Treatment of Reactive Black 5 (RB 5) Dye Using Electrochemical Advance Oxidation Processes (EAOP's)

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Submitted
By

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July 2015

CERTIFICATE

This is to certify that thesis entitled, "**Treatment of Reactive Black 5 (RB 5) Dye Using Electrochemical Advance Oxidation Processes (EAOP's)**" submitted by **Mr. Amanjit Singh** in partial fulfilment of the requirements for the award of **Master of Technology** Degree in **Environmental Science & Technology** at **Thapar University**, **Patiala** is an authentic work carried out by him under our supervision and guidance.

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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I, the undersigned, hereby declare that the research work entitled "**Treatment of Reactive Black 5 (RB 5) Dye Using Electrochemical Advance Oxidation Processes (EAOP's)**" has been carried out by me under the supervision and guidance of ***Dr. Anoop Verma, School of Energy and Environment, Thapar University, Patiala***.

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ABSTRACT

Decolorization and degradation of the Reactive Black 5 (RB 5) has been studied using indirect electrochemical oxidation processes of electro-chlorination and electro-Fenton with graphite and carbon fiber electrodes. The process parameters studies have been done using RSM, Central Composite Design matrix with application of statistical analysis of model along with ANOVA and 3-D response surface graph. Electro-Fenton degradation and decolorization of RB 5 have been studied for pH, catalyst concentration, current applied and distance between the electrodes. The optimized values for various parameters were pH= 5, Catalyst concentration =.40mg/L, Current =342 mA and Distance =3.1cm with experiment results of 89.0% and 68.0% for decolorization and degradation respectively. The carbon cloth electrode gave the 95% dye decolorization and 70% degradation for optimal conditions and similar results were seen with carbon reinforcement with decolorization~ 93% and 67% degradation. However the resistance offer by both of them was higher than the normal electrodes. Electro-chlorination degradation and decolorization of RB5 was studied for pH, current applied and distance between the electrodes. The optimum operational parameters values by RSM were pH= 4.5, Current =381 mA and Distance =1.5 cm. The corresponding values of experiment results were 93% and 68 % for dye decolorization and degradation respectively.

Combination of electro-Fenton and electro-chlorination was also carried for checking the enhance activity for decolorization and degradation. The operating parameters were catalyst amount of.40mg/L, Current at 381 mA, pH 4.5, and Distance between the electrodes as 1.5 cm. The complete Decolorization was observed in 30 minutes of reaction. The amount of dye degradation also saw increment as more than 79% was observed after 40 minutes of reaction.

Carbon as cathode is extremely effective for production of H_2O_2 in presence of physically adsorbed air. In case of anode the carbon is not that effective due low stability, however it is effective for regeneration of Fe^{3+} to Fe^{2+}. Electro Chlorination using carbon electrode is potent as formation potential of Chlorine reactive species is lower than it’s the oxygen evolution potential. Carbon electrodes as anode have stability issues near oxygen evolution potential.

Keywords: - Electrochemical oxidation; Electro-chlorination; Electro-Fenton; Reactive Black 5.

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CHAPTER 1
INTRODUCTION

1.1. Current Scenario

Today world is characterized by various problems from developed to developing countries there are enormous challenges face by the human civilization for its assistance on the earth. On one side of the spectrum the developing world where still a lack of safe water and basic sanitation causing diseases like diarrhea schistosomiasis, trachoma, and soil transmitted Helminthiases (Mara et al., 2010).

The growth and development paradigm of more industrialization and hoard of becoming the developed nation have increased the water problems exponentially. The ever growing industries with increasing amount of effluents generated leads to environmental degradation. One of the significant polluting industry is the textile and dye industry and effluents from textile industries are the major source of water pollution which not only harmful for aquatic life but also to human. The production of dyes is approximately 800,000 tons per year (Levin et al., 2004) and approximately 10-15% of synthetic dyes lost during different processes of textile industry (Langhals, 2004). Other industries using synthetic dyes are paper printing, food, pharmaceutical, leather and cosmetics. In this scenario science and technology not only look to provide the new innovative solutions to the problems but also talk about the implementation and sustainability of that solutions. In growth and development paradigm mode we should not forget the essential conditions to survive on this earth and work for providing better solutions to society.

Fig.1.1 Sarsa river tributaries, solan district (HP)

1.2. Treatment Technologies

Over last few decades the water treatment research has been extensively growing. Rigorous pollution control and legislation in many countries have resulted in an intensive search for new and more efficient water treatment technologies. Because of the extremely diverse features waste that usually contains a mixture of organic and inorganic compounds, no universal strategy of reclamation is feasible and it mainly depends on the nature and concentration of pollutants. As to the treatment of effluents polluted with organic compounds, biological oxidation is certainly the cheapest process, but the presence of toxic, persistent organic pollutants(POP's) molecules may hinder this approach (Sirés et al., 2014). The traditional incineration method poses problems of emission if the treatment conditions are not perfectly controlled, and above all, it can be conveniently applied only for concentrated solutions. Then the special class of oxidation technique known as advanced oxidation processes (AOP's) comes into picture.

Advanced oxidation processes (AOP's) constitute important, promising, efficient, and environmental-friendly methods developed remove pollutants from waters and wastewaters. Defined as the *in situ* generation of a powerful oxidizing agent, such as hydroxyl radicals (•OH), obtained at a sufficient concentration to effectively decontaminate waters.

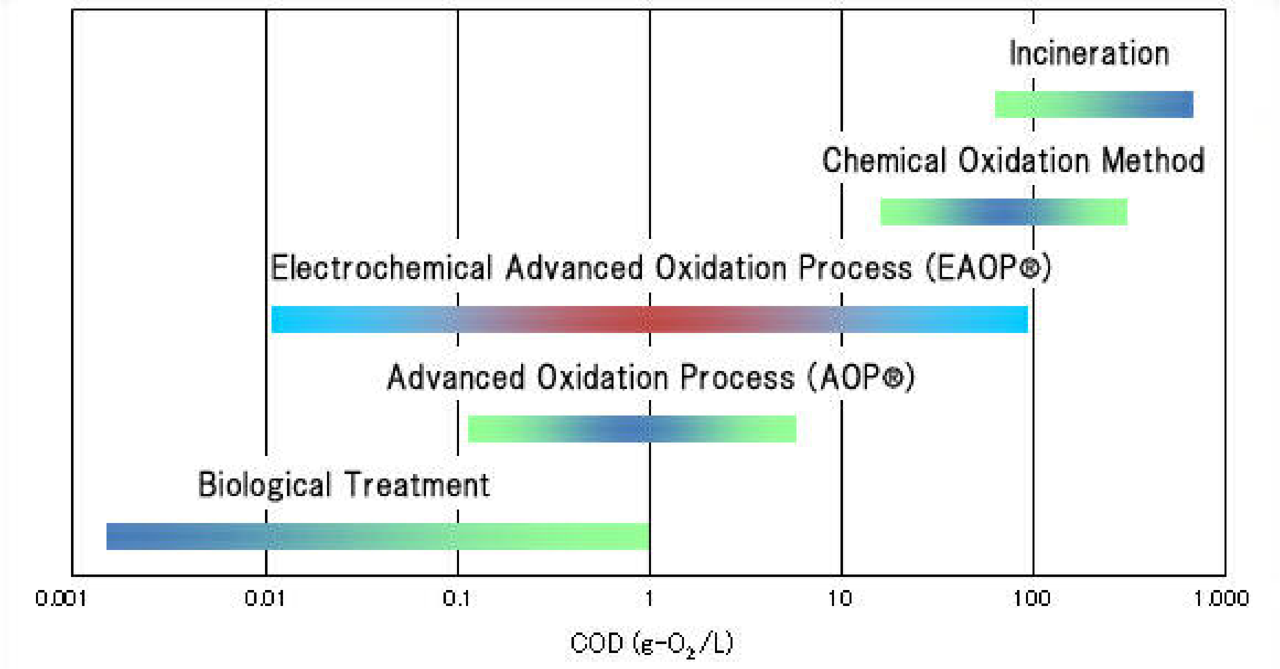

Fig.1.2 Applicability of water technologies based on the amount of organic load.
Source: - Fryda et al., 2003

A large number of AOPs have been developed, which are successfully applied mainly for the treatment of wastewaters, but they are also used in many fields including groundwater treatment, soil remediation, municipal wastewater sludge conditioning, as well as odor and taste removal from drinking water (Fryda et al., 2003). Among the most significantly used AOP is the Fenton and photo-Fenton which is called homogenous catalytic process. It uses the Fenton reagents H_2O_2 and Fe^{2+} salts for the formation of the ·OH. The photo-Fenton uses UV-VIS light to accelerate the formation or regeneration of the Fe^{2+}. This process of the production of ·OH is being used in degradation of various POP's. The only parameter of the control in this is the pH of the solution as acidic conditions are required for the reaction to occur, as higher pH results in reduction of Fe^{2+} to Fe^{3+}. Despite the great deal of work developed by researcher, scanty indications have been in there in bringing about their applications mainly due to pH control and other problems.

The use of semiconductor metal oxides as catalyst in photocatalysis or so called heterogeneous catalysis is other kind of the AOP which is extensively studied with lot of catalysts have been studied with TiO_2 being most interestingly investigated. The use of radiation to form electron and hole pair which by to oxidation and reduction reactions leads to formation of the ·OH which reacts with POPs. The requirement of light for the formation is major step in this. With poor overlapping of the spectrum of TiO_2 and Sun, there have being great affords to develop the doped TiO_2 with broad spectrum. Despite extensive research the industrial application is minute.

In recent years, new AOPs based on the electrochemical technology, i.e., the so-called electrochemical advanced oxidation processes (EAOPs), have been developed (Fryda et al., 2003; Martinez-Huitle and Ferro, 2006). The EAOPs provide several advantages for the prevention and remediation of pollution problems including high energy efficiency, amenability to automation, easy handling because of the simple equipment required, safety because they operate under mild conditions (room temperature and pressure), and versatility as they can be applied to effluents with chemical oxygen demand (COD) in the range of 0.1 to 100 g L^{-1} .

CHAPTER 2
ELECTROCHEMICAL AOP's

Electrochemistry is a technique based on the transfer of electrons, with inherent advantage of the compatibility as main reagent electron is a clean reagent.

The electrochemical processes offer several promising approaches for the prevention and remediation of pollution problems. Among the main characteristics that are attractive as mentioned (Rajeshwar et al., 1994) and reviewed (Martinez-Huitle and Ferro, 2006) are:-

- *Versatility*: These techniques can be applied as direct and/or indirect oxidations. These methods can treat many pollutants with volume varying from micro-liters to millions of liters.
- *Energy efficiency*: These processes require lower temperature with respect to equivalent counterparts (e.g., thermal incineration); the potential can be easily controlled and operational parameters can be designed to minimize power losses.
- *Amenability to automation*: The electrical variables used in the electrochemical processes are particularly suited for facilitating data acquisition, process automation and control.
- *Environmental compatibility*: The electrons are clean and very effective reagent, whose reactivity may be tuned by choosing a suitable electrocatalyst, in order to prevent the production of undesirable metabolites.
- *Cost effectiveness*: The required equipment and operations are generally simple and inexpensive, but diverse considerations must be studied for optimal efficiency.

For the above reasons, intensive research proceeds with the goal of discovering more efficient techniques, processes, materials for the remediation and/or prevention of pollution problems.

2.1. Electrochemical Waste Water Treatment Technologies

The development, design and application of electrochemical technologies in water and wastewater treatment has been focused on particularly in some technologies like electrodeposition, electrocoagulation, electrofloculation, electro-oxidation and electro-Fenton (Panizza et al., 2007; Brillas et al., 2009;Martinez-Hutile et al.,2009). These techniques are discussed below with major emphases on electrochemical-oxidation and electro-Fenton.

2.1.1. Electrodeposition

The recovery of metal in form electromellurgy have being used since 17th century .The electrochemical recovery of metal in metal finishing industry have being used to solve waste management. The electrolytic recovery is the two step procedure in which first is plating and stripping using the carbon electrodes and then physically recuperating the metal (Martínez-Huitle and Brillas, 2009).

2.1.2. Electrocoagulation

The of process generation of the coagulating agents such as Fe^{3+} or Al^{3+} ions is used traditionally in physico-chemical treatment of phase separation. But in this case the generation of the ions is *in situ*, by use of the aluminum or iron electrodes (Martinez-Huitle and Ferro, 2006; Rajeshwa et al., 1994). The metal ions are generated at anode; with release of the hydrogen gas at cathode. Corresponding metal ions evolved from the anodes immersed in the polluted water yield different Fe^{2+} (and/or Fe^{3+}) or Al^{3+} species with hydroxide ion depending on the medium pH (Gregory and Duan, 2001). The species produce act as coagulants for destabilization agents that bring about dyes separation from the wastewater. The use of this technology for the treatment various dyes and industries waste water has being critically reviewed (Martinez-Huitle and Ferro, 2006).

2.1.3. Electroflotation

Electroflotation is a simple process that in which pollutants in water s removed by tiny bubbles of the hydrogen and oxygen gases generated from water electrolysis (Martínez-Huitle and Brillas, 2009). The efficiency dependent on the size of the bubbles with power consumption related to cell design, electrode material and the operation conditions. The major use of electrofloation as reviewed is in mineral recovery, in separation of oil and low density suspended solids followed by plam oil mill effluents and effluents having the oil water emulsion.

2.1.4. Electrochemical Reduction

Electrochemical reduction is the direct electro reduction of compounds or dyes in aqueous solution on suitable cathodes. The reviewers gave reason for low interest in this conventional electrochemical technique is due to poor decontamination of wastewaters in comparison direct and indirect electro-oxidation methods (Martínez-Huitle and Brillas, 2009).

2.1.5. Electrochemical Oxidation

Electrochemical oxidation is an alternative which reviewers date back to 19th century, but major investigation took place in last two decades with focus on the degradation of various pollutants and improving the activity of electrode along with exploration of more electrode materials. What makes it interesting is it's a clean and effective way to produce *in situ* hydroxyl radical (•OH) which are able to destroy a large variety of toxic and POP's. These •OH radicals can be electrochemically produced either directly (via AO process) or indirectly via *in situ* electrocatalytically generated Fenton's reagent or through relative chlorine species (Sirés et al., 2014; Brillas et al., 2009)

These EAOPs using direct electrochemistry or indirect electrochemistry oxidations have advantage over other as these processes:

- Allow rapid degradation of organic pollutants while preventing the formation of new toxic species.
- Lead to total mineralization of organic pollutants.
- Use few or no chemical reagents.
- Have energy costs as low as possible.

Electrochemical-oxidation can be sub divided into following categories

2.1.5.1. Direct Anodic Oxidation

In direct processes, the pollutants that reach the anodic surface are adsorbed onto the electrode surface prior to electron transfer. Oxidation through the generation of physically adsorbed ‘‘active oxygen’’ or chemisorbed oxygen in the oxide lattice (Cameselle et al., 2005). This course for the anodic oxidation using high O_2 evolution overvoltage anodes complete destruction of the organic substrate as explained further in the chapter 3.

In anodic oxidation complete mineralization of any organic pollutant take place but the process rate is controlled by the mass transfer rate, as a result efficiency is not very high, particularly in the treatment of wastewater polluted with organics at low concentrations. (Sirés et al., 2014) .Two very important considerations in the anodic oxidation treatment in water:

- The design and operation conditions (i.e., the inter electrode gap, temperature, electrode size, flow conditions, etc.).
- Suitable electrode materials must be used to enhance the mediated oxidation processes.

2.1.5.2. Indirect Anodic Oxidation

The electro oxidation of pollutants can be performed through different ways. Peroxide, Fenton's reagent, Cl_2, hypochlorite, peroxodisulfate and ozone are prominent oxidants that can be electrochemically produced. These oxidants react with the organic substrates, eventually leading to their complete conversion to CO_2, H_2O and other inorganic components. In mediated mechanisms processes the process rate is controlled volumetrically, and the efficiency increases significantly. In mediated oxidation mechanism an important role is played by salt concentrations, as the result global process is not controlled by mass transfer but by the action of these mediated reagents, resulting in significantly higher efficiencies (Panizza et al.,2009). Thus, low concentration wastewaters can be treated resulting in high current efficiencies. The details mechanism of the process has being explained in further chapter 3 along with literature review.

2.1.5.3. H_2O_2 Electrogeneration For Water Treatment

Hydrogen peroxide formation by the cathodic reduction of dissolved oxygen at high surface area carbon electrodes have being known since 1882 (Martínez-Huitle and Brillas, 2009). More recently, cathodic electrogeneration of H_2O_2, have being successfully applied to the treatment of acidic wastewater containing various contaminants (Brillas et al., 2006; Oturan and Brillas, 2007). The electrogenerated H_2O_2 have being studied using various carbon based cathodes reticulated vitreous carbon (RVC), graphite, and carbon felt cathodes which reduction of dissolved O_2. Other materials in which H_2O_2 can be generated with high yield are either toxic (Hg) or expensive (Au).

- *Electro-Fenton Process*

  The use of electrogenerated H_2O_2 along with catalyst like ferrous ion, to produce hydroxide radical is the electro-Fenton method. The electro-Fenton uses the *in situ* production of H_2O_2 and regeneration of the Fe^{3+} which are required for production of Hydroxide radical .Over the past decade, significant development have be done for effective for the decontamination of wastewater polluted with toxic and persistent pesticides, organic synthetic dyes, pharmaceuticals and personal care products (Sirés et al., 2007; Oturan and Brillas, 2007). The detail process and mechanism has being discussed further in chapter 3.

- *Photo Electro-Fenton (PEF) And Solar Photoelectro-Fenton (SPEF) Processes*

  In this technique, the solution is treatment is done under electro-Fenton conditions and simultaneously irradiated with UV light or Solar light to accelerate the mineralization rate of organics via photo-Fenton process. The degradation action of irradiation is associated with a higher regeneration rate of Fe^{2+} and production of additional •OH from photolysis (Brillas et al., 2009).

- *Sonoelectro-Fenton (SEF) Process*

Sonochemistry has being coupled with various AOP's to give rise to the sonochemical hybrid of the processes. The effect of microbubbles that concentrates energy into microreactor involving the prolysis of the organic by enhancing the reactions with hydroxyl radicals (Brillas et al., 2009) .

- *Other Photoassisted Processes*

The photoperoxi-coagulation (PPC) method, based on the UVA irradiation of a contaminated solution treated by peroxi-coagulation which utilizes an undivided cell containing a sacrificial iron anode and a cathode to generate H_2O_2 .Under these conditions, the Fe^{2+} generated is quickly oxidized by H_2O_2 to yield a Fe^{3+} saturated solution, while the excess of this ion precipitates as $Fe(OH)_3$ (Brillas et al., 2009).The Brillas's group reviews PPC process as practically ineffective because the TOC removal rate was similar to comparable PC treatment since UVA light mainly absorbed (or dispersed) by the $Fe(OH)_3$ precipitate in suspension.

2.1.6. Anodic Oxidation With Electrogenerated H_2O_2

The use of high O_2 over potential anodes make the anodic oxidation and electro generated H_2O_2 an inseparable processes. But together they make efficient and powerful water treatment process. In this the degradation of the organics is done by different oxidizing species such as M(•OH) and other weak oxidizing agents like H_2O_2 and HO_2• produced from H_2O_2 oxidation at the anode. However pollutants undergo similar destruction rate in both cases because their main oxidant is the •OH formed at the anode surface and the weaker oxidants are produced in a low concentration in both cases. So, the disadvantage of this method is the difficulty of achieving the total mineralization of intermediates (Brillas et al., 2009).

CHAPTER 3
LITERATURE REVIEW

Textile industry is one of the water intensive sectors. The wastewater generated during washing purposes and carrier for transporting chemicals to fabric (Tüfekci et al., 2007). As dyes do not bind completely to the fabric and are released in water causing serious problems like mutagenic to human (Chung et al., 1992), damaging biodiversity in aquatic life (Chung and Stevens, 1993).This review is divided to two parts. First part look into various traditional and AOP's methods employed for the removal of the dyes and the recent trends in removal of the reactive dye (model compound RB5). Second part reviews electrochemical AOP's processes, electro-oxidation (Chlorination) and electro-Fenton in details along with the mechanisms and current trends.

3.1. PART 1 (CONVENTIONAL TECHNOLOGIES , AOP'S FOR DYE REMOVAL AND RB 5 REMOVAL)

3.1.1. Conventional Technologies for Dye Removal

Biological and physicochemical methods have been used for the decolorization and degradation of the organic compounds in dye wastewater. With biological resistance of some dyes (Lucas and Peres, 2006) typical dye wastewater treatment methods uses coagulation/flocculation, adsorption and oxidation in combination with biological treatments (Sarasa et al., 1998).

- *Coagulation and Flocculation*

Coagulation and flocculation processes have been widely used as pre-treatments to remove suspended particles and coloring materials prior to biological treatment (Torres et al., 1997). Coagulation is traditionally done using Aluminum (Al) or Iron (Fe) salts. Inorganic polymer flocculants are also currently in use. The chemical coagulation has been successfully used for treatment of textile effluents (Zhu et al., 2007).

- *Adsorption*

Adsorption has been an effective process for color removal from dye wastewater. Use of activated carbon has been found to be effective, but it is too expensive. Many studies have been undertaken to investigate the use of low-cost adsorbents such as peat, bentonite, steel-plant slag, fly ash, china clay, maize cob, wood shavings, and silica for colour removal

(Crini, 2006; Gupta and Suhas, 2009). Various agricultural wastes like rice husk, sugarcane bagasse, pinewood, corncobs, chitosan etc. have also being studied for adsorbtion (Crini, 2006; Ferrero, 2007).

These low cost adsorbents have low adsorption capacities and require large amounts of adsorbents. More over these methods suffer with problems like excess sludge production. They are effective only when effluent volume is small. The disposal of the solid adsorbent itself becomes a big problem.

3.1.2. Advanced oxidation processes (AOPs) for Dye Removal

In the last decade research in the Advance Oxidation processes (AOP's) have grown tremendously. With generation of •OH radicals which possess powerful oxidizing can degrade a wide variety of toxic contaminants (Devi et al., 2009). AOP's have being identified as alternative for dye effluent when conventional waste water treatment technologies are insufficiently effective (Martinez-Huitle and Brillas., 2009).

Various non-photochemical and photo chemical AOP's have being used in treatment of the dyes and have being discussed.

3.1.2.1. Non Photo-Chemical processes

- *Ozonation*:

  Ozonation processes are very effective for degradation of reactive dyes (Liakou et al., 1997) and , removal of toxic pollutants (Gomes de Moraes et al., 2000) from textile effluent. Acidic condition is more favorable for ozonation, so that careful adjustment of the textile effluent pH is required (Baban et al., 2003).

- *Ozonation (O_3) / hydrogen peroxide (H_2O_2):*

  This combine treatment enhances the decomposition of O_3 and accelerates the generation of ·OH which degrades of dyes (Al-Kdasi et al., 2004; Gosavi and Sharma, 2014). At alkaline condition, slow reaction is observed whereas higher pH, maximum H_2O_2 is dissociated in to ·OH (Arslan et al., 1999).

- *Fenton process*

  Process is broadly used for the degradation of reactive dyes due to the coagulation and catalytic oxidation properties (Liu et al., 2007).The main advantage of process is that no energy requirement and effective when high amount of COD reduction is required (Lee and Shoda, 2008; Yonar, 2010).

3.1.2.2. Photo-Chemical Processes

3.1.2.2.1. Homogeneous Photo- chemical process:

- *Ultraviolet lamp (UV):*

  Mainly UV process is used to initiate the oxidizing agent such as hydrogen peroxide and degradation of (Chun and Yizhong, 1999).The main advantage of this process is no mud/slug formation after treatment.

- *$O_3/H_2O_2/UV$:*

  Hydroxyl radicals are remarkable enhance when hydrogen peroxide is added in O_3/H_2O_2 (Contreras et al., 2001).$O_3/H_2O_2/UV$ processes leads to complete decolorization (Mokrini et al., 1997; Perkowski and Kos, 2003).

- *Photo-Fenton process:*

  Hydroxyl radical formation is greatly enhanced by UV lamp (Feng et al., 2003). Efficiency of decolorization of dyes by Fenton process is similar to photo-Fenton process but mineralization process is highly improved in case of photo-Fenton process (Lucas and Peres, 2006).

3.1.2.2.2. Heterogeneous Photolytic chemical process:

Photo-catalyst process using ZnO, TiO_2 with UV and H_2O_2 are widely used for degradation of dyestuff from textile effluent because of complete mineralization can be achieved (Chakrabarti and Dutta, 2004; Sleiman et al., 2007).

3.1.3. Reactive Black 5 (RB 5) Removal

- The oxidative decolorization of RB 5 in aqueous solution has been studied using Fenton and photo-Fenton processes (Lucas and Peres, 2006). Both these methods can effectively remove the color of RB 5 with a little difference between the two processes. As UV lamp has little effect on dye decolorization it is particularly important in dye mineralization.
- Liu et al., (2011) investigated Fenton and Fenton-like reactions to oxidize the commercial azo dye of RB 5 along with different parameters affecting the decolorization efficiency of RB 5. The results evaluated shows higher decolorization efficiency in Fenton oxidation than that of Fenton-like oxidation in the initial stages but the overall efficiency was similar for both systems.

- Rahmani et al., (2010) discussed removal of two azo dyes, Acid Orange 7 (AO 7) and RB 5 by Fenton like reaction using Fe^{2+} and UV light for the production of •OH radicals occur without the addition of hydrogen peroxide. It was observed that high removal of dyes for UV system was obtained at pH=11, while in the Fe^{2+} and Fe^{2+} /UV system, high removal occurred at pH=3. Removal of dye was increased by increasing the iron mass and contact time.
- Dias and Fernando, (2009) degraded RB 5 in a photo-Fenton reactor. The decolorization was completed in a short time of about 3 min reaction. TOC removal is strongly dependent on hydrogen peroxide concentration and ferrous ion catalyst concentration. Based on dye concentration of 55 mg/L, the maximum TOC removal was 90% after 90 minutes reaction with optimal condition on peroxide concentration of 280 mg/L and ferrous ion concentration of 78 mg/L.
- Tantak and Chaudhari, (2006) described two stage sequential process involving Fenton's oxidation followed by aerobic biological treatment, to achieve enhance mineralization of azo dyes, viz. RB 5, Reactive Blue 13 (RB 13) , and AO 7. Results reveal that pH 3 was optimum pH for achieving decolorization of dyes by Fenton's process. Fenton's oxidation process followed by aerobic SBRs treatment provided significant degradation of azo dye.
- Verma et al., (2014) investigated the degradation and decolorization of the RB 5 by dark Fenton, photo-Fenton and Sonophoto-Fenton. Degradation was 50% under Dark Fenton and 92% under photo-Fenton with optimized conditions after 20 minutes. Sonophoto-Fenton treatment enhanced the degradation up to 98% with optimized parameters.
- Iglesias et al., (2013) studied electro-Fenton process using Fe alginate gel beads for the remediation of wastewater contaminated with RB 5 was studied using graphite sheet electrodes. Dye decolorization, reduction of chemical oxygen demand (COD) and energy consumption were studied using RSM, Central Composite experimental design matrix. The optimized parameter values for maximum COD reduction and minimum energy consumption were voltage, 5.69 V, pH 2.24 and iron concentration of 2.68 mM.

3.2. PART 2 (INDIRECT ELECTRO CHEMICAL OXIDATION)

In recent years electrochemical process has been widely studied for the removal of the various pollutants as well as dyes by both direct and indirect oxidation. The idea of indirect oxidation as described by many reviewer is to prevent electrode fouling, avoiding direct electron exchange between the organics and the anode surface and utilize the electro catalytic potential of other anode materials (Bonfatti et al., 2000; Panizza et al., 2007). The oxidizing chemicals can be electrogenerated either by anodic oxidation such as formation of active chlorine, ozone, and persulphate, or by cathodic reduction such as formation of hydrogen peroxide. The main requirements described are the following (Rajeshwar et al., 1994):-

- The potential at which the intermediate species is produced must not be near oxygen evolution potential.
- The intermediate generation rate must be high.
- The reaction rate of the intermediate species and the pollutant must be higher than the rate of any competing reactions.
- Pollutant adsorption must be minimized

Indirect electro-oxidation methods involving the homogeneous reaction of organic pollutants with strong oxidants generated during electrolysis. Two approaches studied are:

- The electro-oxidation (chlorination) with active chlorine, where direct anodic oxidation of chloride ion present in the effluent leads to the formation of free chlorine and/or chlorine–oxygen species that can oxidize organic pollutants in the bulk until overall mineralization.
- The electro-Fenton process in which organics can be mineralized with homogeneous ·OH formed from Fenton's reaction between added catalytic Fe^{2+} and H_2O_2 electrogenerated from O_2 reduction at a suitable cathode.

3.2.1. Electro Chlorination

The use of chlorine-mediated oxidation or electro-chlorination has been reported for oxidation of a wide range of model pollutants and has in particular been shown to be suitable for the treatment of wastewaters with high natural concentrations of sodium chloride.

The major advantages are (Martinez-Huitle and Ferro, 2006):-

- The transport and storage of dangerous chlorine for water treatment is avoided;
- Faster destruction of organic matter than in chemical oxidation;
- The total costs are much lower than conventional chemical technology.

Several disadvantages as reviewed are (Martinez-Huitle and Ferro, 2006):--

- The formation of undesirable toxic chloro-organic derivatives such as chloroform, chlorine–oxygen by-products such as ClO, ClO_3 and ClO_4 which have a high health-risk for living beings.

3.2.1.1. Electro-generation of active chlorine species (Mechanism)

The mechanism of the electro chlorination purposed (Raghu and Basha, 2007).

At anode: Main reaction

$$2Cl^- \longrightarrow Cl_2 + 2e^- \qquad (3.1)$$

At cathode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3.2)$$

In Bulk

$$Cl_2 + H_2O \longrightarrow H^+ + Cl^- + HOCl \qquad (3.3)$$

$$HOCl \longleftrightarrow H^+ + OCl^- \qquad (3.4)$$

$$Dye + OCl^- \longrightarrow CO_2 + H_2O + Cl^- + P \qquad (3.5)$$

The primary reaction occurs at the anodes is chloride ion oxidation with the liberation of Cl_2. The counter reaction at the cathode would be the reduction of the water when no other reducible species are present. As regards to the reactions in the bulk, gaseous Cl_2 dissolves in the aqueous solutions due to ionization.

An explanation of the mediating role of chloride ions have been proposed (Bonfatti et al., 2000). A Schematic diagram of indirect oxidation of pollutant shown in Fig.3.1 shows extended the scheme of the oxygen transfer as carried out by adsorbed oxychloro species, which are considered as intermediates of the chlorine evolution reaction on noble anode (MO_x).

.In the first step, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals

$$MO_x + H_2O \rightarrow MO_x({}^\bullet OH) + H^+ + e^- \qquad (3.6)$$

In the second step, generally the adsorbed hydroxyl radicals interacts with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide MO_{x+1}.But in the presence of Cl ion MOx (•OH) reacts to form adsorbed OCl radicals described in reaction 3.8

$$MO_x(^{\bullet}OH) \rightarrow MO_{x+1} + H^+ + e^- \quad (3.7)$$

$$MO_x(^{\bullet}OH) + Cl^- \rightarrow MO_x(^{\bullet}OCl) + H^+ + 2e^- \quad (3.8)$$

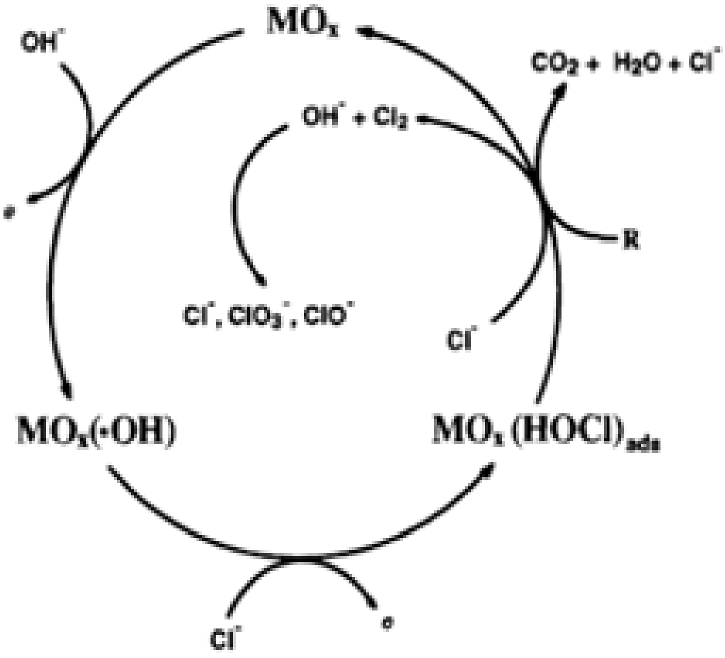

Fig.3.1:- Scheme of chloride mediated electrolysis. Source: - Bonfatti et al, 2000

3.2.1.2. Electrodes for Electro-oxidation (Chlorination)

The catalytic activity towards the oxidation depends on the value of the over potential below mention in the table 3.1 (Awad and Abuzaid, 1997; Martinez-Huitle and Ferro, 2006). The potential of the formation of the typical oxidants reported in literature are as in table 3.2. IrO_2, Pt and graphite show smaller values of the over potential for oxygen. This indicates that effective oxidation of the pollutants at the anodes may occur at very low current density or in presence of high concentration of the mediators such as chlorides. When the current density is high significant decrease of efficiency is expected due to the production of oxygen.

Table 3.1:- O_2 evolution potential at different electrodes

Anode	Value
Pt	1.3
IrO_2	1.6
Graphite	1.7
PbO_2	1.9
SnO_2	1.9
Pb-Sn(93:7)	2.5
TiO_2	2.2
Si/BDD	2.3
Ti/BDD	2.7
DiaChem	2..8
Source:- Martinez-Huitle and Ferro, 2006	

Table3.2:- Formation potential for some chemical reactants

Oxidant	Formation potential
Hydroxyl radical	2.87
Ozone	2.07
Persulphate	2.01
Permanganate	1.77
Hydrogen peroxide	1.77
Chlrine dioxide	1.57
Siver(II)ion	1.5
Chlorine	1.36
dichromate	1.23
Oxygen	1.23
Source:- Martinez-Huitle and Ferro, 2006	

Another difference in behavior of electrodes as given in literature explained by considering two limiting cases: the so-called ‘‘active’’ and ‘‘non-active’’ anodes (Comninellis et al., 2008). The proposed model assumes that the initial reaction in both kinds of anodes corresponds to the oxidation of water molecules leading to the formation of physisorbed hydroxyl where MO_x as denotes reaction 3.6.

The active anodes have higher oxidation states available on the electrode surface and may interact stronger with the adsorbed hydroxyl radicals by further oxidation, forming higher oxides: This occur when higher oxidation states are available for a metal oxide anode, above the standard potential for oxygen evolution showed in reaction 3.7. The surface redox couple MO_{x+1}/MO_x act as mediator in the conversion or partial oxidation of organics on active anodes by chemical decomposition of the higher oxide species from reaction as shown in 3.9

$$MO_{x+1} + R \rightarrow MO_x + RO \qquad (3.9)$$

Non-active electrodes are characterized by weak electrode hydroxyl radical interaction forming physisorbed active oxygen (hydroxyl radicals), which can assist in a complete mineralization of the organics.

$$a\mathrm{M}(^{\bullet}\mathrm{OH}) + \mathrm{R} \rightarrow a\mathrm{M} + m\mathrm{CO_2} + n\mathrm{H_2O} + x\mathrm{H^+} + ye^- \qquad (3.10)$$

In reaction 3.10 R is an organic compound with M carbon atoms and without any heteroatom, which needs a = (2m + n) oxygen atoms to be totally mineralized to CO_2. The oxidative reaction with the surface redox couple MO_{x+1}/MO_x are much more selective than the mineralization reaction with physisorbed heterogeneous hydroxyl radical.

Both the chemisorbed and physisorbed active oxygen undergo a side reactions leading to oxygen evolution resulting in decreased anodic process efficiency and loss of energy:

$$MO_{x+1} \rightarrow MO_x + \tfrac{1}{2}O_2 \qquad (3.11)$$

$$MO_x(^{\bullet}OH) \rightarrow MO_x + \tfrac{1}{2}O_2 + H^+ + e^- \qquad (3.12)$$

The reaction scheme is usually presented as a full oxidation cycle. According to the mechanisms, anodes with low oxygen evolution overpotential such as amorphous carbon, graphite, iridium dioxide, ruthenium dioxide, or platinum have an active behavior, allowing mainly partial oxidation of organics. In contrast, anodes with high oxygen evolution overpotential such as antimony-doped tin oxide, lead dioxide, or boron doped diamond (BDD) have a non-active behaviour and favour complete oxidation of the organics to carbon dioxide.

3.2.1.2.1. Electrodes for Dye wastewater

In Electro Chlorination a special attention is on the kind of anode material chosen. Non-active like conductive diamond electrodes, the most effective anodes in electro-oxidation, are not useful for as they generate appreciable amounts of reactive oxygen species (ROS) and other oxidants species such as peroxodisulphate, peroxodicarbonate and peroxodiphosphate (Kraft, 2007). Nonactive anode like PbO_2 provides a slightly better performance for dyestuffs degradation in chloride solutions (Abu Ghalwa and Zaggout, 2006). The opposite behaviour is reported for active anodes having much higher electrocatalytic power for oxidizing chloride ion than for generating ROS. Among these materials, DSA-type electrodes metals such as Pt and Pt–Ir and graphite have been positively checked active chlorine and their characteristics will be separately detailed below. Few of the most reviewed have being mentioned in Table 3.3.

Table 3.3:- Most popular anodes used for electro-chlorination

Electrode	Compound	C0/mg dm^{-3}	Experimental conditions	j- mA cm^{-2}	Efficiency	Reference
Ti/RuO$_2$	Methylene Blue	80 mg dm^{-3}	1.2 g dm^{-3} Cl$^-$ natural pH, for 95 min	20	100 % Color removal 94% COD decay	Panizza et al., 2007
Ti/RuO$_2$ anode	Procio Black 5B	-----	3.61 g dm^{-3} Cl, pH 10.6, residence time 27 min	25	100 % Color removal 74% COD decay	Raghu and Basha, 2007
Ti/TiO$_2$–RuO$_2$–IrO$_2$ anode	Reactive Black 5B	100 mg dm^{-3}	1.5 g dm^{-3} NaCl, pH 6.2–6.5, for 2 h	36	100%Color removal 53%COD decay	Rajkumar et al., 2007
Ti/TiO$_2$–RhO$_x$	Methylene Blue		0.1 M NaCl at pH 4.0 , 2h	75	100 % Color removal 27 % COD decay	Donaldson et al., 2002
Pt anode	Reactive Orange 4	1000 mg dm^{-3}	20 g dm^{-3} NaCl, pH 9, for 10 h	24	100 %Color removal 81 % COD decay	López-Grimau and Gutiérrez, 2006
Graphite anode	Indigo	200 mg dm^{-3}	30 g dm^{-3} NaCl, natural pH, for 2 h	5 volts	90 %Color removal	Cameselle et al., 2005

Table 3.4 – Most common DSA type anodes used.

Electrode	Compound	Current Density	Reactor Design	Efficiency	Reference
TiO_2–RuO_2–PbO_2, TiO_2–SnO_2 ,TiO_2–RuO_2	Acid Brown 14	30 mA cm^2	Undivided cell	100% decolorization COD removal Varied	Mohan and Balasubramanian, 2006
Ti/TiO_2– RuO_2	Yellow 126 Disperse Red 74 Disperse Blue 139	20 mA cm^2	Undivided cell	42% color removal, 26% COD	Szpyrkowicz et al, 2000
Ti/RuO_2 anode	Procio Black 5B	25mA cm^2	Continuous flow	100% color removal 74% COD	Raghu and Basha, 2007
DSA anode and Stainless steel Cathode	Textile Industry Effluent	100mAcm^2	Undivided flow filter-press cell	100% color removal 53% COD	Vaghela et al.,2005

Table 3.5:- Most used metal and graphite electrode

Electrode	Compound	Current Density	Reactor Design	Efficiency	Reference
Ti/Pt	Reactive Orange 4	24mA /cm^2	Flow reactor Operated in Batch mode	100% Color Removal 81% COD	López-Grimau and Gutiérrez, 2006
Graphite graphite cell	Indigo	5 V	stirred undivided	90% Color Removal	Cameselle et al.,2005
Three Dimentional Graphite	Congo Red	40 mA/cm^2 .	undivided reactor	78% Color Removal at pH 9 and 87% Color Removal at pH 6.	Wang, 2003
Graphite	Methyl Orange	5V	Stirred undivided	100% Color Removal	Cameselle et al., 2005

- *DSA-type electrodes*

Number of papers compared the color removal and COD reduction of some azo and disperse dyes with active chlorine produced by DSA-type anodes. Recently (Mohan and Balasubramanian, 2006;Mohan et al., 2007)TiO_2–RuO_2–PbO_2, TiO_2–SnO_2 or TiO_2–RuO_2were used as anode and a 10 cm^2 stainless steel cathode to treat Acid Brown 14 solution in NaCl at pH 7.0, 30 mA cm^2. Ti/TiO_2–RuO_2– PbO_2 < Ti/TiO_2–SnO_2< Ti/TiO_2–RuO_2 was decreasing order of the reactivity. Other relative oxidation powers for DSA-type electrodes and metal anodes have been reported by ((Szpyrkowicz et al., 2000) when examined the treatment of Disperse Yellow 126, Disperse Red 74 and Disperse Blue 139 in 0.1 M NaCl using a stirred conditions, the best result was with use of a Ti/TiO_2– RuO_2 in undivided cell with a 100 cm2 plate anode at 20 mA cm^2 for 40 min giving 60% current efficiency. More results are needed to ascertain the relative electrocatalytic activity of the large variety of DSA-type electrodes available for the electro-oxidation of organic dyes mediated with active chlorine.

- *Metal anodes*

The use of Ti/Pt for of highly treatment of concentrated dyes effluents have being done (López-Grimau and Gutiérrez, 2006) and reviewed (Martínez-Huitle and Brillas, 2009) following their comparative study on the degradation of Reactive Orange 4 in Na_2SO_4 and NaCl using Ti/Pt anode at pH 9.0 and24 mA cm2 in batch operation mode. Total color removal of this effluent was attained in 90 min and after 10 h of treatment, 81% of COD and TOC decays were reached, with a very high energy cost of 698kWh m^{-3}. From these results, these authors inferred that this method can only be attractive for decolorizing only. Study have revealed that the dye is not oxidized at the Ti/Pt–Ir anode, but only reacts with active chlorine agents in the solution bulk (Martínez-Huitle and Brillas, 2009). Various reviewers found the need of optimizing the configuration of the electrolytic system and parameters such as pH and temperature to obtain the highest oxidation ability of electrogenerated active chlorine using metal electrode.

- *Graphite anode*

The studies on indirect electro-oxidation with active chlorine performed with a graphite anode have been focused to mainly characterize the decolorization process of several organic dyes such as Indigo, Congo Red and Methyl Orange. One of the study is for the treatment of

0.2 gdm^{-3} Indigo in 30 gdm^{-3} NaCl at natural pH using 20 dm^3 solutions in a stirred undivided graphite/graphite cell with 500 cm^2 electrodes separated 50 cm (Cameselle et al., 2005). After application of a cell voltage of at room temperature for 2 h, 90% decolorization efficiency with a very low energy consumption of 1.86$kWhm^{-3}$ was determined. Decorlization of methyl orange using the graphite electrode have being done with 100% color removal (Cameselle et al., 2005). Congo red studied using three dimensional electrode in the undivided cell have being done to achieve removal efficiencies of about 78% at pH 9 and 87% at pH 6 (Wang, 2003).

3.2.1.3. Operating Parameters

The effect of operating parameters such as Cl^- concentration, current density, stirring or flow rate, pH and temperature on the color and COD decays of synthetic dyestuffs effluents has been extensively studied (Panizza et al., 2007; Szyprkowicz et al., 2000; Rajkumar et al., 2007; Raghu and Basha, 2007).

- *pH of the Solution*

The indirect transfer of oxygen to organic molecules can be obtained both on the anode surface through adsorbed oxy-chloro species or in the bulk of the solution through chlorine, hypochlorous acid, or hypochlorite depending on pH.

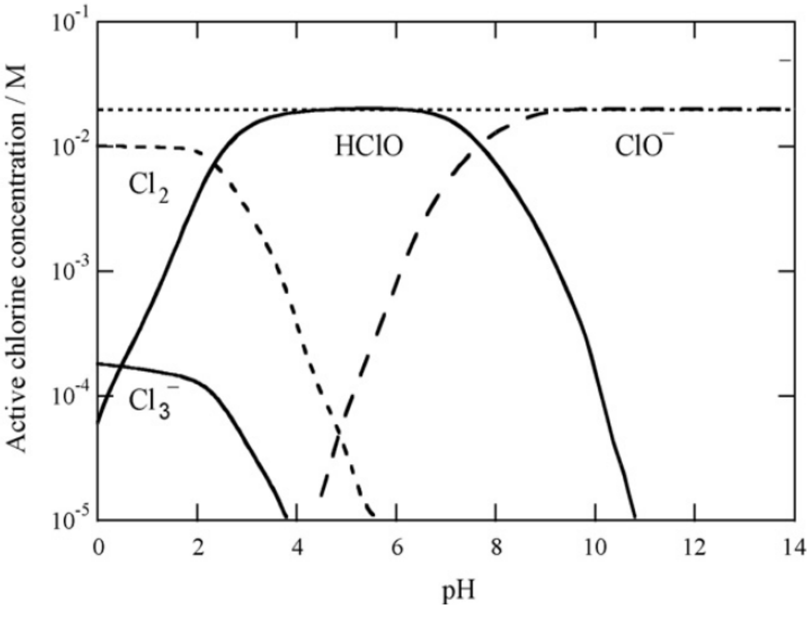

Fig.3.2:-Speciation diagram for Chlorine-Water system
Source: - Martinez-Huitle and Ferro, 2006

Fig.3.2 shows the speciation diagram for (Cl_2 (aq), Cl_3^-, HClO and ClO^-) active chlorine species calculated during the electrolysis of 0.1 M NaCl with a conversion of 0.2 for Cl^-. Cl^{3-} is formed in very low concentration up to pH 4.0, while the predominant species is Cl_2(aq) until pH near 3.0, HClO in the pH range 3–8 and $ClO^-$for pH > 8.0. The mediated oxidation of dyes with these species is then expected to be faster in acidic than in alkaline media because of the higher standard potential of Cl_2(aq) (E_0 = 1.36 V vs. SHE) and HClO (E_0 = 1.49 V vs. SHE) than ClO^- (E_0 = 0.89 V vs. SHE)(Rajeshwar et al.,1994; Martinez-Huitle and Ferro, 2006).

Several studies have reported higher COD destruction when the dyeing solution varies from acidic to alkaline conditions. Azo dye Acid Blue 113 containing NaCl, electrolyzed with a Ti/RuO_2 anode at 10 mA cm^2 it was found that rapidly mineralized occur at pH 9.0 than at pH 7.0 or 4.0. (Mohan et al., 2007). This behavior evidences the complexity of chemical mineralization reactions and wastes reactions involved in the mediated oxidation process, since the degradation rate should be greater in acidic medium with Cl_2(aq) and HClO as active species than in alkaline solutions where the less potent ClO^- acts as oxidant. This trend has been confirmed in study using Ti/TiO_2–RuO_2–IrO_2 mesh anode (Rajkumar and Kim, 2006).

- *Amount of Cl-*

  Higher Cl^-content promotes faster destruction of dyes because of the formation of greater concentration of active chlorine species with the consequent detrimental in ROS production. This behaviour was studied with the Methylene Blue solutions with a Ti/RuO_2 0.5 M Na_2SO_4 anode at 20 mA cm^{-2} (Panizza et al., 2007). A quicker COD removal is mentioned as more Cl^- concentration is added until 2.0 g dm^{-3}.

- *Current Density (j)*

  Increasing current also accelerates dyes mineralization due to the rise in rate of all electrode reactions to produce more oxidizing species. A relevant study on the treatment of the azo dye Procio Black 5B has been reported (Raghu and Basha., 2007). COD reduction increases with increasing j from 10 to 25 mA cm^2, as expected from the faster generation of oxidant ClO-. However the at certain current density the degradation would decrease with rise in oxygen evolution reactions (Martinez Hutile et al.,2006).

- *Stirring in batch reactor*

  A large influence of stirring in batch tank reactors systems on the mediated electro oxidation process of dye has been described provided that they affect the transport of active species. Szpyrkowicz et al., (2009) concluded that increasing stirring favors the decolorization efficiency of a mixture of disperse dyes using a $Ti/TiO_2–RhO_x$ anode, although their mineralization reactions are decelerated causing less COD abatement.

3.2.2. **Electro-Fenton**

EAOP's based on Fenton's reaction chemistry where decomposition of H_2O_2 takes place to produce hydroxyl radicals. Over the past decade, lot of reviews have being published showing significant development for the decontamination of wastewater polluted with organic synthetic dyes, pharmaceuticals and other industrial pollutants (Brillas et al., 2009; Nidheesh and Gandhimathi, 2012).

The major advantages of this method compared with traditional Fenton process are

(i) the on-site production of H_2O_2 that avoids the risks related to its transport, storage, and handling

(ii) The possibility of controlling degradation kinetics to allow mechanistic studies

(iii) The higher degradation rate of organic pollutants because of the continuous regeneration of Fe^{2+} at the cathode, which also minimizes sludge production

(iv) The feasibility of overall mineralization at relatively low cost if the operation parameters are optimized.

3.2.2.1. Mechanism of Electro-Fenton

- *H_2O_2 Electrogeneration for Water Treatment*

H_2O_2 can be continuously supplied to an acidic contaminated aqueous solution contained in an electrolytic cell from the two-electron reduction of oxygen gas, directly injected as pure gas or bubbled air, by reaction 3.13 which takes place more easily than its four-electron reduction to water from reaction 3.14 which has higher *E*° (Agladze et al., 2007).

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (3.13)$$

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (3.14)$$

Oxygen gas is first dissolved in the aqueous phase and further transferred from the bulk to the cathodic surface, where it is reduced to hydrogen peroxide. H_2O_2 production and stability depend on factors such as cell configuration, cathode properties, and operation conditions (Brillas et al., 2009). In a open and undivided cells, when H_2O_2 is gradually accumulated as H_2O_2 is also oxidized to O2 at the anode via $HO_2^•$ as an intermediate shown in reaction 3.15, 3.16 (Brillas et al., 2009).

$$H_2O_2 \rightarrow HO_2^• + H^+ + e^- \tag{3.15}$$

$$HO_2^• \rightarrow O_{2(g)} + H^+ + e^- \tag{3.16}$$

- *Cathodic Fe^{2+} Regeneration*

Fenton reaction uses Fe^{2+} ions and converts to Fe^{3+} along with production of H_2O_2 as seen in reaction 3.17. The Fe^{3+} regeneration is important for continuing the reaction , the Fenton reaction uses H_2O_2 to regenerate Fe^{3+} to Fe^{2+} reaction 3.18 forming $HO_2^•$ which has low oxidative power then $^•OH$. Taking the importance of regeneration photo-Fenton was developed which uses photons or light for regeneration of the Fe^{2+} reaction 3.19. In electro-Fenton uses Fe^{3+} can be cathodically reduced to Fe^{2+} by reaction 3.20, which is known as electrochemical catalysis, with E° 0.77 V/SHE (Aaron et al., 2001). The fast regeneration of Fe^{2+} by reaction 3.20 accelerates the production of •OH from Fenton's reaction 3.17. This enhances the decontamination of organic solutions achieved greater degradation ability. The general mechanism of electro-Fenton in pectoral form has been given by (Oturan, 2000) shown in fig 3.3

$$Fe + H_2O_2 \rightarrow Fe^{3+} + {}^•OH + OH^- \tag{3.17}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^• + H^+ \tag{3.18}$$

$$[Fe(OH)]^{2+} + h\upsilon \rightarrow Fe^{2+} + {}^•OH \tag{3.19}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3.20}$$

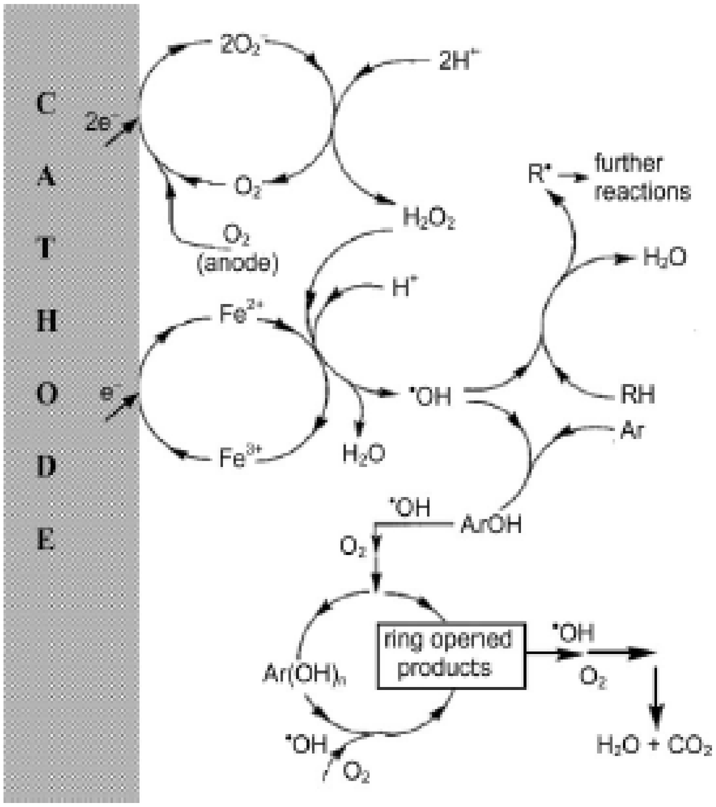

Fig.3.3:- Schematic representation of the main reactions involved in the EF process.
Source: Oturan, 2000

3.2.2.2. Electrodes in Electro-Fenton

Selection of anode and cathode material is one of the significant steps in electro-Fenton process. The various combinations used for degradation of dyes are mentioned in table 3 and are being discussed below

3.2.2.2.1. Anode

Selection of anode is important as it is not only required to complete the reaction but various side reactions also occur with help of anode. The two important parameters looked are (Nidheesh and Gandhimathi, 2012).

- Selection of stable anode. As unstable will cause deterioration of electrode
- Chosing low oxygen over voltage electrode as .High-oxygen overvoltage anode can produce hydroxyl radicals which might be use full but process is termed as combined electro-Fenton not only electro-Fenton.

Pt has been used as an electrode material due to its good conductivity and chemical stability even at high potentials and in very corrosive solutions (Panizza et al., 2009). Pt anode used in degradation of pollutants in electro-Fenton system in different forms such as Pt sheet in waste water degradation (Li et al., 2009) Acid Blue 9 (Khataee et al., 2009) and various azo dyes (Guivarch et al., 2003). Pt gauze has also being used for treating Sunset Yellow dye (Ghoneim et al., 2011) and for treating the dyes in textile waste water (El-Desoky et al., 2010). Indigo Carmine degradation using Pt foil as anode (Flox et al., 2006), Pt flakes used for degradation of Rodhamine B (Yuan et al., 2011) other form also used are Pt grid ,Pt plate , Pt mesh etc.

Boron-doped diamond (BDD) electrode is also used various researchers (Isarain-Chavez et al.,2010 Borra's et al.,2010, Pozzo et al.,2005) for treating various pollutants ,butut it is rarely used for a practical purpose because of its high cost. Other anodes studied are Titanium (Ti) coated with IrO_2/RuO_2 for studies on Reactive Dyes (Huang et al., 2008) and Acid Red 14 (Wang et al., 2005) .

3.2.2.2.2. Cathode

Efficiency of electro-Fenton system depends on cathode also known as working electrode. Mostly the carbon based cathode has been used in the literature but investigations have being done using various newly developed and commercial available electrodes also.

- *Carbon base*

  Graphite or carbon felt are commercially available electrodes which can be modified according to need has being investigated for degradation of Acid Blue 9 (Khataee et al., 2009), various azo dyes (Guivarch et al., 2003),textile waste water (lahkimi et al.,2007), Acid Red 97 (Kayan et al., 2010), Acid Yellow 36 (Ruiz et al., 2011).

  Carbon-polytetrafluoroethylene (PTFE) and graphite- PTFE have also been used for removal of dyes like Methyl red(Zhou.,2007) and Indigo Carmine (Flox et al.,2006). Other forms of carbon electrodes are modified 3d graphite electrode for removal of color from waste water (Wang et al., 2008), reticulated vitreous carbon (RVC) for treatment of Sunset Yellow (Ghonein et al., 2011) and reactive azo dyes (El-Desoky et al., 2010). Carbon sponge, activated carbon fiber (ACF) have also being used for treatment of various waste water.

Table 3.6 :- Mostly used Anodes and Cathodes in electro-Fenton for dye removal

Compound	Anode	Cathode	pH	Removal	Reference
Acid Blue 9	Pt sheet	Graphite felt	2.5-5	90%	Khataee et al., 2009
Basic Red 46	Pt/BDD	CNT-PTFE	3.0	31.7%	Zarei et al., 2010
Various Dyes	Pt	Carbon felt	3.0	89%	Lahkimi et al., 2007
Lissamine Green	Graphite bar	Graphite bar	2.0	100%	Rosales et al., 2009
Methyl red	Pt	Graphite powder/PTFE	3.0	>90%	Ma et al., 2009
Orange II	Pt	Graphite felt	3.0	90%	Daneshvar et al., 2008
Rhodamine B	Pt sheet	$Fe@Fe_2O_3$/ CNT	3; 6; 8	100%	Ai et al., 2007
Sunset Yellow	Pt gauze	RVC	3	97 %	Ghonaeim et al., 2011

- *Non Carbon Electrodes*

Various Non carbon electrodes have also being investigated Boron Doped Diamond (BDD) plate was used as cathode for decolorization of Acid yellow 36 (Cruz-González et al., 2010), Pt flakes, stainless steel , and titanium are some of the recently used working electrodes in wastewater treatment.

- *Composite electrodes*

The usage of composite electrodes is the emerging trend in electro-Fenton system. A noval Fe-CHI/Ni|ACF|Fe-CHI/ Ni sandwich film cathode have being tested for the removal of Rhodamine B (Fan et al., 2010). Other composites tired are Fe@Fe_2O_3/ACF (Li et al., 2009), Cu_2O/ CNTs/PTFE and Fe@Fe_2O_3/ CNT have also used as composite cathodes in electro-Fenton process (Ai et al., 2007).

3.2.2.2.3. Different configurations and comparison of electrodes

The different configurations of different types of electrodes used by various researchers are described in Table 3.7.Investigation had been done for the comparison of different types of the electrodes based upon removal efficiency of different electrodes. Oxidizing power of the four systems (i) a Pt/O_2 diffusion cell (ii) a BDD/O_2 diffusion cell (iii) a Pt/carbon felt cell and (iv) a BDD/carbon felt cell was studied to mineralize chlorophene solutions (Sire's et al., 2007). It was observed that BDD/O_2 diffusion cell has higher efficiency on applying high currents. This has being reported due to formation of hydroxyl radicals that increase the decay rate of organics (Ozcanet al., 2009).

Wang et al., (2005) compared the efficiency of activated carbon fiber and graphite cathodes for removing azo dye and Acid Red 14 from aqueous solution. Reviewers reported that the graphite was the best cathode material for electro generation of H_2O_2 while metal cathodes such as copper, stainless steel, lead and nickel were likely to decompose H_2O_2 (Nidheesh and Gandhimathi, 2012; Rosales et al., 2012). This agrees with the results reported for lissamine Green B dye (LGB) removal from aqueous solution using graphite and stainless steel electrodes (Rosales et al., 2009)**.**The graphite electrodes have higher discoloration rate, moreover, gradual corrosion was detected in stainless steel electrodes.

Table 3.7:- Different configurations used for dye degradation

Reactor Configuration	Compound	Anode	Cathode	Reference
Cylindrical glass cell of 500 mL capacity	Acid Blue 9	Pt sheet of 1 cm^2 area	Graphite felt of thickness=0.4 cm, having an area of 9.5 cm^2	Khataee et al., 2009
Cylindrical cell of 250 mL capacity	Acid Red 97	Pt gauze of area 6 cm2	Carbon felt of size 12.5 cm×4 cm	Kayan et al., 2010
Cylindrical glass cell of 100 mL capacity	Acid Yellow 36	Platinum (geometric area, 4 cm^2)	BDD plate having geometric area of 2 cm^2	Cruz-González et al., 2010
Thermostatic cell of 150 mL in volume	Rhodamine B	Pt sheet (purity: 99.99%) of area 2.0 cm^2	Cu_2O/CNTs/PTFE having an area of 3.0 cm^2	Ai et al., 2007
Glass electrochemical cell of 600 mL capacity	Sunset Yellow	Platinum gauze of an area 3.8 cm^2	RVC sheet of an area of 35 cm2 and thickness of 0.9 cm.	Ghoneim et al., 2011
Cell with a capacity of 0.55 L	Acid Red 14	RuO_2/Ti mesh of area 20 cm_2	20 cm^2 area of ACF felt	Wang et al., 2005
Glass cell of capacity 500 mL	Reactive Dye	Platinum gauze of an area 3.8 cm^2	RVC sheet of dimensions 5 cm×7 cm×0.9 cm	El-Desoky et al., 2010

3.2.2.3. Operating Parameters

- *Catalyst Concentration*

In order to assess the role of initial Fe^{2+} concentration studies were done on the oxidation of azo dye Sunset yellow using different concentration of $FeSO_4$ (Ghoneim et al., 2011). The increase in the concentration increase the decolorization how ever at higher concentration scavenging effect was observed also the increased Fe^{3+} reacts with H_2O_2 to produce $HO_2^{\bullet}$ decreasing the rate of oxidation. The feasibility of using low concentration of Fe^{3+} instead of Fe^{2+} to study the simultaneous decomposition and regeneration of Fe^{2+} ions (Oturan et al., 2010). It was observed that degradation rate reduces when concentration is decreased or increased from the optimal concentration. On reducing the concentration of Fe^{3+} limits the production of Fe^{2+} and on increasing the concentration the scavenging effect occur. The main interaction in Electro Fenton is between Fe^{2+} and H_2O_2 but the fast regeneration of Fe^{2+} also plays a role. Other study to ascertain the catalytic behavior of the Fe^{3+}/Fe^{2+} considering the regeneration of Fe^{2+} was degradation of Orange II under solar light (Bandara et al., 2007). It was observed that regeneration depends on the electrode potential and area, pH, temperature and catalyst content. The availability of the Fe ions depends on the pH as it can modify the oxidation state and cause precipitation or dissolution in bulk (Brillas et al., 2009).

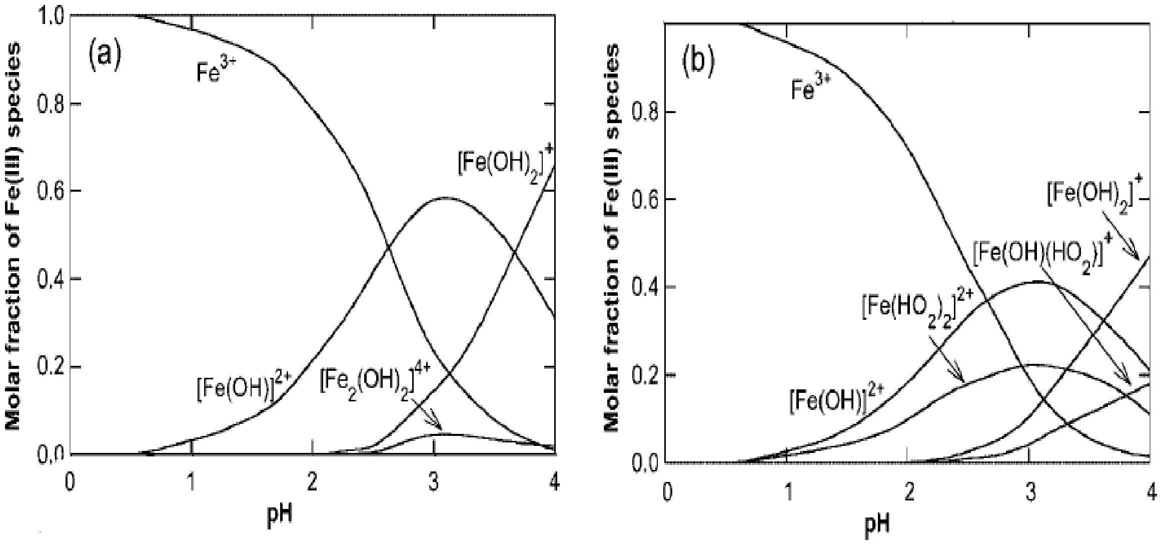

Fig.3.4:- Speciation of soluble Fe(III) species in acidic aqueous medium with 0.1 M $NaClO_4$ at 25 °C: (a) in the absence of H_2O_2 and presence of 1 mM Fe^{3+} and (b) in the presence of 0.5 M H_2O_2 and 0.5 mM Fe^{3+}. Source: - Brillas et al., 2009.

- *pH*

The pH of the reaction medium played an important role in the as it influence the oxidation sate of the ferrous ion. Fig 3.4 give details of the speciation of Fe^{3+} species in acidic solution in absence and presence of H_2O_2 (Brillas et al., 2009).

Acidic conditions favor the formation of hydroxyl radicals efficiently though strict control is necessary (Brillas et al., 2009). pH lower than 2.5 will lead to protons in the bulk surrounding the · OH resulting in less degradation of pollutant (Wang et al., 2010).More over at pH lower than 3 the formation of $[(Fe)^{2+(}H2O)^{2+}]$ occurs which is less reactive (Brillas et al., 2009). The low pH also promotes hydrogen evolution and ·OH scavenging **(**Wang et al., 2008). At higher pH the $Fe(OH)_3$ precipitates resist the Fenton reaction and decrease in the stability of H_2O_2.

The pH 3 as an optimal pH for electro-Fenton is quite contrary to rate of reaction obtained at pH 4 which is about 7 times greater than pH 3 due to formation of $Fe(OH)_2$ which is about 10 times more reactive then Fe^{2+} (Brillas et al., 2009).

To investigate the influence on the pH on the electro-Fenton process, study was conducted on Acid Red 14 and pH ranging from 1.49 to 4.98 (Wang et al., 2010). Apart from giving the similar results it was noticed that at higher pH 3.93 – 4.98 increases the rate of total organic carbon (TOC) as the pH of the solution decrease during the degradation of Acid Red 14 dye. However the change in the pH was not observed in degradation of reactive azo dyes in textile waste water and Electro fenton was found to be best at pH 3(El-Desoky et al., 2010).

The recent studies using the composite electrodes for degradation of Rhodamine B in nutral pH (Li et al., 2009).It was found that cathode $Fe@Fe_2O_3$/ACF was much better in nutral pH however in alkaline medium the residual concentration of Rhodamine B increase. The electro-Fenton applications at neutral pH have being demonstrated for effective degradation of Rhodamine B using Fe-CHI/Ni|ACF|Fe-CHI/Ni sandwich film cathode (Fan et al., 2010) and Fe_0/ACF (Li et al., 2011) for degradation of Orange II.

- *Current density*

The current is the driving force for the reduction of oxygen leading to the generation of hydrogen peroxide at the cathode. Higher applied current means more the quantum of hydrogen peroxide is produced, thus increasing the number of hydroxyl radicals (Sankara Narayanan et al., 2003). Other thing that higher applied current density means is higher applied voltage on the electrochemical system which leads to higher electro-regeneration of ferrous ion from ferric ion (Wang et al., 2010).

However the efficiency of electro-Fenton will be less at higher current density due to the competitive electrode reactions of discharge of oxygen at anode and the evolution of hydrogen at cathode. These reactions inhibit main reaction and lead to decrease in efficiency of electro-Fenton (Nideesh and Gandhimathi et al., 2012). Most of the investigators agree on low current density with values like 10A/m^2, 6.4 A/m^2 as upper limit for electro-Fenton (Zhang et al., 2006). The current value of 300 mA is mentioned after which the rate of degradation becomes constant and side reactions increase (Özcan et al., 2009).

- *Distance between the electrode*

Distance between electrodes is another important factor that affects the efficiency of the electro-Fenton. Distance is linked to energy consumption as decrease in the distance leads to a decrease of the ohmic drop through the electrolyte which is an equivalent decrease of the cell voltage and energy usage (Fockedey and Van Lierde, 2002). Other study reported was COD removal efficiency from landfill leachate. In this study the distance between electrode was varied between 1.3 and 2.1 cm (Zhang et al., 2006). It was observed that efficiency was less for shorter as well as for longer distances. In case of shorter distance Fe^{2+} could be easily oxidized to ferric ion at the anode which reduced the amount of Fe^{2+} for Fenton reaction. Whereas the longer distance causes the limiting mass transfer effect for the regeneration of Fe ions

Many recent reviews) reported insignificant effect of distance on the efficiency of Electro fenton (Nidheesh and Gandhimathi, 2014).However use of long distances caused significant increase in the energy consumption (Atmaca, 2009).

CHAPTER 4
LACUNAE AND OBJECTIVES

4.1. Lacunae

- Lot of scientific data has been published for the use of different type of electrodes for electro-Fenton and electro-oxidation (Chlorination) processes using costly metals and also doping using rare earth metals which make real time application difficult.
- The Indivigual study of the electro-oxidation and electro-Fenton is rarely done as most of researchers are not able to separate the processes
- The process parameters effecting the reactions of both electro-fenton and electro-Chlorination need more investigations as enormous differences in optimized parameters are found in literature.
- The combined electro-Fenton and electro-chlorination technique need to be studied for better removal of pollutants and reduce the residual harmful products.

4.2. Objectives

- Selection of Electrodes for electro-chlorination and electro-Fenton decolorization and degradation study of Reactive Black 5 (RB 5) Dye.
- Process optimization study of process parameters for degradation and decolorization of compound using RSM.
- Combined approach study of electro-chlorination and electro-Fenton for better degradation and decolorization of compound

CHAPTER 5
MATERIAL AND METHODS

In this chapter, materials and methods used to study the electro-Fenton and electro-Chlorination are described in details, including chemicals, instruments, electrodes, batch reactor, analysis along with procedures used.

5.1. Chemicals

In this study, azo dye RB 5 (55% purity, Sigma- Aldrich) was used as model compound for treatment and structure of RB5 is shown below in Fig.5.1. Distilled water was used for making dye solution by dissolving requisite amount of dye. Sodium Sulfate (Anhydrous, Loba Chemie) used for increasing the conductivity of solution. Sodium Chloride (NaCl, S d Fine-chem limited) was used for providing the Cl^- ions and also for increasing the conductivity. Ferrous Sulphate ($FeSO_4.7H_2O$, S d Fine-chem limited) was used as iron source in electro-fenton reaction. For adjusting the pH, H_2SO_4 and NaOH were used.

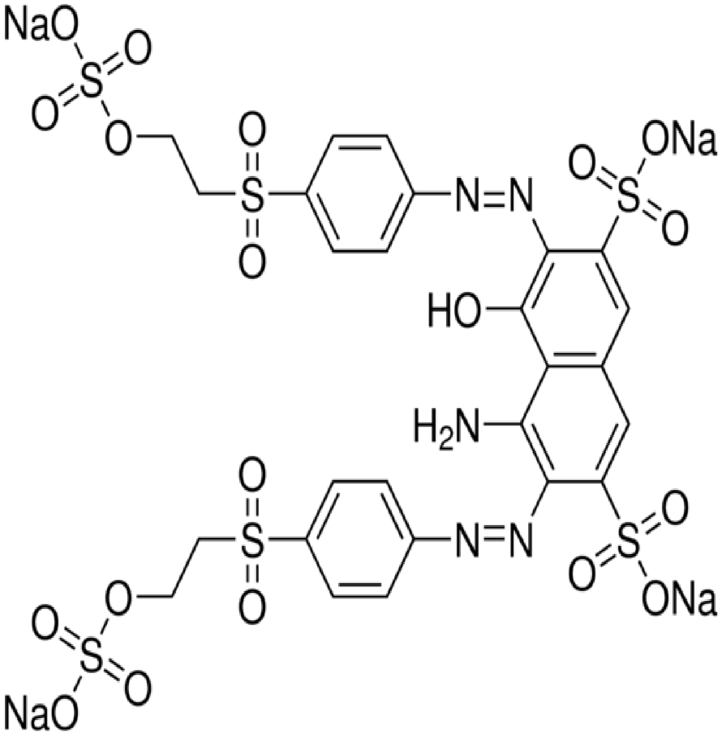

Fig.5.1 Structure of Reactive Black 5 (RB 5)

5.2. Instruments Used

- pH meter

The pH meter (HACH, SensION pH3) was used to adjust the pH of the solution using 0.1N H_2SO_4 and 0.1N NaOH. Instrument was calibrated weekly with freshly prepared buffer solutions (pH 4, 7, 9).

- Conductivity Meter

The Conductivity meter (HACH, SensION+ EC 7) was used to adjust the conductivity of the solution using Na_2SO_4 and NaCl. Instrument was calibrated weekly with buffer solutions (147uS/cm, 1413uS/cm, and 12.88mS/cm).

- UV-Vis Spectrophotometer

UV-Vis spectrophotometer (LABINDIA, model no. T60 U) was used to check Dye degradation at 310 nm and Dye decolorization at 595 nm.

5.3. Reactor

Batch reactor was designed and fabricated using glass for the carrying out the reactions Fig.5.2. The single large reactor was divided into two for carrying out two simultaneous reactions.

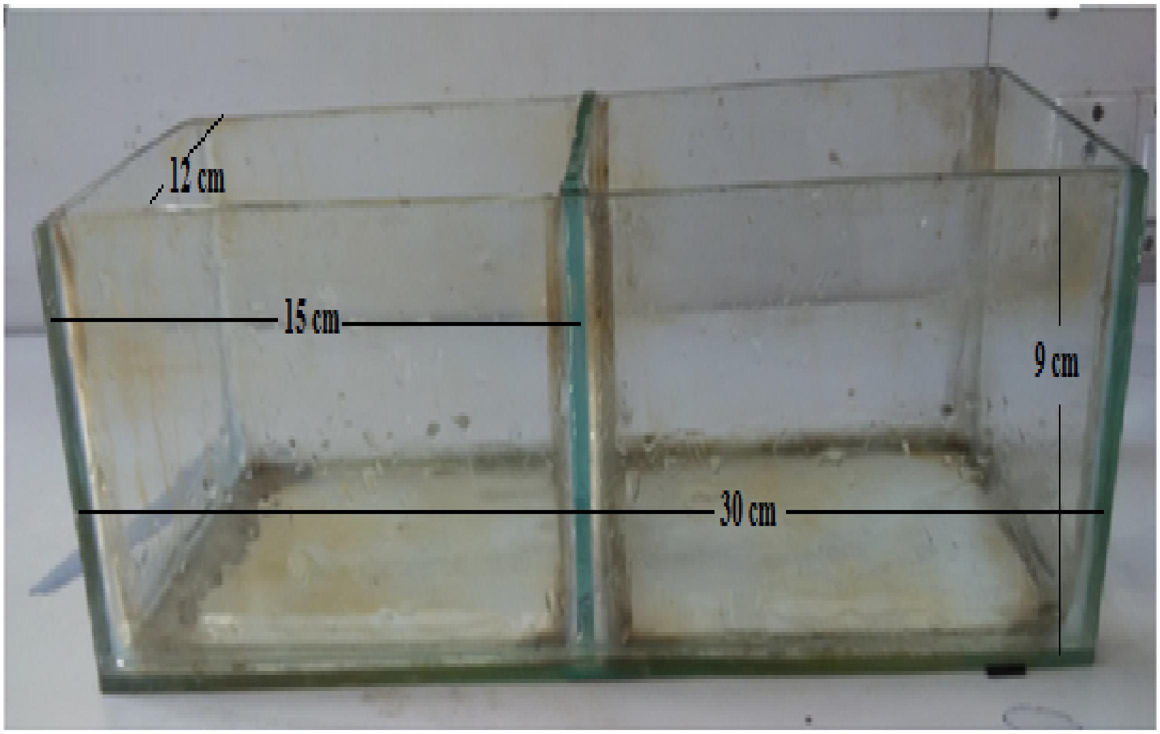

Fig.5.2 Fabricated Glass reactor

5.4. Electrodes

Choosing the electrode is most essential part of the electro-fenton as well as electro-Chlorination. In this study the commercially available graphite materials were chosen as the electrode and desired fabrication was done to be used in reactor.

- *Graphite sticks*

First kind of electrode fabricated was using the graphite pencil sticks (leads). Graphite sticks 2mm*90 mm (Camlin Hi Par) Fig.5.3(a) were purchased from the local market and fabricated using the acrylic sheet to form the single electrode having fifteen (15) sticks horizontally placed without overlapping and vertical sticks for providing the current as shown in Fig.5.3b.The special modifications was done to fit in the air sparger Fig.5.3(c)

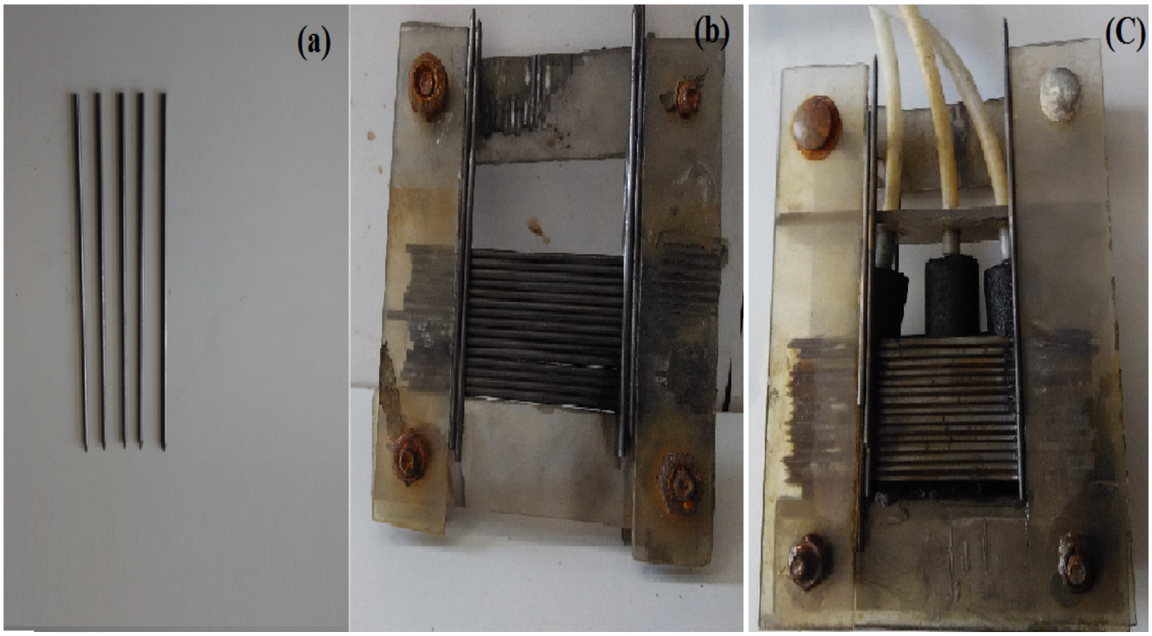

Fig.5.3 Electrodes Used. (a) Graphite pencil sticks (leads),(b) Fabricated electrode ,(C) Modified fabricated electrode

- *Carbon Fiber (Cloth and reinforcement)*

The commercial available carbon fibers were also used. The Avcarb Carbon Cloth (purcsed from M/s Vinpro Tech, Hyderabad) Fig.5.4(a) and commercially available carbon reinforcement (obtained as gift sample from Civil Department research scholars) were used as cathode and compared with fabricated cathode.

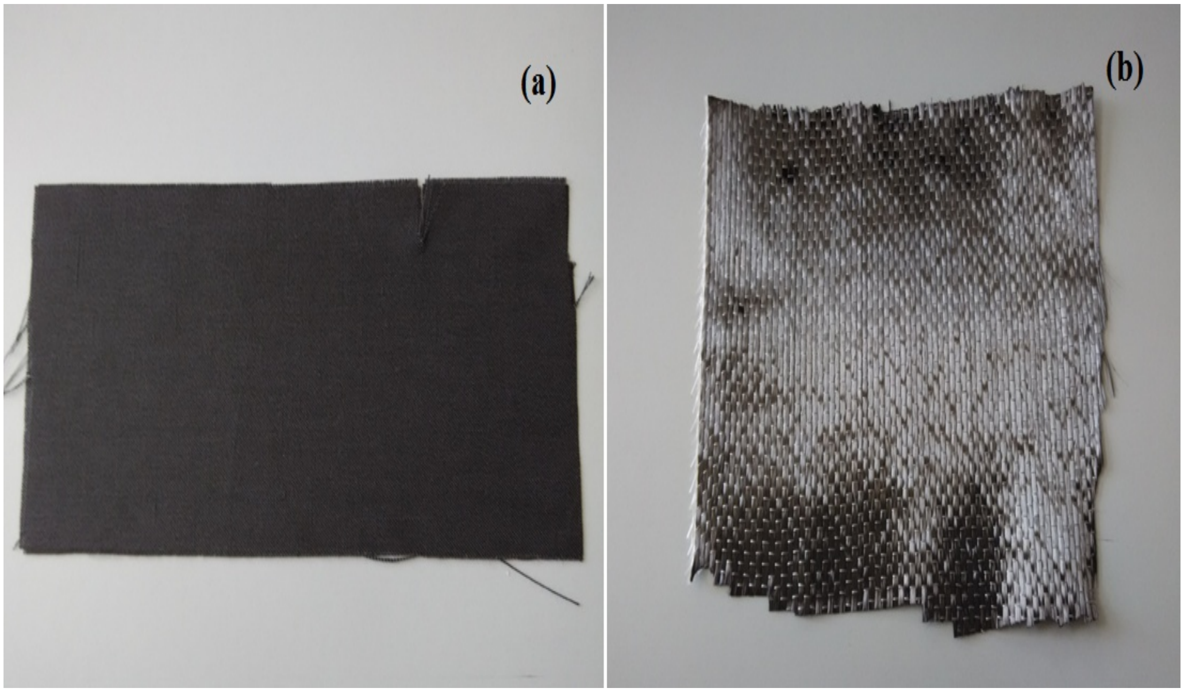

Fig.5.4 Carbon Fibers (a) Carbon Cloth, (b) Carbon Reinforcement

5.5. Air Pump

The air pump used for aeration (Resun AIR-PUMP, ACO-003) had power of 35 W. With air being released at 0.027 MPa with output of 65L/min

5.6. Experimental Setup

The electro-oxidation and electro-Fenton reactions were done in batch reactor made of glass of 4 mm thickness as shown as described in section 5.3. The working volume of the RB 5 solution in the each part of reactor to be treated was chosen as 1 liter. The electrode chosen for the reaction was fabricated described in section 5.4. In case of electro-fenton the cathode chosen was modified electrode fitted with air spargers Fig.5.3(c) and anode chosen was the normal electrode shown in Fig.5.3(b). For electro-chlorination both the electrodes taken were normal electrode shown in Fig.5.3(b). The direct current power supply was used to supply the current during experiment along with magnetic stir was used to agitate the wastewater sample and air supply was used only in electro-Fenton reaction using air pump (65L/min). The schematic diagram of experimental setup was shown in Fig.5.5(a) for electro-Fenton and Fig.5.5(b) electro-chlorination.

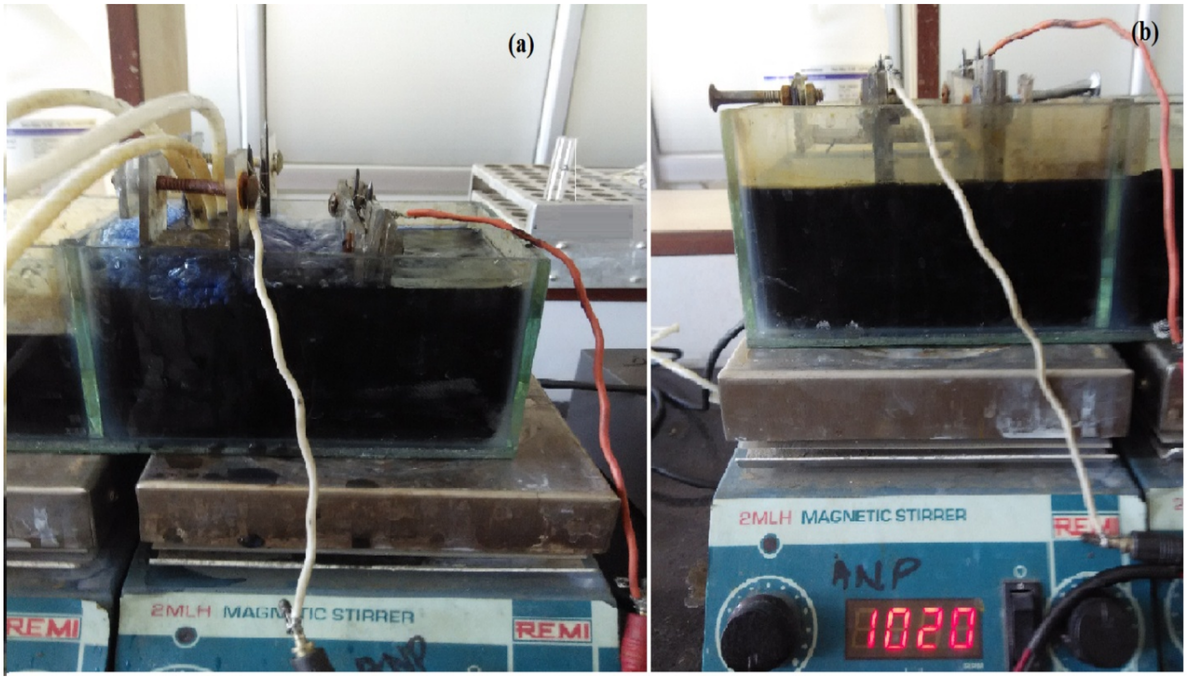

Fig.5.5 Experimental setup for electro-chlorination and electro-Fenton

5.7. Experimental Procedure

Simulated dye wastewater was prepared by dissolving 91 mg RB 5 (55% pure) dye in 1 liter of distilled water to prepare 50 mg/L solution. As the conductivity of the dye is low, for electro-Fenton reactions the conductivity of solution was increased (2.18 mS) using Na_2SO_4. In case of electro-chlorination NaCl (1.75 gm/L) was used keeping the Cl ion concentration and conductivity (2.2 mS) fixed.

The pH of the dye solution was adjusted to the desired level by adding 0.1N NaOH or 0.1 N H_2SO_4 solutions. Spectro-photometric technique was used to measure the concentration of dye in solution after the treatment of sample. Dye degradation was measured at 310 nm and Dye decolorization at 595 nm to determine the %age of degradation of dye and % removal of color.

5.8. RSM

Response surface methodology is a collection of mathematical and statistical techniques that is useful for modeling analysis involving 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 and optimization. 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.

Central composite design (CCD) based on RSM was used for experimental design, which is used to construct second order model efficiently. CCD is first-order (2N) designs augmented by additional centre and axial points to allow estimation of the tuning parameters of a second-order model .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

Design Expert 9 trail version was used for experimental design and 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 for both electro-Fenton and electro-chlorination

For Electro Fenton four operation parameters variables pH 2-6, catalyst concentration 0.025 mg/L – 0.5mg/L current 150 mA - 400mA and distance between the electrodes were considered as input parameters. Table 5.1(a) shows the operational variable conditions used to design the matrix. In case of electro-chlorination three parameters were pH 4-10, current 150 mA - 400mA and distance between the electrodes were considered as input parameters Table 5.1(b).The full factorial design for both obtained by design expert is shown in tables 5.2(a),(b).

Table 5.1 (a)Range of variables and levels of the design model for electro-Fenton

Factor	Name	Units	Minimum	Maximum	Coded Values	
A	pH	----	2	6	-1 =2	1. 0=6
B	catalyst	mg/L	0.025	0.5	-1. =0.025	1. =0.5
C	Current	mA	150	400	-1. =150	1. =400
D	Distance	Cm	0.5	6	-1. =0.5	1. =6

Table 5.1 (b)Range of variables and levels of the design model for electro-chlorination

Factor	Name	Units	Minimum	Maximum	Coded Values	
A	distance	cm	0.5	6	-1. =0.5	1.=6
B	pH	----	4	10	-1.=4	1.=10
C	current	mA	150	400	-1.=150	1.=400

Table 5.2 (a)Full Factorial Design for electro-Fenton

			Factor 1	Factor 2	Factor 3	Factor 4
Std	Block	Run	A:pH	B:catalyst	C:Current	D:Distance
				mg/L	mA	cm
1	Day 2	14	2	0.025	150	0.5
2	Day 1	3	6	0.025	150	0.5
3	Day 1	6	2	0.5	150	0.5
4	Day 2	17	6	0.5	150	0.5
5	Day 1	4	2	0.025	400	0.5
6	Day 2	15	6	0.025	400	0.5
7	Day 2	16	2	0.5	400	0.5
8	Day 1	9	6	0.5	400	0.5
9	Day 1	2	2	0.025	150	6
10	Day 2	18	6	0.025	150	6
11	Day 2	20	2	0.5	150	6
12	Day 1	1	6	0.5	150	6
13	Day 2	11	2	0.025	400	6
14	Day 1	7	6	0.025	400	6
15	Day 1	10	2	0.5	400	6
16	Day 2	13	6	0.5	400	6
17	Day 1	5	4	0.2625	275	3.25
18	Day 1	8	4	0.2625	275	3.25
19	Day 2	12	4	0.2625	275	3.25
20	Day 2	19	4	0.2625	275	3.25
21	Day 3	21	2	0.2625	275	3.25
22	Day 3	25	6	0.2625	275	3.25
23	Day 3	24	4	0.025	275	3.25
24	Day 3	28	4	0.5	275	3.25
25	Day 3	26	4	0.2625	150	3.25
26	Day 3	27	4	0.2625	400	3.25
27	Day 3	29	4	0.2625	275	0.5
28	Day 3	23	4	0.2625	275	6
29	Day 3	30	4	0.2625	275	3.25
30	Day 3	22	4	0.2625	275	3.25

Table 5.2 (b)Full Factorial Design for electro-Chlorination

		Factor 1	Factor 2	Factor 3
Std	Run	A:distance	B:pH	C:current
		Cm	----	Ma
5	1	0.5	4	400
20	2	3.25	7	275
14	3	3.25	7	400
8	4	6	10	400
7	5	0.5	10	400
10	6	6	7	275
4	7	6	10	150
18	8	3.25	7	275
13	9	3.25	7	150
6	10	6	4	400
19	11	3.25	7	275
1	12	0.5	4	150
16	13	3.25	7	275
12	14	3.25	10	275
2	15	6	4	150
15	16	3.25	7	275
11	17	3.25	4	275
9	18	0.5	7	275
3	19	0.5	10	150
17	20	3.25	7	275

CHAPTER 6
RESULTS AND DISCUSSION

The experimental results of degradation and decolorization of the synthetic RB 5 dye wastewater by electro-Fenton and electro-chlorination method using graphite electrodes have being 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. All experiments were conducted in triplicates for reproducibility of the results.

6.1. Reactive Black 5 (RB 5) Dye Compound Characteristics:

- *Absorption Spectra Of RB 5*

The absorption spectrum of RB 5 was recorded with a "UV- vis. Spectrometer (LAB INDIA T60 U). Total 2 peaks were observed in absorption spectra one is at 310 nm (UV range) due to the presence of complex structure and another is at 595 nm due to presence of color as shown in Fig.6.1. Therefore reduction of RB 5 concentration is measured at both wavelength 310 nm and 595 nm.

- *Standard Curve Of RB 5*

Fig.6.2 and Fig.6.3 shows the standard curve for RB 5 which is prepared by plotting the absorbance of known concentration varying from 10mg/L to 100 mg/L at 310 nm and 595 nm against concentration. Value of R^2 is 0.9985 and slope is 0.016 at wavelength 310 nm and R^2 is 0.9981 and slope is 0.0223 at wavelength 595 nm.

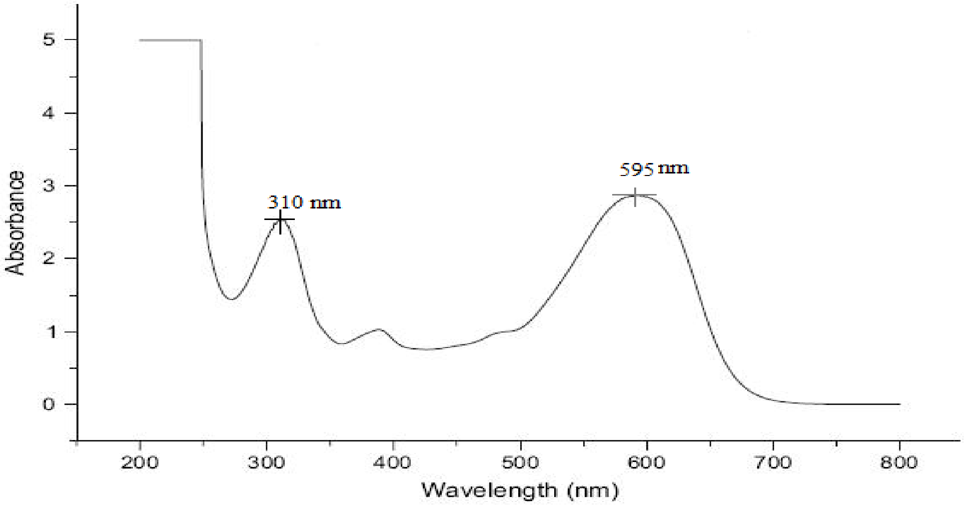

Fig.6.1: Adsorption spectra of RB 5 showing two peaks at 310nm and 595 nm

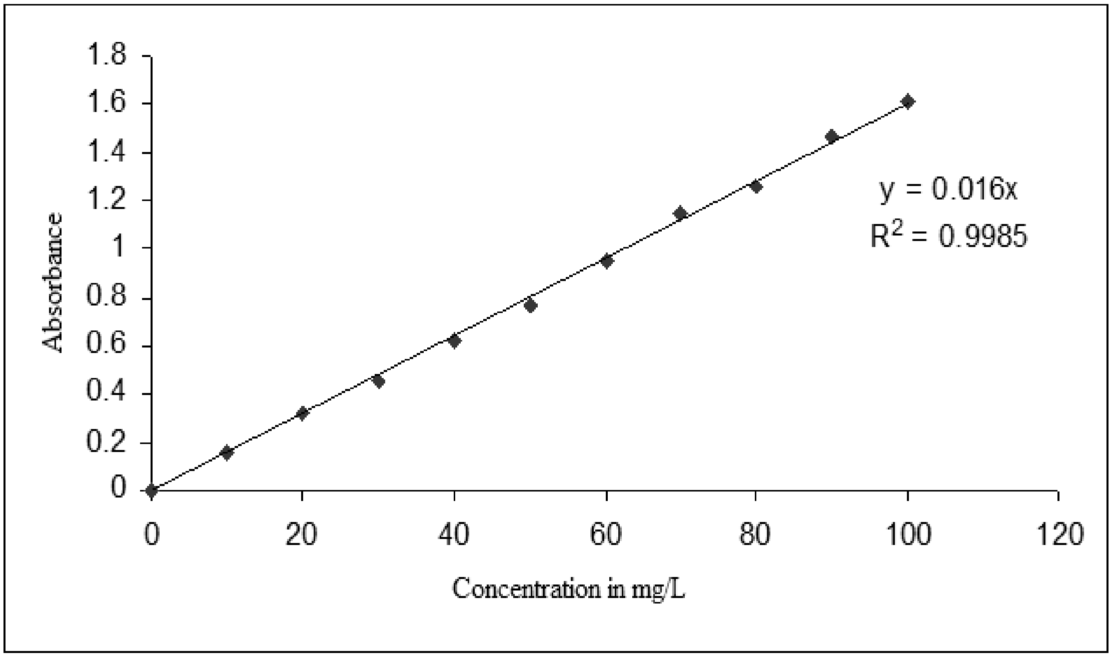

Fig.6.2: Calibration curve of RB 5 at wavelength 310 nm

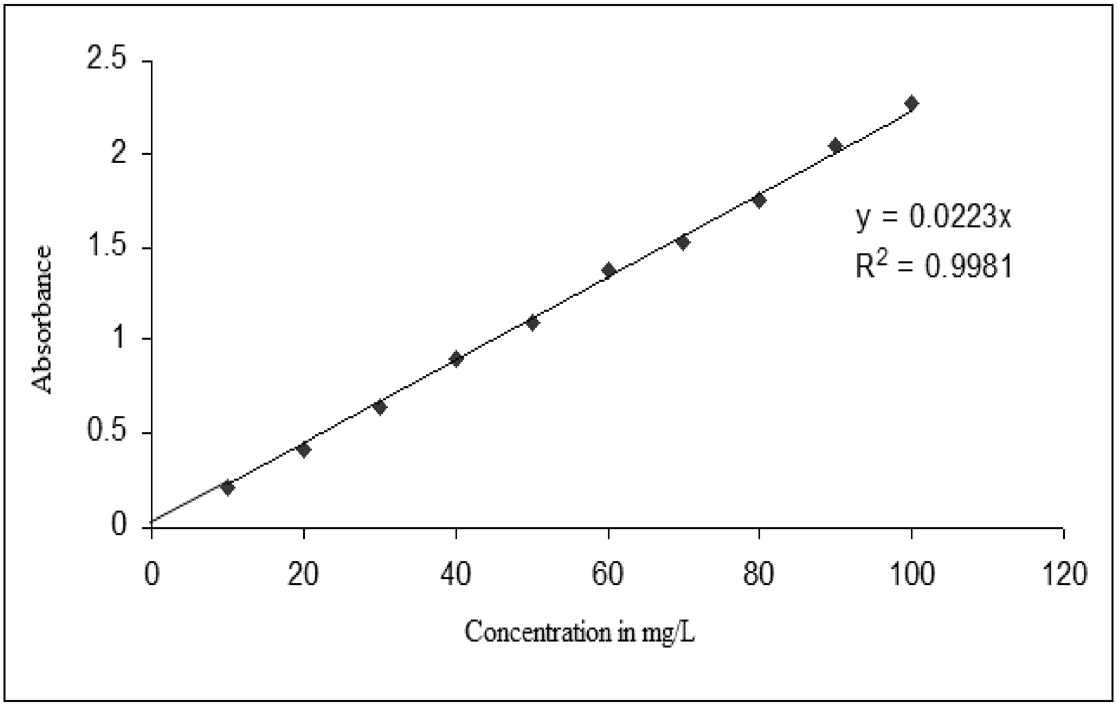

Fig.6.3: Calibration curve of RB 5 at wavelength 595 nm

6.2. Electro-Fenton Treatment of RB 5 Dye

6.2.1. Preliminary Studies

The initial study were conducted for decolorization of RB 5 50 mg/L waste water with added Na_2SO_4 solution to make the conductivity of the solution to 2.18 mS. .The reactions were carried with Fe only, with only current application and combination of both Fe and current keeping all the other parameters like aeration, pH and distance between the electrode and volume of wastewater constant parameters constant.

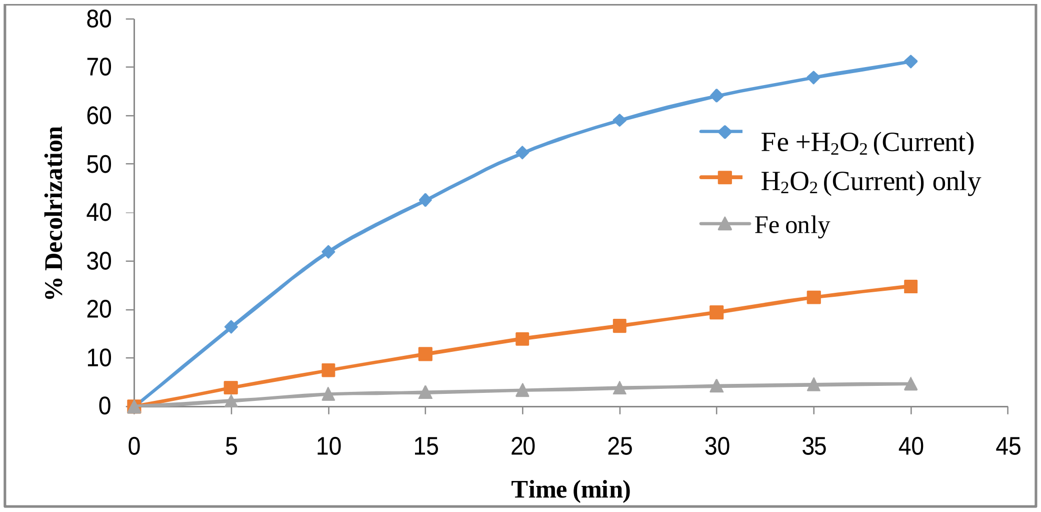

Fig.6.4: Preliminary study of electro-Fenton using graphite electrode, (C_0=50mg/L , pH=3,Current 250 mA,Fe= 0.25mg/L)

The simultaneous presence of the fenton reagents gives the best results as seen from Fig.6.4. As only hydrogen peroxide is not self sufficient to break the complex structure of the dye. The Fe^{3+} ions stability leads to formation of $Fe(OH)_3$ which removes dyes through coagulation and co precipitation.

Further the preliminary degradation and decolorization experiment was conducted at 3pH, 250 mA current and catalyst ($FeSO_4$) amount 0.25 mg/L and 1 liter of RB5 waste water having 2.18 mS conductivity, to study the kinetic of the reaction and to fix the parameters for the RSM optimization. From the preliminary studies Fig.6.5 it can be seen that rate of reaction increases till 40 minutes and then rate starts to become constant. Thus for all the experiments the time of completion of reactions was optimized to 40 minutes. Further the parameters such as pH, catalyst concentration, distance between electrodes and applied current need to be optimized.

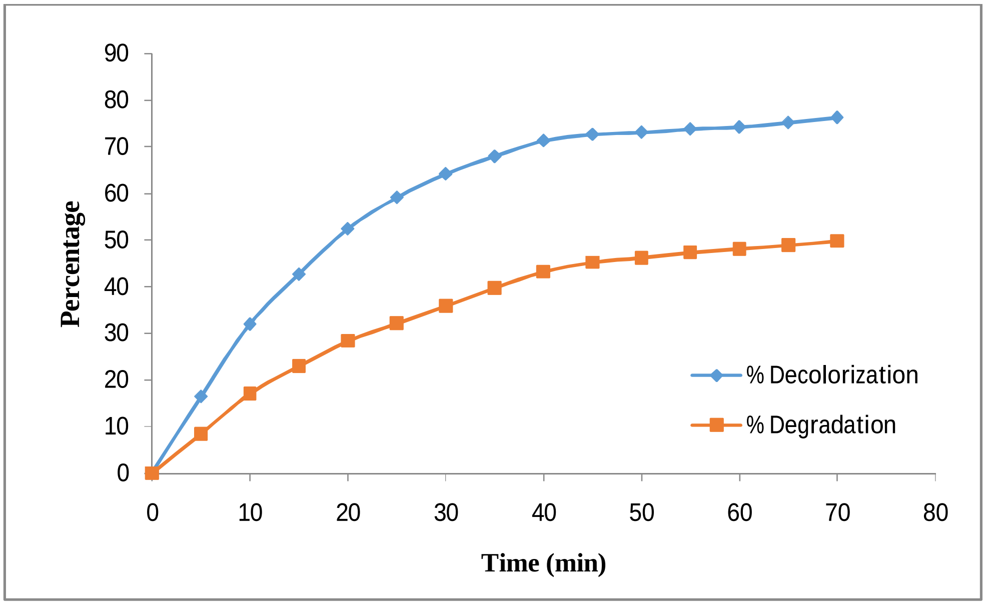

Fig.6.5: Preliminary study of electro-Fenton using graphite electrodes, for degradation and decolorization (C_0=50 mg/L, Current 270 mA, Fe= 0.25mg/L, pH=3)

6.2.2. RSM Optimization For Dye Removal using Electro-Fenton

Central Composite Design (CCD) based on RSM was used for experimental design. Four operation parameters variables pH 2-6, catalyst concentration 0.025 mg/L – 0.5mg/L current 150 mA - 400mA and distance between the electrodes 2cm -6 cm were considered as input parameters and percentage of decolorization , percentage of dye degradation were taken as responses of the system keeping volume one liter as constant and the time of reaction constant as 40 minutes .

- *Statistical Analysis*

  Statistical analysis involves 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. These were performed to establish an optimum condition for the experiments. A total number of 30 simulation experiments designed by RSM, were conducted to study the effects of the four parameters pH, catalyst concentration, current, distance between electrodes on response percentage of dye decolorization (Response 1), percentage of dye degradation (Response 2) keeping the time of reaction constant for 40 minutes.

Table 6.1: Full factorial design used for the electro-Fenton with responses

Run	Factor 1 A:pH	Factor 2 B:catalyst	Factor 3 C:Current	Factor 4 D:Distance	Response 1	Response 2
	pH	mg/L	Ma	cm	Decolorization %	Degradation %
1	6	0.5	150	6	41.6749	34.1694
2	2	0.025	150	6	37.9201	28.5513
3	6	0.025	150	0.5	34.0334	22.3456
4	2	0.025	400	0.5	67.9201	54.7921
5	4	0.2625	275	3.25	77.7631	59.192
6	2	0.5	150	0.5	42.0167	36.1467
7	6	0.025	400	6	69.1117	46.4142
8	4	0.2625	275	3.25	75.2743	57.3785
9	6	0.5	400	0.5	80.5139	65.6279
10	2	0.5	400	6	75.7087	67.5406
11	2	0.025	400	6	69.3103	49.1946
12	4	0.2625	275	3.25	72.0156	55.0061
13	6	0.5	400	6	91.4115	69.311
14	2	0.025	150	0.5	36.7367	26.5817
15	6	0.025	400	0.5	64.9667	48.3721
16	2	0.5	400	0.5	75.9473	68.9111
17	6	0.5	150	0.5	49.2228	36.6171
18	6	0.025	150	6	35.8557	24.8221
19	4	0.2625	275	3.25	71.5737	54.1667
20	2	0.5	150	6	46.5755	38.0033
21	2	0.2625	275	3.25	72.0078	54.9751
22	4	0.2625	275	3.25	76.7825	52.7765
23	4	0.2625	275	6	70.4484	48.1327
24	4	0.025	275	3.25	72.8172	51.4301
25	6	0.2625	275	3.25	70.4899	48.049
26	4	0.2625	150	3.25	43.0005	35.8964
27	4	0.2625	400	3.25	72.3702	54.4121
28	4	0.5	275	3.25	77.7596	59.3135
29	4	0.2625	275	0.5	69.3893	61.4121
30	4	0.2625	275	3.25	74.5946	53.3135

The responses (degradation and decolorization) of electro-Fenton treatment of RB 5 with graphite electrodes were calculated according to the setting of various operational parameters as given in design matrix of experiments and results are shown in Table 6.1. Quadratic model was fitted to the experimental data to obtain the regression equations. Natural log transformation was used for both responses. Sequential model sum of squares Table 6.2(a, b) and model summary statistics Table 6.3(a, b) were tested to decide the adequacy of model.

Table 6.2(a) Sequential model sum of squares for electro-Fenton for % dye decolorization using natural log transformation

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Mean vs Total	508.95	508.95			
Block vs Mean	0.21	0.11			
Linear vs Block	1.77	0.44	20.77	< 0.0001	
2FI vs Linear	0.024	4.004E-003	0.15	0.9873	
Quadratic vs 2FI	0.42	0.11	33.68	< 0.0001	Suggested
Cubic vs Quadratic	0.028	3.518E-003	1.37	0.3780	Aliased
Residual	0.013	2.560E-003			
Total	511.42	17.05			

Table 6.2(b) Sequential model sum of squares for electro-Fenton for % dye degradation using natural log transformation

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Mean vs Total	443.40	443.40			
Block vs Mean	0.14	0.070			
Linear vs Block	2.21	0.55	28.16	< 0.0001	
2FI vs Linear	0.018	2.979E-003	0.12	0.9930	
Quadratic vs 2FI	0.34	0.085	12.18	0.0002	Suggested
Cubic vs Quadratic	0.083	0.010	6.00	0.0321	Aliased
Residual	8.599E-003	1.720E-003			
Total	446.20	14.87			

Table 6.3 (a)Model summary statistics for electro-Fenton for % dye decolorization using natural log transformation

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	
Linear	0.15	0.7832	0.7455	0.6799	
2FI	0.17	0.7938	0.6725	0.3928	
Quadratic	0.056	0.9819	0.9623	0.8655	Suggested
Cubic	0.051	0.9943	0.9694	-4.5905	Aliased

Table 6.3 (b)Model summary statistics for electro-Fenton for % dye degradation using natural log transformation

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	
Linear	0.14	0.8304	0.8009	0.7487	
2FI	0.16	0.8372	0.7414	0.5056	
Quadratic	0.084	0.9657	0.9288	0.7892	Suggested
Cubic	0.041	0.9968	0.9825	-1.9525	Aliased

Sequential model sum of squares showed that quadratic model best fits the experimental data for responses. Higher order models were found to be aliased for responses. The model gives coefficient of determination gives the R^2 value as .9819, .9657 respectively for percentage decolorization and percentage degradation. The adjusted R^2 values as .9623, .9288 and predicted R^2 values as .8655 and .7892 respectively for percentage decolorization and degradation.

A good correlation between the observed and predicted values can be seen in Fig.6.6(a,b). Normal probability and Studentized residual plots which implies the difference between a predicted value and the observed value dividing by the standard error of the residual shown in Fig.6.7(a,b) shows to have close relation with % Normal probability in both degradation and decolorization

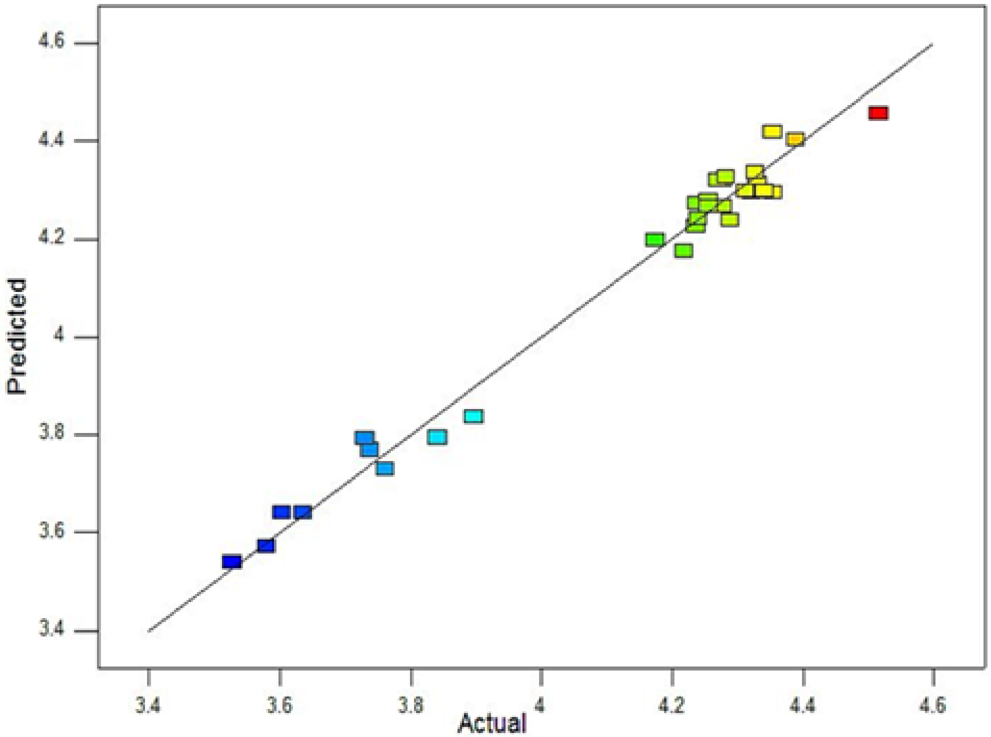

Fig.6.6 (a) Residual plots (actual versus predicted) for %dye decolorization using electro-fenton

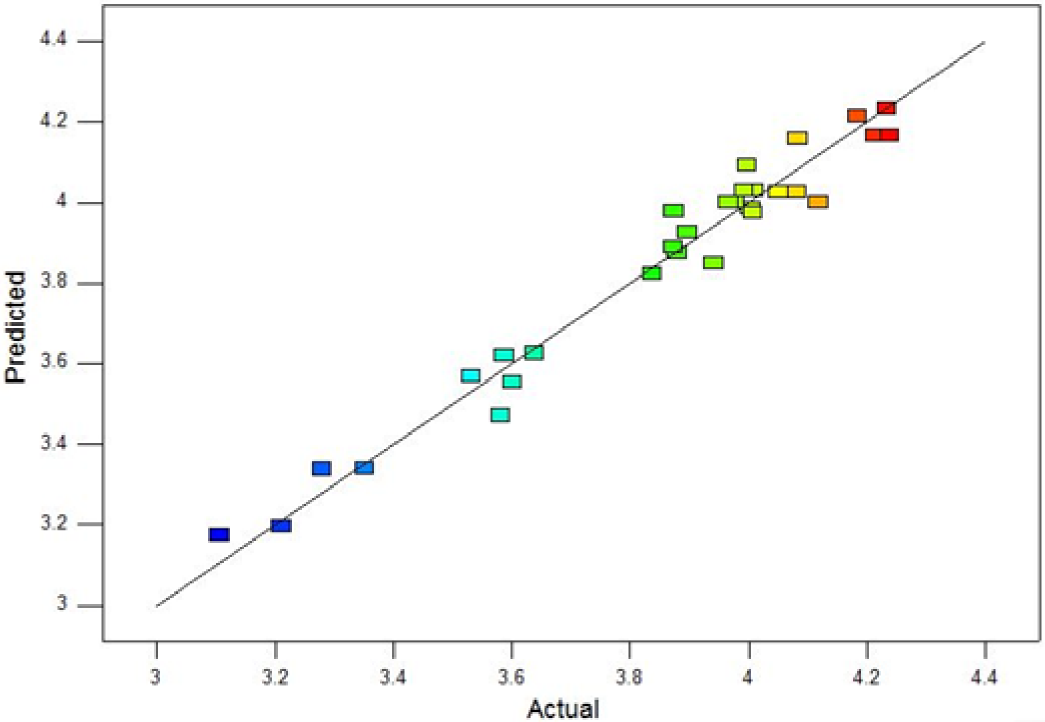

Fig.6.6 (b) Residual plots (actual versus predicted) for %dye degradation using electro-Fenton

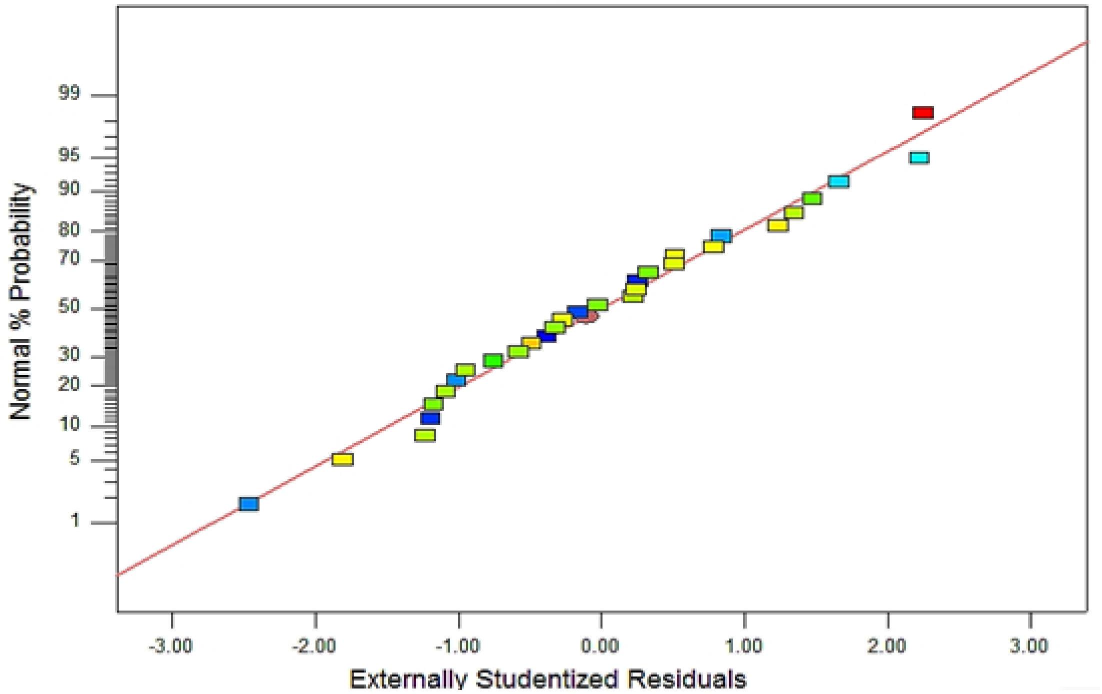

Fig.6.7 (a) Residual Normal plot for % dye decolorization using electro-Fenton

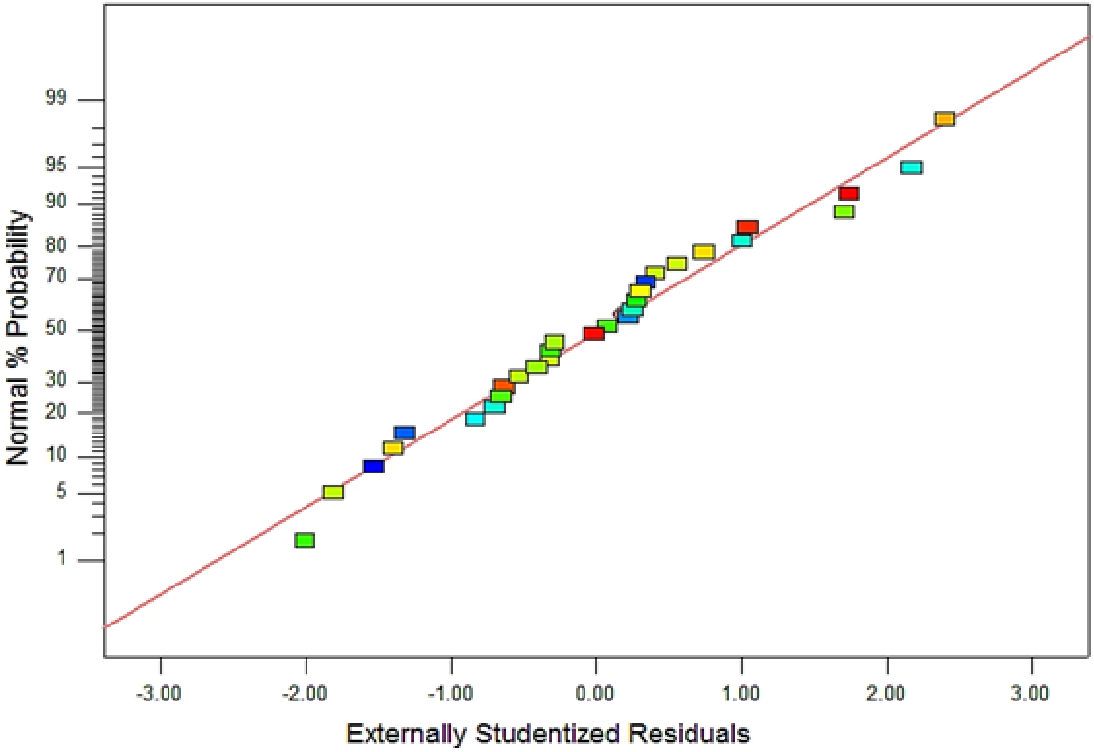

Fig.6.7 (b) Residual Normal plot for % dye degradation using electro-Fenton

The analysis of variance (ANOVA) shows model F-value of 50.25, 26.15 for percentage decolorization and degradation respectively. This implies that model considered is significant for both the responses as shown in Tables 6.4(a,b) 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 catalyst concentration, current, current^2 were highly significant terms for percentage decolorization as well as for percentage degradation.

Table 6.4 (a)ANOVA for electro-Fenton quadratic model % decolorization

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Block	0.21	0.11			
Model	2.22	0.16	50.25	< 0.0001	Highly significant
A-pH	4.799E-004	4.799E-004	0.15	0.7026	
B-catalyst	0.15	0.15	46.25	< 0.0001	Highly significant
C-Current	1.62	1.62	513.68	< 0.0001	Highly significant
D-Distance	3.239E-003	3.239E-003	1.03	0.3290	
AB	0.014	0.014	4.45	0.0548	
AC	5.071E-003	5.071E-003	1.61	0.2267	
AD	3.738E-004	3.738E-004	0.12	0.7360	
BC	1.703E-003	1.703E-003	0.54	0.4752	
BD	6.973E-004	6.973E-004	0.22	0.6458	
CD	2.150E-003	2.150E-003	0.68	0.4235	
A^2	1.667E-003	1.667E-003	0.53	0.4798	
B^2	2.140E-003	2.140E-003	0.68	0.4246	
C^2	0.19	0.19	58.86	< 0.0001	
D^2	5.014E-003	5.014E-003	1.59	0.2292	
Residual	0.041	3.149E-003			
Lack of Fit	0.040	3.998E-003	12.42	0.0309	significant
Pure Error	9.658E-004	3.219E-004			
Total	2.47				

Table 6.4(b)ANOVA for electro-Fenton quadratic model for % degradation

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Block	0.14	0.070			
Model	2.57	0.18	26.15	< 0.0001	Highly significant
A-pH	0.031	0.031	4.43	0.0554	
B-catalyst	0.44	0.44	62.20	< 0.0001	Highly significant
C-Current	jb1.74	1.74	247.84	< 0.0001	Highly significant
D-Distance	2.238E-003	2.238E-003	0.32	0.5817	
AB	9.025E-003	9.025E-003	1.29	0.2770	
AC	2.531E-003	2.531E-003	0.36	0.5583	
AD	1.924E-004	1.924E-004	0.027	0.8710	
BC	1.492E-003	1.492E-003	0.21	0.6522	
BD	9.131E-006	9.131E-006	1.302E-003	0.9718	
CD	4.626E-003	4.626E-003	0.66	0.4313	
A^2	0.011	0.011	1.63	0.2241	
B^2	6.066E-005	6.066E-005	8.652E-003	0.9273	
C^2	0.12	0.12	17.21	0.0011	Highly significant
D^2	2.992E-004	2.992E-004	0.043	0.8395	
Residual	0.091	7.011E-003			
Lack of Fit	0.090	9.049E-003	41.53	0.0054	Significant
Pure Error	6.536E-004	2.179E-004			
Total	2.80				

The final quadratic equation in terms of coded factors for Percentage degradation removal and %age of dye degradation are given below.

Ln(Decolorization)=2.21215342658+.020747459683577*pH-0.012413993543989* catalyst+0.011607799563305*Current+0.039970918091271*Distance+0.06233169831747* pH*catalyst+7.1210155732169e-005 *pH*Current -0.00087882077170585 *pH * Distance -0.00034754573435522*catalyst*Current-0.010108018540154*catalyst*Distance +3.3725844488196e-005*Current*Distance-0.0064068130075633*pH^2 +0.51479470200249 * catalyst^2-1.7295719027472e-005* Current ^{2}-0.0058767345427665* Distance ^{2}

Ln(Degradation) = 1.9743268030745+ 0.084411708371822 * pH + 0.50309092942933* catalyst+0.010205159909731*Current+0.016661031873804*Distance+0.050001137867106 * Ph*catalyst+ 5.0308022375978e-005*Ph*Current + 0.0006305489803405 * Ph*Distance -0.0003253127062763*catalyst*Current-0.0011566656463153*catalyst*Distance 4.9464053884401e-005*Current*Distance-0.01677268150832* Ph^2 +0.086663074185587 * catalyst^2 -1.395391870506e-005*Current^2-0.0014356911641898 * Distance ^{2}

To study the interaction of parameters i.e. pH, catalyst concentration, Current and Distance between electrodes on response 1 and Response 2, 3-D response surface graph were considered.

- *pH and Catalyst Concentration*

Catalyst behavior of the Fe depends on the pH of the solution. Fenton process is mostly optimized in acidic pH as iron species begins to precipitate as ferric hydroxides at higher pH. At lower pH iron form stable complex with H_2O_2 leading to deactivation of catalyst. Fenton reaction is mostly stated to be optimum at pH~3 but the Fig.6.8 shows that decolorization becomes maximum near 4 and becomes constant with pH increasing where as in degradation starts to decrease with pH beyond 5. This may be due to formation of $Fe(OH)_2$ which is more active then Fe^{2+} . Further as reaction proceeds the pH of the reaction decrease due to formation of the acids during the breakdown of the RB 5 dye.

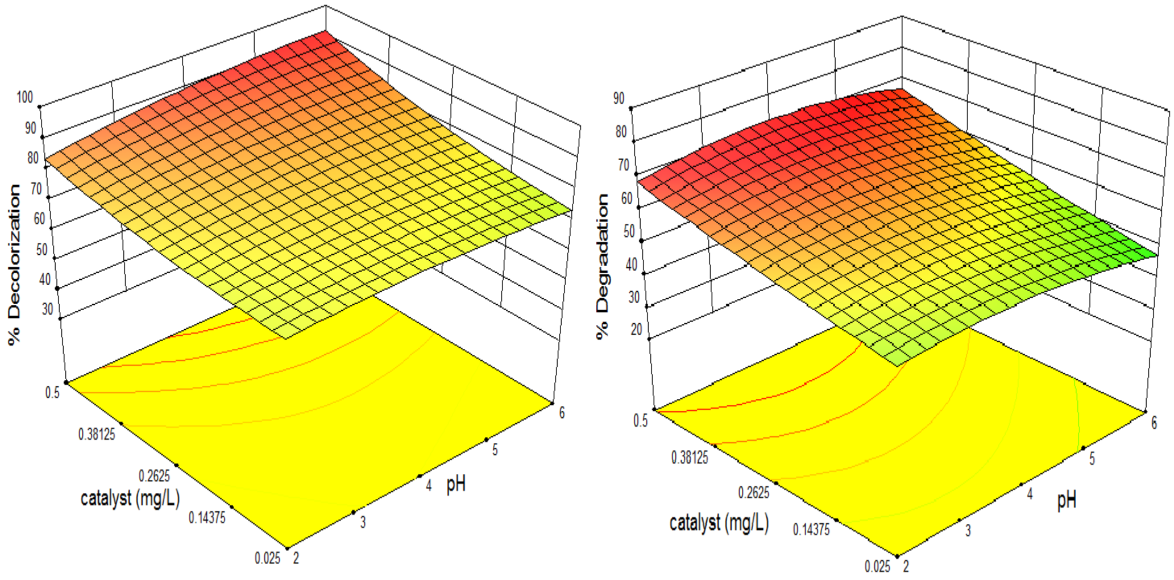

Fig.6.8: Three dimensional response surface graphs for the electro-Fenton between pH and Catalyst concentration

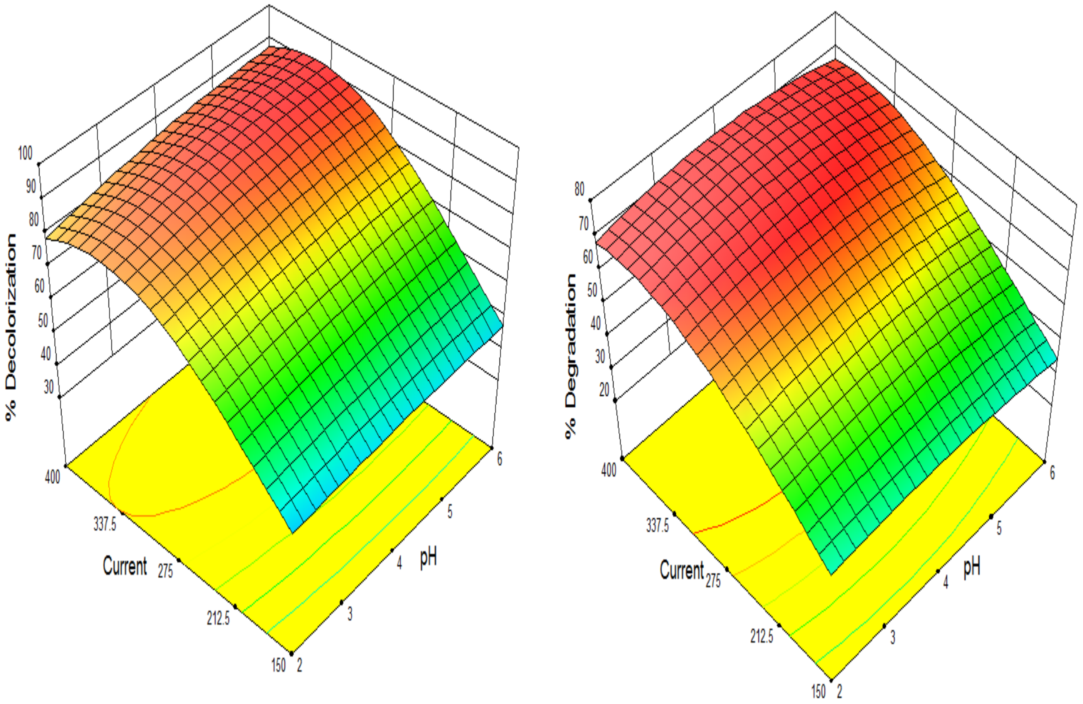

Fig.6.9: Three dimensional response surface graphs for the electro-Fenton between pH and Current

- *pH and Current*

The current or current density affects two process the Fe ion regeneration and H_2O_2 production. Higher applied current increases the quantum of hydrogen peroxide produced and also higher electro-regeneration of ferrous ion from ferric ion. This increases the efficiency of the process and chain fenton reaction. The efficiency of electro-Fenton will be less at higher current density efficiency due to the competitive electrode reactions in the electrolytic cell which include radical scavenging effect of H_2O_2 and the recombination of the hydroxyl radical. Further on increasing the current the discharge of oxygen at anode and the evolution of hydrogen at cathode occur which inhibit main reactions leading to decrease in efficiency of electro-Fenton. pH plays an important role in determining Fe ions nature as explained in pH and Catalyst graphs.

In Fig.6.9 with increase in value of current there is sudden increase of decolorization as well as degradation near 270 mA, with maximum near 342 mA and further degradation becomes constant with little decrease seen in decolorization. In degradation plot we see decrease in degradation with increase in pH beyond 5.

- *pH and Distance between electrodes*

In the electro-Fenton process the decrease in the distance between the electrodes leads to a decrease in the ohmic drop through the electrolyte and then an equivalent decrease of the cell voltage .The efficiency of electro-Fenton system was less for the shorter distance as Ferrous ion could be easily oxidized to ferric ion at the anode and decomposition of H_2O_2 at cathode. Whereas longer distance causes the limiting mass transfer of ferric ion to the cathode surface that governs ferrous ion regeneration

However in Fig.6.10 where distance is correlated with pH there is negligible change in decolorization and degradation with respect to distance between the electrodes when varied 0.5cm-6cm. The change in degradation and decolorization is due to change in pH.

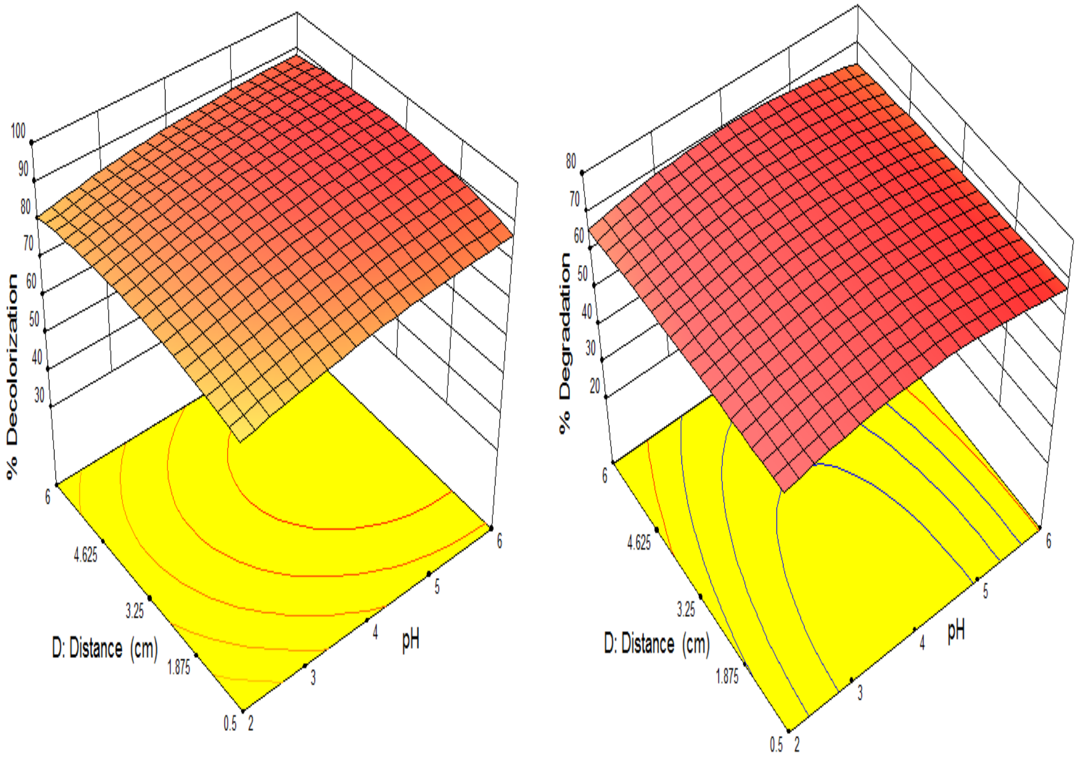

Fig.6.10: Three dimensional response surface graphs for the electro-Fenton between pH and Distance between the electrodes

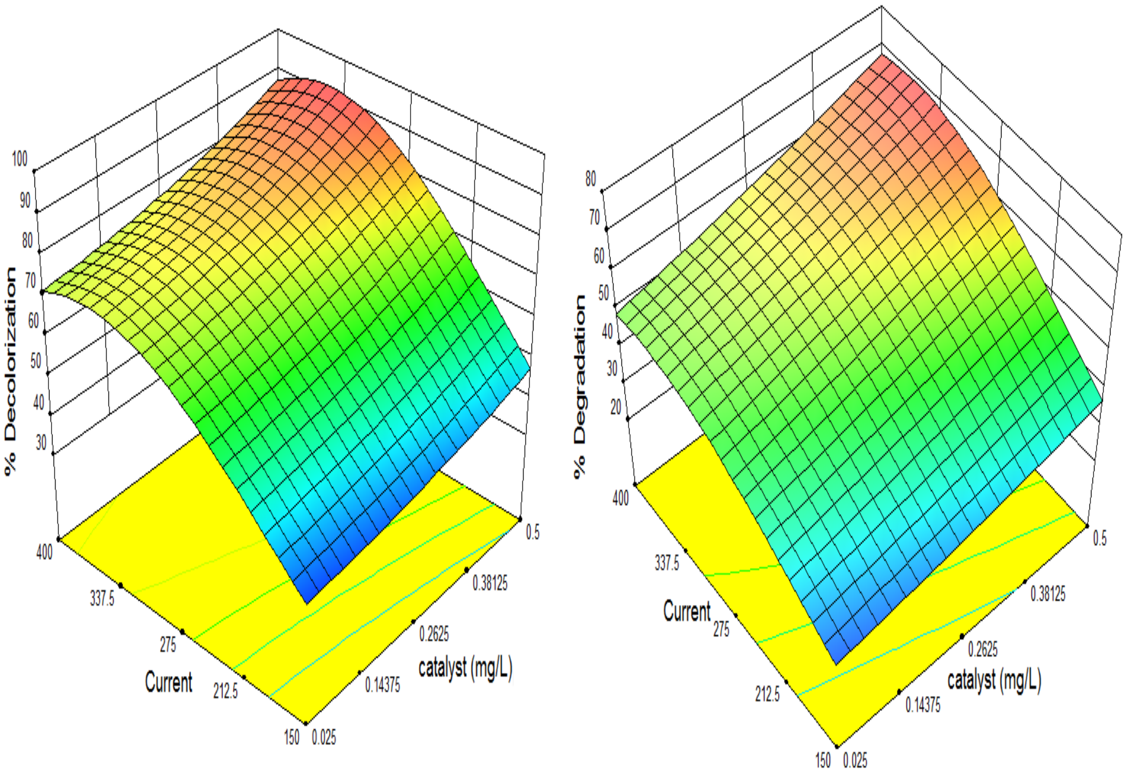

Fig.6.11: Three dimensional response surface graphs for the electro-Fenton between Catalyst concentration and Current

- *Catalyst Amount and Current*

Fe ion and Current have the important relationship. Current which causes the formation of H_2O_2 and also causes the regeneration of ferrous ion for fenton reaction to occur. The increase of current cause faster regeneration of ferric ion and hence more production of peroxide. Amount of Fe ion required as catalyst is less due to regeneration at anode and also by hydroperoxyl radical ($HO_2^{\bullet}$). In general the efficiency of electro-Fenton process increases with Fe^{2+} concentration because there is always some hydrogen peroxide left for reaction thus increasing the concentration of hydroxyl radical. But with increase in initial iron amount ferrous ion can react with the hydroxyl ion decreasing the efficiency of the reaction.

The plot in Fig.6.11 shows the sudden increase in the degradation and degradation with increase in the current near 275mA. The catalyst amount variation from 0.25mg/L-0.5mg/L saw the increase in both decolorization and degradation percentages.

- *Amount of Catalyst and Distance between the electrodes*

The relation between catalyst and distance can be predicted through the other parameter relations. The distance doesn't play the major role in the efficacy of the electro-Fenton process. But catalyst amount is important factor which combines with other factors to increase the percentage decolorization and degradation. The Fig.6.12 also shows higher degradation and decolorization when catalyst amount increased from 0.25mg/L-0.5mg/L with little change with variation in the distance

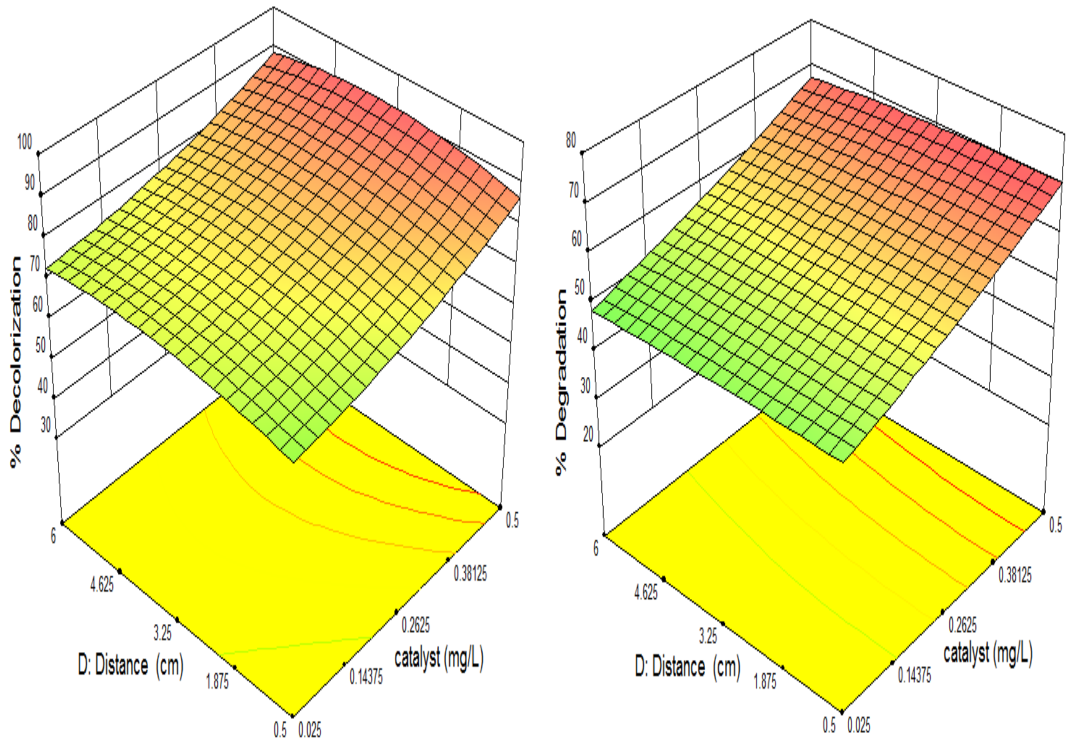

Fig.6.12: Three dimensional response surface graphs for the electro-Fenton between Distance between the electrodes and Catalyst

- *Current and Distance*

As distance is not that major factor in the deciding the efficiency of the electro-Fenton. Current affects both the catalyst amount by regeneration and the H_2O_2 concentration in the solution which effects the decolorization and degradation. As seen from the plot in Fig.6.13 the percentage degradation and decolorization increase with increase in the current value with significant increase beyond 275 mA with little or no changes seen with variation in the distance.

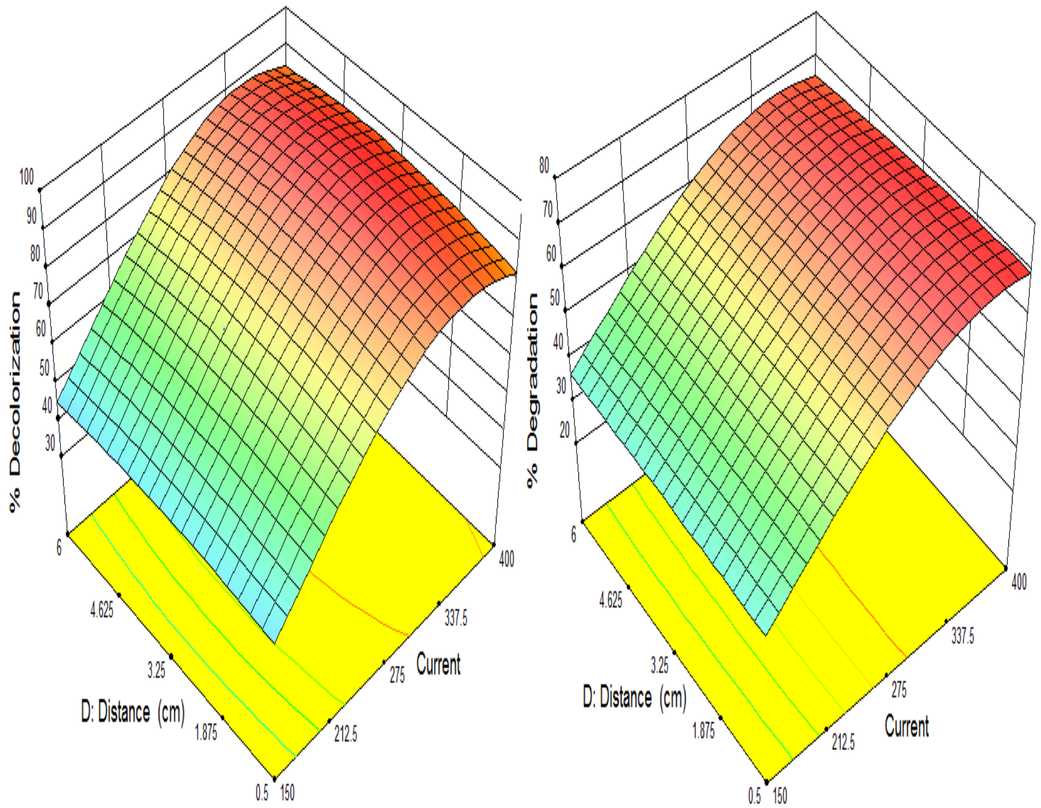

Fig.6.13: Three dimensional response surface graphs for the electro-Fenton between Distance between the electrodes and Current

- *Optimization Analysis*

Electro-Fenton treatment of RB 5 was optimized by RSM in terms of maximization of percentage decolorization and degradation simultaneously. For this purpose some constraints for operational parameters were applied as shown.

Table 6.5 Constraints applied for optimization of electro-Fenton

Name	Goal	Lower Limit	Upper Limit
A:pH	is in range	2	6
B:catalyst	is in range	0.025	0.5
C:Current	is in range	150	400
D:Distance	is in range	0.5	6
% Decolorization	maximize	34.0334	91.4115
% Degradation	maximize	22.3456	69.311

The optimum operational parameters values were obtained by RSM as shown in Table 6.6 and the suggested optimized values of parameters taken were pH= 5, Catalyst concentration =.40mg/L , Current =340 mA and Distance =3.1cm..The corresponding values of responses 1 (% Decolorization) and 2 (% Degradation) were 91.5%, 70.5%, respectively.

- *Carbon Fiber Electrode*

  The electro-Fenton process was also carried out using the carbon fiber cathode. The parameters used were the one optimized by RSM i.e. catalyst amount at 0.49 mg/L, pH 5.0, Current at 342 mA, Distance at 3.9 cm. The resistance offer by both of them was higher than the normal electrode

- *CONFIRMATION RESULTS*

  Electro-Fenton treatment of RB 5 dye was experimentally verified. Experiment was run for 40 min with other process variables obtained by RSM i.e at catalyst amount at 0.49 mg/L, pH 5.0, Current at 342 mA, Distance at 3.9 cm to conform that Optimum responses for percentage decolorization and degradation were 91.5%, 70.5% respectively. Experiment results for optimum process parameters are 89.0% and 68.0 % for percentage dye decolorization and degradation were respectively. The carbon cloth electrode gave the 95% dye decolorization and 70% degradation for the above set of conditions and carbon reinforcement gave similar results with decolorization~ 93% and 67% degradation.

Table 6.6 Optimum conditions for electro-Fenton

No	pH	catalyst	Current	Distance	% Decolorization	% Degradation	
1	5.0	0.40	342	3.1	91.5	70.5	Selected
2	5.1	0.40	340	3.2	91.5	69.5	
3	4.8	0.45	348	3.2	91.4	71.4	
4	4.8	0.50	332	3.5	91.5	70.6	
5	5.0	0.50	357	3.1	91.5	71.2	
6	5.1	0.49	353	4.2	91.5	70.1	
7	5.0	0.49	356	3.5	91.4	70.7	
8	5.0	0.49	334	3.9	91.4	69.8	
9	5.0	0.49	344	4.0	91.6	70.0	
10	5.1	0.49	352	3.7	91.7	70.4	

6.3. Electro-Chlorination Treatment of RB 5 Dye

6.3.1. Preliminary Studies

The initial study were conducted for decolorization of RB 5 (50 mg/L)waste water with added NaCl (1.75 gm/ liter) to make the conductivity of the solution to 2.2 mS. The other parameters such as steering speed, pH and distance between the electrode and volume of wastewater were kept constant. The reactions were carried without adding NaCl solution but making the conductivity 2.2 mS with Na_2SO_4, and with solution having NaCl keeping all the other parameters constant.

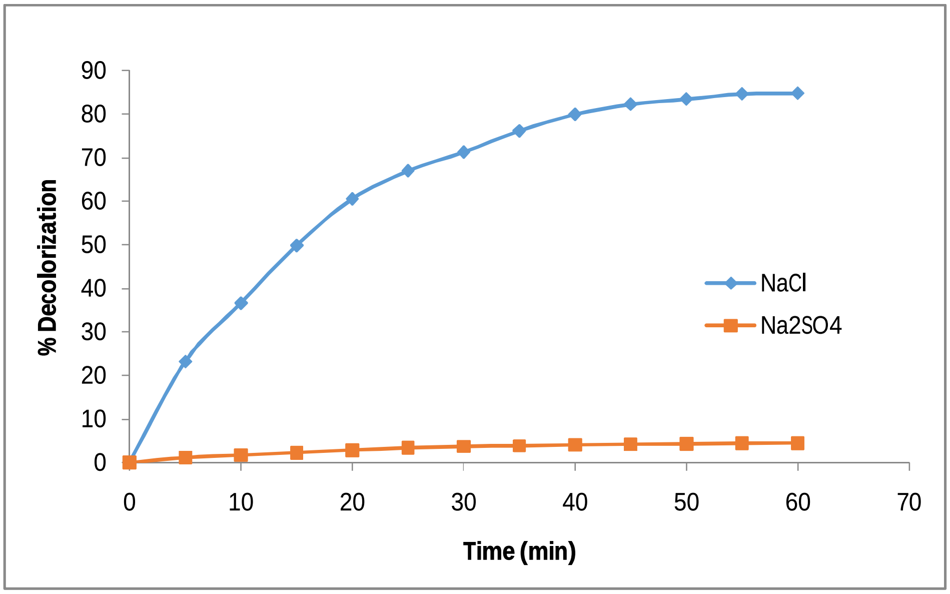

Fig.6.14: Preliminary study of electro-chlorination using graphite electrode, (C_0=50mg/L , pH=6.4,Current 250 mA, Conductivity =2.2 mS)

The NaCl in the solution forms the reactive chlorine species such as (Cl_3^-, HClO and ClO^-) which decolorize the dye solution. Neglible decolorization was seen with the sodium sulfate due to non formation of peroxidisulfate species (SO_4^{2-} /$S_2O_8^{2-}$).

Further the preliminary degradation and decolorization experiment was conducted at 6.4 pH, 250 mA current and 1 liter of RB5 waste water having 2.2 mS conductivity made by adding NaCl (1.75 gm/L), to study the kinetic of the reaction and to fix the parameters for the RSM optimization. From the preliminary studies graph Fig.6.15 it can be seen that rate of reaction increases till 40 minutes from the start of reaction and then starts to reduce. Further the parameters such as pH, distance between electrodes and applied current need to be optimized.

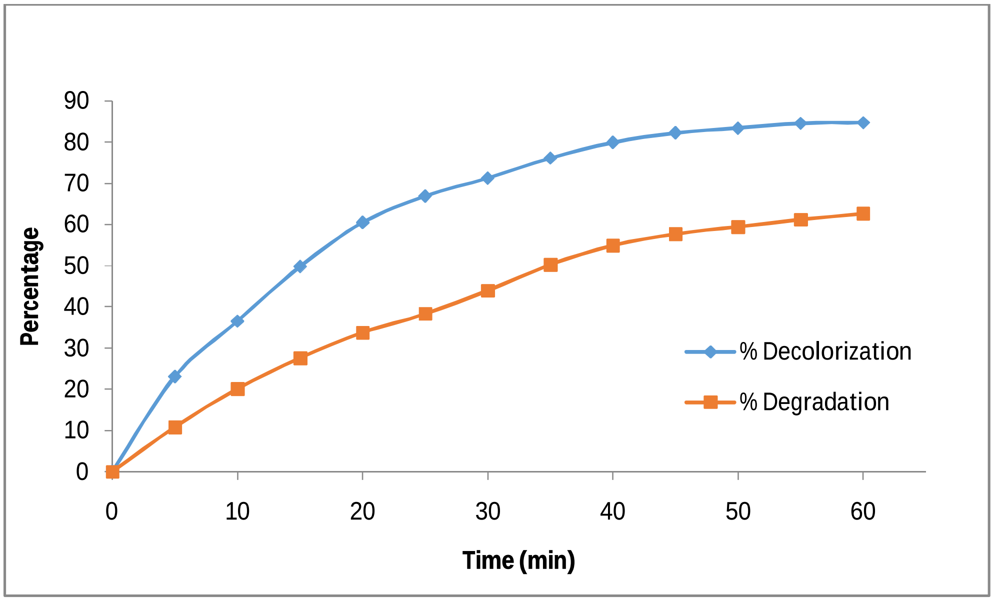

Fig.6.15: Preliminary study of electro-chlorination using graphite electrode, (C_0=50mg/L , pH=6.4,Current 250 mA, Conductivity =2.2 mS)

6.3.2. RSM Optimization for dye removal using Electro-Chlorination

For electro-chlorination optimization of RB5 waste water having the conductivity 2.2 mS was made by adding the known amount of NaCl (1.75gm/L). The operation parameters variables for the electro-chlorination based on the preliminary studies taken into account were pH 4-10, current 150 mA - 400mA and distance between the electrodes were considered as input parameters and percentage of color removal, percentage of dye degradation were taken as responses of the system keeping volume one liter as constant and the time of reaction constant as 40 minutes.

- *Statistical Analysis*

Central composite design (CCD) based on RSM was used for experimental design and 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 experiments. A total number of 20 simulation experiments designed by RSM, were conducted to study the effects of the three parameters pH, current, distance between electrodes on response percentage of dye degradation (Response 1), percentage dye decolorization (Response 2) keeping the time of reaction constant for 40 minutes

Table 6.7 Full factorial design used for the electro-chlorination with responses

Run	Factor 1 A:distance	Factor 2 B:pH	Factor 3 C:current	Response 1 % Decolorization	Response 2 %Degradation
1	0.5	4	400	95.7518	65.1241
2	3.25	7	275	83.8287	55.6091
3	3.25	7	400	90.0389	61.596
4	6	10	400	75.8137	46.5726
5	0.5	10	400	84.5637	57.9444
6	6	7	275	75.9755	44.4668
7	6	10	150	58.9221	28.2688
8	3.25	7	275	84.7943	57.4109
9	3.25	7	150	60.8596	28.2238
10	6	4	400	93.9643	61.891
11	3.25	7	275	81.2676	58.3227
12	0.5	4	150	65.4237	31.7951
13	3.25	7	275	79.004	55.035
14	3.25	10	275	69.807	47.443
15	6	4	150	63.3092	29.2826
16	3.25	7	275	79.567	58.512
17	3.25	4	275	85.9067	59.3965
18	0.5	7	275	86.9271	59.0697
19	0.5	10	150	62.3636	32.0594
20	3.25	7	275	82.45	56.0224

The responses percentage decolorization and degradation of electro-chlorination treatment of RB 5 with graphite electrodes were calculated according to the setting of various operational parameters as given in design matrix of experiments and results are shown in Table 6.7. Quadratic model was fitted to the experimental data to obtain the regression equations. Inverse transformation was used for both responses. Sequential model sum of squares Table 6.8(a, b) and model summary statistics Table 6.9(a, b) were tested to decide the adequacy of model.

Sequential model sum of squares showed that quadratic model best fits the experimental data for responses. Higher order models were found to be aliased for responses. The model gives coefficient of determination gives the R^2 value as .9716, .9812 respectively for Response 1 and 2. The adjusted R^2 values as .9461, .9643 and predicted R^2 values as .8308 and .8785 respectively for response 1 and response 2.

Table 6.8(a) Sequential model sum of squares for electro-chlorination for % dye decolorization using inverse transformation

Source	Sum of Square	Mean Square	F Value	p-value Prob > F	
Mean vs Total	3.425E-003	3.425E-003			
Linear vs Mean	6.381E-005	2.127E-005	26.29	< 0.0001	
2FI vs Linear	8.204E-007	2.735E-007	0.29	0.8296	
Quadratic vs 2FI	9.948E-006	3.316E-006	15.23	0.0005	Suggested
Cubic vs Quadratic	1.267E-006	3.168E-007	2.09	0.2005	Aliased
Residual	9.100E-007	1.517E-007			
Total	3.502E-003	1.751E-004			

Table 6.8 (b) Sequential model sum of squares for electro-chlorination for % dye degradation using inverse transformation

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Mean vs Total	9.551E-003	9.551E-003			
Linear vs Mean	7.040E-004	2.347E-004	13.37	0.0001	
2FI vs Linear	8.316E-006	2.772E-006	0.13	0.9391	
Quadratic vs 2FI	2.539E-004	8.464E-005	45.69	< 0.0001	Suggested
Cubic vs Quadratic	1.059E-005	2.647E-006	2.00	0.2136	Aliased
Residual	7.938E-006	1.323E-006			
Total	0.011	5.268E-004			

Table 6.9(a)Model summary statistics for electro-chlorination for % dye decolorization using inverse transformation

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	
Linear	8.995E-004	0.8313	0.7997	0.7218	
2FI	9.658E-004	0.8420	0.7691	0.1701	
Quadratic	4.666E-004	0.9716	0.9461	0.8308	Suggested
Cubic	3.894E-004	0.9881	0.9625	-4.0636	Aliased

Table 6.9(b)Model summary statistics for electro-chlorination for % dye degradation using inverse transformation

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	
Linear	4.189E-003	0.7149	0.6614	0.5303	
2FI	4.578E-003	0.7233	0.5957	-0.5257	
Quadratic	1.361E-003	0.9812	0.9643	0.8785	Suggested
Cubic	1.150E-003	0.9919	0.9745	-7.6185	Aliased

A good correlation between the observed and predicted values can be seen in Fig.6.16(a, b)

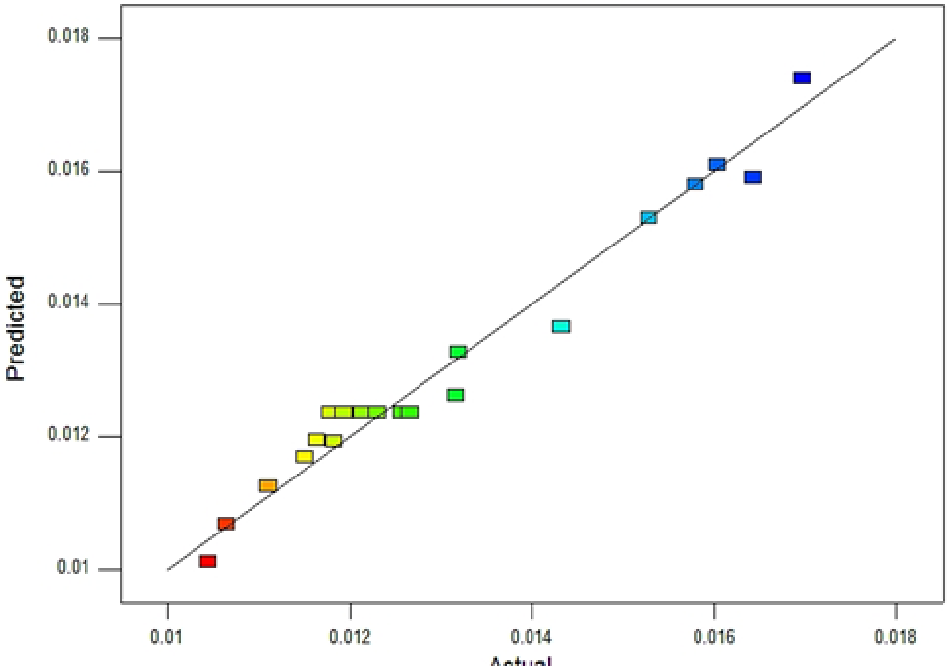

Fig.6.16 (a) Residual plots (actual versus predicted) for %dye decolorization using electro-chlorination

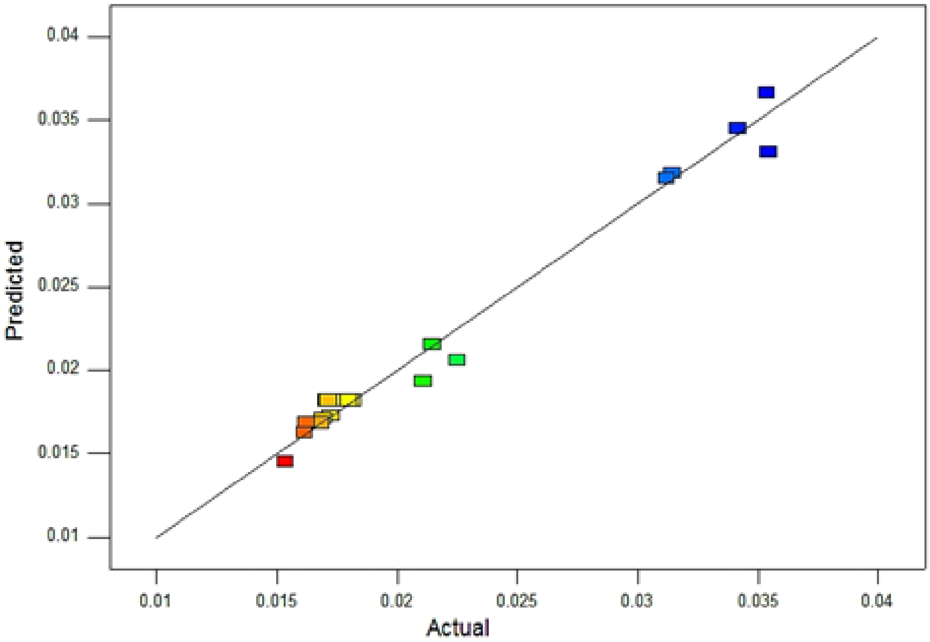

Fig.6.16 (b) Residual plots (actual versus predicted) for %Dye degradation using electro-chlorination

A close relation can also be seen between % normal probability and studentized residual in Fig.6.17(a, b)

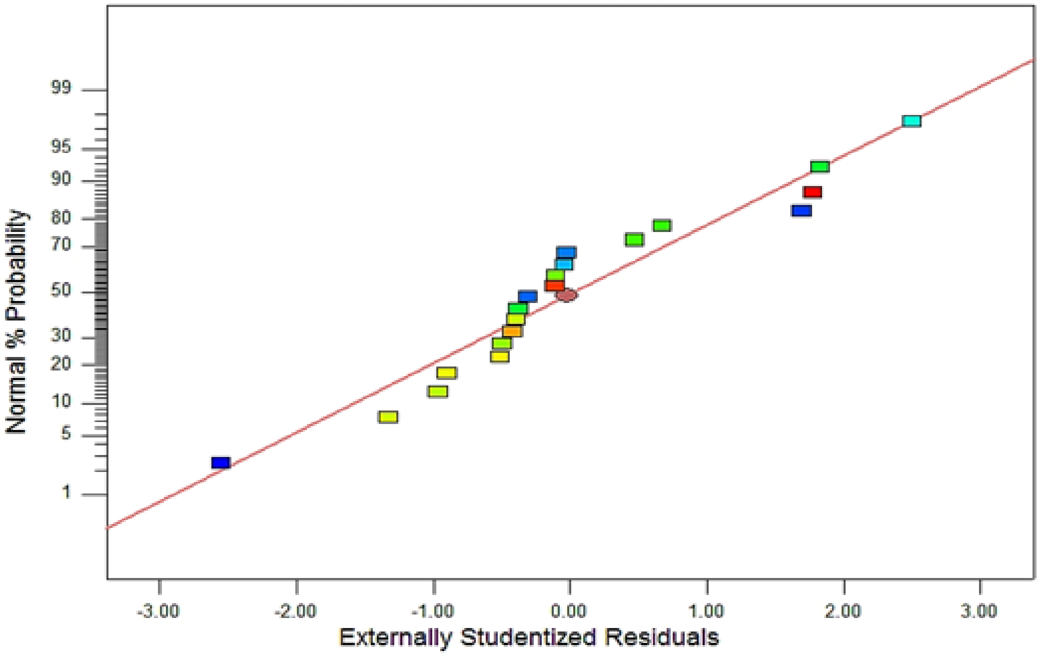

Fig.6.17 (a) Residual Normal plot for % dye decolorization using electro-chlorination

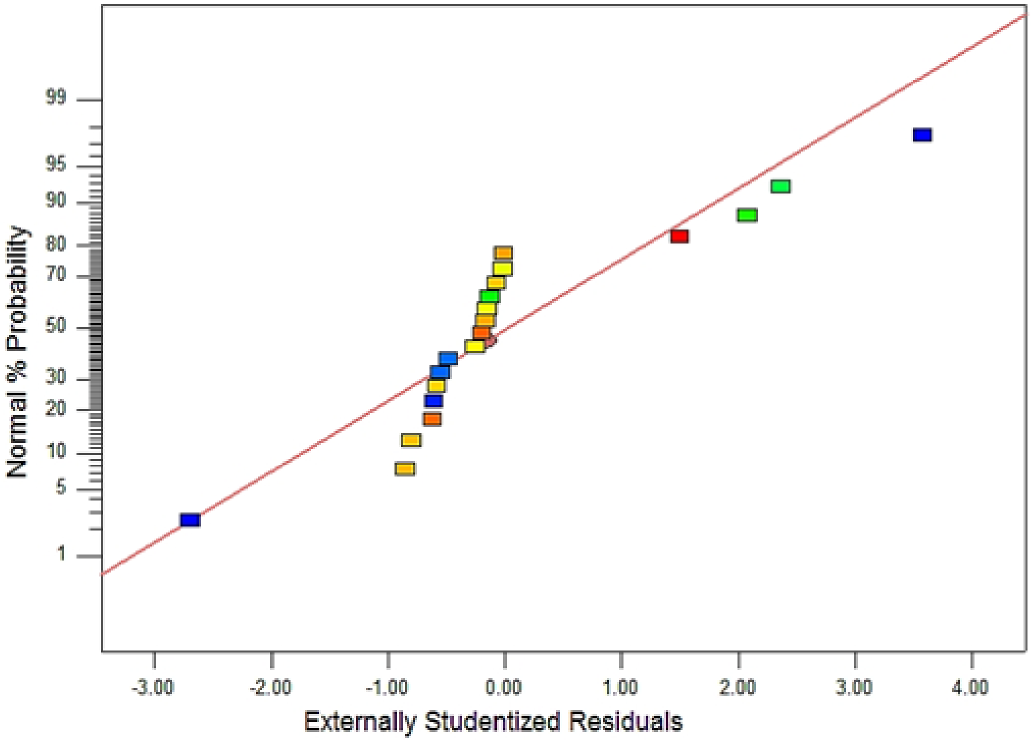

Fig.6.17 (b) Residual Normal plot for % dye degradation using electro-chlorination

The analysis of variance (ANOVA) shows model F-value of 38.06, 57.95 for response 1 and 2 respectively. This model is significant for both the responses as shown in Tables 6.10 (a,b). 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 distance, current, pH and current^2 were highly significant terms for % decolorization as well as for % degradation

Table 6.10(a) ANOVA for electro-chlorination quadratic model % decolorization

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Model	7.458E-005	8.287E-006	38.06	< 0.0001	Significant
A-distance	2.180E-006	2.180E-006	10.01	0.0101	Significant
B-pH	7.294E-006	7.294E-006	33.50	0.0002	Highly significant
C-current	5.434E-005	5.434E-005	249.57	< 0.0001	Highly significant
AB	3.169E-007	3.169E-007	1.46	0.2554	
AC	1.695E-009	1.695E-009	7.785E-003	0.9314	
BC	5.018E-007	5.018E-007	2.30	0.1599	
A^2	1.173E-007	1.173E-007	0.54	0.4798	
B^2	5.405E-007	5.405E-007	2.48	0.1462	
C^2	4.155E-006	4.155E-006	19.08	0.0014	
Residual	2.177E-006	2.177E-007			
Lack of Fit	1.583E-006	3.166E-007	2.66	0.1531	Not significant
Pure Error	5.943E-007	1.189E-007			
Total	7.676E-005				

Table 6.10(b)ANOVA for electro-chlorination quadratic model for % degradation

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Model	9.662E-004	1.074E-004	57.95	< 0.0001	Significant
A-distance	3.047E-005	3.047E-005	16.45	0.0023	Highly significant
B-pH	1.544E-005	1.544E-005	8.33	0.0162	Significant
C-current	6.581E-004	6.581E-004	355.22	< 0.0001	Highly significant
AB	2.996E-006	2.996E-006	1.62	0.2323	
AC	4.348E-007	4.348E-007	0.23	0.6385	
BC	4.885E-006	4.885E-006	2.64	0.1355	
A^2	1.171E-006	1.171E-006	0.63	0.4450	
B^2	2.711E-008	2.711E-008	0.015	0.9061	
C^2	1.263E-004	1.263E-004	68.17	< 0.0001	Highly significant
Residual	1.853E-005	1.853E-006			
Lack of Fit	1.749E-005	3.499E-006	16.95	0.0037	Significant
Pure Error	1.032E-006	2.065E-007			
Total	9.847E-004				

The final quadratic equation in terms of coded factors for percentage decolorization and percentage of dye degradation are given below.

1/(Decolorization)=0.024884603101782+0.00016678087571546*distance .00066698940443074 *pH-6.6729509825677e-005*current+2.4124505620784e-005* distance*pH+4.2343804560895e-008*distance*current+6.678461218482e-007 * pH * current-2.7311204937006e-005*distance^2+4.9257607072449e-005*pH^2+7.8670382192066e-008* current^2

1/(Degradation)=0.06933606493092-0.0002589079736791*distance-0.00024554607482708*pH-0.00031582019208109*current+7.4179479386741e-005*distance *pH-6.7822345921462e-007*distance*current+2.0838669162791e-006*pH*current+ 8.6300980394777e-005*distance^2-1.103252304561e-005*pH^2+4.337086112642e-007* current^2

To study the interaction of parameters i.e. pH, Current and Distance between electrodes on response 1 and Response 2, 3-D response surface graph were considered.

- *pH and Current*

With increase in the Current the rate of all electrode reactions increase which increase the production of the reactive chlorine species. This can be seen from the Fig.6.17 that with increase in current both decolorization and degradation increases. However the decolorization tends to become constant after ~350 mA, but the degradation after becoming constant began to decrease with increase in current due to oxygen evolution reactions. pH decides which chlorine species will be predominant, it is expected that Cl_2 with higher oxidation potential causes maximum degradation and decolorization. As Cl_2 is formed in acidic media more degradation is observed in acidic conditions. This trend can be seen from the Fig6.18 the combined effect can be seen both degradation and decolorization take place at acidic pH and high current density above ~350mA.

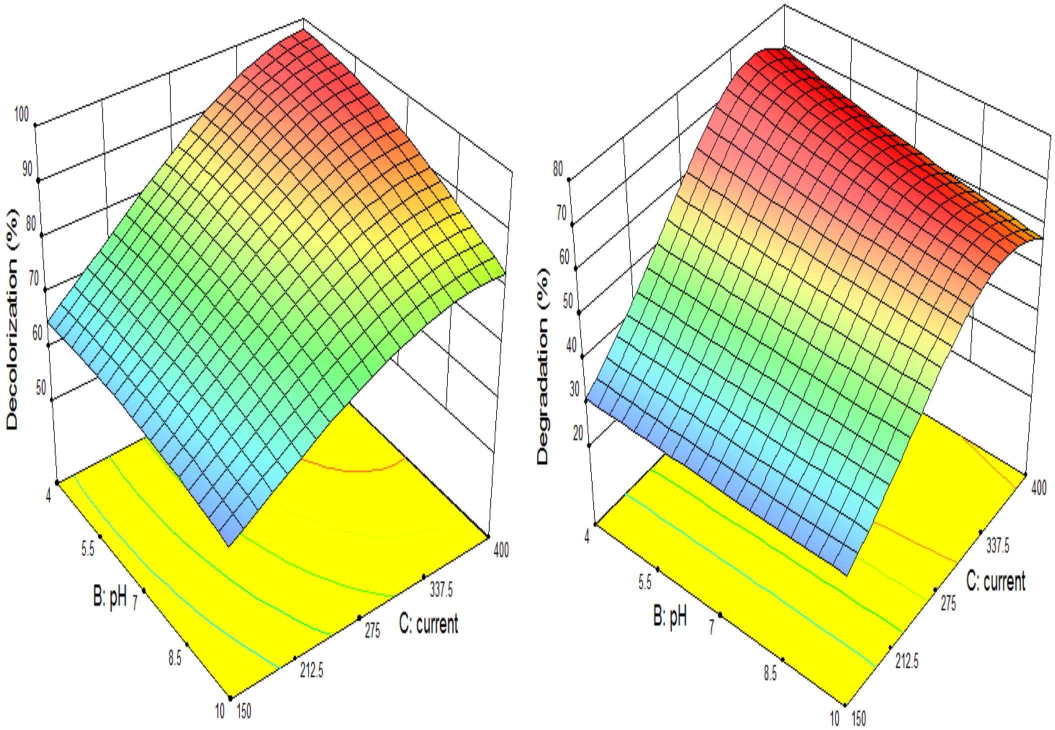

Fig.6.18: Three dimensional response surface graphs for the electro-chlorination between pH and Current

- *Distance between electrode and Current*

Distance decides the change in the ohmic voltage across the electrode. With increase in distance the voltage for supplying the same amount of current increases however it doesn't affect the degradation or decolorization to large extent. The change in degradation and decolorization is observed when distance is varied from 0.5cm-6cm as in Fig.6.19.Which may be due to mass transfer limitation face by Cl^- to reach anode. The increase in current cause increases the chlorine reactive species and hence the increase in decolorization and degradation. With combined effect we see that higher degradation and decolorization occur at smaller electrode gap and high current density.

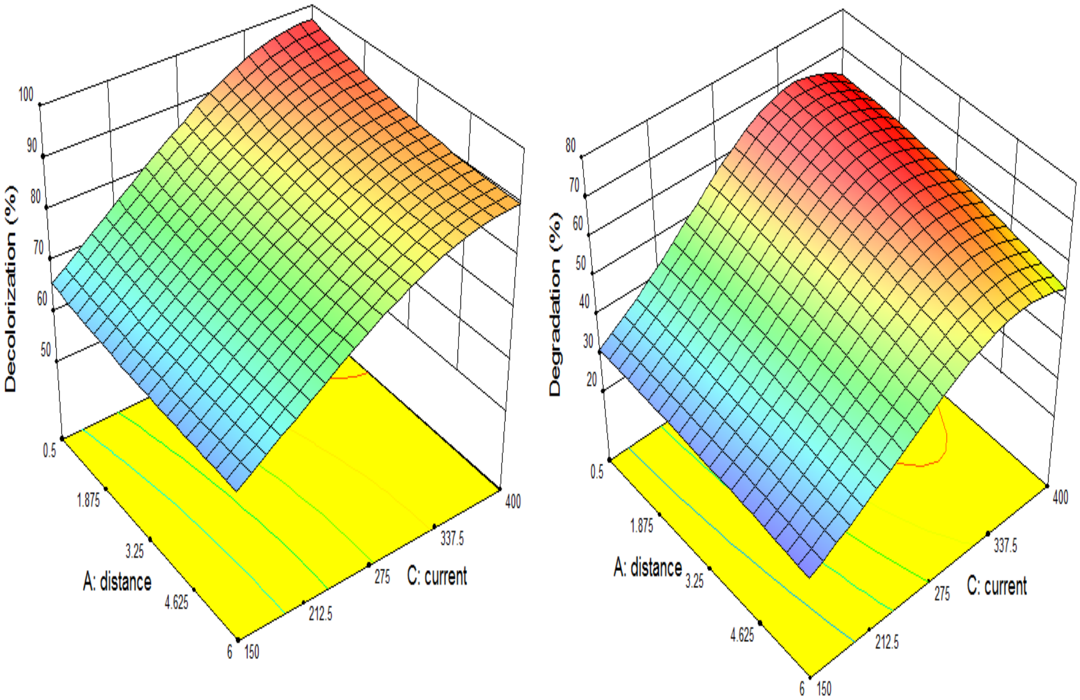

Fig.6.19: Three dimensional response surface graphs for the electro-chlorination between Distance and Current

- *pH and Distance*

The pH as factor decides which chlorine species is present in solution and decides the amount of degradation and decolorization. As distance it just play the role of mass transfer limitations faced by Cl ion for regeneration to reactive chlorine species. The Fig.6.20 shows that amount of decolorization and degradation occur more in acidic medium near pH 4 and in narrow electrode gap

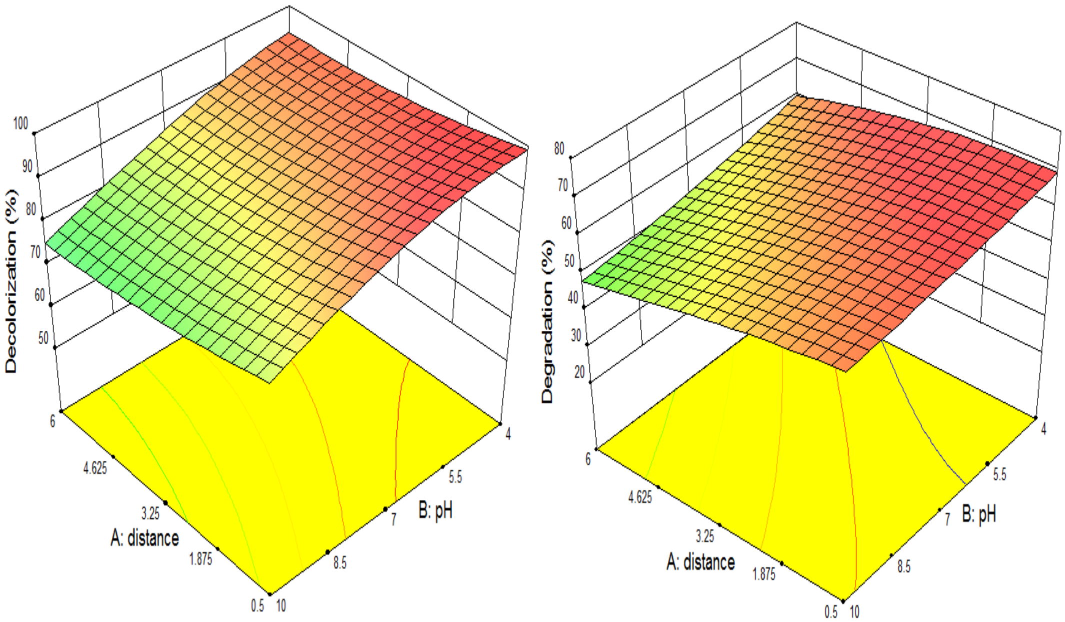

Fig.6.20: Three dimensional response surface graphs for the electro-chlorination between Distance and pH

- *Optimization Analysis*

Electro-chlorination treatment of RB 5 was optimized by RSM in terms of maximization of percentage decolorization degradation simultaneously. For this purpose constraints for operational parameters were applied as shown.

Table 6.11 Constraints applied for optimization of electro-chlorination

Name	Goal	Lower Limit	Lower Limit
A:Distance	is in range	0.5	6
B:pH	is in range	4	10
C:Current	is in range	150	400
% Decolorization	maximize	58.9221	95.7518
% Degradation	maximize	28.2238	65.1241

The optimum operational parameters values by RSM as shown in Table 6.12. The suggested optimized values of parameters were pH= 4.5, Current =381 mA and Distance =1.5 cm. The corresponding values of the responses 1 (% Decolorization) and 2 (% Degradation) were 96.4%, 71.3%, respectively.

Table 6.12 Optimum conditions for electro-chlorination

Number	distance	pH	Current	Decolorization	Degradation	
1	1.50	4.5	381	96.40	71.30	Selected
2	0.50	6.5	381	95.75	66.90	
3	0.50	4.0	400	99.20	69.65	
4	1.20	4.0	393	97.65	71.05	
5	0.75	5.8	387	96.80	67.60	
6	0.80	4.8	366	96.95	71.98	
7	0.90	5.9	393	96.30	66.35	
8	2.00	4.2	386	95.85	71.25	
9	1.50	4.5	398	96.65	68.78	
10	0.75	4.5	382	97.90	71.04	

- *CONFIRMATION RESULTS*

Optimum condition for electro-chlorination of RB 5 dye was experimentally verified. Experiment was run for 40 min with other process variables obtained by RSM i.e at pH 4.5, Current at 381 mA , Distance at 1.5 cm to conform that Optimum responses for response 1 (% Decolorization) and response 2 (% Degradation) 96.4%, 71.3% respectively. Experiment results for optimum process parameters were 93% and 68 %for response 1 (% Decolorization) and response 2 (% Degradation) were respectively.

6.4. Anodic Oxidation along with Electrogenerated H_2O_2 (Combination of electro-Fenton and electro-chlorination)

The combination reaction was carried was carried out using RB 5 50 mg/L solution with added NaCl (1.75 gm/ liter) to make the conductivity of the solution to 2.2 mS. With aeration equivalent to that used in electro-Fenton reaction along with the optimized catalyst amount of.40mg/L. Other parameters were fixed from optimized conditions obtained from electro-chlorination i.e Current at 381 mA, pH 4.5, and Distance 1.5 cm.

The results of this combined approach give better results than both electro-Fenton and electro-chlorination. The complete decolorization was observed in 30 minutes of reaction. The amount of dye degradation also saw increment as more than 79% was observed after 40 minutes of reaction.

CHAPTER 7
CONCUSION

- Degradation and Decolorization of the Reactive Black 5 (RB 5) has been studied using electro-chlorination and electro-Fenton with graphite and carbon fiber electrodes. The Process parameters studies were done using RSM, central composite design matrix.
- Electro-Fenton degradation and decolorization of RB5 was studied for pH, catalyst concentration, Current applied and distance between the electrodes.
  - The Statistical Analysis of model give R^2 values as .9819 and .9657 for percentage decolorization and degradation respectively, which shows a good correlation between the observed and predicted values. ANOVA shows that catalyst concentration, current, current^2 were highly significant parameters for degradation and decolorization of dye.
  - The optimized values for various parameters were pH= 5, Catalyst concentration =.40mg/L, Current =342 mA and Distance =3.1cm with experiment results of 89.0% and 68.0% for decolorization and degradation respectively.
  - The electro-Fenton process carried out using the carbon fiber cathode gave the 95% dye decolorization and 70% degradation for optimal conditions and similar results were seen with carbon reinforcement with decolorization~ 93% and 67% degradation. However the resistance offer by both of them was higher than the normal electrodes.
- Electro-chlorination degradation and decolorization of RB5 was studied for pH, Current applied and distance between the electrodes.
  - The Statistical Analysis of model give R^2 values as .9716, and .9812 for percentage decolorization and degradation respectively, which shows a good correlation between the observed and predicted values. ANOVA shows that distance between the electrodes, current, pH and current^2 were highly significant parameters for degradation and decolorization of dye.
  - The optimum operational parameters values by RSM were pH= 4.5, Current =381 mA and Distance =1.5 cm. The corresponding values of experiment results were 93% and 68 % for dye decolorization and degradation respectively.
- Combination of electro-Fenton and electro-chlorination was also carried for checking the enhance activity for decolorization and degradation. The operating parameters were

catalyst amount of.40mg/L, Current at 381 mA, pH 4.5, and distance between the electrodes as 1.5 cm. The complete Decolorization was observed in 30 minutes of reaction. The amount of dye degradation also saw increment as more than 79% was observed after 40 minutes of reaction.

- Carbon as cathode is extremely effective for production of H_2O_2 in presence of physically adsorbed air. In case of anode the carbon is not that effective due low stability, however it is effective for regeneration of Fe^{3+} to Fe^{2+}. Electro-chlorination using carbon electrode is potent as formation potential of chlorine reactive species is lower than it's the oxygen evolution potential. Carbon electrodes as anode have stability issues near oxygen evolution potential.

CHAPTER 8

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