TREATMENT OF DYE WASTEWATER BY ELECTRO-OXIDATION PROCESS

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Submitted

By

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DECLARATION

I, the undersigned, hereby declare that the research work presented in the M. Tech. dissertstion entitled "**Treatment of Dye Wastewater by Electro-oxidation Process**" has been carried out by me under the supervision and guidance of **Dr. Vikas K. Sangal and Dr. Jai Prakash Kushwaha, Assistant Professor, Chemical Engineering Department,** ***Thapar Universit Patiala***.

Further, I declare that no part of this Dissertation has been submitted for a degree or a other qualification of any other university or examining body in India/elsewhere.

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CERTIFICATE

This is to certify that thesis entitled, "**Treatment of Dye wastewater by Electro-oxidation process**" submitted by **Ms. Parminder Kaur** in partial fulfillment of the requirements for the award of **Masters of Technology** Degree in **Environmental Science & Technology** at **Thapar University, Patiala** is an authentic work carried out by her under our supervision and guidance.

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To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any Degree or Diploma.

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ABSTRACT

Large amount of high strength colored wastewater is produced during dyeing/printing and finishing operations of textile processing. CBSOL LE dyes are reactive dyes developed for wool dyeing. Many physico-chemical treatment techniques like chemical coagulation, adsorption processes and membrane filtration are not preferred generally, for the treatment of such type of dye containing effluents due to costly chemical coagulants, adsorbents, membranes fouling and production of large volume of secondary pollutants. Whereas, non-biodegradability of reactive dyes and high energy requirement, limits the use of biological methods for the treatment of dye containing wastewater. These shortcomings i.e. large volume of secondary pollutants generation and non-biodegradability of dye bearing wastewater can be overcome by the use of electro-oxidation (EO) process. During the EO process, dye is first degraded to some intermediates, and these intermediates are further oxidized to carbon dioxide and water by various chlorine species (HOCl and ClO^{-}).

In the present study, EO of CBSOL LE red wool dye containing wastewater was studied with RuO_2 coated Ti electrode (Ti/RuO_2). Effect of EO processes parameters like pH, current (i) and time (t) on % dye removal (%DR), % color removal (% CR) and energy consumed (EC) was investigated. Also, Artificial neural networks (ANNs) and response surface methodolgy (RSM) were used for modeling and optimization of EO process. The modeling of such EO system having three process variables (pH, i and t) and three response (%DR, % CR and EC) is quite complex. Obsiviously, such problem cannot be solved by simple linear multivariate correlation. Since, Modeling based on ANNs does not require the mathematical description of the phenomena involved in the process. Therefore, ANNs was used for modeling of EO process.

Hyperbolic tangent 'TANSIG' being a sigmoid transfer function was chosen for the input to hidden layer mapping while a purely linear transfer function 'PURELIN' was chosen for the hidden layer to the output layer mapping and the final selected network architecture was trained for 2000 iterations. Number of hidden layer neurons in the ANN architecture was optimized with the reduction in the mean square error. it was found that the optimized neurons for this process was eight. The training versus target gives regression coefficient of 0.995 along with validation, test and all data sets regression coefficient value 0.992, 0.996, 0.995 respectively. Which implied

that training of the ANN model was done accurately and model was ready to stimulate the outputs from a given inputs.

The Stimulated data obtained from AAN modeling was used for the optimization of the process. the optimization was done by central composite design (CCD) under RSM. Three operation parameters variables current (I) 0.25-1.25A, electrolysis time (t) 10-90 min and pH 4-10 was considered as input parameters and %age of color removal, %age of dye degradation and specific electrical energy consumption was taken as responses of the system. Multi-response processes optimization by desirability function approach was used to optimize the EO process which maximize the Y_1 and Y_2 simultaneously and minimize Y_3. The optimum values of operational parameters were found to be I (0.25 A), t (90min) and pH (4.00). At optimum condition, the Y_1 (% dye degradation), Y_2 (% color removal) and Y_3 energy consumed were found to be 91.75%, 99.00%, 2.327 Wh respectively was found. Optimum condition for EO process was experimentally verified. Optimization by CCD under response surface methodology (RSM) vividly underscores interactions between variables and their effects for the dregradation of CBSOL LE red wool dye by EO process and the predictions agree well with the experimental results.

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ABBREVIATIONS

CPCB	Central pollution control board
EO	Electro-Oxidation
CCD	Central Composite Design
ANN	Artificial neural networks
RSM	Response surface methodolgy
ANOVA	Analysis of Variance
Y_1	%age of dye degradation
Y_2	%age of color removal
Y_3	specific electrical energy consumption
DF	Degree of freedom

CHAPTER-1

INTRODUCTION

1.1 GENERAL

Increasing industrialization and urbanization are the causes of environmental pollution. Textile industries are one the huge volume of wastewater generating industries, and amongst the high strength wastewater generating industries (Neill et al., 1999). Common contaminants in textile wastewater include materials containing biochemical oxygen demand and chemical oxygen demand, suspended solids, color and other soluble inorganic and organic substances. Textile industry can be classified into three categories like cotton, woolen, and synthetic fibers depending upon the used raw materials.

Dyes possess certain properties, namely resistance to abrasion, photolytic stability, resistance to chemical and bacterial attack, which make them keep unaltered long time (McMullan et al, 2001, Zollinger, 1987) and are recalcitrant in nature, therefore are very difficult to remove from textile industries wastewaters (EPA625R96004, USA 1996.).

Textile manufacturing is one of the largest industrial producers of wastewater approximately 125-150 l of water are used for 1 kg of textile product. The wastewater from textile processing contains processing bath residues from preparation, dyeing, finishing, slashing and other operations (U.S. EPA, 1995).

During the dyeing process, the dye is dissolved into the process water and it is still there when the process water later is released as effluent. The effluent contains high content of dyestuff, surfactants and other additives that are generally made up of organic compounds with a complex structure. The dissolved dye compounds of the effluent are resistant to light, acids, bases and oxygen as these are the desired properties of the dyed clothes. It is very difficult to treat textile wastewater with conventional methods as these organic compounds have poor bio-degradability. These residues can cause severe pollution if not properly treated before discharge to the environment (U. S. EPA, 1997).

1.2 TEXTILE WASTEWATER CHARACTERISTICS

The treatment of this high strength wastewater is essential due to its strong color, suspended particles, high pH and chemical oxygen demand (COD) (Olmez et al., 2007; Vlyssides et al., 1999; Kim et al., 2003). Variable nature and poor biological degradation (Olmez et al., 2007). The textile industries consume large quantities of water and generate wastewater in proportionate order. Effluent characteristics of the textile industry wastewater are given in Table1.

Tab. 1. EFFLUENT CHARACTERISTICS OF THE TEXTILE INDUSTRY WASTEWATER

PROCESS	COMPOSITION	NATURE
Sizing	Starch, waxes, carboxymethyl cellulose, polyvinyl alcohol	High BOD and COD
Desizing	Starch, glucose, carboxymethyl cellulose, polyvinyl alcohol, fats and waxes	High BOD, COD, suspended solids, dissolved solids
Scouring	Caustic soda, waxes, grease, soda ash, sodium silicate, fibers, surfactants, sodium phosphate	Dark colored, high pH, high COD, dissolved solids
Bleaching	Hypochlorite, chlorine, caustic soda, hydrogen peroxide, acids, surfactants, sodium silicate, sodium phosphate	Alkaline, suspended solids
Mercrizing	Caustic soda	High pH, low COD, high dissolved solids
Dyeing	Various dyes, mordant, reducing agents, acetic	Strongly colored, high COD,

	acid, soap	dissolved solids, low suspended solids, heavy metals
Printing	Pastes, starch, gums, oil mordant, acids, soaps	Highly colored, high COD, oily appearance, suspended solids
Finishing	In organics salts, toxic compounds	Slightly alkaline, low BOD

Source: Olmez et al., 2007

Effluent characteristics of the textile industry wastewater depend upon the processes that are going to be used in the textile industry as shown in Table 2. Except it textile effluent can also contaminated with oils, grease, and waxes while some may contain heavy metals such as chromium, copper, zinc and mercury.

Tab. 2. EFFLUENT CHARACTERISTICS OF THE TEXTILE INDUSTRY WASTEWATER DEPEND UPON THE PROCESSES

Wastewater Type	**COD, mg/L**	**BOD, mg/L**	**TSS, mg/L**	**TDS, mg/L**	**pH**	**Color mg/L**	**References**
Textile wastewater	1411	455	137	2563	7.0	2447	(Yigita et al., 2009)
Textile wastewater	1150	170	150	-	10	1370	(Selcuk 2005)
Textile wastewater	1700	-	-	-	9.7		(Damas et al., 2005)
Desizing	-	200	400	4029	6.8	694	(Venceslau et al., 2008)
Scouring	8000	100-2900	7.6-17.4	184-17400	7.3-13	674	(Bisschops et al., 2003)
Bleaching	1099	878	180	7132	8.5-9.6	-	(Ranganathan et al., 2007)
Mercerising	1600	50-100	600-1900	4300-4600	5.5-9.5	-	(Naveed et al., 2006)
Dyeing	23	11	37	-	8.35	-	(Bruggen et al., 2001)

1.3 ENVIRONMENTAL LEVELS AND STANDARDS

Wastewater that is discharged by dye manufacturing and textile finishing industries has become an environmental concern. The legal requirements concerning discharge of contaminated wastewater are reinforced in many countries and the discharge fees are increasing. According to our experience large international clothes companies are setting a new standard of requirements, often higher than the local legislation requires. According to The Environment (Protection) Rules, 1986 standard for effluents from textile wastewater are in Tab. 3.

Tab. 3 STANDARDS FOR EFFLUENTS FROM TEXTILE INDUSTRY (CPCB)

PARAMETER	CONCENTRATION (mg/L) NOT TO EXCEED, EXCEPT PH
pH	5.5 – 9.0
Total suspended solids	100
Bio-chemical oxygen demand (BOD)	30
Chemical oxygen demand (COD)	250
Total residual chlorine	1
Oil and grease	10
Total chromium as Cr	2
Sulphide as S	2
Phenolic compounds as $\mathbf{C_6H_5OH}$	1

- Where the treated effluent is discharged into municipal sewer leading to terminal treatment plant, the BOD may be relaxed to 100 mg/l and COD to 400 mg/l.
- The quantity of effluent (litre per kilogram of product) shall not exceed 100, 250 and 80 in composite cotton textile industry, composite woolen textile industry and textile processing industry, respectively (CPCB).

1.4 TEXTILE DYEING WASTEWATER RISK

Discharged wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. The importance of the pollution control and treatment is undoubtedly the key factor in the human future. If a textile mill discharges the wastewater into the local environment without any treatment, it will have a serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD5, presence of particulate matter and sediments, and oil and grease in the effluent causes depletion of dissolved oxygen, which has an adverse effect on the aquatic ecological system. Effluent from textile mills also contains chromium, which has a cumulative effect, and higher possibilities for entering into the food chain. Due to usage of dyes and chemicals, effluents are dark in color, which increases the turbidity of water body. This in turn hampers the photosynthesis process, causing alteration in the habitat (Egli, 2007)

1.5 TEXTILE DYEING WASTEWATER TREATMENT PROCESSES

The textile dyeing wastewater has a huge amount of complex components with high concentrations of organic, color and changing greatly characteristics. Due to their high coloration and their salt load, the wastewater resulting from dyeing cotton with reactive dyes is seriously polluted. In the past several years, many techniques have been come into existence that are an economically and an efficient way to treat the textile wastewater such as physicochemical, biochemical, combined treatment processes and other technologies. These technologies are efficient for the textile dyeing wastewater.

1.5.1 Equalization and Homogenization

When the wastewater quality is highly polluted and there is a quantity fluctuation, complex components. Textile dyeing wastewater is generally required a pretreatment to ensure the treatment effective and stable operation. In this process, the regulating tank is set to treat the wastewater and to prevent cotton seed shell and the slurry Settle to the bottom of the tank otherwise it usually mixed the wastewater with air or mechanical mixing equipment in the tank. Generally the hydraulic retention time is about 8 hrs.

1.5.2 Floatation

In the floatation process there is a production of a large number of micro-bubbles in order to form the three-phase substances of water, gas, and solid. Dissolved air under pressure may be added to cause the formation of tiny bubbles which will attach to particles. Under the effect of interfacial tension, buoyancy of bubble rising, hydrostatic pressure and variety of other forces, the micro bubble adheres to the tiny fibers. Due to its low density, the mixtures float to the surface so that the oil particles are separated from the water. So, this method can effectively remove the fibers in wastewater.

1.5.3 Chemical Oxidation

Chemical treatment depends upon the chemical interactions of the contaminants to remove from water and the application of chemicals that either aid in the separation of contaminants from water or helps in the destruction or neutralization of harmful effects associated with contaminants. Chemical treatment methods can be used both as stand-alone technologies and as well as an integral part of the treatment process with physical methods (Ranganathan et al., 2007).

1.5.4 Adsorption

Adsorption is the most used method in physicochemical wastewater treatment, which can mix the wastewater and the porous material powder or granules such as activated carbon and clay or let the wastewater through its filter bed composed of granular materials. Through this method, pollutants in the wastewater are adsorbed and removed on the surface of the porous material or filter.

1.5.5 Aerobic Biological Treatment

According to the oxygen requirements of the different bacteria, the bacteria can be divided into aerobic bacteria, anaerobic bacteria and facultative bacteria. Aerobic biological treatment can purify the water with the help of aerobic bacteria and facultative bacteria in the aerobic environment. Aerobic biological treatment can be divided into two major categories: activated sludge process and bio film process.

1.5.6 Anaerobic Biological Treatment

Anaerobic biological treatment process is methods that make use of the anaerobic bacteria decompose organic matter in anaerobic conditions. Through making use of the anaerobic bacteria and facultative bacteria, the macromolecule, heterocyclic organic matter and other difficult biodegradable organic matter would be decomposed into small molecular organic matter, thereby enhancing the biodegradability of the wastewater and destructing the colored groups of dye molecules to remove part of the color in wastewater. Due to the molecular structure of the organic matter and colored material has been changed by the anaerobic bacteria, its easy to decompose and decolor under the aerobic conditions, which improve the decolorization effect of the sewage. In addition, there are many other processes used in textile dyeing wastewater treatment currently, such as upflow anaerobic sludge bed (UASB), upflow anaerobic fluidized bed (UABF), anaerobic baffled reactor (ABR) and anaerobic biological filter.

1.5.7 Photochemical Oxidation

Photochemical oxidation has many advantages of the mild reaction conditions such as ambient temperature and pressure, powerful oxidation ability and fast speed, etc. It can be divided into 4 kinds, which are light decomposition, photoactivate oxidation, optical excitation oxidation and photocatalysis oxidation. Among them, the photocatalysis oxidation has been more researched and applied currently. This technology can effectively destroy a lot of organic pollutants whose structure is stable and difficult to biologically degrade. Compared with the physical treatment in traditional wastewater treatment process, the most obvious advantages of this technology are significant energy efficiency, completely pollutants degradation and so on. Almost all of the organic matter can be completely oxidized to CO2, H2O and other simple inorganic substances under the light catalyst. However, towards high concentration wastewater, the effect of the photocatalysis oxidation process is not ideal.

1.5.8 Electrochemical oxidation

The mechanism of the electrochemical process treating dyeing wastewater is making use of electrolytic oxidation, electrolytic reduction, electrocoagulation or electrolytic floating destruct the structure or the existence state to make it bleached. It has the advantages of small devices, small area covering, operation and management easily, higher COD removal rate and good bleaching effect, but the precipitation and the consumption of electrode material is great, and the operating cost is high. The traditional electrochemical methods can be divided into power flocculation, electrical float, electro-oxidation, micro-electrolysis and the electrolysis method. With the development of electrochemical technologies and the appearing of a variety of high efficiency reactor, the cost of treatment will decrease largely. Electro-catalytic advanced oxidation process (AEOP) is a new advanced oxidation technology developed recently. Because of its high efficiency, easy operation, and environmental friendliness, it has attracted the attention of researchers. Under normal temperature and pressure, it can produce hydroxyl radicals directly or indirectly through the reactions in the catalytic activity electrode, thus the degradation of the difficultly biodegradable pollutants is effective. It is one of the main directions in future research.

1.6 BENEFITS OF EO FOR TEXTILE WASTEWATER

Physico-chemical treatment methods (Georgiou et al., 2002; Izares et al., 2006) are not preferred generally, for the treatment of such type of dye containing effluents due to expensive chemical coagulants, adsorbents, membranes fouling and production of large volume of secondary pollutants. Whereas, non-biodegradability of reactive dyes and high energy requirement, limits the use of biological methods for the treatment of dye containing wastewater (Chen et al., 2012; Kushwaha et al., 2010). These shortcomings i.e. large volume of secondary pollutants generation and non-biodegradability of dye bearing wastewater can be overcome by the use of electro-oxidation (EO) process. Therefore, EO does not require adding large amount of chemicals to wastewater, as in the case of chemical oxidation, with no generation of secondary pollutants (Chen 2004).

ELECTRO-CHEMICAL METHOD

2.1 GENERAL

Electrochemical treatment may be the promising water treatment technology. Electrochemical treatment is an emerging water treatment technology. The major screened-off area in the electrochemical treatment is

- Electro-Flotation (EF)
- Electro-Coagulation (EC)
- Electro-Oxidation (EO).

EF is a simple process in which hydrogen and oxygen generated from water electrolysis move upwards and takes along with them the pollutant particles to the surface of a liquid body. In EC process the anode material undergoes oxidation and hence, various monomeric and polymeric metal hydrolyzed species are formed. These metal hydroxides remove organics from wastewater by sweep coagulation and/or by aggregating with colloidal particles present in the wastewater to form bigger size flocs and ultimately get removed by settling.

2.2 ELECTRO-OXIDATION

In EO process of wastewater treatment organic contamination are oxidized directly at the surface of the electrode or oxidizing agent is generated electrochemically to perform oxidation. Complete decomposition of organic material by the oxidation of organics produces carbon dioxide and water or other oxides (Chen, 2003). Therefore, no generation of secondary pollutants takes place. The EO of wastewater or wastes can be subdivided in two categories:

- Indirect anodic oxidation (organics are destroyed at the surface of the electrode)
- Direct oxidation (a mediator is electrochemically generated to carry out oxidation)

Indirect electrooxidation involves chlorine species (Cl_2, HOCl and ClO^-) generated anodically and/or hydrogen peroxide (equation 1) with oxygen feeding and the anode is either Pb/PbO_2, $Ti/Pt/PbO_2$, or Pt etc.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

This technique can effectively oxidize many inorganic and organic pollutants at high chloride concentrations. In an indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, and hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by an oxidation reaction of the generated oxidant. All of the oxidants are generated in-situ and are utilized immediately. Among the oxidants, generation of hypochlorite is cheaper, as most of the effluents have a certain amount of chloride which gets converted to chlorine/hypochlorite. The chlorine/hypochlorite so generated oxidizes the pollutants and gets reduced to a chloride ion.

In direct anodic oxidation process, the pollutants are adsorbed on the anode surface followed by destruction by means of the anodic electron transfer reaction. Electro-oxidation of pollutants by direct anodic oxidation is due to generation of physically adsorbed "active oxygen" (adsorbed hydroxyl radicals, •OH) or chemisorbed "active oxygen" (oxygen in the oxide lattice, $MO_{x+1)}$. Following reactions (equation 2-4) are involved in the direct anodic oxidation.

$$\mathbf{MO_x + H_2O \rightarrow MO_x(\bullet OH) + H^+ + e^-} \qquad \textbf{(2)}$$

$$\mathbf{R + MO_x(\bullet OH) \rightarrow CO_2 + H^+ + e^- + MO_x} \qquad \textbf{(3)}$$

$$\mathbf{R + MOx_{+1} \rightarrow RO + MO_x} \qquad \textbf{(4)}$$

2.3 DESCRIPTION OF THE TECHNOLOGY

Electro-oxidation for wastewater treatment goes back to the 19th century, when electrochemical decomposition of cyanide was investigated. Extensive investigation of this technology commenced since the late 1970s (Anglada et al., 2009). During the last two decades, research works have been focused on the efficiency in oxidizing various pollutants on different electrodes, improvement of the electro-catalytic activity and electrochemical stability of electrode materials, investigation of factors affecting the process performance, and exploration of the mechanisms and kinetics of pollutant degradation.

2.3.1 Typical Reactor Designs

The simplest electro-oxidation reactor design is the bi-polar cell. Besides plane electrodes, the cylindrical electrodes can also be employed. In order to design an electrochemical oxidation system, the electrode material, the configuration of the cell and the operating conditions have to be taken into account. Cell configuration one of the most important issues in cell design is to maintain high mass transfer rates as the main reactions that take place in electrochemical oxidation processes take place on electrode surfaces(Anglada et al., 2009).

Two types of electrodes, mainly of two-dimensional and three dimensional constructions exist. The latter guarantee a high value of electrode surface to cell volume ratio. Both types of electrodes can be classified into static and moving electrodes. The use of moving electrodes leads to increased values of the mass-transport coefficient due to turbulence promotion. Among the two-dimensional electrodes, static parallel and cylindrical electrode cells are used in the major reactor designs in current studies of electrochemical oxidation of waste-waters. Cell designs using the parallel plate geometry in a filter press arrangement are widely deployed due to the ease of scale-up to a larger electrode size.

Besides the electrode geometry and configuration, the configuration of the cell, divided and undivided cells has to be considered in the reactor design. In divided cells, the anolyte and catholyte are separated by a porous diaphragm or an ion conducting membrane. For divided cells the choice of the separating diaphragm or membrane is as important as the appropriate choice of electrode materials for proper functioning of the electrolytic process. Overall, the use of divided cells should be avoided whenever possible, because separators are costly and tightening of a divided cell is difficult and encounters a host of mechanical and corrosion problems.

2.3.2 Electrode Material

The choice of electrode material is of paramount importance as it affects the selectivity and the efficiency of the process. The electrode material must have the following properties:

- High physical and chemical stability; resistance to erosion, corrosion and formation of passivation layers.
- High electrical conductivity.
- Catalytic activity and selectivity.
- Low cost/life ratio. The use of electrode materials that are inexpensive and durable must be favoured.

2.3.3 Electrode Types

- Doped-SnO2 electrodes: The conductivity of SnO2 is low, and thus it must be doped to obtain high conductivity and allow it to function as an effective EO electrode (Brian et al., 2014). The most common dopant is Sb, which has resulted in an electrode with high conductivity and a potential for O2 evolution.

- PbO2 electrodes: Early studies of compound oxidation at PbO2 electrodes utilized packed-bed reactors containing oxidized Pb pellets.Later studies explored PbO2 and doped-PbO2 anodes on a variety of substrates.
- Doped- and sub-stoichiometric TiO2: The conductive Magneli phase suboxides of TiO2, and doped-TiO2 are very promising electrode materials for water treatment (Brian et al., 2014).
- Boron-doped diamond electrodes: The most promising and widely studied electrode for EAOPs is BDD. BDD electrodes are commonly produced by the chemical vapor deposition (CVD) method (Brian et al., 2014).
- Ruthenium coated on titanium metal (RuOx–TiOx) electrodes is effective for the removal of organic and inorganic pollutants.
- Others electrodes are like Pt foil electrode, Ti/SnO2–Sb–Pt, graphite electrode etc.

2.3.4 Advantages of Electro-Oxidation

Electro-oxidation degradation (direct and indirect Electro-oxidation) and electro-catalysis of hazardous wastewater have several advantages compared with other treatment methods.

- Electro-oxidation treatment is able to treat very toxic wastes
- This process can operate at room temperature and atmospheric pressure.
- It is a clean technique, it does not need any chemical reagent which may be harmful or expensive.
- It can be easily operated and also optimum safety condition prevails since the oxidizing agents are generated in-situ and utilized during the electro-oxidation process.
- It neither produces any undesirable reaction co-products and sludge.

2.3.5 Disadvantages of Electro-Oxidation

- The main drawback of this process is its high operating cost due to the high energy consumption. Additionally, potential for the formation of chlorinated organics during indirect oxidation by active chlorine needs to be considered.

- The effluent has to be conducting. Unfortunately, not all waste streams will have sufficient conductance and the addition of an electrolyte may be necessary.
- Electrode fouling may occur due to deposition of material on the electrode surface.

Several investigations have been worked on the treatment of textile waste by electro-chemical method are reported below.

(Szpyrkowicz et al., 2000) studied electro-oxidation for the destruction of the pollutants present in dyeing baths containing partially soluble disperse dyes and indicate that electrochemical oxidation, which can lead to substantial decolorization, is promising for the treatment of this kind of wastewater. The efficiency of the treatment depended on the nature of the supporting electrolyte and the bulk pH in the reactor and on the type of the anode material. The best results were obtained in a chloride-rich medium under acidic pH using the Ti/Pt-Ir anode. Cyclic voltammetry study showed no direct discharge of pollutants at the Ti/Pt-Ir anode, it was concluded that the process was mediated by chlorine-hypochlorite species obtained via electro-oxidation of chlorides at the anode and OH. radicals generated during water discharge. Electro-oxidation also proved feasible in the sulfate solution medium as the supporting electrolyte, but the process efficiency was lower. In this case electrooxidation was probably mediated by OH. radicals adsorbed at the anode surface or by persulfates.

(Dogan et al., 2005) studied the electrochemical oxidation of aqueous solution of indigo (1000 ppm) in a batch divided cell for simultaneous colour removal and COD reduction. This solution was prepared at the concentration anticipated in the dyeing unit discharge. A COD reduction of 60% was obtained in 90 min, while decolourization of indigo was achieved completely by electro-oxidation between platinum electrodes. The efficiency of constant potential process was mainly influenced by chloride ions that can form chlorine/hypochlorite species at the anodic potentials and promote the progress of indirect oxidation.

Chloride concentration (0.24 mol dm−3, appox 8.5g dm3), which may be seen as an environmental problem, will decrease significantly during electrolysis, and upon mixing with the plant’s general wastewater after the electrochemical pretreatment, it will be diluted at least 100-fold, and therefore will further decrease below the discharge limits. The current efficiency was not regarded as a problem as it may be related to oxygen evolution or further decomposition of by-products and COD reduction. Cyclic voltammetric and IR studies demonstrated that partial degradation of the dye molecules was achieved. The overall experimental studies indicate that this electrochemical method can be used effectively as a pretreatment stage prior to conventional treatment.

(Rajkumar et al., 2006) concluded that all classes of reactive dyes are degraded by chlorine mediated electrochemical oxidation. Pseudo-first-order rates constant were presented for color and COD removal for various reactive dyes. The energy values given in this paper is only to get some basic idea. Since, the real textile dyeing wastewater contains higher concentrations of chloride than the experimental study, the energetic costs will be definitely be lowered when apply to highly concentrated segregated dye bath during the large-scale operations.The important limitation of the process is the formation of chlorinated organic compounds since the electrochemical oxidation is mediated by active chlorine. All classes of reactive dyes (100 mg/L) showed a complete color removal at a supporting electrolyte concentration of 1.5 g/L NaCl and 36.1 mA/cm2 current density. The chemical oxygen demand (COD) and total organic carbon (TOC) removals were from 39.5 to 82.8% and from 11.3 to 44.7%, respectively, for different reactive dyes. It can be concluded in general that the triazine containing higher molecular weight diazo compounds takes more time for complete de-colorization than the mono azo or anthraquinone containing dye compounds. The degradation rate of mixed dye compounds was affected by reaction temperature,current density, NaCl concentration and initial dye concentration. However, the initial pH of the dye solution ranging from 4.3 to 9.4 did not show significant effect on de-colorization. A complete color removal with 73.5% COD and 32.8% TOC removals were obtained for mixed reactive dyes (200 mg/L) at the end of 120 min of electrolysis under the optimum operating conditions of 4 g/L NaCl concentration and 72.2 mA/cm2 current density.

(Mohan et al., 2007) were carried out Experiments in a batch electrochemical cell for simultaneous color removal and COD reduction in the dye effluent. Due to the strong oxidizing potential of the chemicals produced the effluent COD is reduced substantially in this treatment technique. The influence of effluent initial concentration, pH, supporting electrolyte concentration and the anode material on pollutant degradation has been critically examined. The conclusions that can be made with this study are the COD reduction is significantly effected by the initial pollutant concentration, supporting electrolyte concentration and pH and the treated water can be used for effective dyeing process.

(Raghu et al., 2007) were conducted Experiments at different current densities and selected electrolyte medium using Ti/RuO2 as anode, stainless-steel as cathode in a cylindrical flow reactor. By cyclic voltammetric analysis, the best condition for maximum redox reaction rate was found to be in NaCl medium. During the various stages of electrolysis, parameters such as COD, colour, FTIR, UV–vis spectra studies, energy consumption and mass transfer coefficient were computed and presented. The experimental results showed that the electrochemical oxidation process could effectively remove colour and the chemical oxygen demand (COD) from the synthetic dye effluent. The maximum COD reduction and colour removal efficiencies were 74.05% and 100%, respectively. Reaction mechanism and modeling were proposed for the oxidation of dye effluent. The results obtained reveal the feasibilities of application of electrochemical treatment for the degradation of Procion Black 5B.

(Raghu et al., 2009) studied to reduce the energy cost during electrochemical method because the high energy cost of an electrochemical method is the fatal drawback that hinders its large scale application in wastewater treatment. The traditional single-chamber electrochemical method used in the wastewater treatment mainly focused on anodic oxidation, but hydrogen produced on the cathode and indirect electrochemical treatment involves application of an electrical current to the wastewater containing chloride to convert into chlorine/hypochlorite. The two-compartment electrolytic cell, separated by an anion exchange membrane, had been developed. In the new reactor, indirect oxidation at anode, indirect oxidation by hydrogen peroxide and ultraviolet/hydrogen peroxide (UV/H2O2) at cathode can occur simultaneously. The electrochemically produced hydrogen peroxide at the cathode by reduction of oxygen is affected by passing atmospheric air. Therefore “dual electrochemical oxidation” in one electrochemical reactor was achieved successfully. Compared to a traditional one-cell reactor, this reactor reduces the energy cost approximately by 25–40%, and thus becomes significant in wastewater treatment. Experiments were carried out at different current densities using Ti/RuO2/IrO2 as anode and carbon felt gas diffusion electrode used as a cathode fed with oxygen containing gases to produce hydrogen peroxide. During the various stages of electrolysis, the parameters such as, effect of pH, chemical oxygen demand (COD), colour, energy consumption were monitored. UV–vis spectrometry, Fourier transform infrared spectroscopy (FTIR), high-performance liquid chromatography (HPLC) studies were carried out to assess efficiencies of dye degradationin the dual electrochemical oxidation with and without UV treatment the energy consumption is markedly decreased by 25% (13.58 kWh/kg of COD) and 40% (10.97 kWh/kg of COD) respectively.

(Del et al., 2009) studied the electrochemical treatments in a divided (oxidation and reduction processes) and an undivided cell (oxido-reduction process) to mineralize and decolorize the monoazo dye PMX2R. Degradation of the dye was observed by TOC, TN and COD determinations. UV–Visible as well as HPLC technique was used to explain the differences between the three electrochemical processes studied. The decolorization for all the electrolyses performed followed a pseudo-first order kinetic as HPLC measurements revealed. It was found that oxido-reduction process gave the best result in terms of COD removal where the intermediates generated presented a very high oxidation state. It is very interesting the fact that they were stable in solution after the electrolysis as TOC removal showed. UV–Visible spectra also evidenced that these intermediates did not present aromatic structure. The greatest decolorization rate was obtained when an oxido-reduction was carried out. The reduction process produced a main product whose chemical structure was quite similar to 2-amine-1, 5-naphthalenedisulfonic acid as HPLC and UV–Visible results indicated. Then, final solution showed aromatic structures. TOC and COD removals were not very high. The oxidation process presented a more complex mechanism of decolorization since a higher number of intermediates were generated as HPLC demonstrated. This also involves a smaller decolorization rate.

The behaviors and mechanism of electrochemical decoloration of synthetic-dye water containing Rhodamine 6G were investigated by (Zheng et al., 2012). The effects of solution pH, temperature, and the addition of auxiliaries were explored. Carbon, nitrogen mass balance analyses, UV−vis, FTIR, XPS, and CV spectra were used to systematically study the decoloration mechanism. The obtained results are summarized as follows, pH and temperature played important roles for the electrochemical treatment of wastewater containing Rhodamine 6G. Lower solution pH and lower temperature facilitated the decoloration of the Rhodamine 6G containing water. The addition of auxiliaries did not obviously influence the decoloration efficiency. Complete decoloration of the dye-containing water was obtained within 5 min. TOC analysis implied that 42.3% of Rhodamine 6G was mineralized by the electrochemical treatment within 5 min. Formation of water-insoluble foam and mineralization of the Rhodamine 6G by indirect oxidation were involved during the electrochemical process. UV−vis spectra analysis showed the foam had a different molecular structure from Rhodamine 6G. FTIR, XPS, TOC, and TN analyses indicated that the amine and methyl groups were detached, which changed the dye from a polar into a nonpolar molecule and resulted in formation of a waterinsoluble substance then the water-insoluble substance was floated by the hydrogen bubble generated on the cathode.

(Senthilkumar et al., 2012) investigated degradation of Procion Scarlet a reactive dye in dye effluent is investigated by electrochemical and biological oxidation in individual, combined and integrated methods. They were focused on The Reduction of the COD and colour of the dye effluent containing Procion Scarlet dye. Individual electro oxidation process maximum COD removal of about 80% and colour removal of 97.9% was achieved at an optimum current density of about 10.25 A/dm2 whereas bio-oxidation process reduced COD and colour removal of about 50% and 42.4% respectively. Integrated process reduced the COD and colour removal of 80% and 96.4% respectively at an optimum current density range of 6.84 A/dm2, whereas combined processes showed the COD and colour removal of 90% and 98.5% respectively at an optimized current density of 7.6 and 10.2 A/dm2. After post treatment the treated effluent can be reused.

(Rajkumar et al., 2012) investigated The electro-oxidation process efficiency to removes color and COD from the Reactive Orange 107 contaminated wastewater and Optimization of electro-oxidation process for the treatment of Reactive Orange 107 using response surface methodology. The optimum conditions obtained from the statistical analysis at pH 9.4, NaCl concentration of 0.08 M, and electrolysis time of 16.0 min show maximum color and COD removal of 98%, and 90%, respectively. UV–visible spectrum confirms the decoloration and FTIR spectra show the formation of intermediates.

Several investigations have been worked on the treatment of textile waste by electro-chemical method shown in Tab. 4 and 5.

Tab. 4. REPORTED INVESTIGATIONS WITH THE EFFECT OF TIME AND PH ON THE % COD REMOVAL, % COLOR REMOVAL AND TOC REMOVAL.

NaCl conc.	**Dye**	**Reactor Type**	**Electrode**	**Current Density**	**Time**	**COD Removal**	**Color Removal**	**pH**	**TOC Removal**	**Flow rate**	**Mineralization of dye**	**References**
-	Disperse Yellow 126	undivided cell reactor	Ti/Pt-Ir	1.9 A h dm-3	40 min	39%	90%	4.5	-	-	-	Szpyrkowicz et al., 2000
.08M	Reactive Orange 107	batch electrolytic cell	Graphite electrode	34.96 mA cm−2	16 Min	90%	98%	9.4	-	-	-	Senthilkumar et al., 2012
-	Rhodamine 6G	Pyrex jacketed reactor	RuO2-coated Ti mesh as anode	-	5 min	-	100%	-	-	-	42.3%	Zheng et al., 2012
-	C.I. Reactive Orange 4	divided or undivided electrolytic cell	Ti/SnO2–Sb–Pt and stainless steel used as anode and cathode, respectively	-		An oxido-reduction process was higher than after oxidation		-	an oxidation process was higher than after oxido-reduction	-	-	Del et al., 2009

						process						
-	Procion Black 5B	cylindrical flow reactor	Ti/RuO2 as anode, stainless-steel as cathode	2.5 A/dm2		74.05%	100%	-		10 l/h	-	Raghu et al., 2007
-	All classes of reactive dyes	undivided electrochemical cell	A titanium mesh coated with oxides of titanium, ruthenium and iridium used as anode and cathode is stainless plate	72.2 mA/cm2		73.5%	100%	-	32.8%	-	-	Rajkumar et al., 2006
0.24moldm −3	CI Vat Blue 1: indigo)	batch-type divided electrolytic cell	Pt cage as anode and Pt foil as cathode.	-	90 min	60%	100%	1	-	-	-	Dogan et al., 2005

Tab. 5 REPORTED CONDITIONS FOR THE ELECTRO-OXIDATION TREATMENT OF TEXTILE INDUSTRY WASTEWATERS

Waste type	**Reactor Type**	**Electrode Type**	**Initial COD**	**% COD reduction**	**% color reduction**	**Reference**
Printing & dyeing mill ww	Electrochemical cell (Rectangular)	Expanded graphite/attapulgite anode and copper Cathode	443 g/l	43.5	90.6	Kong et al., 2009
Simulated textile ww	Stainless Steel (Circular)	Stainless steel as cathode and iron as anode	3505 mg/l	53.5	99.3	Korbahti et al., 2009
Simulated textile ww	Membraneless electrochemical reactor (Rectangular)	Platinum coated titanium as anode and stainless steel as cathode	-	-	35 by electrochemical and 92 by electroenzymatic methods	Heecho et al., 2009
Basic Red 29 (BR29) & textile ww	bipolar trickle tower (BTT)	Raschig ring shaped boron-doped diamond (BDD) electrodes	566.45 mg/L.	91	97.2	Koparal et al., 2007

Textile dyeing ww (Reactive Blue 19) (RB-19)	bench-top reactor (Rectangular)	Titanium mesh coated with TiO2-RuO2-IrO2 as anode and stainless steel as cathode	-	55.8	100	Rajkumar et al., 2007
Textile effluent (Acid Brown 14)	glass beaker of 100 ml capacity	Ti/TiO2, RuO2 coated mesh as anode and stainless steel as cathode	4800 mg/l	-	-	Mohan et al., 2007
Textile effluent	Batch type electrocoagulation and electrooxidation reactors (Rectangular)	$RuO_2/IrO_2/TaO_2$ coated titanium Rods and graphite rods used as anode and cathode	530 mg/l	93 % with graphite and 54 % with RuO2/IrO2 /TaO2 coated titanium	-	Rajua et al., 2009
Simulated textile ww	Pyrex glass electrochemical reactor (Rectangular)	Iron electrodes used as anode and cathode	3505 mg/	93.9	99.5	Korbahti et al., 2008
Simulated wastewaters	Filter-press electrochemical	boron-doped diamond electrode supported on a	-	-	90	Leonardo et al., 2007

containing the Blue Reactive 19 dye	reactor (Rectangular)	niobium substrate (Nb/BDD) and pure Ti–Pt/b-PbO2 electrodes, or doped with Fe and F				
Levafix Blue CA and Levafix Red CA reactive azo-dyes	Glass electrochemical cell (reactor) (Rectangular)	reticulated vitreous carbon cathode and a platinum gauze anode	-	90	100	Desokya et al., 2010
Textile dye wastewater containing Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes	Pyrex glass electrochemical reactor (Rectangular)	Iron electrodes used as anode and cathode	950 mg/g, 690 mg/g and 740 mg/g	32, 37 and 33	100	Korbahti et al., 2008
Mixture of exhaust dyeing solutions at a textile	Pyrex glass (Rectangular)	Aluminium and Iron electrodes used as anode and cathode connected in three modes monopolar	2031 g/m^3	63 and 65	-	Kobya et al., 2003

factory		parallel (MP-P), monopolar serial (MP-S), and bipolar serial(BP-S)				
Textile wastewater effluent	Electrolytic Cell (Rectangular)	Aluminium electrodes used as anode and cathode	4800 mg/l	97	99	Aouni et al., 2009

3.1 RESEARCH GAP

The studies reported in the open literature for textile wastewater treatment by EO method explains the treatment efficiency in terms of color removal and/or COD removal.

- Even if there is color removal, however, the dye may be present in wastewater in its degraded form. Therefore, observation of both color removal and dye degradation simultaneously explains the true treatment efficiency.
- Energy consumption during the EO treatment is very important aspect in view of operating cost, which is lacking in literature available.
- During the EO process, dye is first degraded to some intermediates, and these intermediates are further oxidized to carbon dioxide and water (Sundarapandiyan et al., 2010) by various chlorine species (HOCl and ClO^-) as discussed earlier. Therefore, in point of view of disposal of treated wastewater, identification of various degraded dye intermediates and chlorinated organic compounds formed is important.
- No study was reported on CBSOL LE red wool dye degradationby EO process.

CHAPTER-4

OBJECTIVES

In the present study, EO of CBSOL LE red wool dye containing wastewater was studied with RuO_2 coated Ti electrode (Ti/RuO_2).

- To study the effect of EO processes parameters like pH, current (i) and time (t) on % dye degradation(%DR), % color removal (% CR) and energy consumed (EC).
- Modeling of degradation and color removal of CBSOL LE red wool dye by EO process with Artificial neural networks (ANNs) .
- Optimization of degradation and color removal of CBSOL LE red wool dye by EO process using Response surface methodolgy (RSM).

CHAPTER-5

EXPERIMENTAL SETUP AND PROCEDURE

5.1 GENERAL

In EO process of wastewater treatment organic contamination are oxidized directly at the surface of the electrode or oxidizing agent is generated electrochemically to perform oxidation. This chapter reports the use of electro-oxidation for the treatment of textile wastewater with Ti/RuO_2 as a cathode and aluminum plate as an anode. Experiments were conducted in a batch setup to investigate the effects of current (I), pH, time on %age of removal, %age of color removal and specific energy consumed in Wh.

5.2 LAB SCLAE EXPERIMENTAL SETUP

The electro oxidation reactor was fabricated with acrylic plexi glass sheet of thickness 5mm having the working volume of 1.5 *l*. Ti/RuO2 and aluminium electrodes having the dimensions of 100x85x1 mm were used as anode and cathode respectively. The direct current power supply (DIGITECH, Roorkee, India, Model: 4818A10) was used to supply the current during experiments. Magnetic stir was used to agitate the wastewater sample . The schamatic diagram of experimental setup was shown in Figure no.1.

FIGURE NO.1 Electro-Oxidation set up

5.3 PREPARATION OF THE SAMPLE

CBSOL LE dyes are metal free reactive dyes developed for wool dyeing. These dyes form covalent bond with wools amino acids during the dyeing process. Simulated dye wastewater was prepared by dissolving 100 mg CBSOL LE red wool dye in 1 *l* of distilled water.

5.4 EXPERIMENTAL PROCEDURE

The pH of the dye solution was adjusted to the desired level by adding 0.1N NaOH or 0.1 N HC*l* solutions. NaCl was used to maintain the conductivity of the solution upto 10^{-3} mS. Electrodes were clean with successive rinses of water to remove the carbon deposited during the reaction. The electrode spacing was fixed to 1 cm. DC power supply was provided for EO process. Spectro-photometric technique was used to measure the concentration of dye in solution after the treatment of sample. At 270nm the absorbance was measured to determine the %age of dye removal. 504 nm the absorbance of the sample was measured to determine the %age of color removal and wavelength 504 nm scanning plot.

5.5 ANN MODELING

ANN is relatively basic models based on the neural structure of the brain i.e. ANN's are stimulated by biological neural systems as shown in Figure no. 2. Neurons are simple processing units of ANN. An artificial neuron is a computational model inspired from natural neurons. The complexity of real neurons is highly abstracted when modelling artificial neurons. Each network of ANN consists of artificial neurons which are grouped in a layer and have parallel relation to each other. ANN network consist of inputs which are multiplied by weights to maintain the strength of the respective signals, and then computed by a mathematical function which determines the activation of the neuron. Adjusting of weights to process the information is called learning or training. The first neural model by McCulloch and Pitts has been developed hundreds of different models considered as ANN in 1943. Presently an ANN which learns using the backpropagation algorithm for learning the appropriate weights is one of the most common models used in ANN. ANN are now commonly used in many areas of research (Aleboyeh et al., 2008) predict decolorization of azo dye by UV/H_2O_2 using artificial neural networking. Two types of ANNs commonly used are Kohonen self organizing mapping and Multilayered feed forward neural network trained by backpropagation algorithm. (Slokar et al.,1999) discuss about the use of ANN for modelling of H_2O_2/UV decoloration process. (Salari et al., 2009) discuss about the electrochemical treatment of dye solution containing C.I Basic Yellow 2 by the peroxi-coagulation method and modelling of the experimental results was done by ANN. (Bhatti et al 2011) discuss about the RSM and ANN modeling for electrocoagulation of copper from simulated wastewater by Multi objective optimization using genetic algorithm approach.

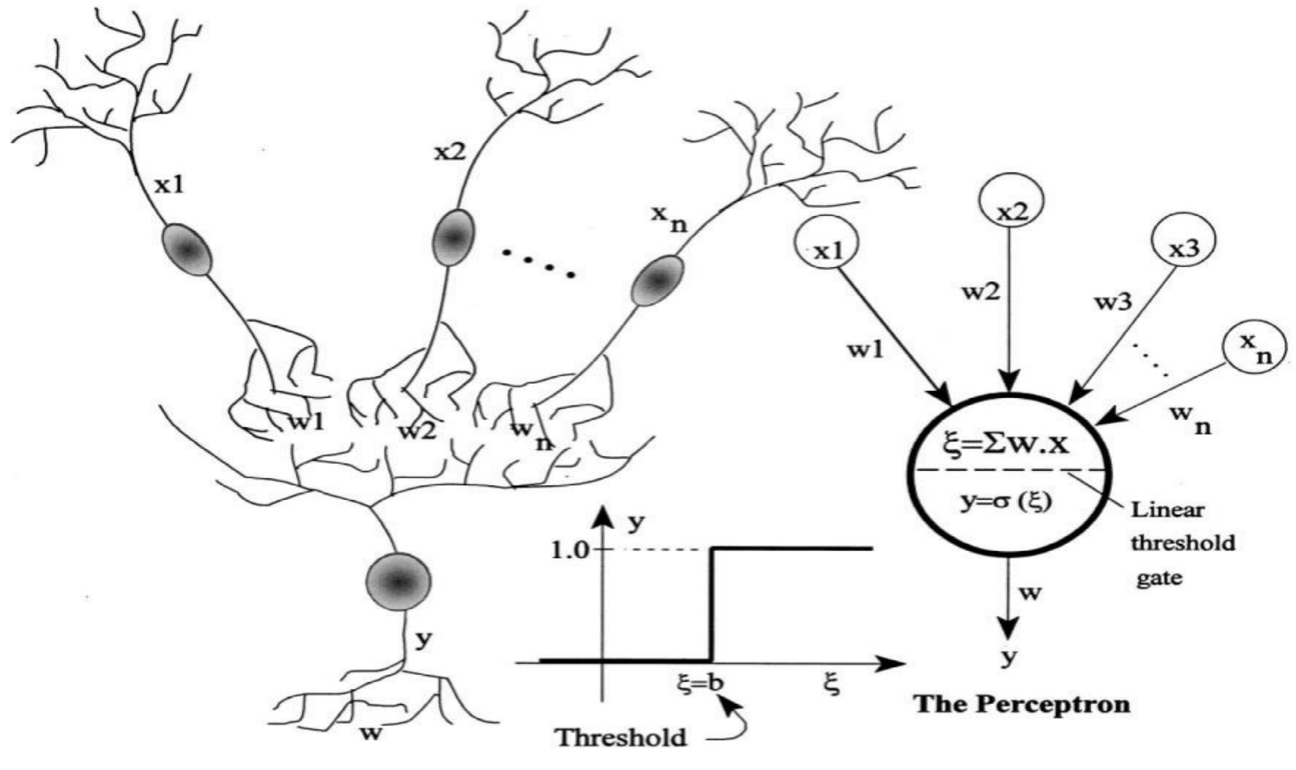


FIGURE NO. 2 ANN based on natural neuron structure

5.5.1 The Backpropagation Algorithm

The backpropagation algorithm is used in layered feed-forward ANNs. This means that the artificial neurons are organized in layers, and send their signals “forward”, and then the errors are propagated backwards. The network receives inputs by neurons in the input layer, and the output of the network is given by the neurons on an output layer. There may be one or more intermediate hidden layers. The backpropagation algorithm uses supervised learning, which means that we provide the algorithm with examples of the inputs and outputs we want the network to compute, and then the error or difference between actual and expected results is calculated. The backpropagation algorithm is to reduce this error, until the ANN learns the training data. The training begins with random weights, and the goal is to adjust them so that the error will be minimal. The activation function of the artificial neurons in ANNs implementing the backpropagation algorithm is a weighted sum. The activation depends only on the inputs and the weights. If the output function would be the identity (output=activation), then the neuron would be called linear. The perceptron is an algorithm for supervised classification of an input into one of several possible non-binary outputs. It is a type of linear classifier. But these have severe limitations. The most common output function is the sigmoidal function. The sigmoidal function is very close to one for large positive numbers, 0.5 at zero, and very close to zero for large negative numbers. This allows a smooth transition between the low and high output of the neuron. The output depends only in the activation, which in turn depends on the values of the inputs and their respective weights. The goal of the training process is to obtain a desired output when certain inputs are given. Since the error is the difference between the actual and the desired output, the error depends on the weights, and we need to adjust the weights in order to minimize the error. Figure no. 3 shows backpropagation algorithm.

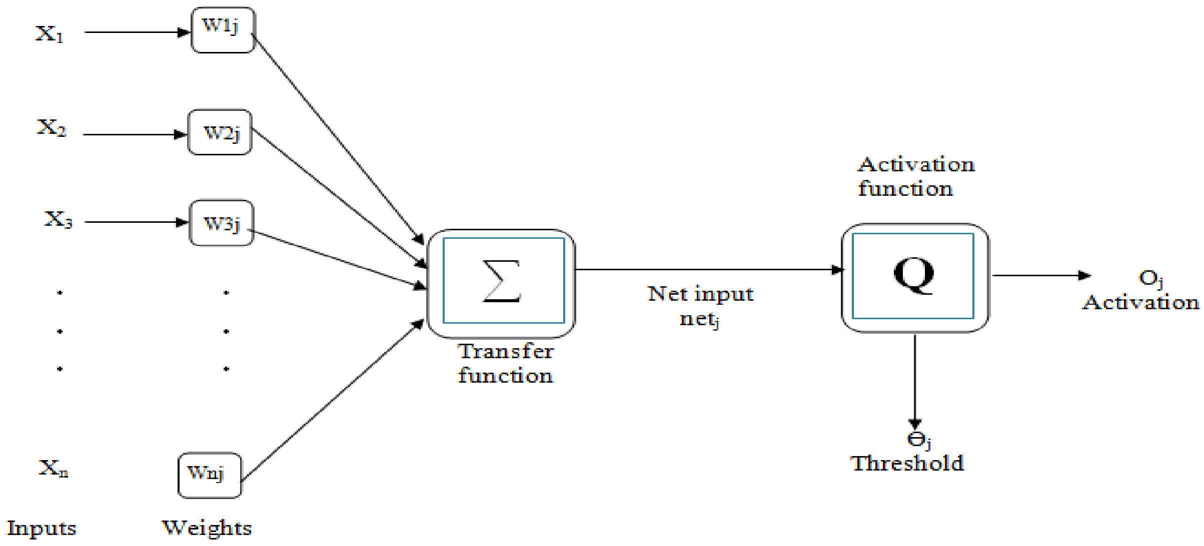


FIGURE NO. 3 Backpropagation Algorithm

5.6 RSM OPTIMIZATION

Response surface methodology is a collection of mathematical and statistical techniques that are useful for modeling analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response. The application of RSM to design optimization is aimed at reducing the cost of expensive analysis methods and their associated numerical noise. An important aspect of RSM is the design of experiments. These strategies were originally developed for the model fitting of physical experiments, but can also be applied to numerical experiments. The objective of design of experiment is the selection of the points where the response should be evaluated. Most of the criteria for optimal design of experiments are associated with the mathematical model of the process. Generally, these mathematical models are polynomials with an unknown structure, so the corresponding experiments are designed only for every particular problem. The choice of the design of experiments can have a large influence on the accuracy of the approximation and the cost of constructing the response surface. In a design of experiment, screening experiments are performed in the early stages of the process, when it is likely that many of the design variables initially considered have little or no effect on the response. The purpose is to identify the design variables that have large effects for further investigation. Central Composite Design based on RSM was used for experimental design. There are certain authors which used Response Surface Methodology (RSM) for the optimization of the process (Rajkumar et al., 2012) used central composite design to optimize the electro-oxidation process for Reactive Orange 107 dye, (bahadhir et al., 2008) used central composite design for five factors to optimize the electro-oxidation process and (Samane et al., 2013) used RSM for the optimization of electro-coagulation process.

5.6.1 Central Composite Design

A second-order model can be constructed efficiently with central composite designs (CCD). CCD is first-order (2^N) designs augmented by additional centre and axial points to allow estimation of the tuning parameters of a second-order model. The practical development of a CCD often arises through sequential experimentation. (2^N) designs have been used to fit a first order model, the model has exhibited lack of fit and the axial runs are then added to allow the quadratic terms to be incorporated into the model. Central composite design for N=3 as shown in Figure no. 4. There are two parameters in the design that must be specified, the distance of the axial runs from the design center and the number of center points.

The CCD is very efficient design for fitting the second order model.

$$Y = b_o + \sum_{i=1}^{3} biXi + \sum_{i=1}^{3} biiXi^2 + \sum_{i=j}^{2} \sum_{i=j+1}^{3} bijXij$$

Where, Y is response; bo, bi, bii, bij are constant coefficients and Xi the uncoded independent variables. The significant terms in the model were found by analysis of the variance (ANOVA) for each response. The model adequacies were checked by predicted-R^2, adjusted-R^2, R^2, and prediction error sum of squares.

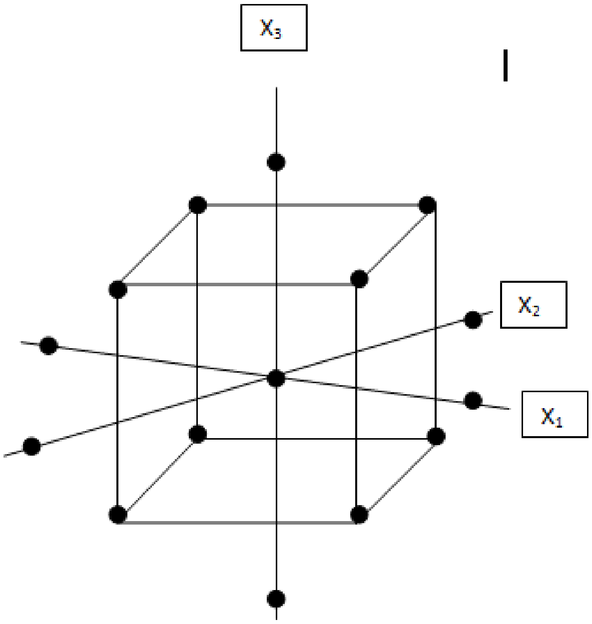


FIGURE NO. 4 central composite design for N=3

Rotatability is important for the second order model to provide good predictions throughout the region of interest. So, it is required that the model have a reasonably consistent and stable variance of the predicted response at a point. A CCD is made rotatable by the choice of the distance of an axial run. The distance of an axial run depends upon the number of points in the factorial portion of the design to yield a rotatable CCD. Rotatability is a spherical property it makes most sense as a design criterion when the region of interest is a sphere. However ,it is not important to have exact rotatability to have a good design infact for a spherical region of interest, the best choice of the distance of an axial run (a) from the prediction variance viewpoint for the CCD is to be set $a=N^{1/2}$. This design is called as spherical CCD, puts all the factorial and axial design points on the surface of a sphere of radius $N^{1/2}$.

5.6.2 Desirability

The desirability function approach to simultaneously optimizing multiple equations was originally purposed by Harrington. It is an approach to translate the functions to common scale, combine them using the geometric mean and optimize the overall metric. There are three responses therefore multiresponse process optimization by the desirability function approach was used for the optimization of the EO process parameters. The desirability function approach is one of the most widely used methods for the optimization of multiple response processes

One-sided desirability di is given by:

$$d_i = \begin{cases} 0 & \text{if Yi <=Yi\_min} \\ \left[\dfrac{y_i - y_{i-\min}}{y_{i-\max} - y_{i-\min}}\right]^r & \text{if Yi\_min < Yi < Yi\_max} \\ 1 & \text{if Yi >=Yi\_max} \end{cases}$$

Where Yi is response value, Yi-min and Yi-max are minimum and maximum acceptable values of response i, and r is a weight and a positive constant used to determine scale of desirability. The desirability (d_i) lies between 0 and 1, representing the closeness of a response to its ideal value. In multiresponse process optimization, the desirability function transforms each response in to a corresponding desirability value between 0 and 1 (Sangal et al., 2013). All the desirability functions are combined to form a composite desirability function, which converts multiresponses into a single response. The individual desirability functions are combined in order to obtain the overall desirability, D as follows:

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

Where 0<=D<=1, and k is the number of responses.

If all of the quality characteristics reach their ideal values d_i is 1for all i. Consequently, the total desirability is also 1. If any one of the responses does not approach its ideal value, the d_i is less than 1 for that response and the total desirability is therefore also less than 1.

CHAPTER-6

RESULTS AND DISCUSSION

6.1 GENERAL

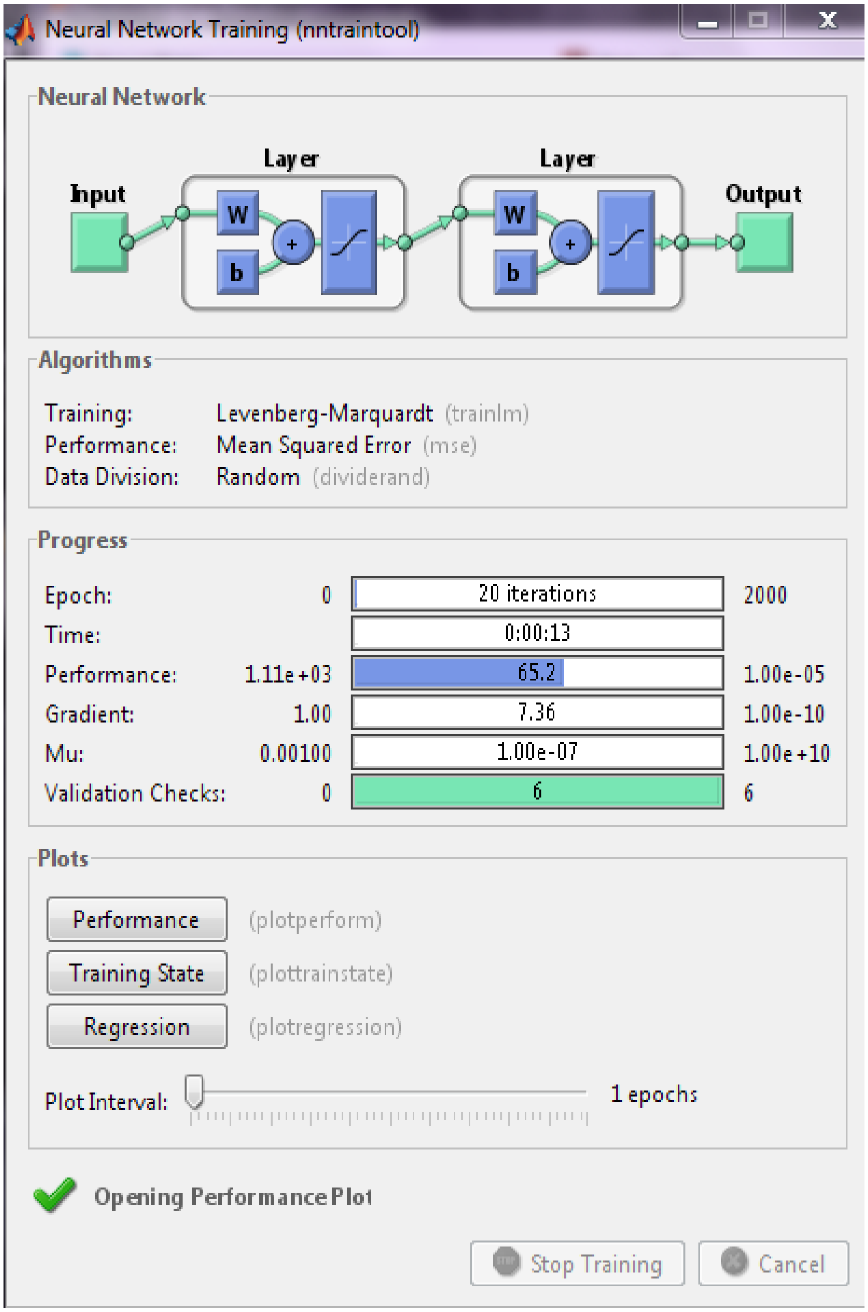
The experimental results of dye degradation and color removal from a synthetic CBSOL LE dye wastewater by electro-oxidation method with Ti/RuO_2 coated plate as an anode and aluminum plate as a cathode have been discussed in this chapter. The treatment process shows a considerable color removal and dye degradation, the results and their interpretation have been discussed in detail.

6.2 RESULTS AND DISCUSSION

6.2.1 MODELING OF EO PROCESS WITH ANN

The modeling of EO process having three process variables (pH, i and t) and three response (%DR, % CR and EC) is quite complex. Obsiviously, such problem cannot be solved by simple linear multivariate correlation (Salari et al., 2009). Since, Modeling based on ANNs does not require the mathematical description of the phenomena involved in the process. Therefore, ANNs was used for modeling of EO process.

Model was designed with sigmoid transfer functions. We had chosen pH, time and current as input variables and % of color removal, % of dye degradation and specific electrical energy consumption as output variables. Selection of optimum number of hidden layer neurons in the ANN architecture is most important step. A number of training runs were performed out to look out for the best possible weights in error back-propagation framework. MATLAB (The Mathworks, Inc. ver. 7.6) computing environment was chosen to generate neural network model from the data. Preprocessing of the inputs and output was done by randomization to make the neural network training more efficient. Hyperbolic tangent 'TANSIG' being a sigmoid transfer function was chosen for the input to hidden layer mapping while a purely linear transfer function 'PURELIN' was chosen for the hidden layer to the output layer mapping and the final selected network architecture was trained for 2000 iterations shown in Figure no. 5.



Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Epoch:	0	20 iterations	2000
Time:		0:00:13	
Performance:	1.11e+03	65.2	1.00e-05
Gradient:	1.00	7.36	1.00e-10
Mu:	0.00100	1.00e-07	1.00e+10
Validation Checks:	0	6	6

(plotperform)
(plottrainstate)
(plotregression)

Plot Interval: 1 epochs

✓ Opening Performance Plot

FIGURE NO. 5 Network training

Figure no.6 shows the performance plot which provides the information about the training of network by comparing the performance of testing, training and validation with best. This plot was between mean square error of training network and epochs taken by the network to become trained.

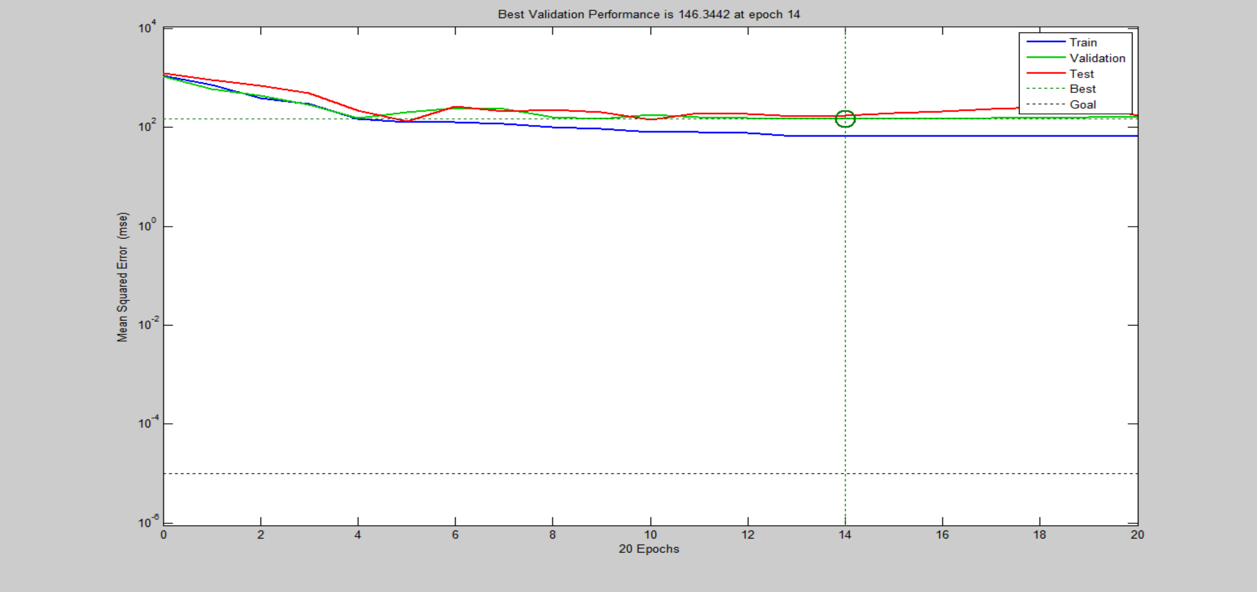


FIGURE NO. 6 Performance plot

Number of hidden layer neurons in the ANN architecture was optimized with the reduction in the mean square error. Optimized neurons for the process were eight as shown in Figure no. 7. Increase in the number of hidden layer neurons compromises the generalization ability of the ANN at the cost of minimizing the training data set error. We had trained the model with 8 neurons in the first layer or input layer and 8 neurons in the second or output layer. The training function was trainlm.

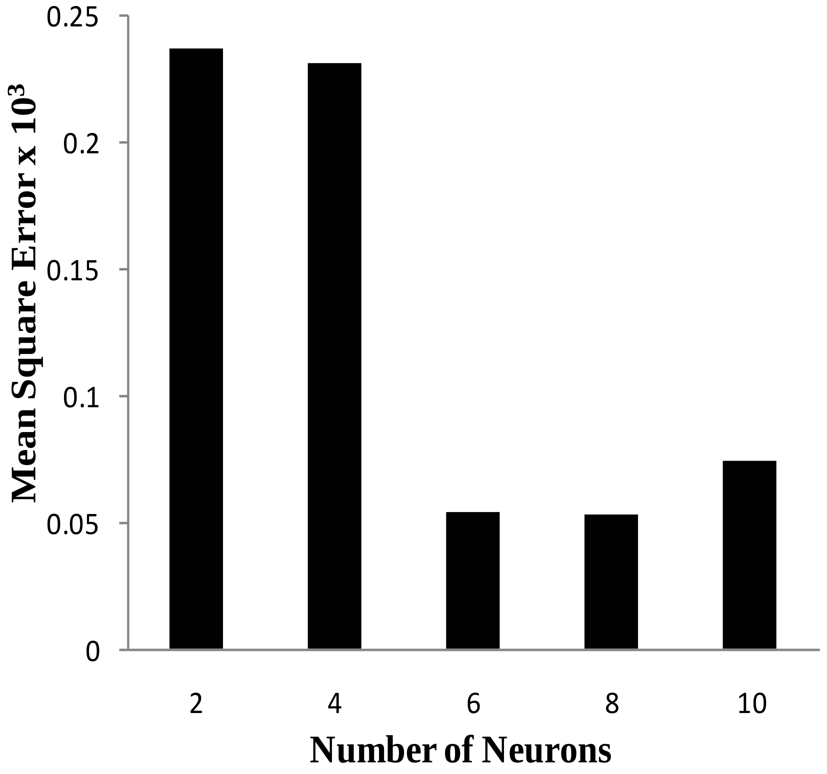
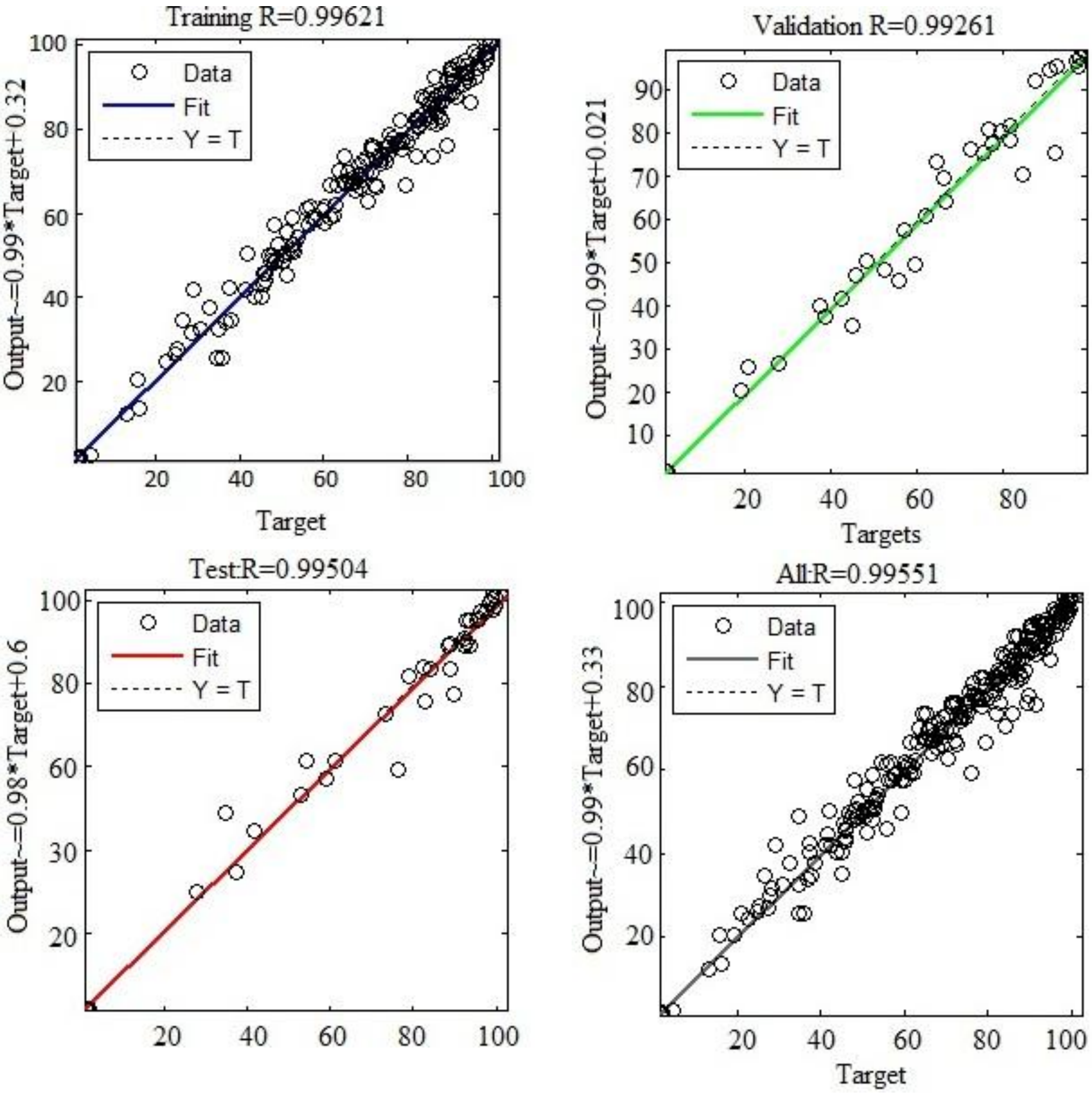


FIGURE NO. 7 Effect of the number of hidden layer neurons on the performance of neural network

The regression plots of the trained network are shown in Figure no. 8. The training versus target gives regression coefficient of 0.995 along with validation, test and all data sets regression coefficient value 0.992, 0.996, 0.995 respectively. Which implied that training of the ANN model was done accurately and model was ready to stimulate the outputs from a given inputs.



Training R=0.99621

Validation R=0.99261

Test:R=0.99504

All:R=0.99551

FIGURE NO. 8 The regression plots of the trained network

The function sim simulates a network. The output was predicted from a given input after stimulation of the network. The ANN model reduce the experimental work, with the generation of this ANN model without performing experiments we can predict the output values by artificial intelligence.

6.2.2 RSM OPTIMIZATION

6.2.2.1 Central composite design (CCD)

Central Composite Design based on RSM was used for experimental design. The stimulated data from ANN was analyzed using Design Expert trail 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 Stimulated data obtained from AAN modeling require optimization. Three operation parameters variables current (I) 0.25-1.25A, electrolysis time (t) 10-90 min and pH 4-10 was considered as input parameters and %age of color removal, %age of dye degradation and specific electrical energy consumption was taken as responses of the system. Tab. 6 shows various operational variables and their levels whereas simulated experimental design matrix.

A total number of 20 simulation experiments designed by RSM, were conducted to study the effects of the three parameters pH, current, time on response %age of dye degradation (Y_1), %age of color removal (Y_2) and specific electrical energy consumption (Y_3). Full Factorial Design used for the electro-oxidation of textile wastewater as shown in Table no 7.

Tab. 6 RANGE OF VARIABLES AND LEVELS OF THE DESIGN MODEL

FACTORS	**VARIABLES**	**Range of actual and coded variables**		
		(-1)	**(0)**	**(+1)**
A	pH	5.50	7	8.50
B	Time (min)	30	50	70
C	I(A)	0.50	0.75	1.00

TAB. 7 FULL FACTORIAL DESIGN USED FOR THE ELECTRO-OXIDATION OF TEXTILE WASTEWATER.

Std	**Run**	**Block**	**pH**	**t (min)**	**I(A)**	**% dye removal, Y_1**	**% color removal, Y_2**	**energy consumed(Wh), Y_3**
1	1	Block 1	5.50	30.00	0.50	41.55	59.03	0.995
16	2	Block 1	7.00	50.00	0.75	62.24	79.81	2.297
14	3	Block 1	7.00	50.00	1.25	80.49	94.32	7.283
3	4	Block 1	5.50	70.00	0.50	62.89	81.45	2.221
19	5	Block 1	7.00	50.00	0.75	62.24	79.81	2.297
10	6	Block 1	10.00	50.00	0.75	68.02	89.12	3.124
8	7	Block 1	8.50	70.00	1.00	97.77	98.98	4.825
9	8	Block 1	4.00	50.00	0.75	80.63	90.84	2.844
6	9	Block 1	8.50	30.00	1.00	93.68	92.04	3.31
11	10	Block 1	7.00	10.00	0.75	43.79	50.85	0.602
18	11	Block 1	7.00	50.00	0.75	62.24	79.81	2.988
13	12	Block 1	7.00	50.00	0.25	30.82	53.46	0.813
15	13	Block 1	7.00	50.00	0.75	62.24	79.81	2.988
4	14	Block 1	8.50	70.00	0.50	52.79	75.58	2.546
12	15	Block 1	7.00	90.00	0.75	80.49	92.53	5.377
20	16	Block 1	7.00	50.00	0.75	62.24	79.81	2.988
17	17	Block 1	7.00	50.00	0.75	62.24	79.81	2.988
7	18	Block 1	5.50	70.00	1.00	89.96	98.25	6.217
5	19	Block 1	5.50	30.00	1.00	83.72	76.41	3.005
2	20	Block 1	8.50	30.00	0.50	32.61	55.33	1.357

The stimulated data was analyzed using Design Expert trail 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.

6.2.2.2 Statistical Analysis

The responses ($Y_{1,}$ Y_2 and Y3) by electro-oxidation of textile wastewater with aluminum plate as a cathode and Ti/RuO2 as an anode were calculated according to the setting of various operational parameters as given in design matrix of experiments and results are shown in Tab. 7. Quadratic model was fitted to the simulated data to obtain the regression equations. Inverse transformation was used for Y_1 and Y_3. Sequential model sum of squares and model summary statistics were tested to decide the adequacy of model. The results about the adequacy of model were shown in Tab. 8 - 10 for the responses $Y_{1,}$ Y_2 and Y_3 respectively. Sequential model sum of squares showed that quadratic model best fits the simulated data for responses $Y_{1,}$ Y_2 and $Y_{3.}$ Higher order models were found to be aliased for responses.

Tab. 8 SEQUENTIAL MODEL SUM OF SQUARES FOR % DYE DEGRADATION USING INVERSE TRANSFORM (Y_1).

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	5.684E-003	1	5.684E-003			
Linear	5.779E-004	3	1.926E-004	19.81	< 0.0001	
2FI	6.197E-005	3	2.066E-005	2.87	0.0772	
Quadratic	8.692E-005	3	2.897E-005	43.12	< 0.0001	Suggested
Cubic	4.403E-006	4	1.101E-006	2.85	0.1215	Aliased
Residual	2.316E-006	6	3.860E-007			
Total	6.418E-003	20	3.209E-004			

Tab. 9 SEQUENTIAL MODEL SUM OF SQUARES FOR % COLOR REMOVAL (Y_2).

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Mean	1.259E+005	1	1.259E+005			
Linear	3434.80	3	1144.93	30.79	< 0.0001	
2FI	144.59	3	48.20	1.39	0.2897	
Quadratic	402.15	3	134.05	27.77	< 0.0001	Suggested
Cubic	45.54	4	11.38	25.00	0.0007	Aliased
Residual	2.73	6	0.46			
Total	1.300E+005	20	6498.31			

Tab.10 SEQUENTIAL MODEL SUM OF SQUARES FOR ENERGY CONSUMED (Y_3).

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Mean	186.4467	1	186.4467			
Linear	50.99176	3	16.99725	46.75921	< 0.0001	
2FI	1.437397	3	0.479132	1.422505	0.2810	
Quadratic	2.441433	3	0.813811	4.20082	0.0364	Suggested
Cubic	1.220754	4	0.305189	2.555616	0.1462	Aliased
Residual	0.716513	6	0.119419			
Total	243.2546	20	12.16273			

The model gives coefficient of determination predicted R^2 value of 0.9287, 0.9073, 0.8018 for $Y_{1,}$ Y_2 and Y_3 respectively, adjusted R^2value of 0.9826, 0.9772, 0.9352 for $Y_{1,}$ Y_2 and Y_3 respectively and R^2 value of 0.9908, 0.9880 and 0.9659 for $Y_{1,}$ Y_2 and Y_3 respectively This advocates a good correlation between the observed and predicted values as shown in Figure no. 9-11. The predicted values were closer to the actual values. Figure no. 12-14 shows close relation between % Normal probability and Studentized residual. Which was implies that the difference between a predicted value and the observed value dividing by the standard error of the residual have close relation with % Normal probability.

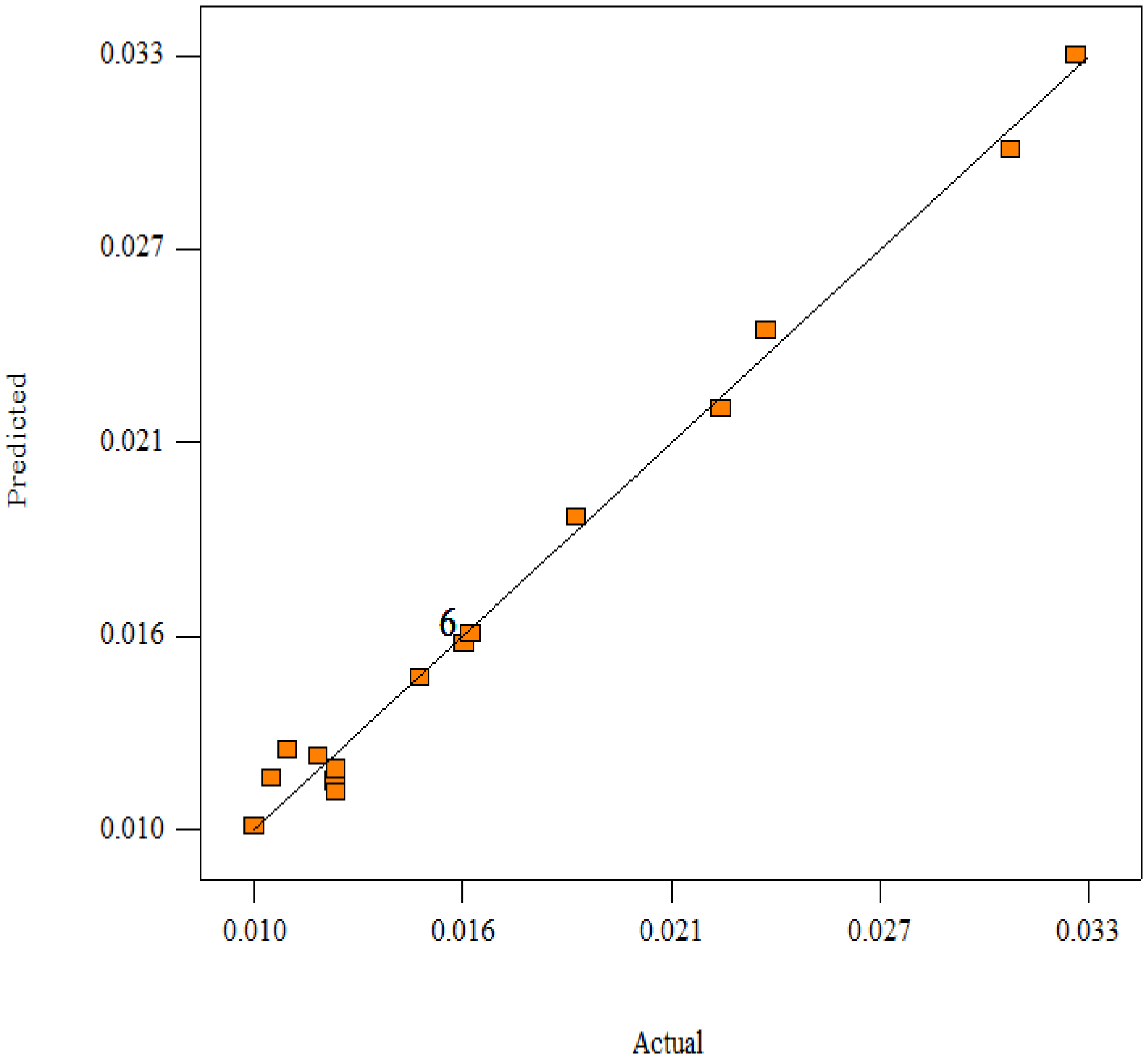


FIGURE NO. 9 Residual plots (actual versus predicted) for electro-oxidation of CBSOL red LE wool dye for %Dye degradation

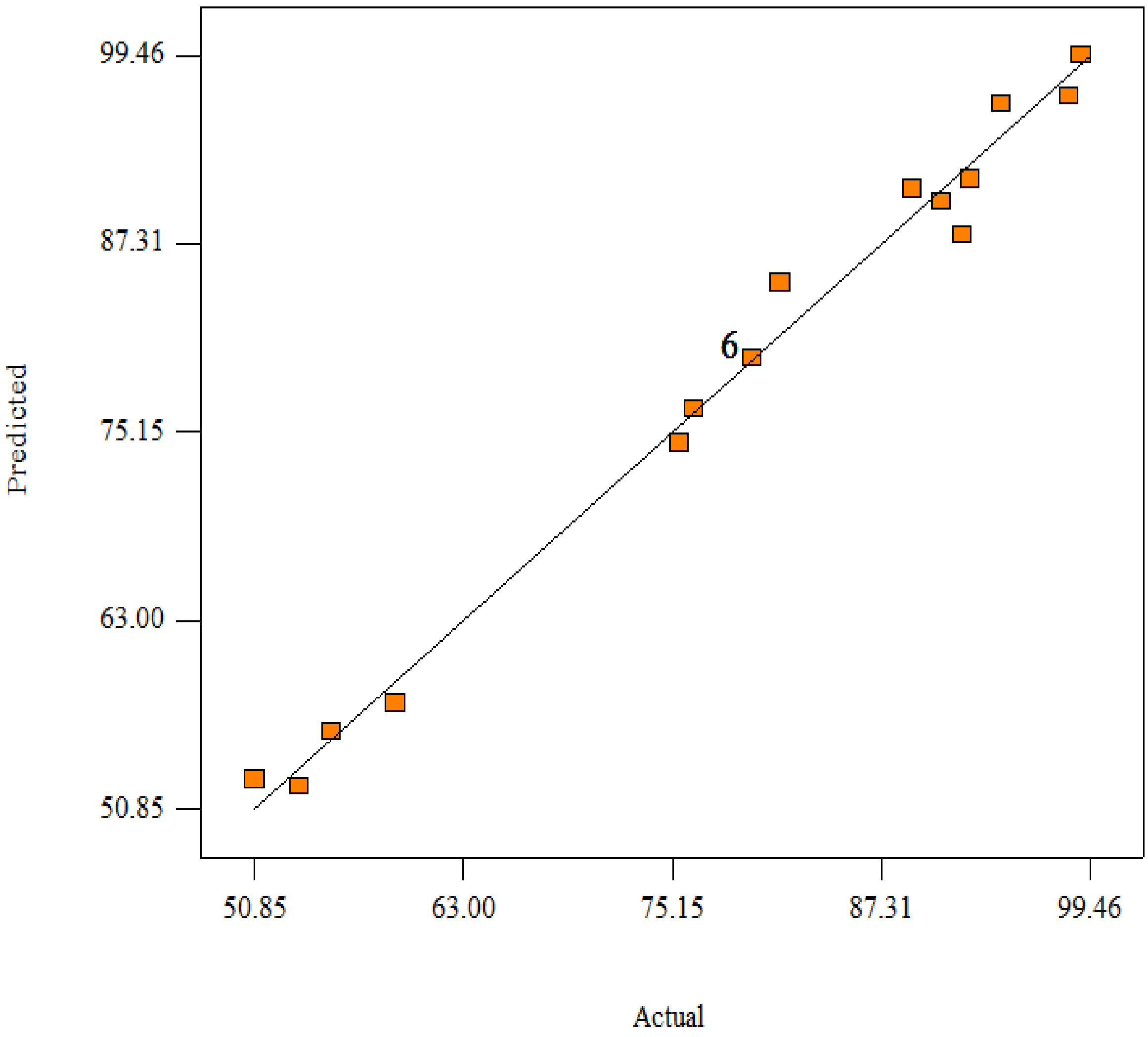


FIGURE NO. 10 Residual plots (actual versus predicted) for electro-oxidation of CBSOL red LE wool dye of %Color Removal

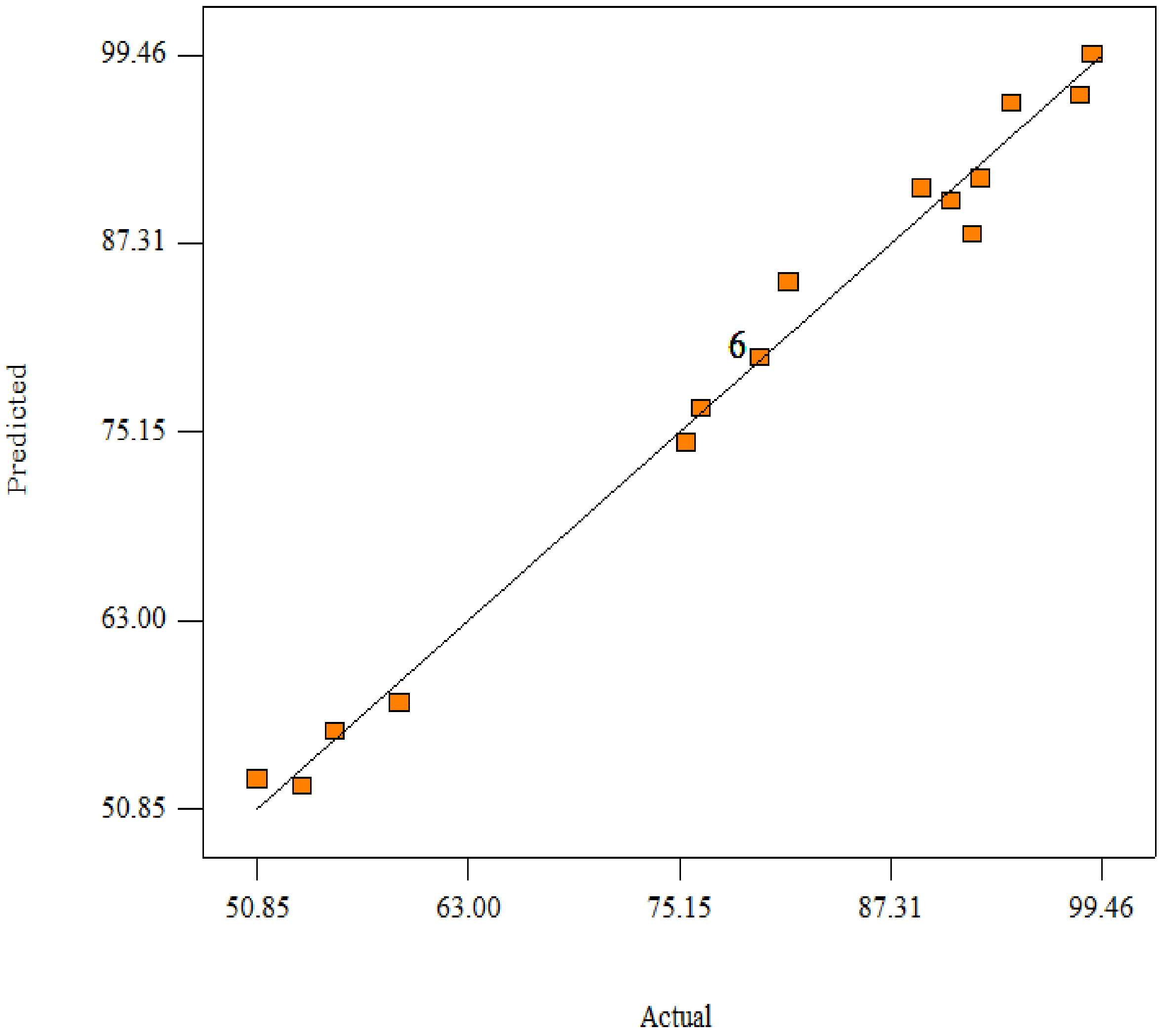


FIGURE NO. 11 Residual plots (actual versus predicted) for electro-oxidation of CBSOL red LE wool dye of Energy consumption

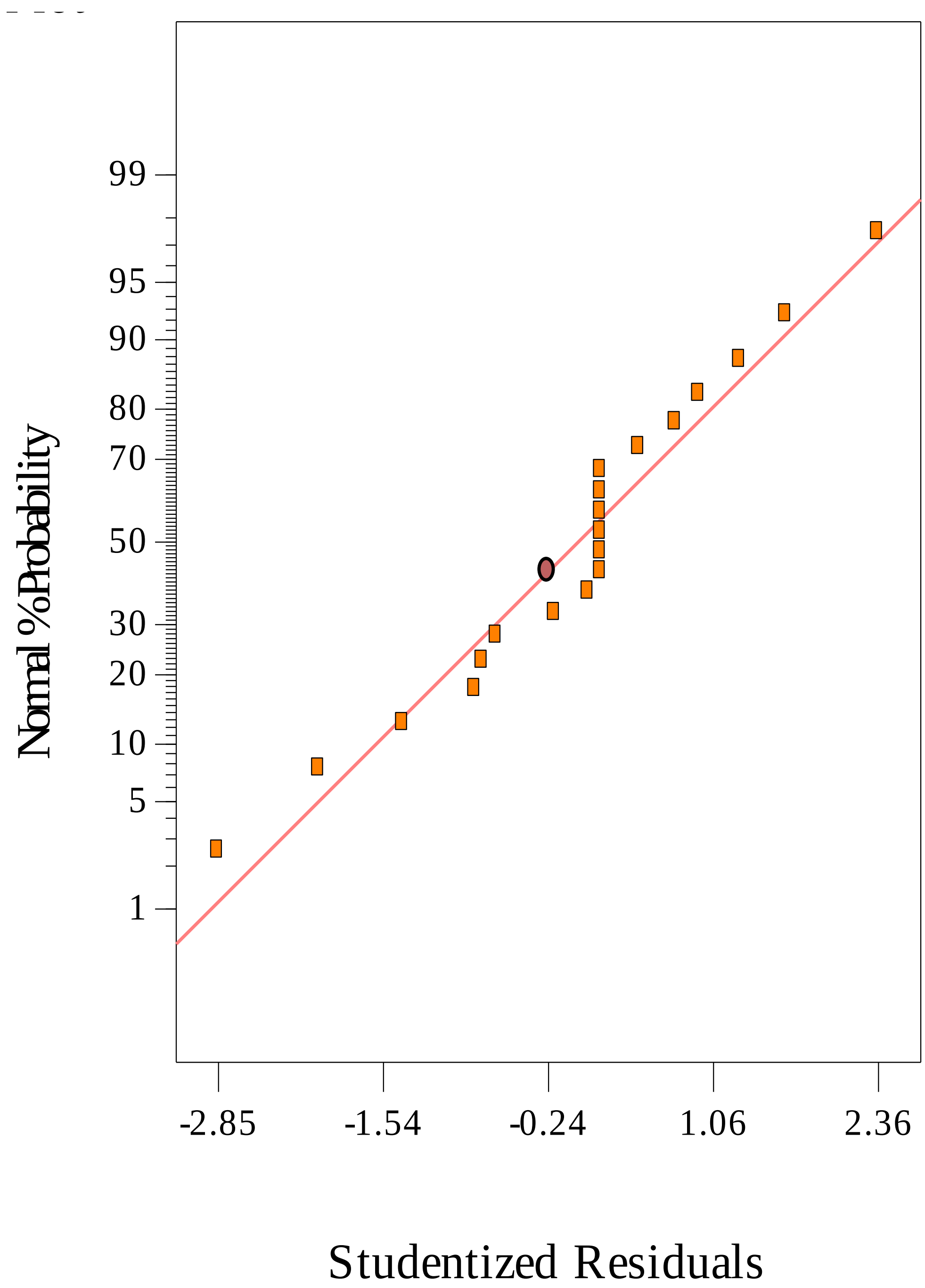


FIGURE NO. 12 Residual plots for electro-oxidation of CBSOL red LE wool dye of %Dye degradation

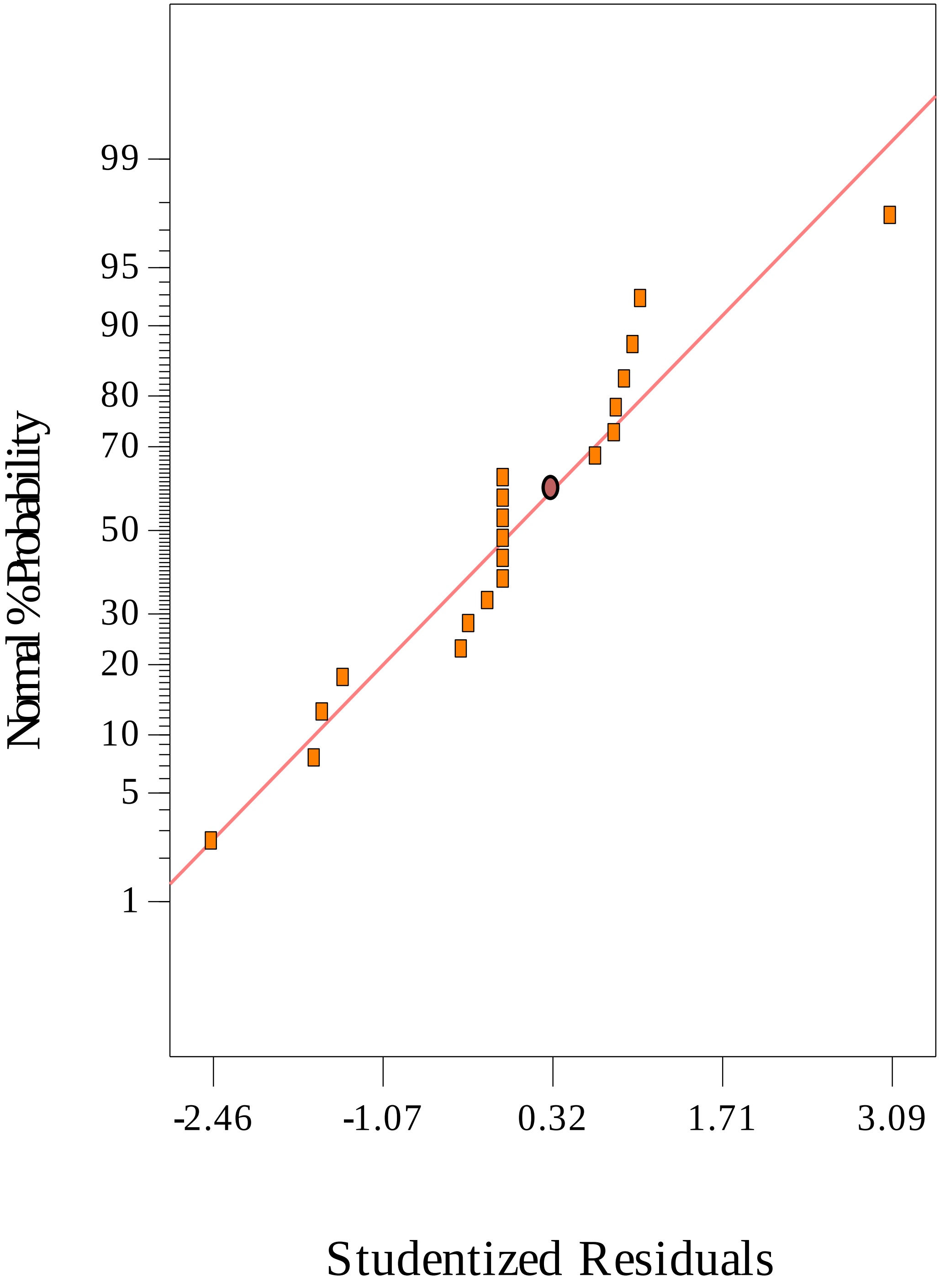


FIGURE NO. 13 Residual plots for electro-oxidation of CBSOL red LE wool dye of %Color Removal

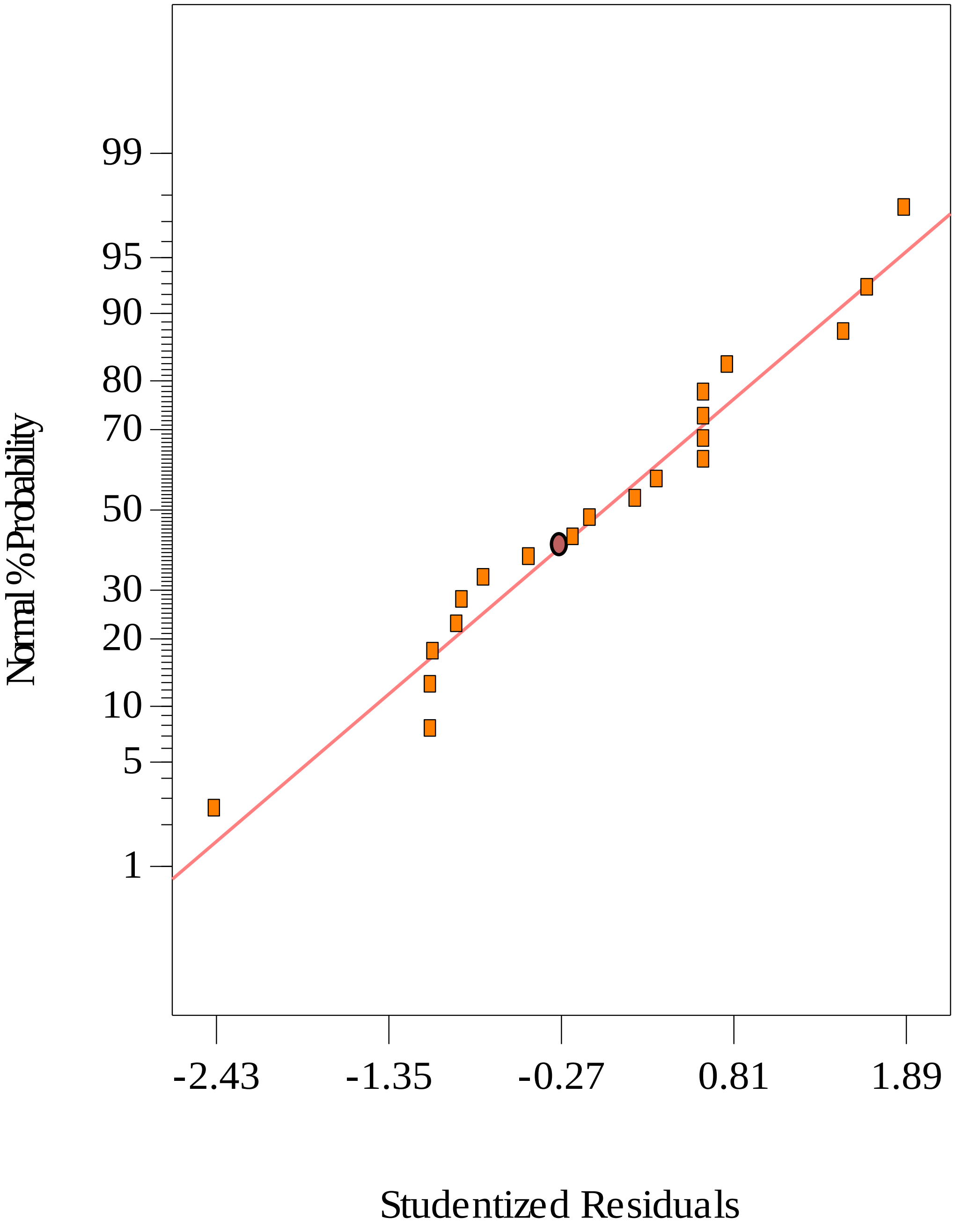


FIGURE NO. 14 Residual plots for electro-oxidation of CBSOL red LE wool dye of Energy consumption

The analysis of variance (ANOVA) shows model F-value of 120.19, 91.65, 47.58 for Y_1, Y_2 and Y_3 respectively. This implies that model considered is significant for Y_1, Y_2 and Y_3

responses as shown in Tab. 11 - 13 for model terms to be significant, “prob>F” values should be less than 0.05 “prob>F” values larger than 0.100 indicates that model term are insignificant.

The response surface models shows that time, current, current^2, time X current, were highly significant terms for (%degradation of dye) Y_1 response. pH, pH^2, Time^2, pH X current were significant terms for Y_1 response. pH X Time was not a significant terms for Y_1 response as shown in Tab. 11.

Tab. 11 ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL FOR %DEGRADATION OF DYE USING INVERSE TRANSPOSE.

Source	**Sum of Squares**	**DF**	**Mean Square**	**F-Value**	**P- value Prob > F**	
Model	7.268E-004	9	8.075E-005	120.19	< 0.0001	Significant
Ph	9.122E-006	1	9.122E-006	13.58	0.0042	
Time (T)	1.102E-004	1	1.102E-004	164.00	< 0.0001	Highly significant
Current(I)	4.586E-004	1	4.586E-004	682.52	< 0.0001	Highly significant
pH^2	1.214E-005	1	1.214E-005	18.07	0.0017	
Time^2	2.649E-006	1	2.649E-006	3.94	0.0752	
current^2	5.854E-005	1	5.854E-005	87.12	< 0.0001	Highly significant
pH X Time	1.259E-006	1	1.259E-006	1.87	0.2010	
pH X Current	1.740E-005	1	1.740E-005	25.90	0.0005	
Time X Current	4.331E-005	1	4.331E-005	64.46	< 0.0001	Highly significant
Residual	6.719E-006	10	6.719E-007			
Lack of Fit	6.719E-006	5	1.344E-006			
Pure Error	0.000	5	0.000			
Cor Total	7.335E-004	19				

Time, current, were highly significant terms for response Y_2 (% of color removal) as shown in Tab.12. Current^2, time^2, pH^2, time X current, pH X current, pH X time are significant terms for Y_2 response. pH is insignificant parameter for response Y_2 response.

Time, current were highly significant terms for Y_3 response (energy consumed) $current^2$ were significant for Y_3 response. pH, pH^2, pH X time, $time^2$, time X current, pH X current were insignificant terms for response Y_3 as shown in Tab.13.

Tab. 12 ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL FOR % OF COLOR REMOVAL

Source	**Sum of Squares**	**DF**	**Mean Square**	**F-Value**	**P- value Prob > F**	**Sum of Squares**
Model	3981.54	9	442.39	91.65	< 0.0001	Significant
pH	0.70	1	0.70	0.15	0.7110	
Time (T)	1497.88	1	1497.88	310.31	< 0.0001	Highly significant
Current(I)	1936.22	1	1936.22	401.12	< 0.0001	Highly significant
pH^2	171.86	1	171.86	35.60	0.0001	
$Time^2$	96.40	1	96.40	19.97	0.0012	
$current^2$	49.85	1	49.85	10.33	0.0093	
pH X Time	36.42	1	36.42	7.55	0.0206	
pH X Current	84.05	1	84.05	17.41	0.0019	
Time X Current	24.12	1	24.12	5.00	0.0494	
Residual	48.27	10	4.83			
Lack of Fit	48.27	5	9.65			
Pure Error	0.000	5	0.000			
Cor Total	4029.81	19				

Tab. 13 ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL FOR ENERGY CONSUMED DYE USING INVERSE TRANSPOSE.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	54.87059	9	6.096732	31.47079	< 0.0001	significant
pH	0.0016	1	0.0016	0.008259	0.9294	
Time (T)	17.41393	1	17.41393	89.88916	< 0.0001	significant
Current(I)	33.57623	1	33.57623	173.3175	< 0.0001	significant
pH^2	0.049307	1	0.049307	0.254519	0.6248	
$Time^2$	0.052417	1	0.052417	0.27057	0.6143	
$current^2$	2.420659	1	2.420659	12.49523	0.0054	
pH X Time	0.375845	1	0.375845	1.940076	0.1938	
pH X Current	0.393385	1	0.393385	2.030616	0.1846	
Time X Current	0.668168	1	0.668168	3.449024	0.0929	
Residual	1.937267	10	0.193727			
Lack of Fit	1.300626	5	0.260125	2.042949	0.2259	not significant
Pure Error	0.636641	5	0.127328			
Cor Total	56.80786	19				

The final quadratic equation in terms of coded factors for %age of color removal, %age of dye degradation and specific electrical energy consumption are given below.

Final Equation in Terms of Coded Factors:

1.0/(% dye degradation) (Y_1) = 0.016+7.551Error-004*pH-2.624 Error -003*time-5.354E-003*current -6.950 Error -004*pH^2+ 3.246 Error -004* time 2 +1.526 Error -003* current 2-3.967E-004 * pH * time -1.475 Error -003*A* current +2.327 Error -003 * time * current **(5)**

% color removal (Y_2) = 79.95+0.21* pH +9.68* time +11.00* current +2.61* pH 2-1.96 * time 2-1.41*current 2-2.13* pH * time +3.24* pH * current -1.74* time * current **(6)**

Energy consumed (Y_3) = 2.73+1.000E-002 * pH +1.04 * time +1.45* Current+0.044* pH^2 +0.046 *$time^2$+0.31 * $current^2$-0.22 * pH * time -0.22 * pH * Current + 0.29* time * Current **(7)**

6.2.2.3 Effects of pH, Time, Current on responses Y_1, Y_2 and Y_3

To study the interaction of parameters i.e pH, time, current on Y_1, Y_2 and Y_3 responses for Electro-oxidation of CBSOL LE red wool dye, 3-D response surface graph were considered.

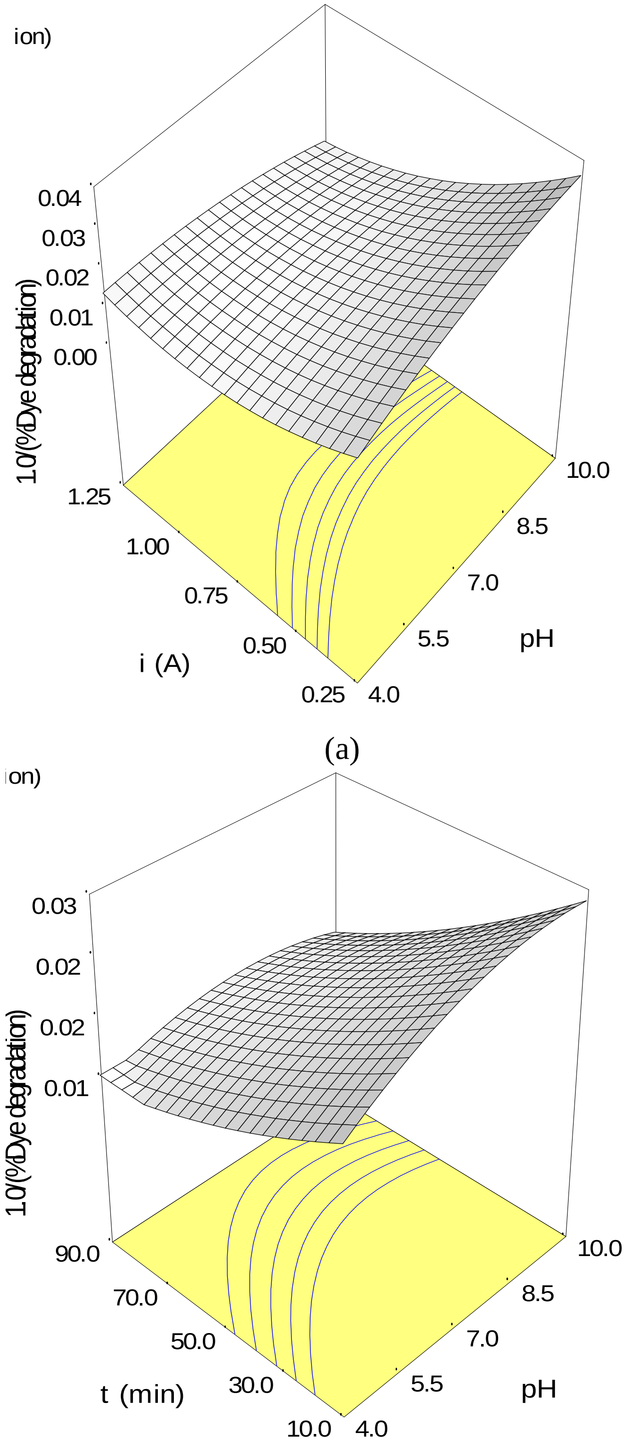
%dye degradation, Y_1 was found to increase with decrease in current from 0.25 to ≈0.75 A. decreasing i beyond ≈0.75 A showed marginal effect on the %dye degradation (Fig.13 a). This can be observed true for the pH value from 4 to ≈7. For each pH> 7.0, increasing i values first increases Y_1 up to i≈ 0.75, thereafter, for all values of increased current Y_1 was found to decreased. It can also be observed that increasing pH at high value of i favored higher removal. Therefore, it may be concluded that lower i value is preferable at acidic pH range, while in basic pH range higher i value is required for the CBSOL LE red wool dye degradation.

Fig. 13b shows 3-D response surface graph for pH and t versus %dye degradation, Y_1. It can be seen increasing pH value lowered the Y_1 value. This can be seen true for all values of t. Unlike pH, increased t value increases Y_1 value for each value of pH.

Fig. 14a explains the effects of pH and i on % color removal, Y_2. It was found that decreasing pH at lower values of i deceases Y_2 value. While at higher current the decreasing pH value increased Y_2, and complete color removal was found for current 1-1.25 A at highly basic pH.

In Fig. 14b, it can be observed that increasing t value and current, i always increases the % color removal, Y_2.

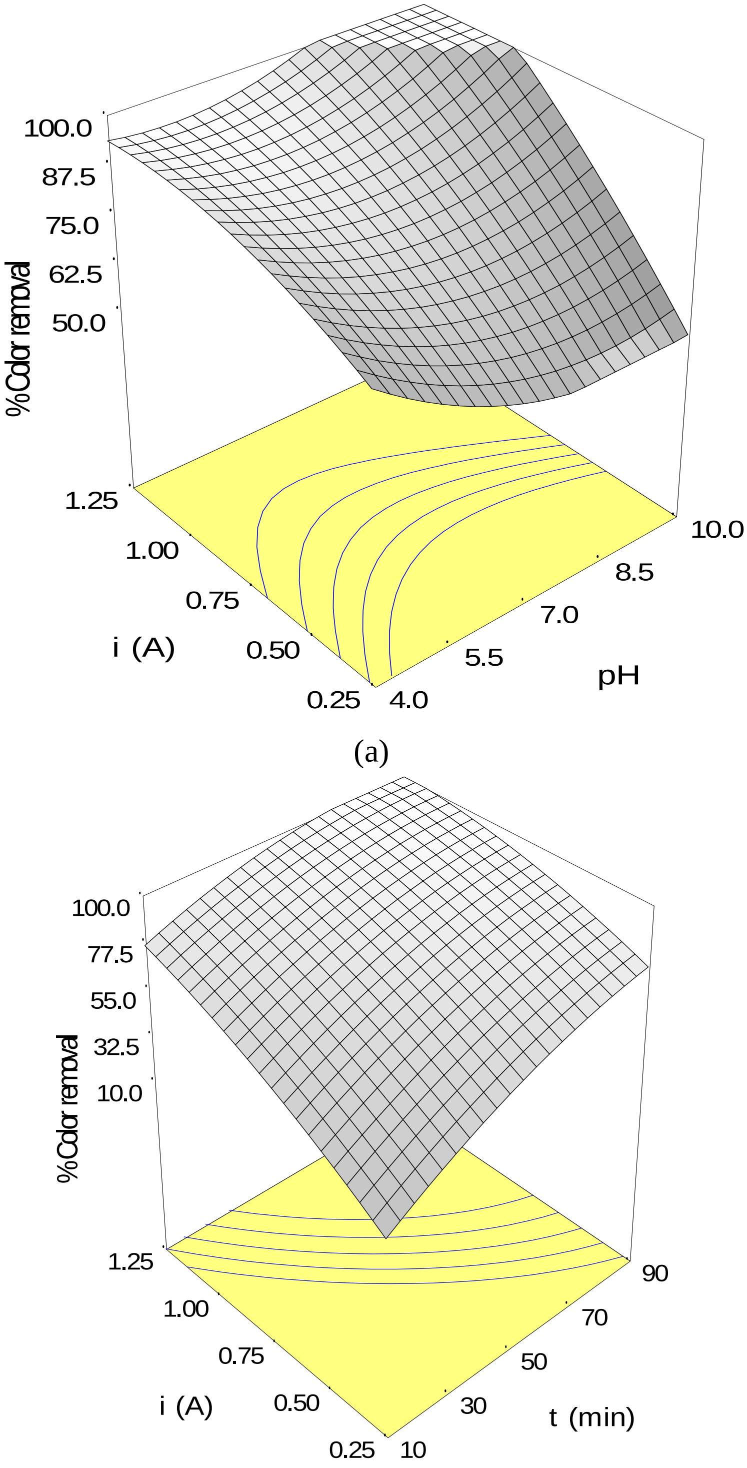
Fig. 15a and b shows effect of pH, t and i on the energy consumed, Y_3. With increase in pH, it was found that Y_3 value always increases with i up to 0.75 A. For i>0.75 A, Y_2 value was found to gradually decreased (Fig. 15a). Same trend was found with pH and t for energy consumed.



(a)

(b)

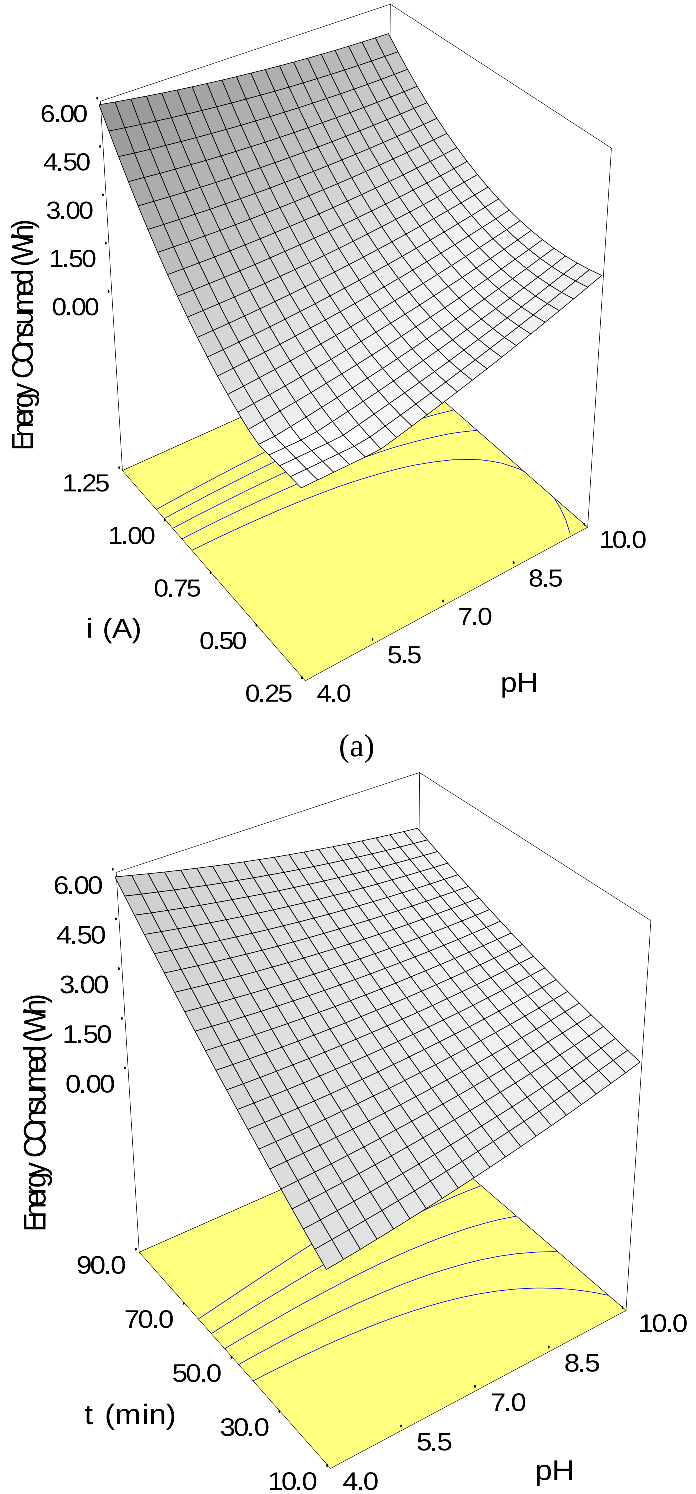
Fig. 13a, b. Three dimensional response surface graph for the electro-oxidation of textile wastewater for %dye degradation



(a)

(b)

Fig. 14a, b. Three dimensional response surface graph for the electro-oxidation of textile wastewater for %Color removal



(a)

(b)

Fig. 15a, b. Three dimensional response surface graph for the electro-oxidation of textile wastewater for %Energy Consumed

6.2.2.4 Optimization Analysis

Electro-Oxidation of textile wastewater was optimized by RSM in terms of maximization of response $Y_{1,}$ maximization of response Y_2 and minimization of response Y_3 simultaneously with the help of desirability (D) function approach. For this purpose some constraints for operational parameters were applied as shown in Tab. 14.

Tab. 14 CONSTRAINTS APPLIED FOR OPTIMIZATION OF ELECTRO-OXIDATION OF TEXTILE WASTEWATER

Variables	Goal	Lower Limit	Upper Limit
pH	is in range	4	10
T	is in range	10	90
J	is in range	0.25	1.25
1.0/(% dye removal)	maximize	30.82	97.77
% color removal	maximize	50.85	98.98
energy consumed)	minimize	0.602	7.283

Electro-Oxidation of textile wastewater was optimized by RSM in terms of maximization of response $Y_{1,}$ maximization of response Y_2 and minimization of response Y_3 simultaneously with the help of desirability (D) function approach. The overall Desirability (D) was 1.000. The optimum values of operational parameters suggested by RSM as shown in Tab. 15. These optimized values of parameters were I=0.25 A, t=90min and pH=4.00. The responses Y_1 (%dye degradation), Y_2 (% color removal) and Y_3 energy consumed 91.75%, 99.00%, 2.327 Wh respectively.

Tab. 15 OPTIMUM CONDITIONS FOR ELECTRO-OXIDATION OF TEXTILE WASTEWATER

Variables	Optimum values
I(A)	0.25
T (min)	90 min
pH	4.00

6.2.3 CONFORMATION RESULTS

Optimum condition for electro-oxidation of textile wastewater was experimentally verified. Experiment was run for 90 min at current was 0.25 and pH 4.00 to conform that stimulated data from ANN was practically feasible. Optimum responses for optimum process parameters were Y_1 (%dye removal)), Y_2 (% color removal) and Y_3 energy consumed 91.75%, 99.00%, 2.327 Wh respectively. Experiment results for optimum process parameters for Y_1 (%dye degradation), Y_2 (% color removal) and Y_3 energy consumed were 89.87%, 96.71%, 2.02875 Wh respectively.

The comparison between the optimum and experimental results as shown in Tab. 16

Tab. 16 COMPARISON BETWEEN THE RESULTS

Responses	**Predicted value**	**Experimental value**
% Dye degradation (Y_1)	91.75%	89.87%
% Color removal (Y_2)	99.00%,	96.71%,
Energy consumed (Y_3)	2.327 Wh	2.02875 Wh

Optimization by CCD under response surface methodology (RSM) vividly underscores interactions between variables and their effects for the dregradation of CBSOL LE red wool dye by EO process. The predictions agree well with the experimental results.

CHAPTER 7

CONCLUSION

From the present study for the degradation CBSOL LE red wool dye wastewater by electro-oxidation method with Ti/RuO_2 coated plate as an anode and aluminum plate as a cathode following major conclusions were drawn.

Modelling of EO process by ANN

- Modeling for the degradation CBSOL LE red wool dye wastewater by EO process was done susssessfully by ANNs. It was concluded that optimized neurons for the process was eight.
- The training versus target gives regression coefficient of 0.995 along with validation, test and all data sets regression coefficient value 0.992, 0.996, 0.995 respectively. Which implied that training of the ANN model was done accurately and model was ready to stimulate the outputs from a given inputs.

Optimization by CCD under response surface methodology (RSM)

- The model gives coefficient of determination R^2 value of 0.9908, 0.9880 and 0.9659 for % Dye degradation (Y_1), % Color removal (Y_2) and Energy consumed (Y_3) respectively This advocates a good correlation between the observed and predicted values.
- The response surface models shows that time, current, $current^2$, time X current, were highly significant terms for Y_1 response, Time, current, were highly significant terms for response Y_2 and Time, current were highly significant terms for Y_3 response.
- These optimized values of process parameters were I=0.25 A, t=90min and pH=4.00 for the degradation CBSOL LE red wool dye wastewater by EO process.
- At the optimum condition, the actual % Dye degradation (Y_1), % Color removal (Y_2) and Energy consumed (Y_3) were 89.87%, 96.71%, 2.02875 Wh respectively.

- Lower i value is preferable at acidic pH range, while in basic pH range higher i value is required for the CBSOL LE red wool dye degradation. Increasing t value and current, i always increases the % color removal, Y_2.
- Optimization by CCD under response surface methodology (RSM) vividly underscores interactions between variables and their effects for the dregradation of CBSOL LE red wool dye by EO process and the predictions agree well with the experimental results.

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