electro coagulation has a long history as a water treatment technology having been employed to remove a wide range of pollutants.

3.1 DESCRIPTION OF THE TECHNOLOGY

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

Different types of arrangement of electrodes in EC are:

(i) A simple arrangement of an EC cell with a pair of anodes and a pair of cathodes in parallel arrangement is shown in Figure 2.1. It essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a direct current power source. The experimental set up also requires a resistance box to regulate the current density and a multimeter to read the current values. The conductive metal plates are commonly known as ‘sacrificial electrodes’. The sacrificial electrodes may be made up of the same or of different materials.

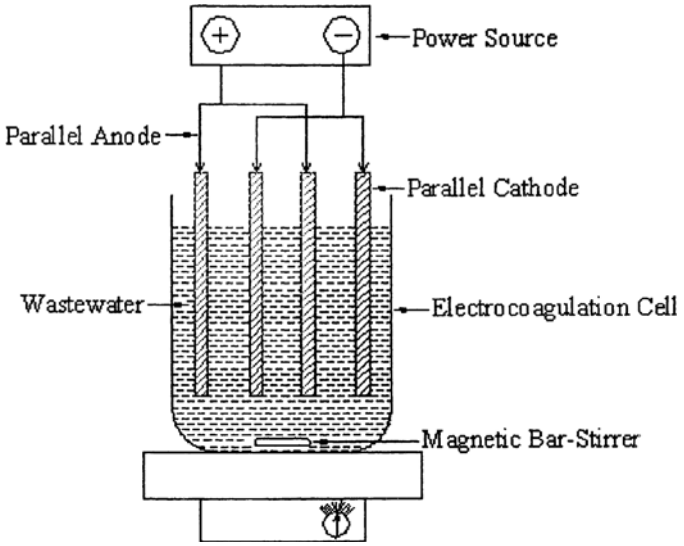


Figure 3.1. Bench-scale EC reactor with monopolar electrodes in parallel connection

(ii) An arrangement of an EC cell with monopolar electrodes in series is shown in Figure 2.2. As can be seen from Figure 2.2, each pair of 'sacrificial electrodes' is internally connected with each other, and has no inter connections with the outer electrodes. This arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections.

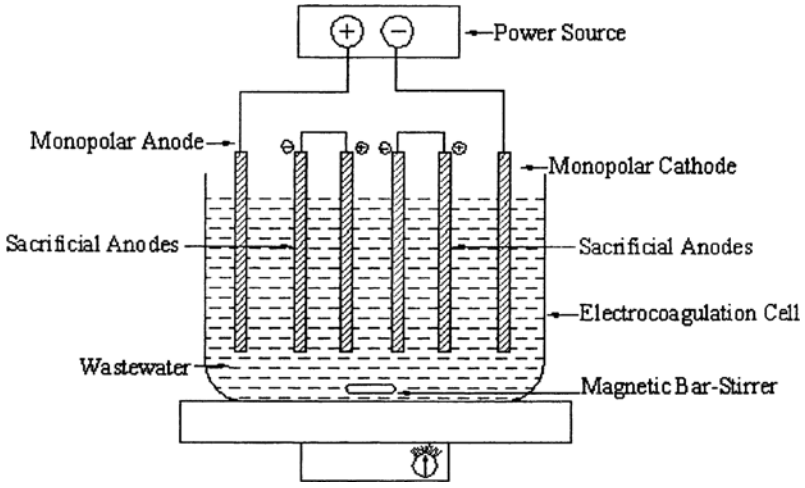


Figure 3.2. Bench-scale EC reactor with monopolar electrodes in series connection

In series cell arrangement, a higher potential difference is required for a given current to flow because the cells connected in series have higher resistance. The same current would, however, flow through all the electrodes. On the other hand, in parallel arrangement the electric current is divided between all the electrodes in relation to the resistance of the individual cells.

(iii) An arrangement of an EC cell with bipolar electrodes in parallel is shown in Figure 2.3. The sacrificial electrodes are placed between the two parallel electrodes without any electrical connection. Only the two mono polar electrodes are connected to the electric power source with no interconnections between the sacrificial electrodes. This cell arrangement provides a simple set-up, which facilitates easy maintenance during use. When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared to the parallel side beside it. The sacrificial electrodes in this case are also known as bipolar electrodes.

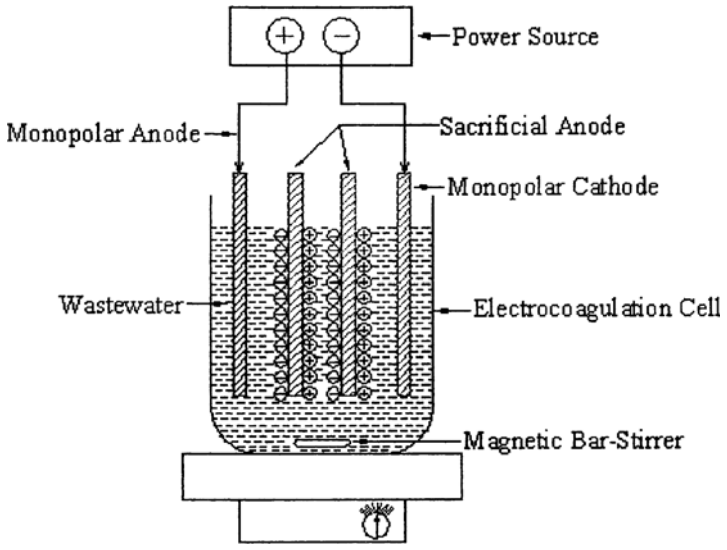


Figure 3.3. Bench-scale EC reactor with bipolar electrodes in parallel connection

3.2 THEORY OF EC

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

- **a.** Generation of metal ions by electrolytic oxidation of the 'sacrificial electrode
- **b.** Subsequent formation of gelatinous metal hydroxides
- **c.** Coagulation and subsequent adsorption of pollutants and contaminants on gelatinous metal hydroxides

The destabilization mechanism of the contaminants, particulate suspension, has been described in broad steps and may be summarized as follows:

1. Compression of the diffuse double-layer around the charged species, which is achieved by the interactions of ions generated by dissolution of the sacrificial electrode, due to passage of current through the solution.
2. Charge neutralization of the ionic species present in wastewater, which is caused by the counter ions, produced by the electrochemical dissolution of the sacrificial electrode. These counter ions reduce the electrostatic inter particle repulsion sufficiently so that the Vander Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
3. Floc formation, and the floc formed as a result of coagulation creates a sludge blanket that adsorb and bridges colloidal and suspended particles. (Mollah et al., 2001; Balasubramanian et al., 2009).

Reaction types involved in the EC process as described by (Tchamango et al., 2010) are:

For aluminum electrode:

Mechanism

At anode:

$Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e-$

$Al^{3+}{}_{(aq)} + 3\ H_2O_{(l)} + O_{2(g)} \rightarrow Al(OH)_{3(s)} + 3H+_{(aq)}$

At cathode:

$3H_2O_{(aq)} + 3\ e- \rightarrow 3OH + 3/2H_{2\ (g)}$

Overall:

$Al_{(s)} + 3\ H_2O_{(l)} + OH_{(g)} \rightarrow Al\ (OH)_{4(s)} + 3/2\ H_{2\ (g)}$

3.3 ADVANTAGES OF EC

EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running. It is a low sludge producing technique and the sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Flocs formed by EC are similar to chemical floc, 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. 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. 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. 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 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.

3.4 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 may be expensive in many places. 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. Gelatinous hydroxide may tend to solubilize in some cases (Mollah et al., 2001).

3.5 ADSORPTION THEORY

Adsorbent surfaces contain unsaturated bonds and this bond is responsible for the reactant molecules to get attached to the surface. The degree of interaction depends on the nature of adsorbate and the adsorbent. Depending on the nature of interaction, adsorption is classified as either physical or chemical also called as physisorption and

chemisorption adsorption respectively. Physisorption is caused by the forces of molecular interaction, which include dipole and dispersive forces and thus, physisorption is a result of the same forces that cause condensation and solidification of fluid phases. On the opposing, chemisorption involves interaction of electrons of the adsorbate and adsorbent resulting in the formation of a chemical bond. Unfortunately, it is not always easy to determine experimentally predict whether physi- or chemi-sorption is taking place. Table 2.1 gives a comparison between physical and chemical adsorption. If the heat of adsorption is very large or if the adsorption has higher activation energy than the latent heat of evaporation, then the adsorption is clearly chemisorption. Unfortunately, often the heat of adsorption is about 40-50 kJ/mol. In this case, it is very difficult to determine whether the adsorption is physical or chemical. Other criteria, which are helpful in distinguishing between these two types of adsorption, are electrical conductivity (which changes appreciably upon adsorption) and FTIR spectroscopy.

3.5.1 ADSORPTION PROCESS

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites. The transport of components from the solution phase into the pores of the adsorbent particles may be controlled either by one or more of the following steps: film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface. It is necessary to calculate the slowest step involved among these steps to identify the controlling step during the adsorption process (Srivastava and Srivastava et al., 2009). The external mass transfer controls the adsorption process for the systems that have poor mixing, dilute concentration of adsorbate, small particle sizes of adsorbent and higher affinity of adsorbate for adsorbent. Whereas, the intraparticle diffusion controls the adsorption process for a system with good mixing, large particle sizes of adsorbent, high concentration of adsorbate and low affinity of adsorbate for adsorbent (Aravindhan et al., 2007).

As the adsorbate concentration increases, adsorption occurs in three stages. First, a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and is associated with a change in free energy that is a characteristic of

the forces that hold it. Second, as the fluid concentration is further increased, second, third etc., layers form by physical adsorption. The numbers of layers which can form are limited by the size of the pores. Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore.

The parameters that affect the adsorption process are initial pH (pH_i), adsorbent dose (m_{ad}), contact time (t), initial pollutant concentration (C_o) and temperature (T).

Table 3.1. Comparison between physisorption and chemisorption

Property	**Physisorption**	**Chemisorption**
Heat of adsorption	Low (< 2-3 times latent heat of evaporation)	High (> 2-3 times latent heat of evaporation)
Rate of adsorption	Rapid, non activated, Reversible	Activated, may be slow and irreversible
Rate of desorption	Activation energy for desorption equals heat of adsorption	Activation energy for desorption may be larger than heat of adsorption
Temperature range over which adsorption occurs	Close to condensation temperature of the adsorbate	Occurs at a wide range of temperatures and at temperatures much above the condensation temperature.
Electrical conductivity	Electrical conductivity of the catalyst not affected	May affect electrical conductivity of catalyst

Source: (Ruthven, 1984).

3.5.2 ADSORPTION ISOTHERM

Equilibrium adsorption equations are required in the design of an adsorption system and their subsequent optimization (Sharma et al., 2010). Therefore it is important to establish the most appropriate correlation for the equilibrium isotherm curves.

Srivastava et al., (2007) have discussed the theory associated with the most commonly used isotherm models. Various isotherms namely Freundlich, Langmuir, Redlich-Peterson (R-P) and are widely used (Table 2.2).

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, whereas in the Langmuir theory the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. The R-P isotherm incorporates three parameters and can be applied either in homogenous or heterogeneous systems.

Table 3.2: Various isotherm equations for the adsorption process

Isotherm	Equation	Reference
Freundlich (3.1)	$q_e = K_F C_e^{1/n}$	(Freundlich, 1906)
Langmuir (3.2)	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	(Langmuir, 1918)
R-P (3.3)	$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$	(Redlich and Peterson et al., 1959)

K_R: R–P isotherm constant (l/g), a_R: R–P isotherm constant (l/mg), β: Exponent which lies between 0 and 1, C_e: Equilibrium liquid phase concentration (mg/l), K_F: Freundlich constant (l/mg), 1/n: Heterogeneity factor, K_L: Langmuir adsorption constant (l/mg), q_m: adsorption capacity (mg/g).

CHAPTER- 4

MATERIALS AND METHODS

4.1 General

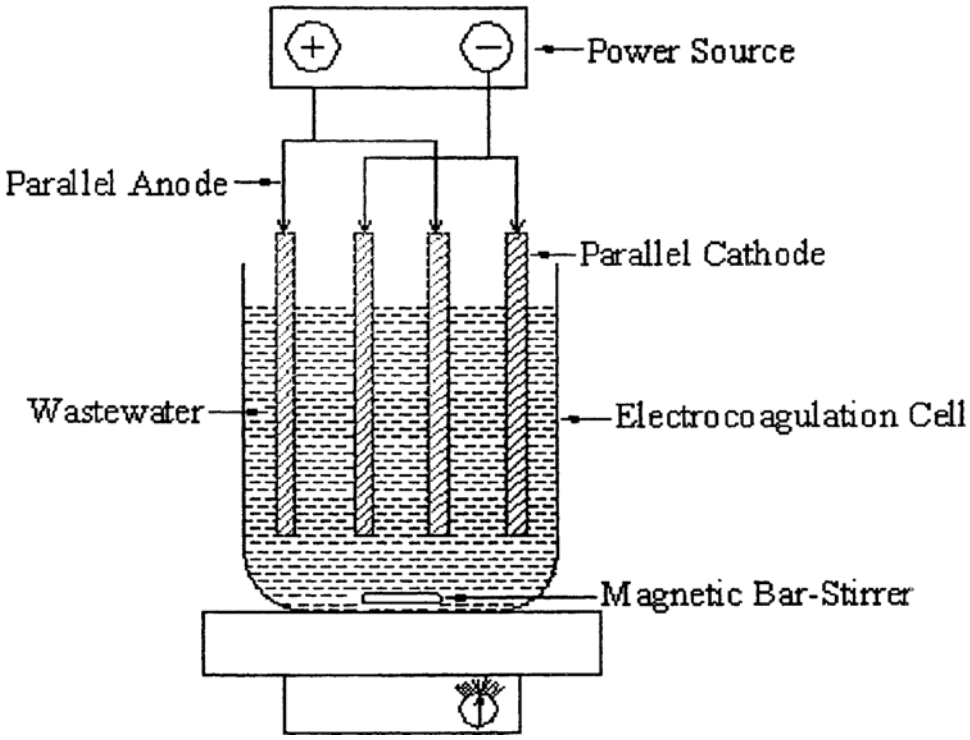
This chapter reports explanation of the materials and experimental methods adopted during the electrochemical treatment (ECT) of synthetic textile wastewater (STW) using aluminum (Al) electrode. The experimental detail includes experimental set- up, chemicals and electrodes used and various studies performed during the STW treatment by ECT have been explained in detail.

4.2 Materials and Methods

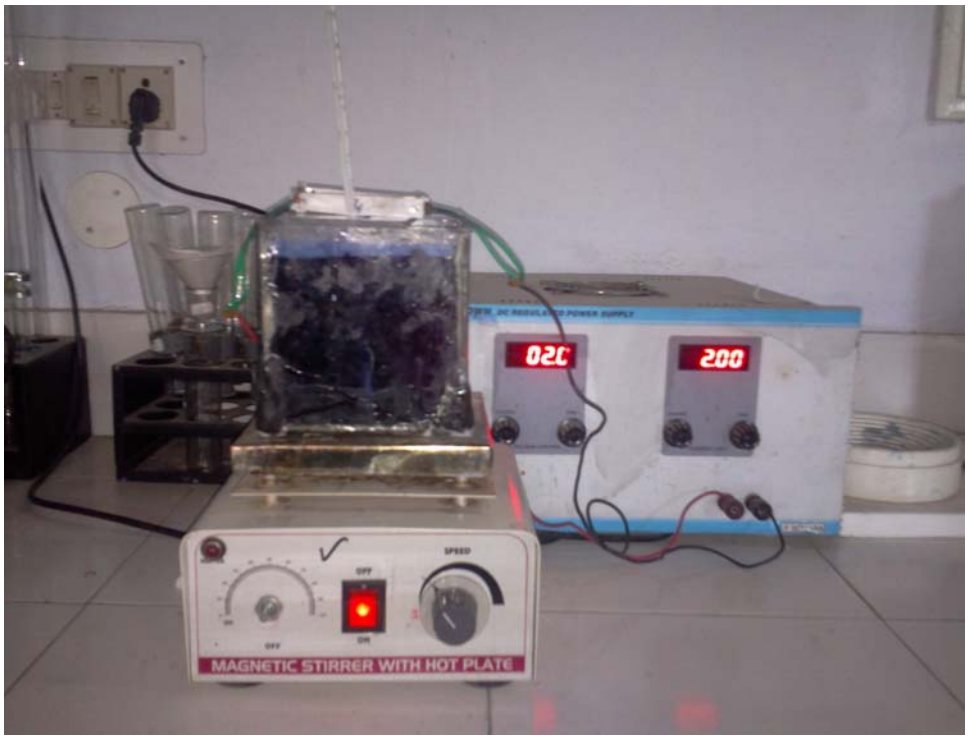
4.2.1. Reactor

Fig. 4.1 shows schematic and actual setup of the experiment. The reactor having a volume of 1.728 liter (12 cm length x 12 cm width x 12 cm depth) was fabricated with Plexiglas sheet of thickness 5 mm. Aluminum plates (8.4cm x 8.4 cm) with a thickness of 1 mm were used as the electrodes for the experiment. Mono-polar electrodes connected in parallel were used in the experiments. Two pairs of electrodes were used for the study. The spacing between two electrodes in ECT cell was maintained constant to 01 cm during the experiments. Magnetic stirrer was used to agitate the solution. A regulated direct current power supply (0-30 V,15 A, Make Crown Electronics Delhi, India) was used for the experiments.

Cleaning of the electrodes before and after the experiments was done by ordinary detergent and 15% HCl solution followed by washing with water for perfect cleaning. To maintain a fixed inter-electrode distance non conducting wire was used as the electrode separator.



(a) Schematic diagram of lab-scale batch experimental setup



(b) Actual setup of experiment

Fig.4.1

4.2.2. Feed to Reactor

The synthetic textile wastewater (STW) was prepared by dissolving commercial grade reactive black dye with other chemicals as listed in table 4.1, in distilled water(DW). Amount of various chemicals dissolved in DW were taken as reported by Korbahti et al., 2008. The prepared STW showed 3148 mg/l of COD.

Table 4.1. Amount (mg/l) of various chemical dissolved in DW to prepare STW

S.No.	Chemical	Amount
1	Dextrin	1600
2	Sucrose	640
3	Sodium Carbonate	700
4	Acetic Acid	160 µl/l
5	Sodium Hydroxide	1200
6	Sodium Chloride	5000
7	Reactive Black Dye	200

4.2.3. Experimental Design and Experimental Procedure

Three factors and five level full factorial central composite (CC) design, based on response surface methodology (RSM) were used and data obtained were analyzed by Design-Expert trial version. RSM is an effective statistical tool for collection of mathematical and statistical information useful for optimizing processes and can be used to evaluate the relative significance of several affecting parameters even in the presence of complex interactions. The main advantage of RSM is the reduced number of experiments needed to provide sufficient information to optimise the process.

Three operational parameters, namely J: 14.17–308.64 mA/cm^2; t: 30–180 min and pH: 4–10, have been taken as input parameters and percentage COD removal (Y_1), percentage Dye removal (Y_2), and specific energy consumed (KWh per litre of effluent treated) (Y_3) have been taken as a responses of the system. By conducting preliminary experiments for COD and dye removal at various operational parameters, working

range of parameters were (not shown here). Table 4.2 shows various operational variables and their levels whereas actual experimental design matrix is given in Table 4.3.

A total of 20 experiments, designed by RSM (Table 4.3), were conducted to study the effects of the three parameters on responses Y_1, Y_2 and Y_3. The pH of the STW was adjusted to desired level by adding 0.1 N NaOH or 0.1 N HCl solutions.

At the start of experiment, the STW with initial COD concentration 3148 mg/l was adjusted to desired *pH*, as per that particular run. Time, *t*, was measured when power supply was switched on. *J* was maintained constant during the run. After the desired *t*, samples were taken from the reactor and its final COD and dye concentration was measured. The percentage COD removal was calculated using the following relationship:

$$\text{Percent COD removal}(Y_1) = \frac{(COD_0 - COD_f)100}{COD_0} \qquad \textbf{4.1}$$

where, COD_o is the initial COD concentration, and COD_f is the final COD concentration (mg/l) after *t* (min).

A PC based UV-Vis spectrophotometer was used for determination of the dye concentration in the STW. For this purpose following steps were followed:

- The system was switched on and warmed up.
- Thoroughly clean cuvettes were used.
- Both of the cuvettes were filled with distilled water to get the reference.
- One cuvette was then emptied and filled with the solution for which the concentration was to be measured; the other cuvette stays as a reference.
- The absorbance value at 597 nm was used to find the absorbance.

Fig. 4.2 shows the calibration plot for calculation of dye concentration and % dye removal was calculated by using the following relationship:

$$\text{Percent COD removal}(Y_2) = \frac{(C_0 - C_f)100}{C_0} \qquad \textbf{4.2}$$

Where, C_o is the initial dye concentration, and C_f is the final dye concentration (mg/l) after *t* (min).

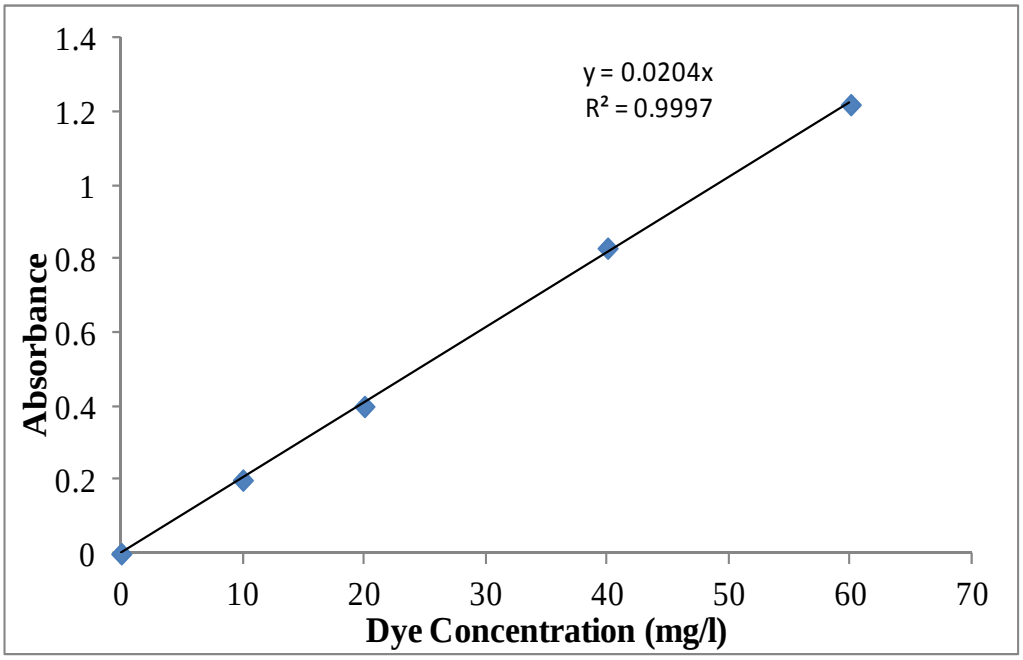


Fig. 4.2. Calibration plot for calculation of dye concentration

Table 4.2. Range of Variables and levels of the design model for Al electrode

Factor	Variable	Range of actual and coded variables				
		-2	-1	0	1	2
A	Initial pH	4	5.5	7	8.5	10
B	Time of electrolysis, *t* (min)	30	67.5	105	142.5	180
C	Current density, *J* (mA/m^2)	14.17	17.72	21.26	24.8	28.34

Table 4.3. Full Factorial Design Used for the ECT of STW by Aluminum Electrodes

Std Order	pH	Time, t (Min)	J (mA/cm^2)
1	5.5	67.5	17.72
2	8.5	67.5	17.72
3	5.5	142.5	17.72
4	8.5	142.5	17.72
5	5.5	67.5	24.8
6	8.5	67.5	24.8
7	5.5	142.5	24.8
8	8.5	142.5	24.8
9	4	105	21.26
10	10	105	21.26
11	7	30	21.26
12	7	180	21.26
13	7	105	14.17
14	7	105	28.34
15	7	105	21.26
16	7	105	21.26
17	7	105	21.26
18	7	105	21.26
19	7	105	21.26
20	7	105	21.26

The data obtained from the experiments was analyzed using Design-Expert trial version. Three analytical steps: adequacy of various models test (sequential model sum of squares and model summary statistics), analysis of variance (ANOVA) and the response surface plotting were performed to establish an optimum condition for the responses.The data obtained by the experiments set suggested were fitted to a second-order polynomial model equation:

$$Y = b_o + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i=j}^{3} \sum_{i=j+1}^{4} b_{ij} X_{ij} \qquad \textbf{4.3}$$

Where, Y is Response; b_o, b_i, b_{ii}, b_{ij} are constant coefficients and X_i the uncoded independent variables. The significant terms in the model were found by analysis of variance (ANOVA) for each response. The model adequacies were checked by R^2, adjusted-R^2, predicted-R^2 and prediction error sum of squares (PRESS). A good model will have a large predicted R^2, and a low PRESS.

4.2.4. Multi-response optimization

There are three responses in this study, therefore, multi-response processes optimization by desirability function approach was used to optimize the electrochemical treatment. The desirability function approach is one of the most widely used methods in industry for the optimization of multiple response processes.

Simultaneous optimization combines all the different response requirements into one composite requirement.

One-sided desirability d_i is given by:

$$d_i = \begin{cases} 0 & if \quad Y_i \le Y_{i-\min} \\ \left[\dfrac{Y_i - Y_{i-\min}}{Y_{i-\max} - Y_{i-\min}}\right]^r & if \ Y_{i-\min} < Y_i < Y_{i-\max} \\ 1 & if \ Y_i \ge Y_{i-\max} \end{cases} \qquad \textbf{4.4}$$

Where, Y_i is response values, $Y_{i\text{-}min}$ and $Y_{i\text{-}max}$ is minimum and maximum acceptable values of response i, and r is a weight and a positive constant, used to determine scale of desirability.

Among the multi-response optimization techniques, desirability function approach is one of the most frequently used in practice (Derringer et al., 1980). The desirability lies between 0 and 1 representing the closeness of a response to its ideal

value. If a response falls within the unacceptable intervals, the desirability is 0, and if a response falls within the ideal intervals or the response reaches its ideal value, the desirability is 1. Meanwhile, when a response falls within the tolerance intervals but not the ideal interval, or when it fails to reach its ideal value, the desirability lies between 0 and 1. The more closely the response approaches the ideal intervals or ideal values, the closer the desirability is to 1.

In the multi-response processes optimization, desirability function transforms each response to a corresponding desirability value between 0 and 1. All the desirability is combined to form a composite desirability function which converts a multi-response into a one single response. The individual desirability functions are combined in order to obtain the overall desirability D, as follows:

$$D = (d_1 \times d_2 \times d_3 .....)^{\frac{1}{k}} \qquad \textbf{4.5}$$

Where, $0 \leq D \leq 1$and k is the number of responses.

If all of the quality characteristics reach their ideal values, the desirability d_i is 1 for all i. Consequently, the total desirability is also 1. If any one of the responses does not reach its ideal value, the desirability d_i is below 1 for that response and the total desirability is below 1. If any one of the responses cannot meet the quality requirements, the desirability d_i is 0 for that response. Total desirability will then be 0.

4.2.5. Analytical Methods

COD was measured by titration method using open reflux digestion unit (Spectra lab, 2015D), and double beam UV visible spectrophotometer (Electronic Corporation India Ltd., UV 5704SS) was used to measure the dye concentration. Scanning electron microscope (SEM, JEOL, JSM-6510LV, Japan) was employed to understand the morphologies of the generated sludge by the ECT of STW and to study the distribution of the elements in the sludge energy dispersive X-ray (EDX) was conducted. For the SEM/EDX, the samples were first ground to make the samples homogeneous and then spread on sample holders in such a manner to produce flat surfaces. After this the samples were gold coated using sputter coater to provide conductivity to the samples, and then the SEM and EDX spectra were taken.

CHAPTER – 5

RESULT AND DISCUSSION

5.0. GENERAL

This chapter reports electrochemical treatment (ECT) of synthetic textile wastewater (STW) in batch with Aluminum (Al) electrode. Results obtained during the treatment of STW and their interpretations have been discussed in detail.

The optimization of the process for the removal of COD and color, and consumption of electrical energy has been mentioned using central composite design based on response surface methodology (RSM). Analysis of variance (ANOVA) has also been mentioned. Finally, physico-chemical characterizations of the EC generated solid residues (scum and sludge) and treated effluent presented to understand their disposal.

5.1. RESULTS AND DISCUSSION

5.1.1. Statistical Analysis

The responses (Y_1, Y_2 and Y_3) by ECT of STW by the Al electrode were measured according to the conditions of various operational parameters as given in design matrix and the results are shown in Table 5.1. Linear, interactive, quadratic and cubic models were fitted to the experimental data to obtain the regression equations. In order to decide about the adequacy of various models, sequential model sum of squares and model summary statistics were tested and results are given in Table 5.2, Table 5.3 and Table 5.4 for responses Y_1, Y_2 and Y_3, respectively. Sequential model sum of squares showed that quadratic model best fits the experimental data for responses Y_1 and Y_2, and linear model for Y_3. Cubic model was found to be aliased for all three responses. For quadratic model, p value was lower than 0.05, and this was used for further study as per sequential model sum of squares test for responses Y_1 and Y_2.

The model gives coefficient of determination (R-squared) value of 0.9187, 0.9103 and 0.9116 for Y_1, Y_2 and Y_3, respectively, and adjusted R-squared value of 0.8455, 0.8295 and 0.8321 for Y_1, Y_2 and Y_3, respectively, which advocates a good correlation

between the observed and the predicted values. As also shown in figure 5.1, 5.2 and 5.3 that actual value and predicted value close to each other.

The analysis of variance (ANOVA) results showed F-value of 12.55, 11.27 and 11.46 for Y_1, Y_2 and Y_3, respectively, implying that models is significant (Table 5.5, Table 5.6 and Table 5.7). Value of "Prob>F" less than 0.0500 indicate model terms are significant. Values greater than 0.1000 indicate the model terms are not significant. ANOVA table obtained from the response surface models shows that time, pH^2, t^2, J^2 and pHxJ are significant terms for Y_1; pH, t, t^2, tx.J are significant terms for Y_2; and t and J are significant terms for Y_3.

The final quadratic equation in terms of coded factors for COD removal (Y_1), Dye removal (Y_2) and energy consumption per litre of effluent treated are given below:

$$Y_1 = 47.45 + 7.72B - 3.18A^2 - 4.91B^2 + 5.71C^2 - 5.56AC \quad \textbf{5.1}$$

$$Y_2 = 88.16 - 2.91A - 7.84B - 3.10B^2 - 3.84BC \quad \textbf{5.2}$$

$$Y_3 = 0.00894 + 0.003171B + 0.002659C \quad \textbf{5.3}$$

Table 5.1. Full factorial Design used and responses for the ECT of STW by aluminum electrodes

pH	Time, t (Minute)	J (mA/cm^2)	%COD removal (Y_1)		% Dye Removal (Y_2)		Specific Energy Consumed (Y_3)	
			Actual	Predicted	Actual	Predicted	Actual	Predicted
5.5	67.5	17.72	28.94	31.33	79.9	78.58	0.00403	0.00259
8.5	67.5	17.72	45.44	41.42	67.11	68.46	0.00497	0.00435
5.5	142.5	17.72	44.83	43.20	96.13	98.14	0.00851	0.00893
8.5	142.5	17.72	55.54	62.83	91.27	95.64	0.0101	0.01069
5.5	67.5	24.8	50.12	44.37	94.61	89.66	0.00722	0.00791
8.5	67.5	24.8	29.06	32.24	83.11	80.52	0.01076	0.00966
5.5	142.5	24.8	48.28	53.85	95.78	93.86	0.0147	0.01425
8.5	142.5	24.8	52.09	51.25	91.59	92.34	0.02161	0.01601
4	105	21.26	30.5	30.98	95.6	98.39	0.00875	0.00754
10	105	21.26	40.5	38.47	88.97	86.75	0.00928	0.01105
7	30	21.26	9.48	12.35	56.62	60.09	0.0027	0.00296
7	180	21.26	47.66	43.24	94.36	91.47	0.0141	0.01564
7	105	14.18	70.77	69.53	91.67	88.18	0.00467	0.00398
7	105	28.34	71.31	71.00	91.91	95.97	0.0126	0.01462
7	105	21.26	50.1	47.45	82.54	88.16	0.0091	0.00929
7	105	21.26	50.5	47.45	90.44	88.16	0.00875	0.00929
7	105	21.26	48.5	47.45	87.75	88.16	0.00875	0.00929
7	105	21.26	49	47.45	89.71	88.16	0.00823	0.00929
7	105	21.26	38	47.45	87.75	88.16	0.00858	0.00929
7	105	21.26	50.13	47.45	90.2	88.16	0.00858	0.00929

Table 5.2. Sequential model Sum of Square for COD removal

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	41473.28	1	41473.28			
Linear	1012.14	3	337.38	1.99	0.1556	
2FI	295.47	3	98.49	0.53	0.6691	
Quadratic	2109.98	3	703.33	23.25	< 0.0001	Suggested
Cubic	177.88	4	44.48	2.14	0.1934	Aliased
Residual	124.68	6	20.78			
Total	45193.44	20	2259.67			

Table 5.3 Sequential model Sum of Square for dye removal

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	152603.94	1	152603.94			
Linear	1181.11	3	393.70	9.18	0.0009	
2FI	147.63	3	49.21	1.19	0.3529	
Quadratic	371.36	3	123.78	7.39	0.0068	Suggested
Cubic	122.70	4	30.67	4.10	0.0613	Aliased
Residual	44.85	6	7.47			
Total	154471.6	20	7723.58			

Table 5.4. Sequential Model Sum of Square for Energy Consumption

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	$1.73x10^{-3}$	1	$1.73x10^{-3}$			
Linear	$2.86x10^{-4}$	3	$9.54x10^{-5}$	30.14	< 0.0001	Suggested
2FI	$1.94x10^{-5}$	3	$6.45x10^{-6}$	2.68	0.0903	
Quadratic	$1.52x10^{-6}$	3	$5.06x10^{-7}$	0.17	0.9142	
Cubic	$1.87x10^{-5}$	4	$4.69x10^{-6}$	2.56	0.1461	Aliased
Residual	$1.10x10^{-5}$	6	$1.84x10^{-6}$			
Total	$2.06x10^{-3}$	20	$1.03x10^{-4}$			

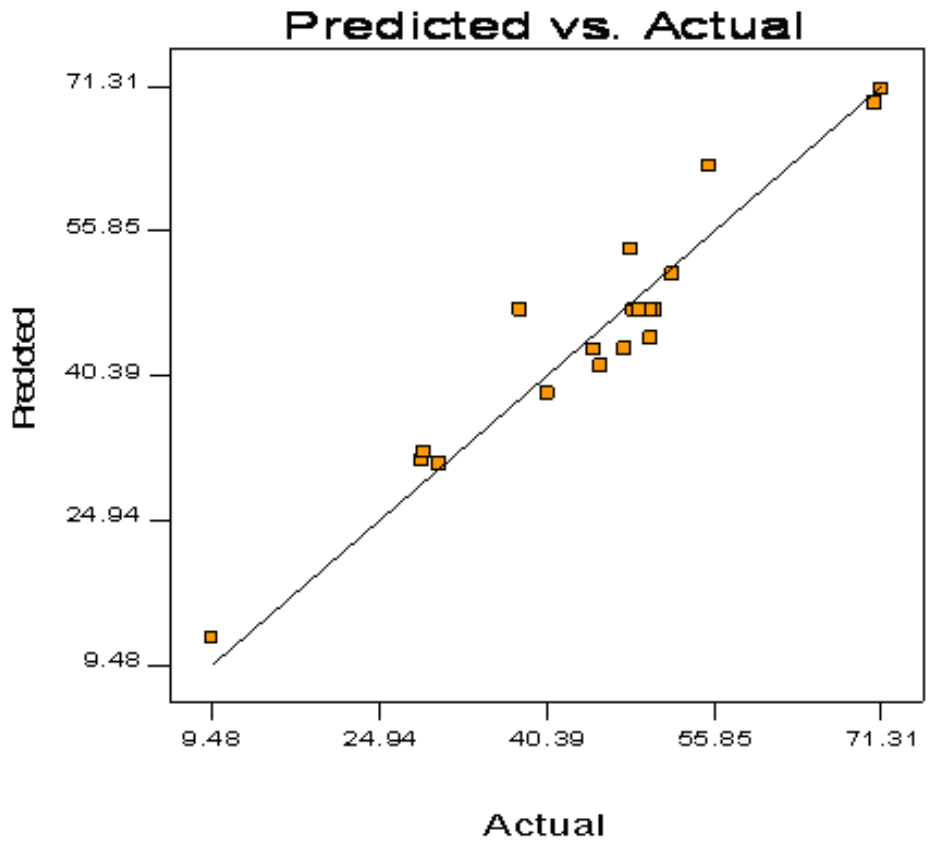


Figure 5.1. Comparison of Actual result with Predicted result for COD Removal

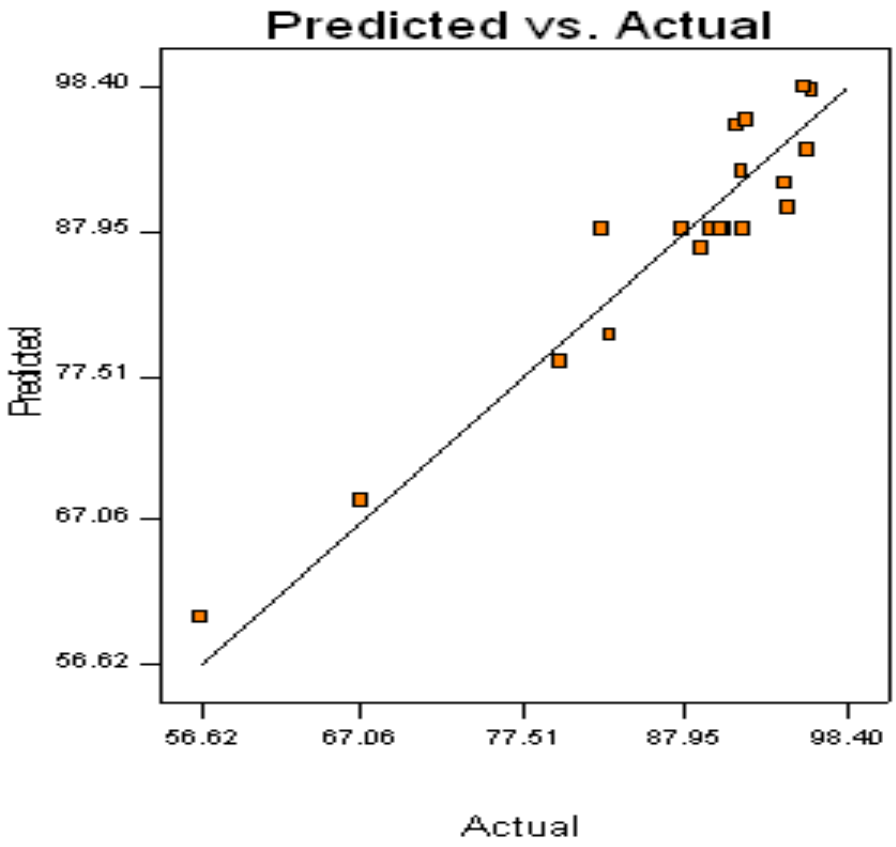


Figure 5.2. Comparison of Actual result with Predicted result for Dye Removal

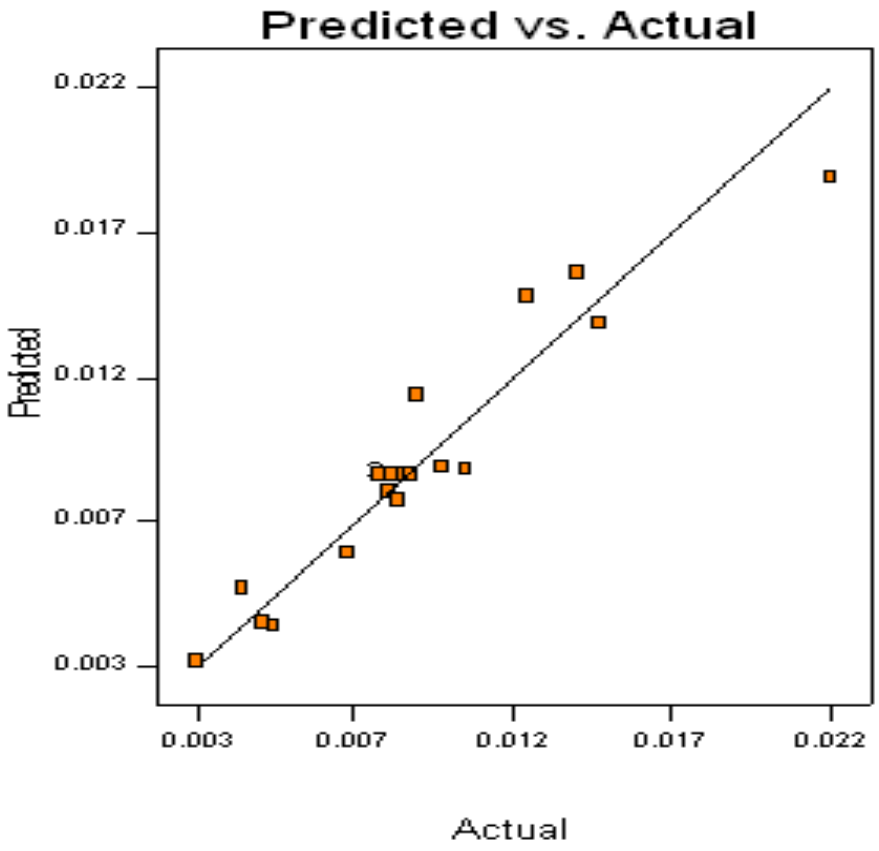


Figure 5.3. Comparison of Actual result with Predicted Result for Energy Consumption

Table 5.5. ANOVA for COD Removal

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	3417.60	9	379.73	12.55	0.0002	significant
A	56.10	1	56.10	1.85	0.2032	not significant
B	953.88	1	953.88	31.53	0.0002	significant
C	2.16	1	2.16	0.07	0.7947	not significant
A^2	254.25	1	254.25	8.40	0.0159	significant
B^2	606.76	1	606.76	20.05	0.0012	significant
C^2	818.32	1	818.32	27.05	0.0004	significant
AB	45.50	1	45.50	1.50	0.2481	not significant
AC	247.08	1	247.08	8.17	0.0170	significant
BC	2.88	1	2.88	0.09	0.7640	not significant
Residual	302.56	10	30.26			
Lack of Fit	186.63	5	37.33	1.61	0.3070	not significant
Pure Error	115.92	5	23.18	12.55		
Cor Total	3720.16	19				

Table 5.6. ANOVA for Dye Removal

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	1700.09	9	188.89	11.27	0.0004	significant
A	135.72	1	135.72	8.10	0.0174	significant
B	984.70	1	984.70	58.77	< 0.0001	significant
C	60.68	1	60.68	3.62	0.0862	not significant
A^2	30.59	1	30.59	1.83	0.2064	not significant
B^2	240.93	1	240.93	14.38	0.0035	significant
C^2	24.12	1	24.12	1.44	0.2579	not significant
AB	29.03	1	29.03	1.73	0.2174	not significant
AC	0.48	1	0.48	0.03	0.8689	not significant
BC	118.12	1	118.12	7.05	0.0241	significant
Residual	167.55	10	16.75			
Lack of Fit	123.93	5	24.78	2.84	0.1383	not significant
Pure Error	43.63	5	8.73			
Cor Total	1867.65	19				

Table 5.7. ANOVA for Energy Consumption

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	3.07×10^{-4}	9	3.41×10^{-5}	11.46	0.0004	significant
A	1.23×10^{-5}	1	1.23×10^{-5}	4.136	0.0694	not significant
B	1.61×10^{-4}	1	1.61×10^{-4}	54.02	< 0.0001	significant
C	1.13×10^{-4}	1	1.13×10^{-4}	37.97	0.0001	significant
A^2	1.32×10^{-6}	1	1.33×10^{-6}	0.44	0.5201	not significant
B^2	1.44×10^{-7}	1	1.44×10^{-7}	0.05	0.8304	not significant
C^2	4.54×10^{-7}	1	4.54×10^{-7}	0.15	0.7043	not significant
AB	2.02×10^{-6}	1	2.02×10^{-6}	0.68	0.4294	not significant
AC	7.84×10^{-6}	1	7.84×10^{-6}	2.63	0.1358	not significant
BC	9.50×10^{-6}	1	9.50×10^{-6}	3.19	0.1043	not significant
Residual	2.98×10^{-5}	10	2.97×10^{-6}			
Lack of Fit	2.94×10^{-5}	5	5.87×10^{-6}	71.97	0.0001	significant
Pure Error	4.08×10^{-7}	5	8.16×10^{-8}			
Cor Total	3.37×10^{-4}	19				

5.1.2. Effects of J, t and pH on Y_1, Y_2 and Y_3

Three-dimensional response surface graphs for responses Y_1 and Y_2 by various experimental factors *J, t* and *pH* are shown in Fig. 5.4 and Fig. 5.5 by Al electrode.

At anode, Al^{3+} and OH^- ions get generated due to oxidation of Al electrode.

$$Al\ (s) \rightarrow Al^{3+}\ (aq) + 3e \qquad \textbf{5.4}$$

$$3H_2O\ (l) + 3e \rightarrow 3/2\ H_2\ (g) + 3OH^- \qquad \textbf{5.5}$$

Above reactions react to form monomeric species such as $Al\ (OH)^{2+}$, $Al\ (OH)_2^+$, $Al_2\ (OH)_2^{4+}$ and $Al\ (OH)_4^-$ and various polymeric species such as $Al_6\ (OH)_{15}^{3+}$, $Al_7\ (OH)_{17}^{4+}$, $Al_8\ (OH)_{20}^{4+}$, $Al_{13}O_4\ (OH)_{24}^{7+}$, and $Al_{13}\ (OH)_{34}^{5+}$ [Bayramoglu et al. 2003] and the concentration of these species depends on the aluminum concentration in the solution and solution pH. percentage of various aluminium hydroxides products can be calculated from the following stability constants: [Duan et al., 2003]

$$Al^{3+} + H_2O \rightarrow Al\ (OH)^{2+} + H^+ \quad pK_1=4.95 \qquad \textbf{5.6}$$

$$Al\ (OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad pK_2=5.6 \qquad \textbf{5.7}$$

$$Al\ (OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \quad pK_3=6.7 \qquad \textbf{5.8}$$

$$Al\ (OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+ \quad pK_4=5.6 \qquad \textbf{5.9}$$

It may be seen from above equations that the hydrolysis constants cover a very narrower range and are compressed into pH region approximately 5-6, and the dominant soluble species are Al^{3+} and $Al\ (OH)_4^-$ at low and high pH, respectively.

The results ishown in Fig. 5.4a and Fig. 5.5a explains the %COD removal and %dye removal at various pH. Fig. 5.4a shows that response Y_1 first increases on increasing pH upto pH≈7.0 for each value of J. For pH> 7.0 there is very minute change in response Y_1. Therefore it may be concluded that Y_1 increases with increasing pH in the range of pH 4-7 and then remaining almost constant for pH>7. Precipitation and adsorption are the two major interaction mechanisms which are applicable at different pH ranges for the removal of COD. At low pH values, metal species Al^{3+} and

various other aluminum hydrolysed cations products is generated at the anode and bind anionic colloidal particles present in the STW and their solubility and precipitation occurs. After precipitation, adsorption of organic substances on amorphous metal hydroxide precipitates reduces the COD. It may be concluded that COD abatement rates decreased with increasing the initial reaction pH particularly when the initial pH value was above 7. Opposite result was found for %dye removal with increasing pH (Fig. 5.5a). On increasing pH, response Y_2 was found to decrease from pH=4.0-7.0. For pH>7.0 change in responses value Y_1 and Y_2 was marginal.

Faraday's law describes the relationship between current density (J), time (t) and the quantity of anode material that dissolves in the solution. It is given as:

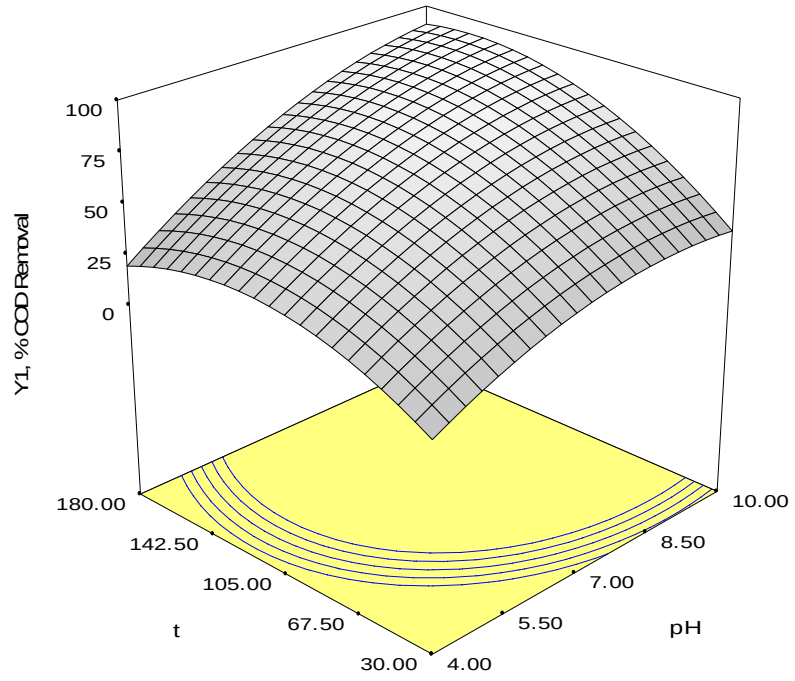
$$w = \frac{MJt}{ZF} \qquad \textbf{5.10}$$

Where, w is the theoretical amount of ion produced per unit surface area by current density J passed for duration of time, t**.** Z is the number of electrons involved in the oxidation/reduction reaction, M is the atomic weight of anode material and F is the Faraday's constant (96486 C/mol). for Al, Z =3. M is the atomic weight (g/mol) of anode material, for Al, M =26.9815 g/mol; and F is the Faraday's constant (96486 C/mol).

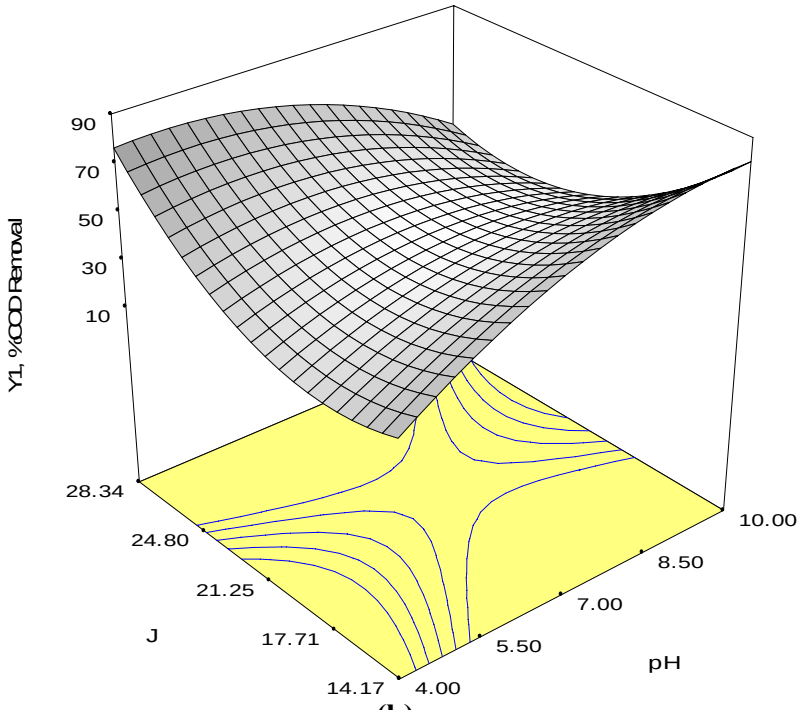
The removal efficiency of pollutants depends directly on the concentration of aluminum ions generated by the metal electrodes, which depends upon the t and J as per Faradays law. When the value of t and J increases, an increase occurs in the concentration of metal ions and their hydroxide flocs. As a result, an increase in t and J increases the removal efficiency. It may be seen in Fig. 5.4 and Fig. 5.5b that increasing t increases value of responses Y_1 and Y_2 upto t≤100, but for t>100 there is very marginal change in value of responses Y_1 and Y_2 and are nearly constant. At higher t, higher amount of Al^{3+} is generated and hence higher removal efficiency is found, but for t>100 minutes it may be concluded that all the removable COD and dye are already removed from the solution at t≤100.

Fig. 5.4b and Fig. 5.5 also shows dependency of J on responses Y_1 and Y_2. Fig. 5.4b shows that for J≤16 did not improve response Y_1. But for J>16, increasing J increases response Y_1. At lower values of J, Al^{3+} generation from electrode is not sufficient to remove COD, but at higher J, higher amount of J is produced and hence higher removal of COD. Form Fig. 5.5, it is clear that increasing J always improves Y_2 due to higher generation of Al^{3+} as per Faraday's law.

Fig. 5.6 shows the effect of *J*, *t* and *pH* on specific energy consumed (Y_3, kWh/litre of effluent treated). It may be seen in Fig. 5.6 that energy consumed always increased with *t* for all pH and J. Increasing t at lower pH showed lower specific energy consumed. Also at lower value of t increasing J showed slower increase in Y_3. However, at higher values of t, increasing J showed rapid increase in Y_3.



(a)



(b)

Fig. 5.4. Three-dimensional response surface graphs for the ECT of STW (a) Y_1, versus *t* and *pH* at *J* = 14.17 mA/cm^2 (b) Y_1, versus *J* and *pH* at *t* = 102 min.

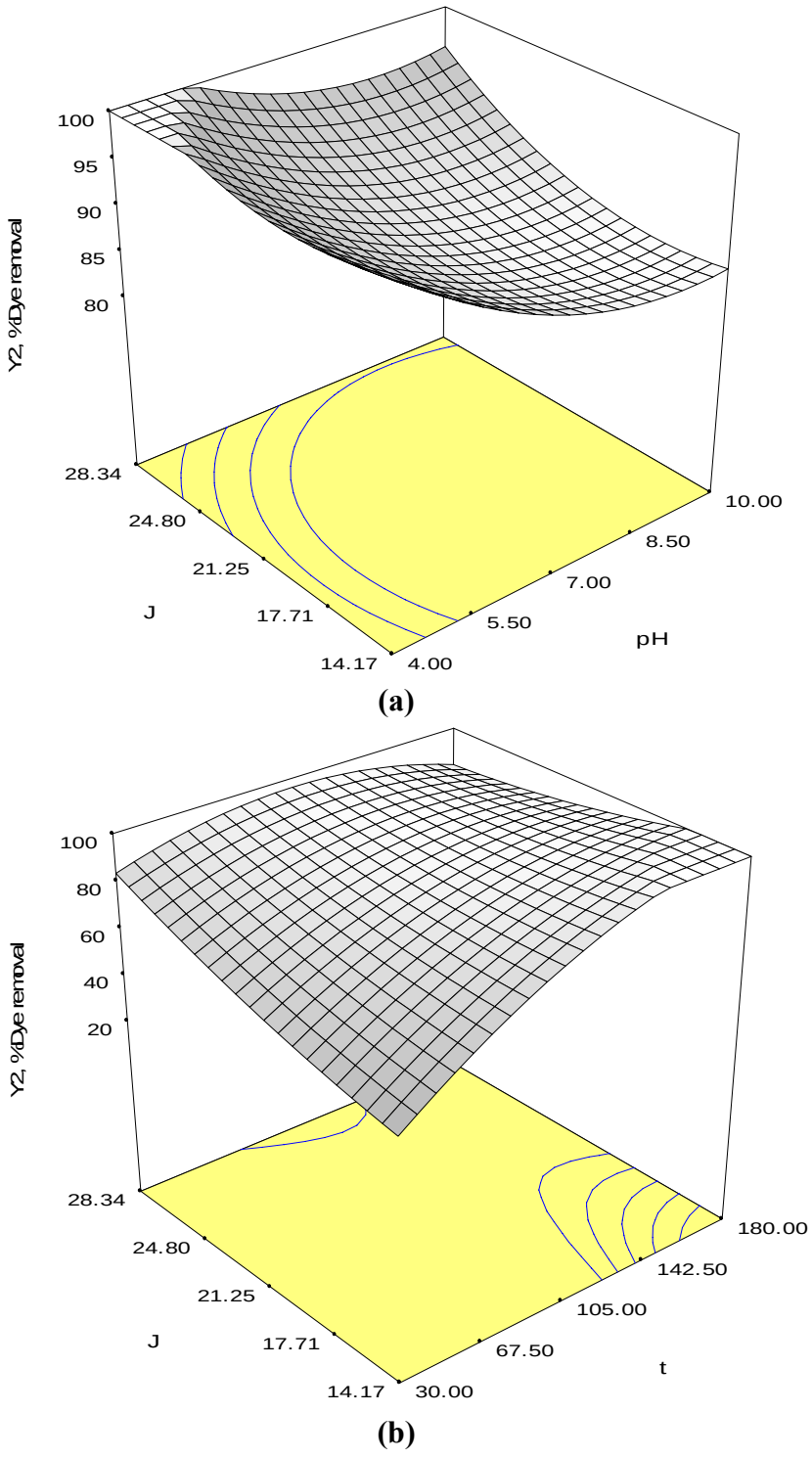
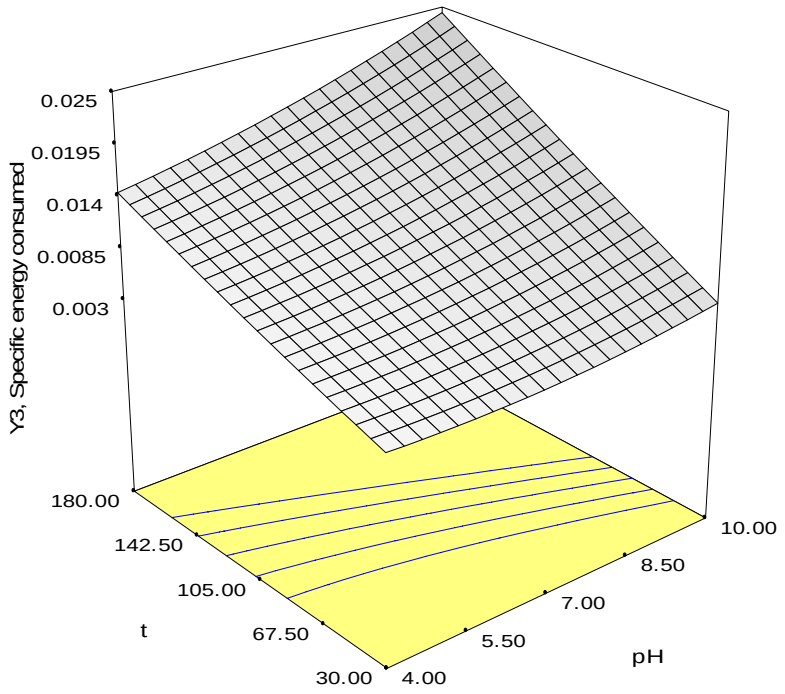
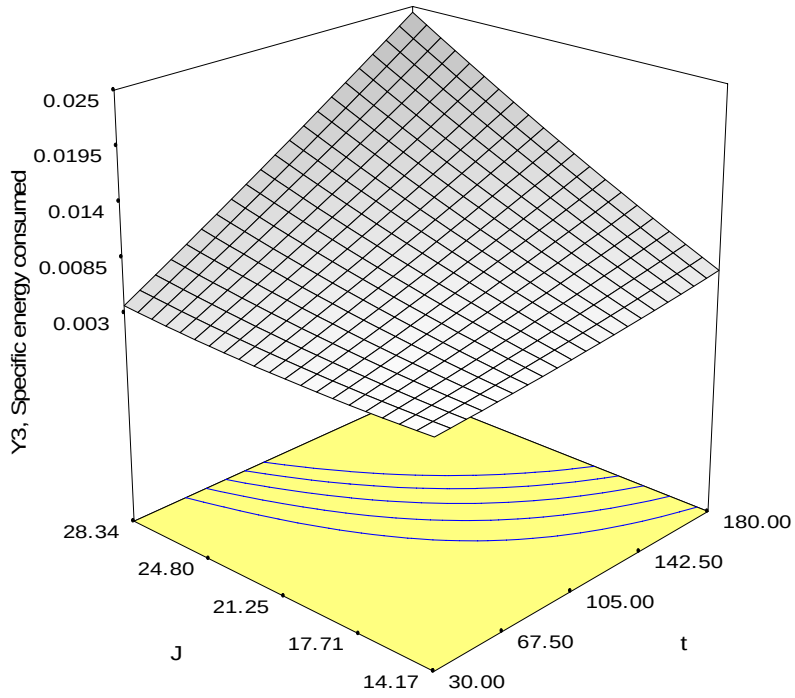


Fig. 5.5. Three-dimensional response surface graphs for the ECT of STW (a) Y_2, versus *J* and *pH* at *t*=102 min, (b) Y_2, versus *J* and *t* at *pH*= 6.25.



(a)



(b)

Fig. 5.6. Three-dimensional response surface graphs for ECT of STW (a) Y_3 versus *J* and *t* at *pH* = 6.25 (b) Y_3 versus *t* and *pH* at *J* = 14.17 mA/cm^2.

5.1.3. Optimization Analysis

ECT treatment of STW was optimized for response Y_1 and Y_2 to be maximized while Y_3 to be minimized. Desirability function approach was utilized to get the maximum Y_1 and Y_2 while minimum Y_3 simultaneously, since the optimum conditions for responses Y_1, Y_2 and Y_3 are not same. The constraints applied for the optimization of various operational parameters is given in Table 5.8.

The optimum values of operational parameters were found to be J = 14.17 mA/cm^2, t = 102 min and pH = 6.25 which produced overall *D* = 0.734. The responses Y_1, Y_2 and Y_3 were 62%, 89.17% and 0.0047 kWh/litre of effluent treated, respectively (Table 5.9 and 5.10).

In order to confirm the result found by optimization, three verification runs were conducted with the optimized set of operational parameters. The average value of responses Y_1, Y_2 and Y_3 were found to be 63.41%, 90.93% and 0.0035 kWh/litre of effluent treated, respectively, which are very close to predicted values (Table 5.10).

Since optimum pH was found to be 6.25, $Al(OH)_3$, $Al(OH)_2^+$ and $Al(OH)^{2+}$ are the species which are responsible for coagulation and subsequent adsorption of COD and dye from the wastewater.

At optimized set of operational parameters, dissolved amount of aluminum electrodes after ECT of STW was found to be 2.6975 g, whereas, theoretical corresponding value calculated from Faradays law was found to be 1.129 g. This showed current efficiency as 238.9%. Gao et al. (2010) has also reported higher value of current efficiency.

Table 5.8. Constraints applied for the optimization of ECT of STW by Al electrode.

Variables	Objective	Lower Limit	Upper Limit
J (mAcm^{-2})	minimize	14.17	28.34
t (min)	minimize	30	180
pH	is in range	5	7

Table 5.9. Optimum condition for ECT of STW by Al electrode.

Variables	Optimum values
J ($mAcm^{-2}$)	14.17
t (min)	102
pH	6.25

Table 5.10. Experimental and predicted values of Y_1, Y_2 and Y_3 at optimum condition.

Parameters		Values
D		0.734
Y_1	**Pre**	62.2%
	Exp	63.41%
Y_2	**Pre**	89.17%
	Exp	90.93%
Y_3	**Pre**	0.0047
	Exp	0.0035

5.1.4. Kinetics of COD and Dye removal

At optimized set of operational parameters (J = 14.17 mA/cm^2, t = 102 min and pH = 6.25), kinetic study for COD removal and dye removal was also performed at temperature 30 ºC and 50 °C.

The kinetic data were analyzed by using the first-order degradation kinetic equation. The first-order rate equation can be written as:-

$$dC_At/dt=kC_A \quad \textbf{5.11}$$

Where C_A= COD concentration and k is kinetic constant

The integration of the above equation (5.11) with the boundary conditions to t=t and C_{Ao}=COD_o at t=0; and C_A=COD_f at t=t gives

$$\ln(COD_f/COD_o) =-kt \quad \textbf{5.12}$$

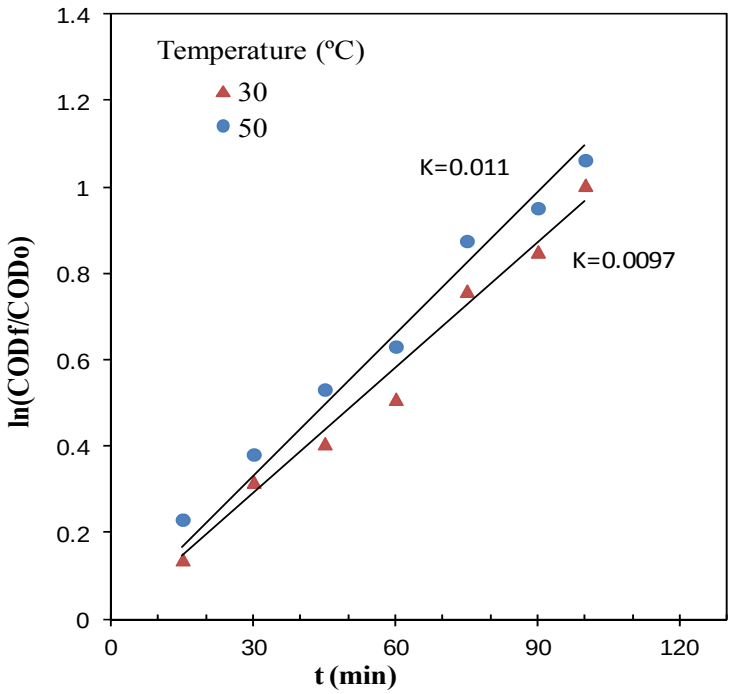
Where, COD_f= Final COD of treated STW, COD_o= Initial COD of STW and t is time for electrolysis.

Similarly for Dye Removal the above equation (5.12) can be written as

$$\ln (D_f/D_o) =-kt \quad \textbf{5.13}$$

Where, D_f= Final dye concentration of treated STW, D_o= Initial dye concentration in STW

The plot of ln (COD_f/COD_o) versus t and ln (D_f/D_o) versus t should show a straight line if the kinetic data fits the first order kinetic and Fig 5.7 shows plot of ln (COD_f/COD_o) versus t and ln (D_f/D_o) versus t which confirms the data are best fitted to this first order kinetic model. The rate constant (k) was calculated for Dye and COD from the slope of the plots of ln (D_f/D_o) versus t and ln(COD_f/COD_o) versus t, respectively. The plot shows that the k for dye removal and COD removal at 30°C was 0.0205 min^{-1} and 0.0097 min^{-1} and at 50°C was 0.037 min^{-1} and 0.011 min^{-1}, respectively. These results indicate that the rate constant increases with increase in temperature in both cases indicating higher COD and dye removal at higher temperature.



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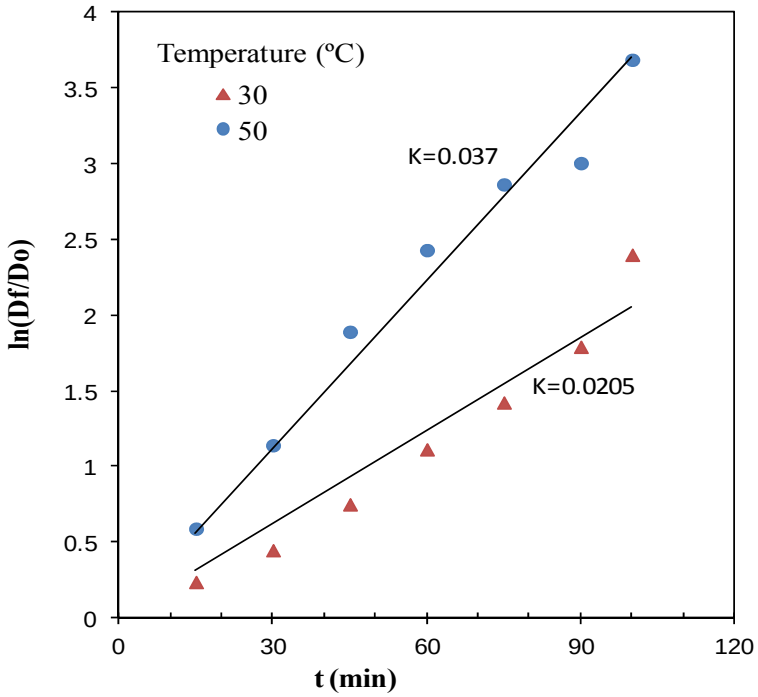


(b)

Fig. 5.7. Kinetic study at optimized set of operational parameters, for COD and dye removal

5.1.5. Physico-Chemical Analysis of Residues

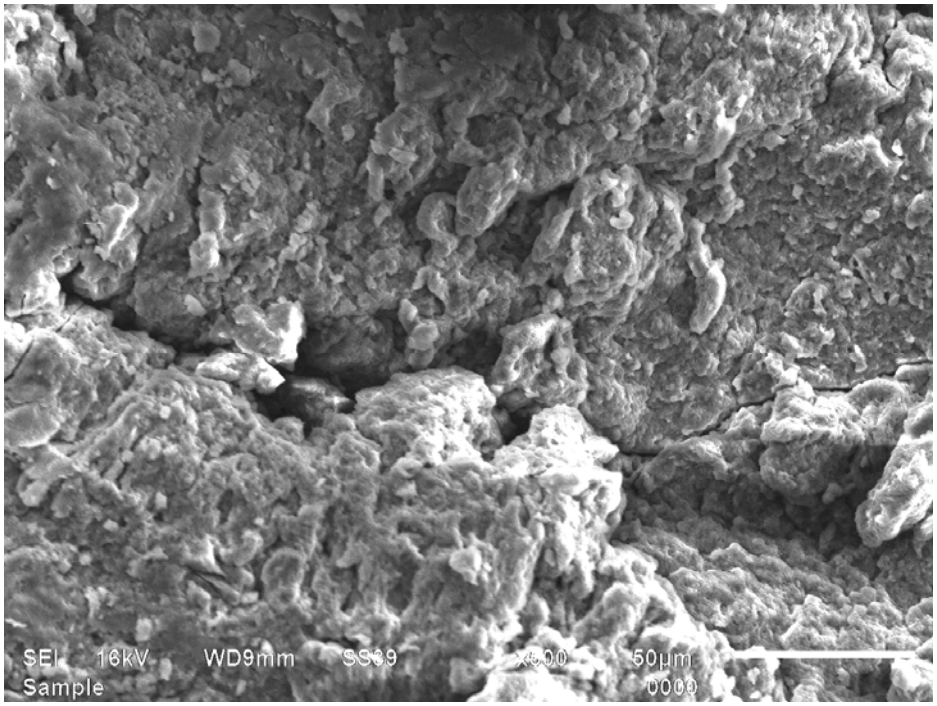
Residues of ECT of STW were examined by conducting SEM and EDX analysis. SEM images of dried residues are shown in Fig. 5.8. This figure shows that the sludge is having harder texture as compared to scum. Scum (Fig. 5.8b) has puffy texture with pores of varying sizes on the surface. The puffy texture of scum is due to the evolution of hydrogen gas from cathode during the ECT.

EDX was conducted to study the distribution of the elements in sludge and scum generated at optimum condition.

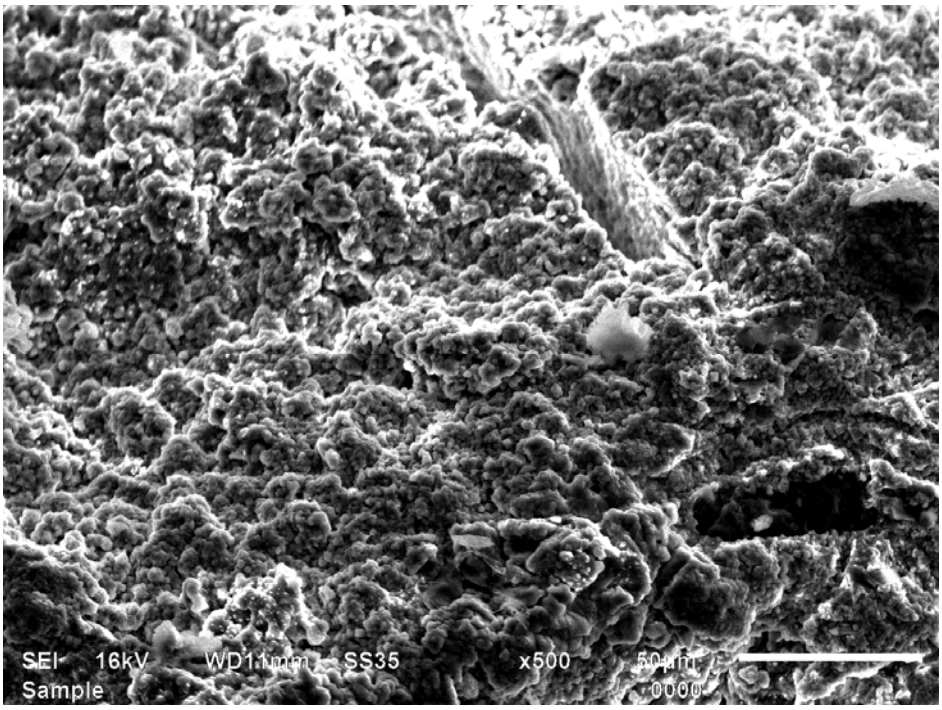
EDX analysis showed the presence of 45.47% C, 5.46% Al, 1.89% Cl, 2.12% Fe. 23.66% Cu and 21.39%Zn in sludge, whereas scum was found to contain 23.02% C, 14.95% O, 36.51% Na, %.46% Al, and 20.06% Cl, respectively. Thus, sludge is found to contain higher amount of carbon as compared to scum.

Aluminum mass balance was also performed for sludge and scum generated at optimum condition and calculation is shown in Table 5.11.

Treated STW contained 25.12 mg/l of aluminum. EPA prescribed a limit of 0.2 mg/l in national secondary drinking water regulations. Treated STW COD content was found to be 1152 mg/l, which also does not meet the standard for discharge of environmental pollutants set by the Indian government. Obviously, the treated effluent will require further treatment by other method to remove the remaining COD, aluminum, etc. For this purpose, adsorption of treated STW was conducted.



(a)



(b)

Fig. 5. 8. SEM images of generated (a) sludge (b) scum by ECT of STW.

Table 5.11 Al mass balance calculation at optimum condition

Total aluminum introduced	
Aluminum in STW (mg/l)	2.06
Total aluminum in STW (g)	0.309
Aluminum eroded by ECT (g)	2.6975
Total aluminum (g)	3.0065
Total aluminum in residues and treated STW	
Sludge produced (g)	9.3
Total aluminum in sludge (g)	0.50778
Scum produced (g)	1.1
Total aluminum in scum (g)	0.06006
Al in treated STW (mg/l)	25.12
Total aluminum in treated STW (g)	2.512
Total aluminum (residues + treated STW) (g)	3.07984
% Error	-2.43

5.1.6. Adsorption of Electrochemically Treated STW

For adsorption of electrochemically treated STW activated carbon (AC) was used as adsorbent. For every experiment, a known amount of the adsorbent was introduced into 250 ml stoppered conical flasks in which 100 ml of the electrochemically treated STW of known COD and initial pH was already present. This adsorbent-adsorbate mixture was kept in a temperature-controlled shaker at a constant speed of 150 rpm at 30 ºC temperature for 22 h to attain the equilibrium. After 22 h, adsorbent was separated from the STW and analysed for residual COD concentration. The percentage removal of COD was calculated using the equation 4.1.

The adsorption of STW by the AC was studied over a pH range of 2–10 at 30 ºC at dosage value of 20 g/l. Dosage of adsorbent study was carried out by varying the dosages of AC in the range of 5-40 g/l at the optimum pH and 30 ºC.

Isothermal experiments were performed at 30 ºC with initial COD concentrations of 300, 600, 900 and 1152 mg/l at optimum pH and optimum dosage of AC. Langmuir isotherm (equation 3.2) was used to represent the adsorption equilibrium data.

The adsorbents were separated from the STW after 22 h and analysed for equilibrium COD (COD_e). The equilibrium adsorption uptake, q_e (mg/g), was calculated using the following relationship:

$$q_e = \frac{(COD_0 - COD_e)}{w} V \qquad \textbf{5.14}$$

Where, V is the volume of the STW (l) and w is the mass of the adsorbent (g).

The Chi-square error analysis function was used to find out best fit isotherm model. It is given as:

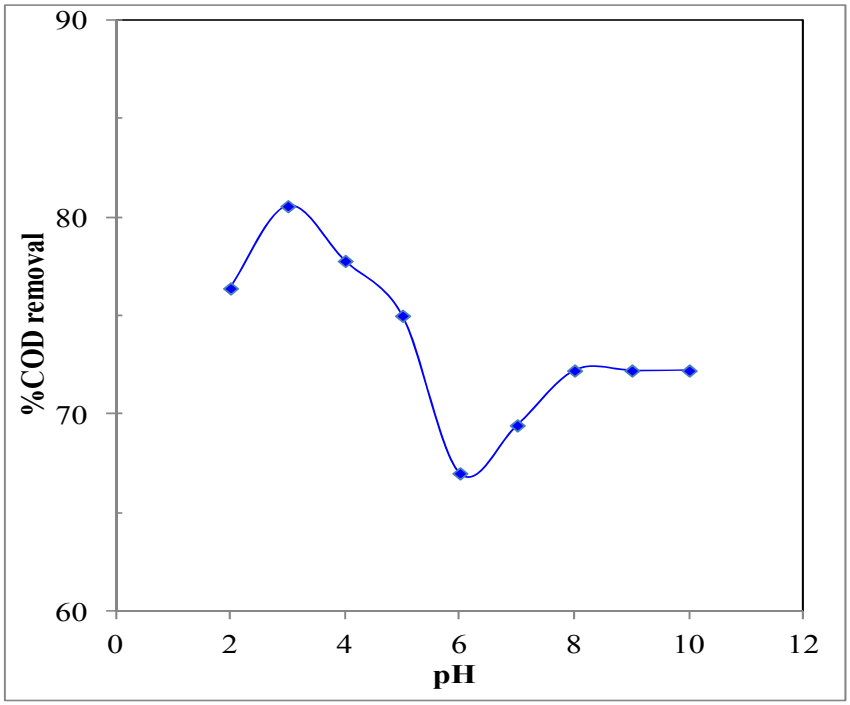
$$CHI^2 = \sum_{i=1}^{n} \frac{(q_{e,i,\exp} - q_{e,i,cal})^2}{q_{e,i,\exp}} \qquad \textbf{5.15}$$

In this equation, the subscript ‘exp’ and ‘cal’ represent the experimental and calculated values of q_e.

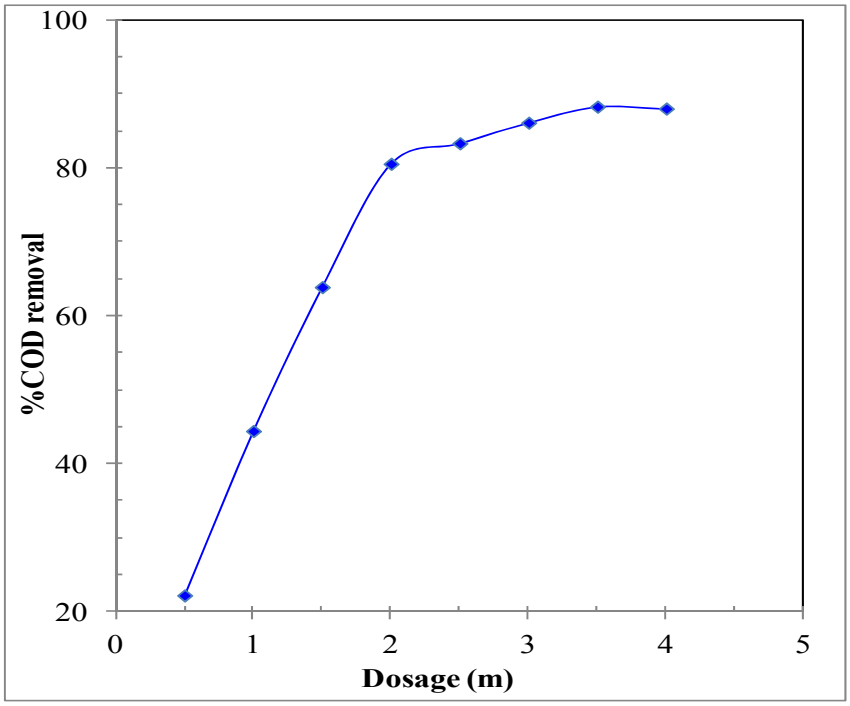
5.1.6.1. Effect of initial pH and dosage of AC: The initial pH value of the STW is an important parameter in the process of adsorption which greatly affect COD removal. Fig. 5.9a represents the effect of initial pH on the COD removal of electrochemically treated STW by AC. For this, highest removal efficiency of 80.56% was obtained at pH= 3.0. Higher or lower initial pH lowers the COD removal. Minimum COD removal of 67% was found at pH=6.0. For pH>6. 0, COD removal again increases upto pH=8.0 giving 72.22% COD removal and after this COD removal becomes constant.

Fig. 5.9b shows effect of AC dosage on the COD removal efficiency. It was found that an increase in AC dosage increased COD removal up to a certain value and thereafter the removal efficiency remained almost constant. An increase in the removal with the increase in dosage may be due to availability of greater surface area and the availability of more adsorption sites. At dosage ≥ 35 g/l the change in COD removal is marginal and remains almost constant to 88.28% (135mg/l of COD). This revels that for dosage≥ 35 g/l the removal efficiency more depends upon the COD concentration of the STW and less depends upon the dosage.

5.1.6.2. Isotherm modelling: Data obtained from the isothermal study were fitted to Langmuir isotherm. Fig. 5.10 shows fitting of Langmuir isotherm. Data points show experimental values and solid line shows fitting of Langmuir isotherms. The parameters, R^2 and CHI^2 values were found to be 0.95 and 1.43, respectively, which shows good correlation between experimental and predicated data from Langmuir isotherm. Value of Langmuir isotherm parameters K_L and q_m were found to be 0.00004 l/mg and 4509.02 mg/g, respectively. A high q_m value indicates a higher affinity of adsorbate to adsorbent.



(a) Effect of initial pH



(b) Effect of AC dosage

Fig. 5.9. (a) Effect of initial pH (b) Effect of AC dosage

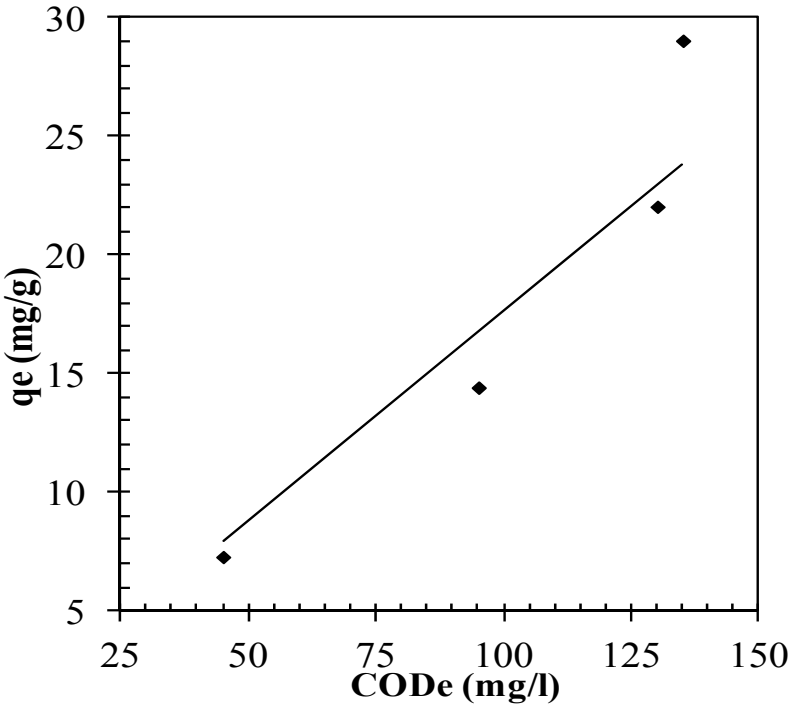


Fig. 5.10. Equilibrium adsorption isotherms at 30 ºC. Experimental data points given by symbols and the lines predicated by Langmuir isotherm model. time= 22 h, COD_o=300-1152 mg/l, Dosage of AC= 35 g/l and pH= 3.0

CHAPTER-6

CONCLUSION

On the basis of the results and discussion for the treatment of synthetic textile wastewater (STW) by electrochemical treatment (ECT) following major conclusions were found:

- Optimum condition for the ECT of STW was to be pH=6.25, J=14.17 mA/cm2, time=102 minute.
- At the optimum condition, actual COD removal (Y_1), Dye removal (Y_2) and specific energy consumed (kWh per litre of STW treated) (Y_3) were 63.41% (1152 mg/l residual COD), 90.93% and 0.0035 KWh/ per litre of STW treated, respectively.
- Coagulants $Al(OH)_3$, $Al(OH)_2^+$ and $Al(OH)^{2+}$ were found to be responsible for coagulation and subsequent adsorption of COD and dye from the STW.
- First order kinetics fitted the kinetic data for COD removal and dye removal. Kinetic constant for dye removal and COD removal at 30°C was 0.0205 min^{-1} and 0.0097 min^{-1} and at 50°C was 0.037 min^{-1} and 0.011 min^{-1}, respectively, which indicated removal increases with increase in temperature.
- Aluminium in treated STW, sludge and scum was 25.16 mg/l, 0.50778g and 0.06006 g, respectively.

Adsorptive treatment of electrochemically treated STW with activated carbon concluded:

- Optimum condition for the adsorptive treatment of STW was found to be: initial pH ≈ 3.0, adsorbent dose of 35 g/l and contact time ≈22 h.
- At the optimum condition, 88.28% COD removal were found (135mg/l of residual COD).
- Langmuir isotherm was found to fit the equilibrium data by showing R^2=0.95.
- Value of Langmuir isotherm parameters K_L and q_m were found to be 0.00004 l/mg and 4509.02 mg/g, respectively. A high q_m value indicates a higher affinity of adsorbate to adsorbent.

CHAPTER -7

REFERENCES

A. Alaton, I. Kabdaslı, Y. Sahin, "Effect of operating parameters on the electro coagulation of simulated acid dye bath effluent", The Open Environmental & Biological Monitoring Journal, 1 (2008) 1-7.

A. Alinsafi, M. Khemis, M.N. Pons, J.P. Leclerc, A. Yaacoubi, A. Benhammou, A. Nejmeddine, "Electro-coagulation of reactive textile dyes and textile wastewater", Chemical Engineering and Processing, 44 (2005) 461–470.

A. Geethakarthi, B.R. Phanikumar, "Adsorption of reactive dyes from aqueous solutions by tannery sludge developed activated carbon: Kinetic and equilibrium studies", International Journal of Environment Science and Technology, 8 (3) (2011) 561-570.

A. Srivastava, V.C. Srivastava, "Adsorptive desulfurization by activated alumina", Journal of Hazardous Material, 170 (2009) 1113-1140.

A.K. Golder, N. Hridaya, A.N. Samanta, S. Ray, "Electro coagulation of methylene blue and eosin yellowish using mild steel electrodes", Journal of Hazardous Materials, B127 (2005) 134–140.

A.R. Khataee, V. Vatanpour, A.R.A. Ghadim, "Decolorization of acid blue 9 solution by UV/Nano-TiO2, Fenton, Fenton-like,electro-Fenton and electrocoagulation processes" , Journal of Hazardous Materials, 161 (2009) 1225–1233.

B. Merzouk, K. Madani, A. Sekki, "Using electro coagulation electro flotation technology to treat synthetic solution and textile wastewater", Desalination, 250 (2010) 573–577.

B.K. Korbahti, A. Tanyolac, "Electrochemical treatment of simulated textile wastewater with industrial components and Levafix Blue CA reactive dye: Optimization through response surface methodology", Journal of Hazardous Materials, 151 (2008) 422–431.

C. Phalakornkule, S. Polgumhang, W. Tongdaung, B. Karakat, T. Nuyut, "Electrocoagulation of blue reactive, red disperse and mixed dyes and application

in treating textile effluent", Journal of Environmental Management, 91 (2010) 918–926.

D. Georgiou, P. Melidis, A. Aivasidis, "Use of a microbial sensor: inhibition effect of azo-reactive dyes on activated sludge", Bioprocess and Biosystem Engineering, 25 (2002) 79-83.

D. Ghosh, C.R. Medhi, H. Solanki, M.K. Purkait, "Decolorization of Crystal Violet Solution by Electrocoagulation", Journal of Environmental Protection Science, 2 (2008) 25 – 35.

E. Butler, Y.T. Hung, R.Y.L. Yeh, M.S.A. Ahmad, "Electro coagulation in wastewater treatment", Water, 3 (2011) 495-525.

E.O. Aluyor, O.A.M. Badmus, "COD removal from industrial wastewater using activated carbon prepared from animal horns", African Journal of Biotechnology, 7 (21) (2008) 3887-3891.

F. Ntuli, D.I. Omoregbe, P.K. Kuipa, E. Muzenda, M.Belaid, "Characterization of Effluent from Textile Wet Finishing Operations", Proceedings of the World Congress on Engineering and Computer Science 2009, Volume I, October 20-22, 2009, San Francisco, USA

F. Othman, J. Sohaili, M.F. Ni'am, Z. Fauzia, "Enhancing Suspended solids removal from wastewater using Fe Electrods", Malaysian journal of civil Engineering, 18 (2006) 139-148.

F.K. Bangash, A. Manaf, "Dyes Removal from Aqueous Solution using Wood Activated Charcoal of Bombax Cieba Tree", Journal of the Chinese Chemical Society, 52 (2005) 489-494.

G. Annadurai, R.S. Juang, D.J. Lee, "Use of cellulose-based wastes for adsorption of dyes from aqueous solutions", Journal of Hazardous Materials, B92 (2002) 263–274.

G. Guven, A. Perendeci, A. Tanyola, "Electrochemical treatment of simulated beet sugar factory wastewater", Chemical Engineering Journal, 151 (2009) 149–159.

G.B. Raju, M.T. Karuppiah, S.S. Latha, D.L. Priya, S. Parvathy, S. Prabhakar, "Electrochemical pretreatment of textile effluents and effect of electrode materials on the removal of organics", Desalination, 249 (2009) 167–174.

H. Patel, R.T.Vashi, “Treatment of Textile Wastewater by Adsorption and Coagulation”, E-Journal of Chemistry, 7(4) (2010) 1468-1476.

H. Zhian, K. khalipour, H. khandani, “The removal Acid Red Dye 88(AR88) from aqueous solution by electrocoagulation”, World applied Sciences Journal, 3 (2011) 558-563. H.R. Guendy, “Treatment and Reuse of Wastewater in the Textile Industry by Means of Coagulation and Adsorption Techniques” Journal of Applied Sciences Research, 6(8) (2010) 964-972.

H.M.F. Freundlich, “Over the adsorption in solution”, Journal of Physical Chemistry, 57 (1906) 385-471.

I. Langmuir, “The adsorption of gases on plane surfaces of glass, mica and platinum”, Journal of American Chemical Society 40 (1918) 1361-1403.

I.A. Sengil, M. Ozacar, “The decolorization of C.I. reactive black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes”, Journal of Hazardous Materials, 161 (2009) 1369–1376.

J. Duan, J. Gregory, “Coagulation by hrdrolysing metal salts”, Advanced Journal of Colloid and Interface Science, 100–102 (2003) 475–502.

J. Liang, L. Cui, X. Wang, J.L. Liu, H. Wang, Y. Liu,” Study on the Treatment of Dye Wastewater by Electro-coagulation”, Department of chemistry and environment, School of Science, Shenyang University of Technology, 110023 Shenyang, China.

J.P. Khuswaha,V.C. Srivastava, I.D. Mall, “Studies on Electrochemical Treatment of Dairy Wastewater Using Aluminum Electrode” AIChE Journal,2010.

J.W. Lee, S.P. Choi, R. Thiruvenkatachri, W.G. Shim, and H. Moon, “Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes”, Dyes and Pigments, 69 (2006)196 – 203.

K. Charoenlarp and W.Choyphan, “Reuse of dye wastewater through colour removal with electrocoagulation process”, International Conference on the Role of Universities in Hands-On EducationRajamangala University of Technology Lanna, Chiang-Mai, Thailand 23-29 August 2009.

K. Chithra, N. Balasubramanian, “Modeling Electrocoagulation through Adsorption Kinetics”, Journal of Modelling and Simulation of Systems, 1 (2010) 124-130.

K. Vijayaraghavan, S.W. Won, Y.S. Yun, “Treatment of complex Remazol dye effluent using sawdust- and coal-based activated carbons”, Journal of Hazardous Materials, G Model (2009) HAZMAT-9415.

M. Bayramoglu, M. Eyvaz, M. Kobya, “Treatment of the textile wastewater by electro coagulation”, Chemical Engineering Journal, 128 (2007) 155–161.

M. Chaudhuri, E.S. Elmolla, R.B. Othman, “Removal of reactive dyes from aqueous solution by adsorption on coconut coir activated carbon”, 2nd International Conference on Engineering Technology, 8-10 December 2009, Kuala Lumpur.

M. Kashefialasl, M. Khosravi, R. Marandi, K.Seyyedi, “Treatment of dye solution containing colored index acid yellow 36 by electro coagulation using iron electrodes”, Journal of Environment Science and Technology, 2 (2006) 365-371.

M. Kobya, E. Demirbas, O.T. Can, M. Bayramoglu, “Treatment of levafix orange textile dye solution by electro coagulation”, Journal of Hazardous Materials, B132 (2006) 183–188.

M. Kobya, O.T. Can, M. Bayramoglu, “Treatment of textile wastewaters by electro coagulation using iron and aluminum electrodes”, Journal of Hazardous Materials, B100 (2003) 163–178.

M. Suzuki, T. Fujii, “Concentration dependence of surface diffusion coefficient of propionic acid in activated carbon particles”, AIChE Journal, 28 (1982) 380-385.

M.J. Iqbal, M.N.Ashiq, “Adsorption of dyes from aqueous solutions on activated charcoal” © 2006 Elsevier B.V. All rights reserved.

M.T. Karuppiah, G.B. Raju, S.S. Latha, S. Parvathy, S. Prabhakar, “Treatment of wastewater from synthetic textile industry by electro-coagulation”, Chemical Engineering Journal, 144 (2008) 51–58.

M.Y.A. Mollah, R. Schennach,, J.R. Parga, D.L. Cocke, “Electrocoagulation (EC)-science and applications”, Journal of Hazardous Materials, B84 (2001) 29–41.

M.Y.A. Mollah, S.R. Pathak, P.K. Patil, M. Vayuvegula, T.S. Agrawal, J.A.G. Gomes, M. Kesmez, D.L. Cocke, “Treatment of orange II azo-dye by electro coagulation technique in a continuous flow cell using sacrificial iron electrodes”, Journal of Hazardous Materials, B109 (2004) 165–171.

M.Y.A. Mollaha, M. Paul, J.A.G. Gomes, M. Kesmez, J. Pargad, D.L. Cocke, “Fundamentals, present and future perspectives of electro coagulation”, Journal of Hazardous Materials, B114 (2004) 199–210.

N. Daneshvar, H.A. Sorkhabi, A. Tizpar, “Decolorization of orange II by electro coagulation method”, Separation and Purification Technology, 31 (2003) 153-162.

N. Daneshvar, H.A. Sorkhabi, M.B. Kasiri, “Decolorization of dye solution containing Acid Red 14 by electro coagulation with a comparative investigation of different electrode connections”, Journal of Hazardous Materials, B112 (2004) 55–62.

N.K. Amin, “Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith”, Desalination, 223 (2008) 152–161.

O. Redlich, D.L. Peterson, “A useful adsorption isotherm”, Journal of physical Chemistry 63 (1959) 1024-1026.

O.T. Can, M. Bayramoglu, M. Kobya, “Decolorization of reactive dye solutions by electro-coagulation using aluminum electrodes”, Industrial and Engineering Chemistry Research, 42 (2003) 3391-3396.

P. Izares, Fabiolamartianez, Carlosjimeanez, Justolobato, M. Rodrigo, “Coagulation and electro coagulation of wastes polluted with dyes”, Environmental Science and Technology, 40 (2006) 6418-6424.

P. Izares, Fabiolamartianez, Carlosjimeanez, Justolobato, Manuela, Rodrigo, “Coagulation and electro coagulation of wastes polluted with dyes”, Environment Science and Technology, 40 (2006) 6418-6424.

P. Sivakumar, P.N. Palanisamy, “Adsorption studies of basic red 29 by a nonconventional activated carbon prepared from euphorbia antiquorum l”, International Journal of chemtech Research, 1(3) (2009) 502-210.

R. Ahlawat, V.C. Srivastava, I.D. Mall, S. Sinha, “Investigation of the Electro-coagulation Treatment of Cotton Blue Dye Solution using Aluminium Electrodes” Clean , 36 (10 – 11),2008.

R. Aravindhan, J.R. Rao, B.U. Nair, “Removal of basic yellow dye from aqueous solution by adsorption on green algae Caulerpa scalpelliformis”, Journal of Hazardous Material, 142 (2007) 68–76.

R. Kant, V.K. Rattan, “Adsorption of dye green B from a textile industry effluent using two different samples of activated carbon by static batch method and continuous process”, Indian journal of chemical Technology, 16 (2009) 240-244.

S. Gao, M. Du, J. Tian, J. Yang, J. Yang, F. Ma, J. Nan, “Effects of chloride ions on electro-coagulation-flotation process with aluminum electrodes for algae removal”, Journal of Hazardous Materials, 182 (2010) 827–834.

S. Tchamango, C.P. Nanseu-Njiki, E. Ngameni, D. Hadjiev, A. Darchen, “Treatment of dairy effluents by electrocoagulation using aluminium electrodes”, Science of the Total Environment, 408 (2010) 947–952.

T. Robinson, G. McMullan, R. Marchant, P. Nigam, “Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative”, Bioresource Technology, 77 (2000) 247-255.

T.H. Kim, C. Park, E. Shin, S. Kim, “Decolorization of reactive dye by continuous electro-coagulation process”, Desalination, 150 (2002) 165-175.

U. Tezcan, E. AYTAC, “Treatment of Textile Wastewaters by Electrocoagulation Method”, 2nd International Conference on Chemical Engineering and Applications (IPCBEE) Vol. 23 (2011), IACSIT Press, Singapore.

V.A. Shenai, Technology of textile processing volume II: Chemistry of dyes and principles of dyeing, 1977, Bombay: Sevak.

V.C. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, “Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamic study”, Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 272 (2006) 89-104.

W. Miled, A. Haj Said, S. Roudesli, “Decolorization of High Polluted Textile Wastewater by Indirect Electrochemical Oxidation Process”, Journal of textile and apparel, Technology and management, 6(3) spring2010.

www.miga.orrg/miga_ documents/Dyemanufacturing.pdf.

X. Lu, L. Liu, R. Liu, J. Chen, “Textile wastewater reuse as an alternative water source for dyeing and finishing processes”, Desalination,258 (2010) 229–232.

Y. Anjaneyulu, N.S. Chary, D. Samuel, S. Raj, “Decolorization of industrial effluents – available methods and emerging technologies – a review”, Reviews in Environmental Science and Biotechnology, 4 (2005) 245–273.

Y. S. Al-Degs, M.I. El-Barghouthi , A.H. El-Sheikh, G.M. Walker, “Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon”, Dyes and Pigments, (2007) 1-8.

Y.C. Sharma, B. Singh, Uma, “Fast Removal of Malachite Green by Adsorption on Rice Husk Activated Carbon”, The Open Environmental Pollution & Toxicology Journal, 1 (2009) 74-78.

Y.C. Sharma, Uma, A.S.K. Sinha, S.N. Upadhyay, “Characterization and Adsorption Studies of Cocos nucifera L. Activated Carbon for the Removal of Methylene Blue from Aqueous Solutions”, Journal of Chemical Engineering Data, 55 (2010) 2662–2667.

Y.S. Ho, G. McKay, “Pseudo-second order model for adsorption processes”, Process Biochemistry, 34 (1999) 451-465.