STUDY OF ELECTROCOAGULATION AND COMBINED ELECTROCOAGULATION-OXIDATION PROCESSES FOR DYE REMOVAL

A Thesis Report Submitted
in partial fulfillment of the requirements for
the award of degree of

MASTER OF TECHNOLOGY
IN
CHEMICAL ENGINEERING

Submitted by

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DECLARATION

I hereby declare that thesis entitled **"Study of Electrocoagulation and Combined Electrocoagulation-Oxidation Processes for Dye Removal"** is an authentic record of my study carried out as requirements for the award of degree of **M.Tech. (Chemical Engineering)** at **Thapar University, Patiala**, under the guidance of **Dr. R. K. Gupta**, Assistant Professor, **Department of Chemical Engineering** and **Mr. V. K. Sangal**, Assistant Professor, **Department of Chemical Engineering**, Thapar University, Patiala during **July 2009 to July 2010**. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.

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This is to certify that above declaration made by the student concerned is correct to the best of our knowledge and belief.

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ABSTRACT

Dyeing and finishing are the two most important processes usually applied in textile manufacturing industries. These two processes generate considerable amount of wastewater, which may contain high color, suspended solids (SS), pH, temperature, biological oxygen demand (BOD), chemical oxygen demand (COD), and low biodegradability. However, the major problem is strong color wastes that are lost after the dyeing process up to 50%**.** The discharge of dyeing wastewater into streams and rivers causes several problems. Therefore, it is necessary to treat dye wastewater before discharged into water.

The purpose of this study was to investigate the effects of the operating parameters, such as pH, treatment time, and current density on COD removal from synthetic water sample prepared by dissolving *Brilliant Cresyl Blue* dye in distilled water.

Better COD removal was observed with increasing current density. It was found that for current density equal to 14.53 mA/cm^2 (with 5.5 A current) with four electrodes gave better result as compared to 9.25 mA/cm^2 and 11.88 mA/cm^2. It was possible to bring the residual COD in the treated water within the permissible limit in 75 minutes of electrolysis time. pH 6 was found to be appropriate for the treatment.

The comparison of COD removal by EC alone and with EC and oxidation combined was carried out. Hydrogen peroxide was used as oxidant. The results showed that the COD removal efficiency increased from 87% to 97% with 1.5 ml/l of H_2O_2 dose and from 87% to 94% with 1.0 ml/l of H_2O_2 dose. This increased COD removal results due the formation of hydroxyl radicals. Also, the treatment time decreased from 90 min to 60 min in case of combined process.

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CHAPTER -1

INTRODUCTION

The textile industry is one of the industries that consume huge amounts of water and chemical products. Large amounts of chemically different dyes are used for various industrial applications. Dyeing and finishing are the two most important processes usually applied in textile-manufacturing industries. These two processes generate considerable amount of wastewater, which may contain high color, suspended solids (SS), pH, temperature, biological oxygen demand (BOD), chemical oxygen demand (COD), low biodegradability (Vlyssides et al., 1999; Kim et al., 2002; Mollah et al., 2004). However, the major problem is strong color wastes that are lost after the dyeing process up to 50%**.** The discharge of dyeing wastewater into streams and rivers causes several problems, in particular, are not only aesthetic pollutants by nature of their color, but may interfere with light penetration in the receiving bodies of water, thereby disturbing biological processes. Furthermore, dye effluent contains chemicals, which are toxic, carcinogenic, mutagenic, or teratogenic in various microbiologic, fish species (Daneshvar et al., 2004). Therefore, it is necessary to treat dye wastewater before discharged into water.

The conventional treatments methods of wastewater containing dyestuff are physico-chemical and biological methods. Most of these conventional methods are becoming inadequate and insufficient; because of the dye effluent contain mainly complex aromatic molecular structures. Compounds are often constructed to resist fading on exposure to sweat soap water, light or oxidant agents and this renders them more stable and less amenable to biodegradation (Carneiro et al., 2005). A simple and efficient treatment process for the dyeing wastewater is essentially necessary. Electro-coagulation process is shown to be an effective and reliable technology. Electro-coagulation is very effective in removing organic pollutants including dyeing wastewater. Electro-coagulation is simple in operation and requires little space. The sludge produced during electro-coagulation process is less as compared to coagulation process.

1.1 Minimal national standards (MINAS) for industrial effluents

The Central Pollution Control Board (CPCB), Delhi, under powers vested in it through the water (Prevention and control of pollution) Act, 1974, has prescribed effluent standards for various quality parameters. For dye effluents, the COD limit is 250 mg/l. Taking in to account the treatability of the effluent from the technical feasibility point of view, the cost of treatment and cost burden that can be boomed by industry, CPCB has noticed industry specific MINAS. The MINAS will be binding for all industrial units throughout the country.

1.2 Dyeing wastewater treatment technology

Many techniques are available, including a variety of filters, chemical dosing, and reverse osmosis for treatment of dye effluents.

For a technique to be successful it needs to satisfy a number of criterions, including: -

i. It must be cost effective, producing results, which are cheaper than dumping and purchasing more water. Both the capital and operating costs must be low and the results as good as tap water for the technique to be successful.
ii. It must remove the contaminants producing water, which can be reused in the same application, or as a replacement for water in another application.
iii. It must not in itself produce great amounts of waste.
iv. It must operate reliably and have low downtimes.

There are many techniques for the treatment of dye effluents.

1.2.1 Adsorption

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterized by surface properties such as surface area and polarity. Adsorption operations, employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters. This method is an efficient alternative used to remove low organic concentration in wastewater. The used activated carbon adsorbent, is not suitable for insoluble dyes, so the costs of adsorbent used for treating textile effluent is high and exceed that of chemical coagulation (Daneshvar et al., 2003).

1.2.2 Coagulation-Flocculation

Chemical coagulation has been used for decades to destabilize suspensions and to effects precipitation of soluble metal species, as well as other in organic species from aqueous streams, thereby permitting their removal through sedimentation or filtration, alum, lime and/or polymers have been the chemical coagulants used. These processes, however, tend to generate large volumes of sludge with high bound water content that can be slow to filter and difficult to dewater.

The process of destabilization is known as coagulation and agglomeration of neutralized particles to form the bigger flocs is known as flocculation. The neutralization of the negative surface of the colloid is accomplished by the addition of cations in the case of inorganic coagulants. The trivalent ions are ten times more effective than the divalent ion. Trivalent iron and aluminum salts are widely used in all the water coagulation treatments. Although the exact method by which coagulation is accomplished can not be determined, four mechanisms are thought to occur. These include ionic layer compression, adsorption and charge neutralization, entrapment in a flocculent mass, and adsorption and intraparticle bridging. Figure 1 shows the different stages of coagulation and flocculation mechanism.

1.2.3 Membrane technology

The principle of micro filtration and ultra filtration is physical separation. The extent to which dissolved solids, turbidity and microorganisms are removed is determined by the size of the pores in the membranes. Substances that are larger than the pores in the membranes are totally removed. Substances that are smaller than the pores of the membranes are partially removed, depending on the construction of a refuse layer on the membrane. Micro filtration and ultra filtration are pressure-dependent processes, which dissolved solids and other substances from water to a lesser extent than nano-filtration and reverse osmosis. Capacity of membrane technology is as shown in Figure 2.

Micro filtration

Membranes with a pore size of 0.1 – 10 µm perform micro filtration. Microfiltration membranes remove all bacteria. Only part of the viral contamination is caught up in the process, even though viruses are smaller than the pores of a micro filtration membrane. This is because viruses can attach themselves to bacterial biofilm. Micro filtration can be implemented in many different water treatment processes when particles with a diameter greater than 0.1 mm need to be removed from a liquid.

Ultra filtration

For complete removal of viruses, ultra filtration is required. The pores of ultra filtration membranes can remove particles of 0.001 – 0.1 µm from fluids.

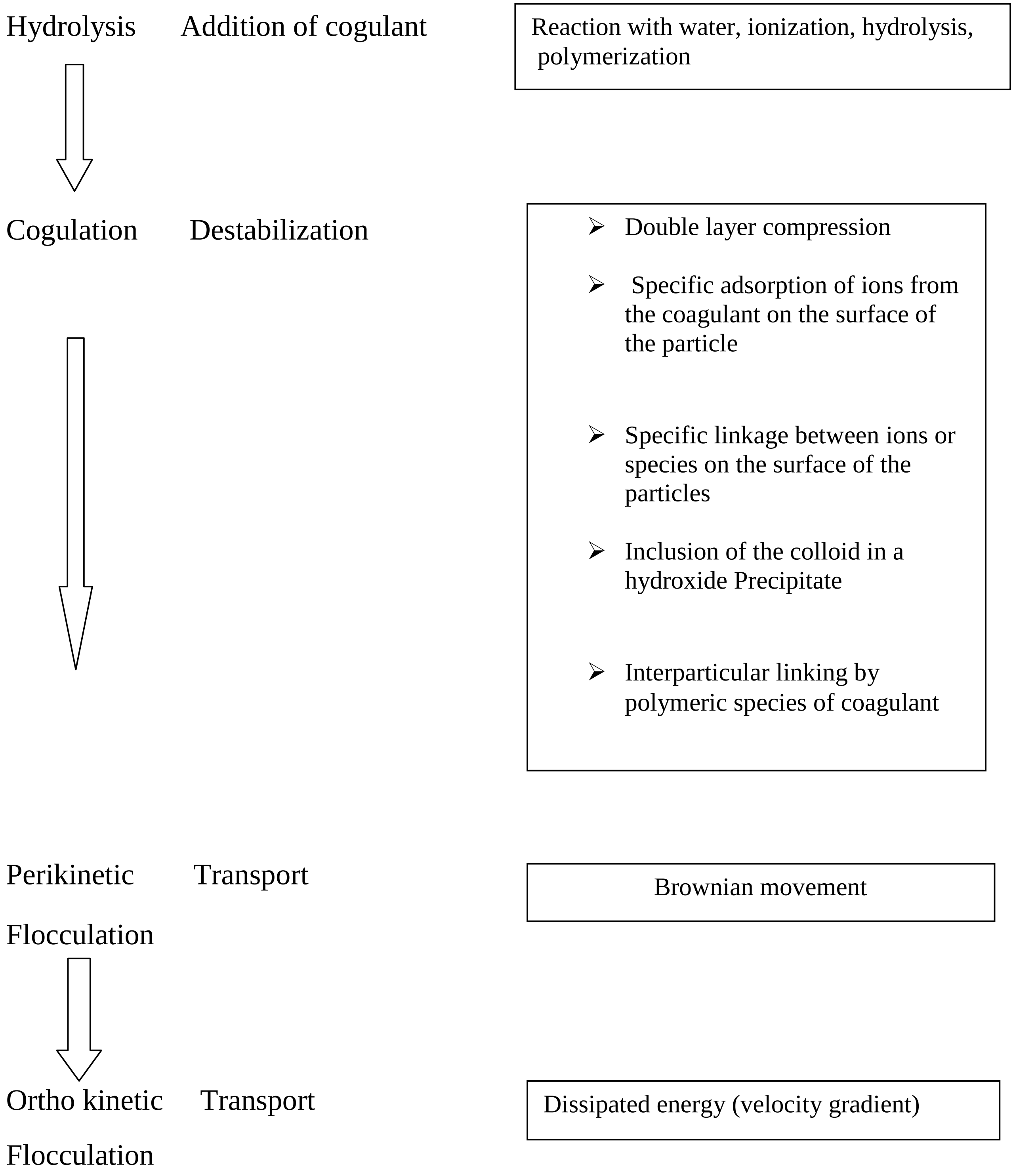


Figure 1: Different stages of coagulation and flocculation mechanism

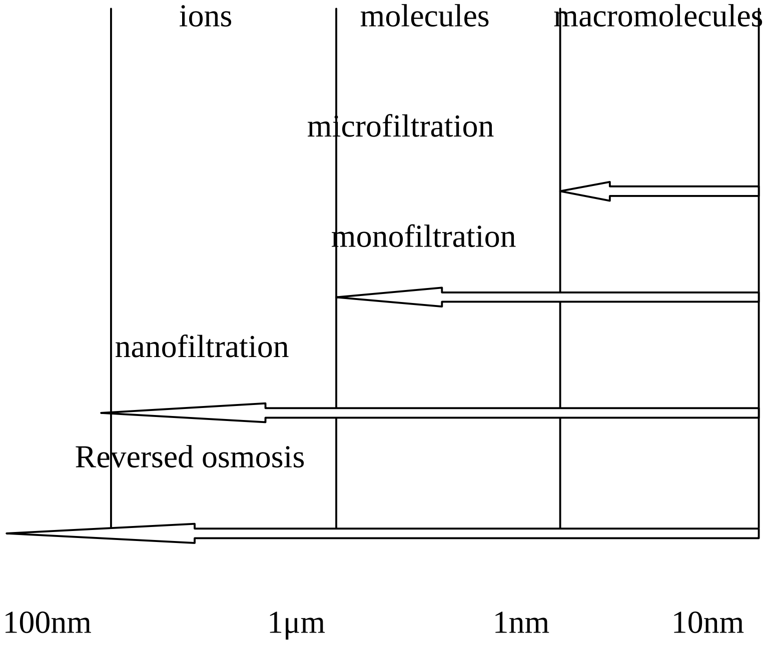


Figure 2: Capacity of membrane technology

Nano filtration

Nano filtration is a technique that has prospered over the past few years. Today, nano filtration is mainly applied in drinking water purification process steps, such as water softening, discoloring and micro pollutant removal. Nano filtration is a pressure related process, during which separation takes place, based on molecule size, mainly used for the removal of two valued ions and the larger mono valued ions like heavy metals. This technique can be seen as a coarse RO (reversed osmosis) membrane. Because nano filtration uses less fine membranes, the feed pressure of the NF system is generally lower compared to RO systems. Also the fouling rate is lower compared to RO systems.

Reverse osmosis

In the reversed osmosis process water is forced across a membrane, leaving the impurities behind. The permeability of the membrane can be so small, that practically all impurities, salt molecules, bacteria and viruses are being separated from the water.

1.2.4 Biological method

Biological method (aerobic and anaerobic) is used for decreasing the BOD, COD and TOC of dyeing wastewater but inadequate for the treatment of solutions containing bio-refractory. Soluble dyes have high molecular weight compounds and are not easily degraded by bacteria (Sanroman et al., 2004).

1.2.5 Advanced oxidation methods

Advanced oxidation processes make use of oxidants to reduce COD/BOD levels, and to remove both organic and oxidisable inorganic components. The processes can completely oxidize organic materials to carbon dioxide and water, but it is not necessary to operate these processes to that level of treatment. Advanced oxidation processes are particularly appropriate for effluents containing refractory, toxic or non-biodegradable materials. These processes offers several advantages over biological or physical processes However, advanced oxidation processes often have a higher capital and operating costs compared with biological process.

UV-H_2O_2 Process

UV /oxidation processes generally involve generation of *OH through UV photolysis of conventional oxidants, including hydrogen peroxide (H_2O_2).

$$H_2O_2 + \text{light energy (hv)} \rightarrow 2\ {}^*OH$$

UV-TiO_2 Process

The metal semiconductors are used to destroy environmental contaminants by means of light-induced redox reactions. These reactions, involve generation of conduction band electrons and valence band holes by UV irradiation of semiconductor materials such as titanium dioxide (TiO_2).

Photo Fenton process

Several metals have a special oxygen transfer properties which improve the use of hydrogen peroxide. Some metals have a strong catalytic power to generate highly reactive hydroxyl radicals (.OH). The iron catalyzed hydrogen peroxide has been called Fenton's reaction.

Fenton process may be used for organic pollutant destruction, toxicity reduction biodegradability improvement, BOD/COD removal, Odor and color removal and destruction of resin in radioactive contaminated sludge.

After addition of the iron and the hydrogen peroxide, they are going to react together to generate some hydroxyl radicals as it shows in the following equations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + .OH + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + .OOH + H^+$$

The typical range for the iron dose is 1 part of Fe per 5-25 parts of H_2O_2. After that the hydroxyl radicals are going to react with the pollutants to oxidize them. The hydroxyl radicals can react according four type of reactions with the pollutants:

- Addition: $.OH + C_6H_6 \rightarrow (OH)C_6H_6$
- Hydrogen Abstraction: $.OH + CH_3OH \rightarrow .CH_2OH + H_2O$
- Electron Transfer: $.OH + [Fe(CN)6]4^- \rightarrow [Fe(CN)6]3^- + OH^-$
- Radical Interaction: $.OH + .OH \rightarrow H_2O_2$

During the Fenton's reaction all the parameters are adjusted to promote the first two kinds of reaction between the pollutant and the hydroxyl radicals.

Ozone

Ozone is a molecule that consists of three oxygen atoms (O_3), with negative electric charge. The ozone molecule is very unstable and has a short half-life. Therefore, it will decay after sometime into its original form of oxygen as,

$$2O_3 \longrightarrow 3O_2$$

In the food industry for example ozone is used for disinfection and in the paper- and textile industry it is used for the oxidation of wastewater. The main benefit of ozone is its clean character, because it only oxidizes materials, with forming almost no byproducts. Because ozone has a strong recognizable odor, very low concentrations will soon be perceived. This makes it generally safe to work with ozone.

1.2.6 Electro-coagulation

The EC technology offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions. The technology removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species. These species neutralize the electrostatic charges on suspended solids and oil droplets to facilitate agglomeration or coagulation and resultant separation from the aqueous phase. The treatment prompts the precipitation of certain metals and salts.

1.2.7 Combined Electrocoagulation and oxidation

EC + H_2O_2 *Mechanism*

Recently the use of hydroxyl radicals in aqueous medium has been suggested to promote the oxidation of toxic pollutants in the effluent to be treated (Andreozzi et al., 1999). The hydroxyl radical is an extremely powerful oxidant. Hung et al., (1993) have discussed the advantages and disadvantages of several advanced oxidation processes and have concluded that the methods based on hydrogen peroxide to promote the formation of hydroxyl radical are the most promising approaches, since these methods do not involve the use of particularly dangerous chemicals, their operation is relatively simple and they are, in relative terms, not very expensive. These methods show more efficient mass transport properties than those involving other hydroxyl radical promoting species such as ozone (Huang et al., 1993; Peralta et al., 2005).

Hydrogen peroxide decomposition is highly sensitive to the presence of dissolved substances and solid surfaces, and it has been well documented that H_2O_2 heterogeneously decomposes to a higher or lesser extent by direct interaction with the solid surfaces. Miler et al., (1999) proposed a mechanism at the electrode surface (S) as following:

$S + H_2O_2 \leftrightarrow S^+ + OH^- + OH^\cdot$

$S^+ + H_2O_2 \leftrightarrow S + H^+ + HO_2^\cdot$

$S^+ + HO_2^\cdot \leftrightarrow H^+S + O_2$

$S + HO_2^\cdot + H^+ \leftrightarrow S^+ + H_2O_2$

$S + HO^\cdot \leftrightarrow S^+ + OH$

In acidic media (bulk solution) the reduction half reaction for the hydrogen peroxide is (Glaze et al,. 1999).

$$H_2O_2 + 2\,e^- + 2\,H^+ \leftrightarrow 2H_2O$$

The hydrogen peroxide will form the hydroxyl radical at the cathode as, (Bard et al,. 1985)

$$H_2O_2 + e^- + H^+ \leftrightarrow H_2O + OH^\cdot$$

The aqueous media is agitated with the injection of air. Some of the Al^{3+} ions produced in the anode can be reduced at the cathode. Then, the aluminum will react in the solution as, $H_2O_2 + 3\,H^+ + Al \leftrightarrow 3\,OH^\cdot + Al^{3+} + 3H_2O$

A chain reaction occurs between the hydroxyl radical and an organic compound R as, (Ksibi et al,. 2006)

$RH + OH^\cdot \leftrightarrow R^\cdot + H_2O$

$R^\cdot + O_2 \leftrightarrow ROO^\cdot$

$ROO^\cdot + RH \leftrightarrow ROOH + R^\cdot$

Therefore, the main advantage of adding H_2O_2 to produce this hydroxyl radical, which will react with the organic pollutants present in the wastewater.

CHAPTER-2

ELECTRO-COAGULATION

Electro-coagulation is a technique involving the electrolytic addition of coagulating metal ions directly from sacrificial electrodes. These ions coagulate with pollutants in the water, in a similar manner to the addition of coagulating chemicals such as alum and ferric chloride, and allow the easier removal of the pollutants. The electrolytic addition of these ions has a number of advantages over their addition chemically. There is no addition of anions meaning no increase in salinity of the treated water. The system produces half to one third of the sludge. Greater activity means less metal ions required and a wider range of pollutants can be removed. In electro flocculation, the pollutants are removed by the bubbles, which are generated during the process, capturing the coagulated pollutants and floating to the surface.

In an EC process the coagulating ions a produced ‘in situ’ and it involves three successive stages.

[1] Formation of coagulants by electrolytic oxidation of the sacrificial electrode**.**
[2] Destabilization of the contaminants, particulate suspension, and breaking of emulsions.
[3] Aggregation of the destabilized phases to form flocs.

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

- Compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode.

- Charge neutralization of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic inter-particle repulsion to the extent that the Vander Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
- The floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles still remaining in the aqueous medium.
- The solid oxides, hydroxides and oxy-hydroxides provide active surfaces for the adsorption of the polluting species.

A simple electro-coagulating reactor with one anode and one cathode is shown in Figure 3. When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the EC process. The mechanisms of removal of ions by EC will be explained with aluminum, since this metal has been extensively used to clarify wastewater.

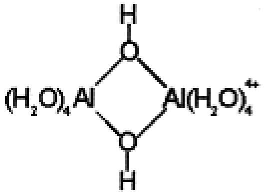
The electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as Al^{3+} and $Al(OH)_2^+$ at low pH, which at appropriate pH values are transformed initially into $Al(OH)_3$ and finally polymerized to $Al_n(OH)_{3n}$ according to the following reactions:

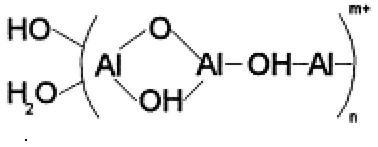
$$Al \longrightarrow Al^{3+}_{(aq)} + 3e^-$$

$$Al^{3+}_{(aq)} + 3H_2O \longrightarrow Al\ 3H^+_{(aq)}$$

$$nAl(OH)_3\ A \longrightarrow Al_n(OH)_{3n}$$

Depending on the pH of the aqueous medium other ionic species, such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ may also be present in the system. Examination of the pE–pH equilibrium diagram reveals that under appropriate conditions various forms of charged multimeric hydroxo Al^{3+} species may be formed. For example, the structures of dimeric and polymeric Al^{3+} hydroxo complexes are shown below:





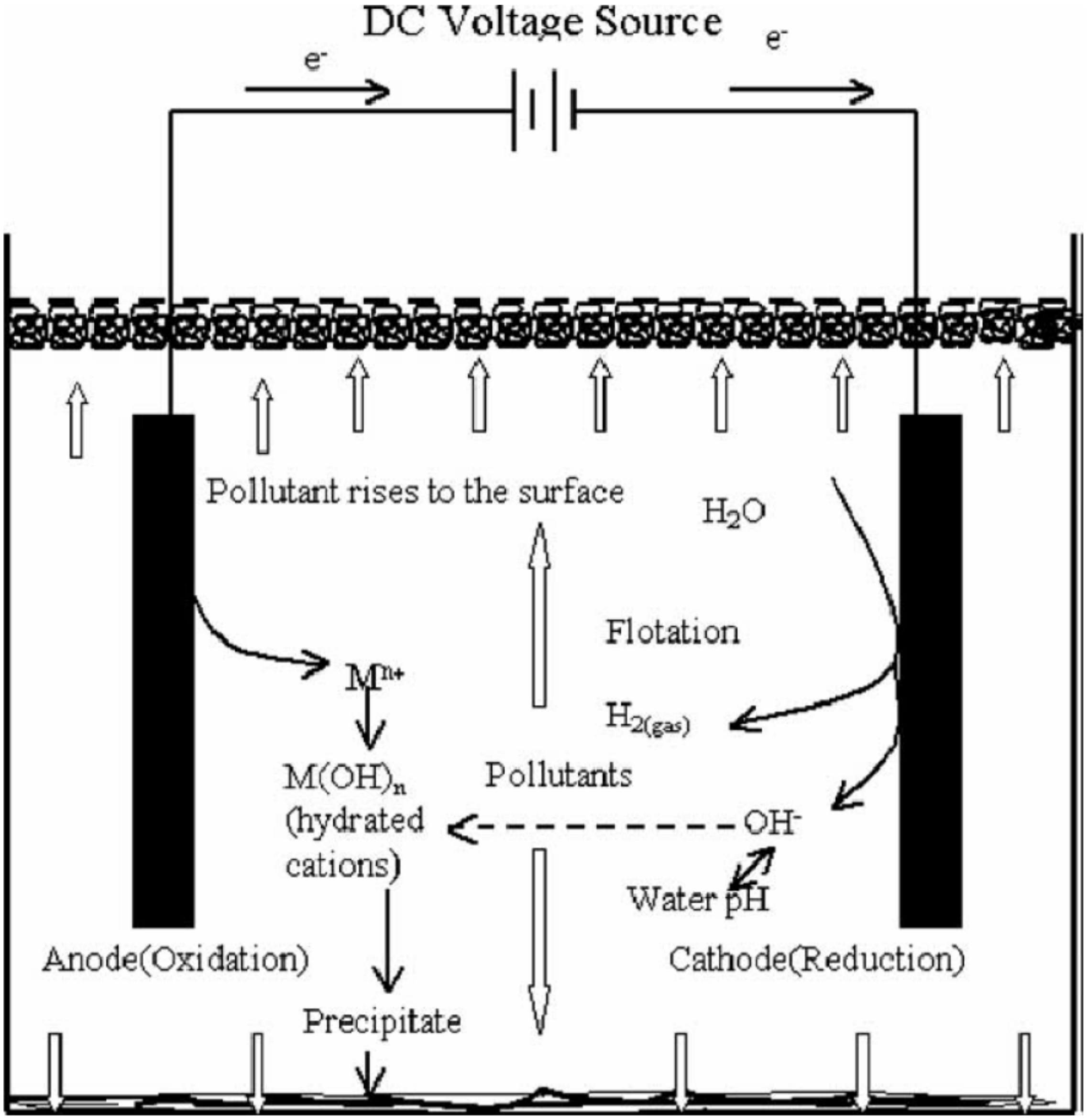


Figure 3: Schematic diagram of bench scale two electrode electro-coagulation cell

These gelatinous charged hydroxo cationic complexes could effectively remove pollutants by adsorption to produce charge neutralization, and by enmeshment in a precipitate. (Mollah et al., 2001)

The advantages of this are that the aluminum is much more active, requiring less metal for the removal of the same pollutants, and they can remove more material. In applying the aluminum via a sacrificial anode, the cathode releases hydrogen gas, which can operate like the air bubbles in a dissolved air flotation unit. This system automatically adds its own flocculating agent and generates its own gas bubbles, in a controlled manner, enabling suspended solids, oils/greases and other pollutants to be removed cheaply. In electro-coagulation, sacrificial electrodes are used and the passage of an electric current through the water from the electrodes causes the metal to go into solution as the ions, via the anode reactions:

$$Al + 3e^- \longrightarrow Al^{3+}$$

At the cathode, the reaction is more typically

$$2H_2O + 2e^- \longrightarrow 2(OH)^- + H_2$$

In this manner, the same effect is achieved as would be done using chemical dosing, but without the addition of any anions, leaving the residual salinity of the water practically unaltered. The cathode reaction results in a slight increase in the pH of the treated water, usually about 1 pH unit, depending upon the starting pH and the degree of treatment required. The pollutants are then removed in a similar manner to that associated with chemical coagulation, namely filters, settling or similar. Electroflocculation is a term used to describe the use of electro-coagulation to coagulate the pollutants, plus the cathode bubble generation to float the pollutants to the surface. In this regard, electroflocculation is similar to dissolved air flotation (DAF), with one major difference that there are no chemicals to be added and consequently no increase in the salinity of the treated water. The electroflocculation process generates the coagulating ions and the gas bubbles in one action, without the need for additional compressed air/bubble generation equipment. Best results are achieved with a pH in the range $3.5 < pH < 9$.

To improve the performances of an EC it may be necessary to interchange the polarity of the electrode intermittently. However, a two-electrode EC cell is not suitable for wastewater treatment, because for a workable rate of metal dissolution the use of electrodes with large surface area is required. Performance improvement has been achieved by using EC cells with monopolar electrodes either in parallel or series connections.

Different types of arrangement of electrodes in EC are:

(i) A simple arrangement of an EC cell with a pair of anodes and a pair of cathodes in parallel arrangement is shown in Figure 4. It essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a direct current power source. The experimental set up also requires a resistance box to regulate the current density and a multimeter to read the current values. The conductive metal plates are commonly known as ‘sacrificial electrodes’. The sacrificial electrodes may be made up of the same or of different materials (Pretorius et al., 1991).

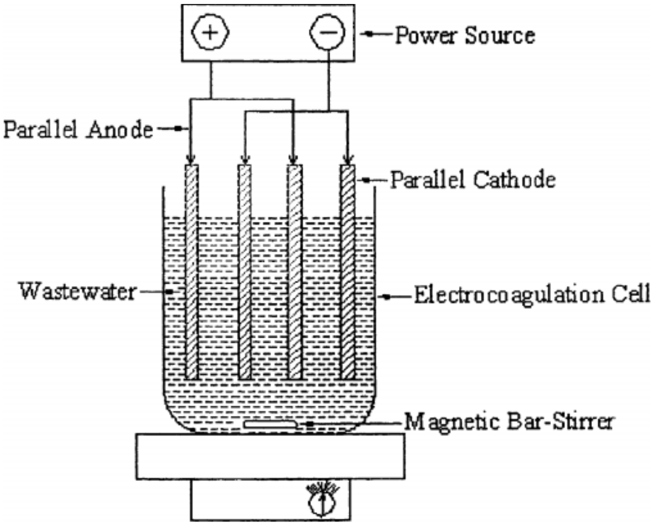


Figure 4: Bench-scale EC reactor with monopolar electrodes in parallel connection

(ii) An arrangement of an EC cell with monopolar electrodes in series is shown in Figure 5. As can be seen from Figure 5, each pair of ‘sacrificial electrodes’ is internally connected with each other, and has no inter connections with the outer electrodes. This arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections (Pretorius et al., 1991).

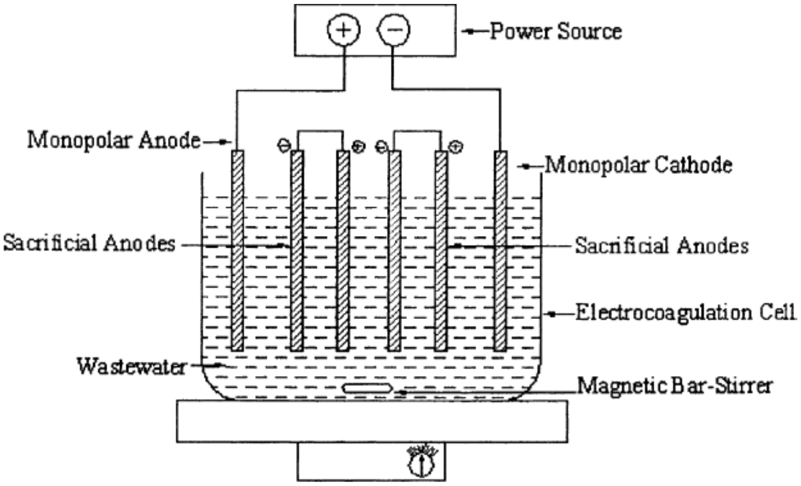


Figure 5: Bench-scale EC reactor with monopolar electrodes in series connection

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

(iii) An arrangement of an EC cell with bipolar electrodes in parallel is shown in Figure 6. The sacrificial electrodes are placed between the two parallel electrodes without any electrical connection. Only the two mono polar electrodes are connected to the electric power source with no interconnections between the sacrificial electrodes. This cell arrangement provides a simple set-up, which facilitates easy maintenance during use. When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared to the parallel side beside it. The sacrificial electrodes in this case are also known as bipolar electrodes (Pouet et al., 1995, and Mameri et al., 1998).

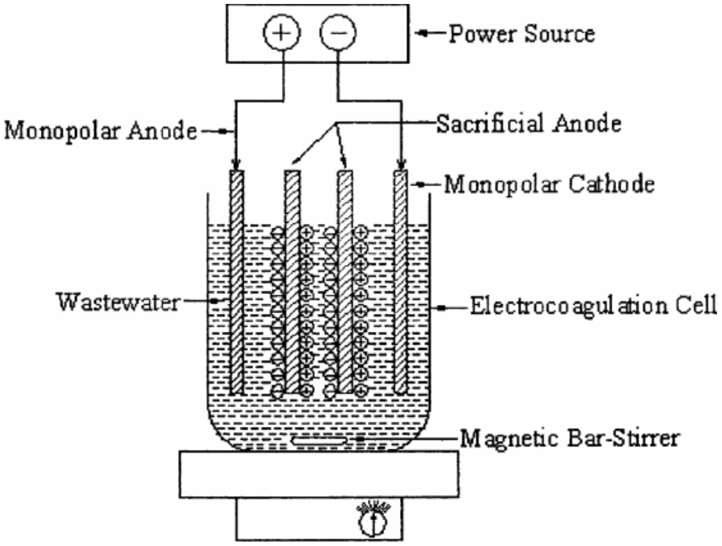


Figure 6: Bench-scale EC reactor with bipolar electrodes in parallel connection

The amount of metal dissolved or deposited is dependent on the quantity of electricity passed through the electrolytic solution. A simple relationship between current density (A cm$-^2$) and the amount of substances (M) dissolved (g of Mcm$-^2$) can be derived from Faraday's law.

$$w = \frac{itM}{nF}$$

where w is the quantity of electrode material dissolved (g of Al cm^{-2}), i the current density (A cm^{-2}), t the time in s; M the relative molar mass of the electrode concerned, n the number of electrons in oxidation/reduction reaction, F the Faraday's constant, 96,500Cmol^{-1}.

It is expected that there should be an agreement between the calculated amount of substances dissolved as a result of passing a definite quantity of electricity and the experimental amount determined. Usually a good agreement is obtained although significant error may be introduced if sufficient attention is not given to the geometry of the electrode assembly as well as the optimum conditions of operation of the EC cell. One area of uncertainty is in the measurement of potential of the EC cell. The measured potential is the sum of three components as,

$$\eta_{AP} = \eta_{k} + \eta_{Mt} + \eta_{IR}$$

where η_{AP} is the applied over potential (V), η_{k} the kinetic over potential (V), η_{Mt} the concentration over potential (V), η_{IR} the over potential caused by solution resistance or IR-drop.

The IR-drop is related to the distance (*d* in cm) between the electrodes, surface area (*A* in m^{2}) of the cathode and specific conductivity of the solution (*k* in mS m^{-1}) and current (*I* in A) electrodes.

$$\eta_{IR}=I\ d/Ak$$

The IR-drop can be easily minimized by decreasing the distance between the electrodes and increasing the area of cross-section of the electrodes and the specific conductivity of the solution.

Concentration overpotential (η_{Mt}), also known as mass transfer or diffusion overpotential is caused by the change in concentration occurring in the proximity of the electrode surface due to electrode reaction. This overpotential is caused by the differences in electrolytic species concentration between the bulk solution and the electrode surface. This condition occurs when the electrochemical reaction is sufficiently rapid to lower surface concentration of electrolytic species below that of the bulk solution. The concentration overpotential is negligibly small when reaction rate constant is much smaller than the mass transfer coefficient.

The mass transport overpotential (η_{Mt}, V) can be reduced by increasing the masses of the metal ions transported from the anode surface to the bulk of the solution and can be achieved by enhancing the turbulence of the solution. It can also be overcome by passing electrolyte solution from anode to cathode at a higher velocity by using some mechanical means.

Kinetic overpotential (also called activation potential) has its origin in the activation energy barrier to electron transfer reactions. The activation overpotential is particularly high for evolution of gases on certain electrodes. Both kinetic and concentration overpotential increase as the current increases.

Advantages of EC

- EC requires simple equipment and is easy to operate.
- The electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring less maintenance.
- Wastewater treated by EC gives palatable, clear, colorless and odorless water.
- It is a low sludge producing technique. Sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides.
- Flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.
- The EC process avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used.
- The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
- The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

Disadvantages of EC

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

CHAPTER 3

LITERATURE REVIEW

The textile industry is one of those industries that consume considerable amounts of water. The water employed in the dyeing and finishing processes eventually ends up as wastewater that needs to be treated before final discharge. Frequent changes of dyestuff employed in the dyeing process cause considerable variation in the wastewater characteristics, particularly pH, color and wastewater COD value. Large pH fluctuation is especially troublesome because the pH tolerance of conventional biological and chemical treatment systems is very limited. Hence without proper pH adjustment, normal operation of the treatment processes is essentially impossible. Strong color is another important component of the textile wastewater that is very difficult to deal with combination of strong color and high dissolved solid content resulting in high turbidity of the wastewater. The strong color of wastewater if not removed would cause disturbance to the ecological system of the receiving waters. Traditional methods for dealing with the wastewater consist of biological, physical, chemical and their various combinations. The work of several researchers pertaining to textile wastewater is discussed below:

Gursesa et al. (2002) studied the decolorization of strong colored solutions containing the reactive textile dyes by electrocogulation. The experiments were statistically designed and carried out according to a 24 full factorial design with two replicate and four center points. This design was extended with eight additional axial points. Then, the non-linear regression was applied on the data by using MINITAB software. The variables chosen for this work are mixing rate, cell voltage, electrolysis time and current density. Results showed that the effective variables on decolorization process are cell voltage, electrolysis time and current density. In addition, to determine the effect of dye and electrode type on decolorization, the additional experiments were carried out. It was determined the dye and electrode type are important on the decolorization process.

Kim et al. (2002) investigated the effects of the operating parameters, such as current density, electrode number, electrolyte concentration, electrode gap, dyestuff concentration, pH of solution and inlet flow rate, on decolonization by continuous electrocogulation. The dye removal efficiencies and reaction rate constants from the curves following the first-order relationship. In addition, the operating parameters were also searched for minimum power consumption. The behaviors of decolorization according to dyestuff types, i.e., disperse dye and reactive dye, were also examined.

Daneshvar et al. (2003) studied the decolorization of orange II by the direct current electrocogulation (EC). The effect of initial pH, rate of stirring, concentration of dye, electrodes distance, current density, water temperature etc were studied. The optimum operating range for each of these operating variables was experimentally determined. The experimental results revealed that the color of orange II in aqueous phase was effectively removed (98%) and also the chemical oxygen demand (COD) reduced (84%), when iron was used as sacrificial anode and the concentration of orange II was B 200 ppm. The optimum current density was 34.62 A/m^2 for effectively removing of orange II. The EC 1method is found to be quite effective in removing of orange II.

Mollah et al. (2004) studied treatment of orange II dye solution in a flow cell using sodium chloride as an internal electrolyte. In this technique dye solutions were passed through a flow-through EC apparatus consisting of a flow-through cell, the electrode assembly, the feed pump and the DC power supply unit. The cell contained five parallel iron electrodes, which form four parallel cells. Experiments were run at 25 ^{0}C under various electrolyte concentrations, dye concentrations, current density, flow rate of the solution, and pH at direct current range of 2–5 A. Various number of recycles of the treated dye solution were also performed at the same dc current range. Optimum conditions to get high removal efficiency were experimentally determined. It was found that 98.5% of the dye was removed from the solution under the optimum conditions.

Daneshvar et al. (2004) investigated the variables that influence the efficiency of decolorization of a solution containing an azo dye (Acid Red 14) by electrocogulation

(EC) and compare the efficiency of different electrode connections for color removal. Current density, time of electrolysis, inter-electrode distance, and pH of the solution was the variables that most influenced color removal. The effect of each variable was studied separately using synthetic wastewater in a batch mode. The efficiency of the method tested was determined by measurement of color removal and reduction of Chemical Oxygen Demand (COD). For dye solutions with COD of approximately 30 ppm and dye concentrations less than 150 ppm, high color removal (93%) was obtained when the pH ranged from 6 to 9, time of electrolysis was approximately 4 min, current density was approximately 80 A/m^2, the temperature was approximately 300 K, and interelectrode distance was 1 cm. During the EC process under these conditions, the COD decreased by more than 85%. In the second series of experiment, the efficiency of EC cells with monopolar electrodes in series and parallel connections and an EC cell with bipolar electrodes were compared with results using a simple electrochemical cell. The experimental results showed that an EC cell with several electrodes was more effective than a simple electrochemical cell in color removal. The results also showed that an EC cell with monopolar electrodes had a higher color removal efficiency than an EC cell with bipolar electrodes. Furthermore, within an EC cell, the series connection of the monopolar electrodes was more effective for the treatment process than the parallel connection in color removal.

Mollah et al. (2004) studied the electrocogulation that is currently experiencing both increased popularity and considerable technical improvements. There has been relatively little effort to better understand the fundamental mechanisms of the processes, particularly those that could provide design parameters to optimize the performances of this relatively simple and inexpensive technique. This work presents an in-depth discussion and consideration of the factors that need to be addressed for optimum performance of this technology. Recent improvements of this technique and the theoretical model studies are also reviewed.

Golder et al. (2005) studied the electrocogulation (EC) of aqueous dye solutions of two different industrial dyes in a batch stirred cell. Experiments were carried out with 200 mg/l individual concentration of methylene blue (MB) and eosin yellowish (EY) in presence of NaCl as electrolyte. Effect of operating time and current density on the decolorization of dye solutions, reduction of chemical oxygen demand (COD) and variation in conductivity, pH during treatment has been studied. Small difference between color diminution and COD reduction has been found with the progress of treatment. First-order rate equation for dye removal has been developed from the experimental results. Sludge formation during EC and problems associated with this solid waste generation and disposal has been assessed. Electric power consumption of 1.5KWh reduces 0.21 and 0.11 kg COD from 0.24 and 0.14 kg of initial COD for MB and EY, respectively, starting from 200 mg/l dye concentration.

Song et al. (2007) investigated the variables that influence the efficiency of color removal from a solution containing an azo dye (C.I. Reactive Black 5, abbreviated here as RB 5) by the combination of ozonation and electrocogulation at iron electrodes. Several working parameters, such as initial pH, initial dye concentration, current density, salt (K_2SO_4) concentration, temperature, ozone flow rate and distance between the electrodes, were studied in an attempt to achieve higher color removal efficiency. The experimental results revealed that the color of RB 5 in the aqueous phase was removed effectively. Under the conditions of an initial dye concentration of 100 mg/L, initial pH of 5.5, current density of 10 mA/cm^2, salt concentration of 5000 mg/l, temperature of 20 ^{0}C, ozone flow rate of 20 ml/min (ozone dose 0.20 g/h), and interelectrode distance of 1 cm, the color-removal efficiency reached 94%, corresponding to a reduction in COD of more than 60%. The energy consumption of the technique was approximately 33 kWh/kg of COD removal.

Bayramoglu et al. (2007) presented the comparative results with respect to electrode configurations on the economic performance of treatment of textile wastewaters by electrocogulation (EC) process. Aluminum and iron electrode materials were used as sacrificial electrode in parallel and serial connection modes. Various direct and indirect cost items including electrical, sacrificial electrodes, labor, sludge handling, maintenance and depreciation costs were considered in the calculation of the total cost per m^3 of wastewater taken from a textile plant with a capacity of 1000m^3 per day. The results showed that monopolar-parallel mode (MP-P) was the most cost-effective for Fe and Al electrodes. These electrodes showed similar results in removal efficiency of COD and turbidity, but Fe electrode was preferred due to its low cost. pH 7 for Fe electrode and pH 5 for Al electrode were found suitable in terms of removal efficiency of COD and turbidity from textile wastewater. Meanwhile, 30A/m^2 of current density and 15 min of operating time were found to be sufficient for Fe and Al electrodes. Finally a comparative study showed that EC was faster and more economic; consumed less material and produced less sludge, and pH of the medium was more stabilized as compared to chemical coagulation (CC) for percentage removal efficiency of COD and turbidity from textile wastewater. The treatment cost of EC at optimum conditions was 3.2 times cheaper than that of CC.

Wu et al. (2008) studied the decolorization efficiency of Procion Red MX-5B in electrocogulation (EC), UV/TiO2 and ozone-related systems. The effectiveness of energy input was also determined. The decolorization rate constants of these EC, UV/TiO2 and ozone-related systems fitted pseudo-first-order kinetics and the values were in the order O_3 (24 W) > O_3(16 W) > O_3(16 W)/EC (8 W) > UV/TiO2/O_3 (8 W)/EC (8 W) > O_3 (10 W) > UV/O_3 (8 W)/EC (8 W) > UV/O_3(8 W) > O_3 (8 W) > UV/TiO2/O_3 (8 W) > O_3 (8 W)/EC (8 W) > O_3(4 W)/EC(4 W) > UV/TiO2/EC (8 W) > UV/TiO2 > UV/EC (8 W) > EC (8 W). The decolorization rate constants increased with the total power input. Additionally, the decolorization efficiency could be promoted by combining UV with O_3, UV with EC, EC with UV/TiO2 and EC with UV/O_3. This study revealed that combining EC with UV/TiO2 or UV/O_3 can trigger a Fenton or Fenton-like reaction, which accelerates the rate of decolorization. The solution pH of O_3, UV/O_3 and UV/TiO2 systems declined during decolorization; in contrast, the pH increased to 7.4 in the UV/EC system. The effective energy consumption constant did not increase with the total power input and reached maximum at a total power input of approximately 10-16 W.

Valero et al. (2008) studied the feasibility of the use of an electrocogulation system (EC) directly powered by a photovoltaic (PV) array using a reactive textile dye Remazol Red

RB 133. They proposed an effective methodology to adjust the EC–PV system operation conditions depending on solar irradiation has been proposed. The current flow ratio, Jv, is established as the control parameter.

Raju et al. (2008) studied the treatment of wastewater from a textile industry, that produces synthetic polyester cloths, employing electrochemical techniques. The sample was initially subjected to electrocogulation to remove suspended solids. Mild steel and aluminum electrodes were tried as anodes; and aluminum was found to be effective for the removal of suspended solids. Using aluminum as anode, the chemical oxygen demand (COD) concentration of the effluent which was initially at the level of 1316 mg/l could be reduced to 429 mg/l by electrocogulation. After electrocogulation, the effluent was further subjected to electro oxidation using graphite and RuO2/IrO2/TaO2 coated titanium as anodes. During the electro oxidation tests, both COD and chloride ion were simultaneously estimated; and the effect of Cl^- ion is discussed. The measurements revealed the depletion of Cl^- ion concentration implying the generation of free chlorine during electro oxidation. The depletion of Cl^- ion concentration and the COD removal were observed to be comparatively high in the presence of graphite electrode. The effects of electrode materials and current density on COD removal are discussed. The instantaneous current efficiency (ICE), mass transfer coefficient and energy consumption were estimated.

Raju et al. (2009) studied the purification of textile wastewater by electrocogulation and electro oxidation techniques. The suspended solids were removed to the extent of 97% from its initial concentration of 1565 mg L/l by electro-cogulation. The initial COD of 530 m/l reduced to 246 mg/l using mild steel as anode. After electrocogulation, the effluent was further subjected to electro oxidation using two different materials viz. graphite and RuO2/IrO2/TaO2 coated titanium as anodes. The COD was removed to the extent of 90–93% using graphite and 54% using RuO2/IrO2/TaO2 coated titanium. Graphite electrode has exhibited higher CE values of 40%, whereas RuO2/IrO2/TaO2 coated titanium yielded only 11%. The energy consumption, EOI, CE values clearly indicated the superior performance of graphite electrodes. Graphite materials exhibit EOI values (0.21–0.35) with less energy consumption and efficient anodic oxidation of organics compared to RuO2/IrO2/TaO2 coated titanium. The processed water can be safely treated by reverse osmosis to recover the water for reuse.

Eyvaz et al. (2009) studied the electro-coagulation of two textile dyes from aqueous solutions using different power supplies. Aluminium electrodes were used as sacrificial electrodes in parallel connection modes. Direct current (DC) was obtained from a DC power supply operated at galvanostatic mode while alternating pulse current (APC) was obtained by a time relay integrated with DC power supply. Dye and TOC removal efficiencies with DC and APC were compared. Furthermore, various cost items were used to calculate the total operation cost of both DC and APC systems by means of TOC and dye removal. They have concluded the following points:

- Higher removal efficiencies of TOC and dye can be acquired in shorter operation times by using APC system (e.g. 5 min of operation time). Thus, it can be said that anode–cathode polarization reduces the reaction time which is necessary for metal hydroxides removing TOC and dye from aqueous solutions.
- For RY dye, TOC and dye removal percentages increase until a certain operation time, and then they decrease so long as DC system goes on working. It may be due to the cathode passivization arisen from accumulation of contaminants on the cathode material. Therefore, electrode surfaces are needed to be cleaned and then put into use again. The system can be used to overcome these drawbacks of DC system.
- Fill-and-draw periods of reactor could be easily increased for batch EC processes by using time relay to eliminate cathode passivization.

Canizares et al. (2009) studied the influence of the pH of the waste in the coagulation with aluminum by conventional and electrochemical dosing. The pH has significant influence on the coagulant species along with the charge of the aluminum hydroxide precipitates and this information has been used to interpret the results obtained in the treatments (by both coagulation methods) of a synthetic oil-in-water emulsion and an actual effluent of a door-manufacturing factory. Results showed that a simple change in the pH of the wastes can result in a significant change in the efficiency of the coagulation process, and that if the same pH conditions are found at the end of the treatment, the efficiencies of the solution-dosing and of the electrochemical dosing technologies are very similar.

Khataee et al. (2009) has made a comparison study between UV/Nano-TiO_2, Fenton, Fenton-like, electro-Fenton (EF) and electrocogulation (EC) treatment methods to investigate the removal of C.I. Acid Blue 9 (AB9) which was chosen as the model organic contaminant. Results indicated that the decolorization efficiency was in order of Fenton > EC > UV/Nano-TiO_2 > Fenton-like > EF. Desired concentrations of Fe^{2+} and H_2O_2 for the abatement of AB9 in the Fenton-based processes were found to be 10^{-4}M and $2\times^{10-3}$ M respectively. In the case of UV/Nano-TiO_2 process, we have studied the influence of the basic photo catalytic parameters such as the irradiation time, pH of the solution and amount of TiO_2 nanoparticles on the photo catalytic decolorization efficiency of AB9. It was stated that the complete removal of color, after selecting desired operational parameters could be achieved in a relatively short time, about 25 min. The most effective decomposition of AB9 was observed with 150 mg/l of TiO_2 nanoparticles in acidic condition. The effect of operational parameters including current density, initial pH and time of electrolysis were studied in electro-coagulation process. The results indicated that for a solution of 20 mg/l AB9, almost 98% color were removed, when the pH was about 6, the time of electrolysis was 8 min and the current density was approximately 25A/m^2 in electro-coagulation process.

Merzouk et al. (2010) investigated the effects of the operating parameters, such as pH, initial concentration, current density, inter-electrode distance and conductivity on the treatment of a synthetic wastewater in the batch electro-coagulation (EC)-electroflotation (EF) process. The optimal operating condition were determined and applied to a textile wastewater. Initially a batch type EC-EF reactor was operated at various current densities ranging from 11.55 to 91.5 mA/cm^2 and various electrode gaps (1, 2 and 3 cm). For solutions with 300 mg/l of silica gel , good turbidity removal (89.6 %) was obtained without any coagulant when the current density was 11.55 mA/cm^2, and with initial pH at 7.6, conductivity at 2.1 mS/cm^2 the treatment time was 10 min and the electrode gap was

1 cm. Application of the optimal operating parameters on a textile wastewater showed a high removal efficiency for the following variables: suspended solid (SS) 85.5 %, turbidity 76.2%, biological oxygen demand (BOD_5)8 8.9%, chemical oxygen demand (COD) 79.7% and color over 93 %.

Objectives of the present work

The following objectives were set for the present work:

- To investigate the treatment efficiency of the electro-coagulation process for COD removal from synthetic water sample prepared using brilliant crysel blue dye.
- To study the effect of pH and current density on the COD removal for electro-coagulation process.
- To study the kinetics of COD removal for electro-coagulation process.
- To study the effect of combined oxidation and electro-coagulation process on COD removal.

CHAPTER 4

EXPERIMENTAL SETUP AND PROCEDURE

Direct current electro-coagulation technique was used for dye removal from synthetic wastewater samples. Electrolysis was conducted in a batch setup to investigate the effect of pH, current density and on COD removal.

4.1 Lab scale electro-coagulation setup

EC reactor with mono-polar electrodes connected in parallel was used in the experiments. The reactor having a volume of 3.2 liter (13.2 cm lenght × 13.2 cm width×17.9 cm depth) was fabricated with acrylic sheet of thickness 5 mm. Aluminum plates (12.2 cm × 7.8 cm) with a thickness of 0.5 mm were used as the electrodes for the experiments. A regulated direct current supply (0–30 V, 15 A, Make Crown Electronics Delhi, India) was used for the experiments. The experimental setup is shown in Figure 7.

Fig 7: Electro-coagulation set up

4.2 Preparation of sample

The synthetic samples were prepared by dissolving *Brilliant Cresyl Blue* dye (procured from S.D. Fine Chemicals, Mumbai) in distilled water. The chemical structure formula is $C_{17}H_{2O}N_3OCl.1/2\ ZnCl_2$ and its molecular weight is 386. For the preparation of sample 200 mg of the dye was dissolved per liter of distilled water. The pH of the sample was adjusted using NaOH/concentrated H_2SO_4.

4.3 Experimental procedure

The complete experimental procedure is as follows:

1. The sample solution was prepared as required.
2. The pH of the solution was adjusted by adding either H_2SO_4 or NaOH as per the requirement.
3. Before each experiment, the electrodes were abraded with sand paper to remove scale and then cleaned with successive rinses of water and $H_2SO_{4.}$
4. The electrodes were weighed before and after each run.
5. The inter-electrode spacing was kept at 1 cm for all the experiments.
6. DC power supply was used to pass 3.5, 4.5, and 5.5 A current at 4.5 V.
7. Proper agitation was done by using magnetic stirrer.
8. The samples were taken for residual COD analysis.

4.4 Analysis of COD in sample

The COD analysis of the of sample is as follows:

1. COD analysis of the sample was done with the following ratio (1:2:3) where $K_2Cr_2O_7$ was taken first, then sample volume as above prescribed limit and sulfuric acid reagents was added .
2. Sample was put in COD digester for 2 hour for digestion.
3. After 2 hour sample was titrated with FAS solution.

CHAPTER 5

RESULT AND DISCUSSION

The experimental results of COD removal from synthetic dye water solution by electro-coagulation process are presented in this chapter. The treatment process has to ensure that COD in the treated dye water solution is well below the permissible limit.

5.1 Effect of influent pH on COD removal

Effect of initial pH of the sample on COD removal was investigated at current density of 9.25 mA/cm^2. The pretreated sample have the initial COD equal to 1360 mg/l. After EC run of 90 minutes and a settling time of 30 minutes the treated water samples were analyzed for the residual COD. results has been discussed at current density of 9.25 mA/cm^2, 4.5 V and at an inter-electrode distance is 1 cm. The pretreated sample have the initial COD of 1360mg/l. The treated dye water sample is analyzed after each run with the settling time of the sample was 30 minute. The results are shown in Table 1 and Figure 8.

Table 1: Effect of influent pH on COD removal

Sr no.	pH	Residual COD in sample (mg/l)
1	5	320
2	6	180
3	7	240
4	8	280

The COD measurements of the different sample were made. At low pH (pH = 5) and high pH (pH = 8) the sufficient sludge formation did not take place. Therefore, the adsorption of dye could not perform effectively at low or high pH. The residual COD was found to be minimum for an initial pH equal to 6. At low pH, the solution protons are reduced at cathode to H_2 and the same proportion of hydroxide ions cannot be produced Daneshvar et al. (2003). For further experiments the pH was kept at 6.

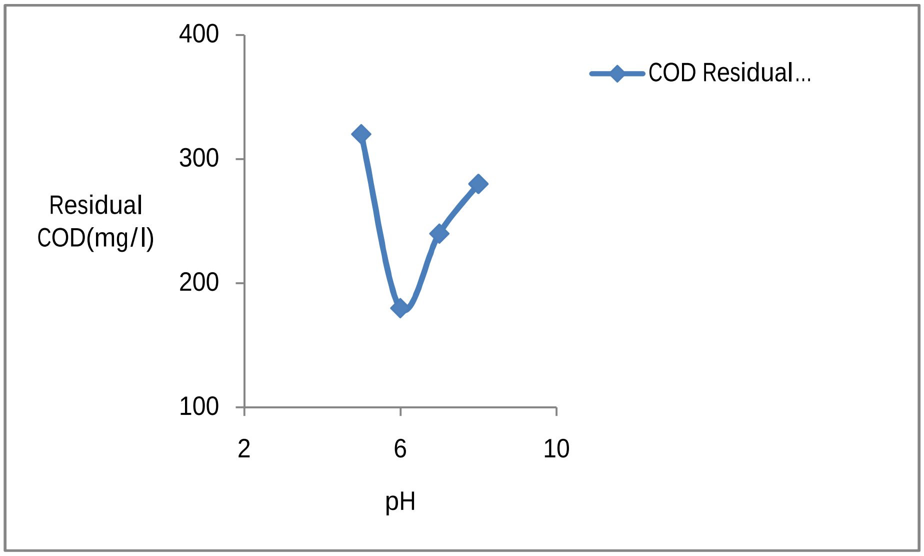


Figure 1: Effect of influent pH on COD Removal, at current density of 9.25 mA/cm^2 With reaction time of 90 minute.

5.2 Variation in pH with electro-coagulation time:

The effect on sample pH change with EC time is investigated. The initial pH and current density for this study was kept at 6 and 9.25 mA/cm^2 respectively. The inter-electrode distance was kept at 1 cm. Results are shown in Table 2 and Figure 9.

Table 2: Variation of pH with time in electro-coagulation process

Sr. No.	Time (min)	pH
1	0	6
2	15	6.34
3	30	6.58
4	45	6.84
5	60	7.07
6	75	7.35
90	90	7.56

The pH of the sample increased with time. The pH increase in electro-coagulation process is attributed to the formation of H_2 gas at the cathode, also a slight increase in pH may be caused by the formation of ionic species such as $Al(OH)^{2+}$ (Mollah et al., 2004).

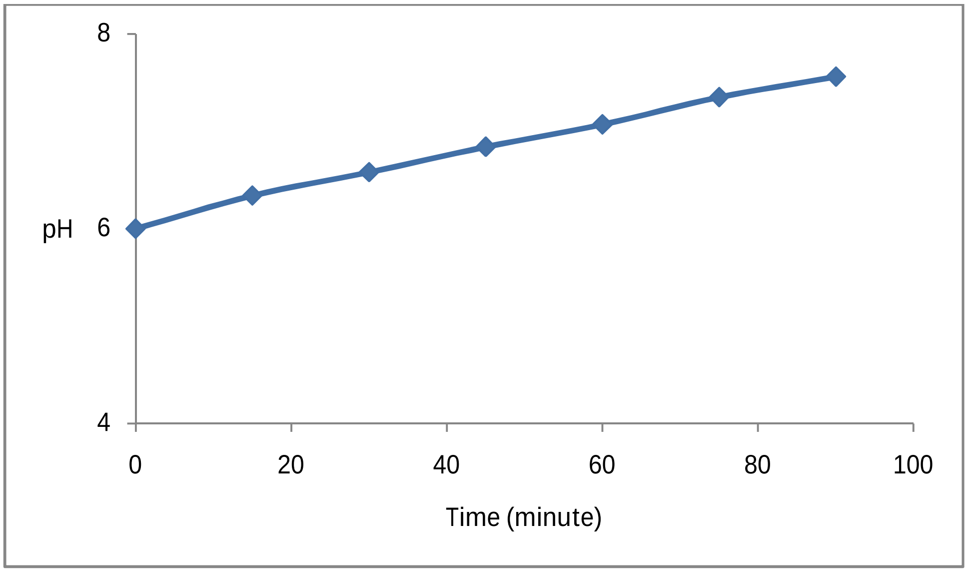


Figure 9: Variation of pH with time in electro-coagulation process.

5.3 Effect of current density on COD removal

The COD removal by electro-coagulation process is affected by applied current density. Different set of experiments were performed for current density varying from 9.25 to 14.53 mA/cm^2, inter-electrode distance was kept at 1 cm. It was found that the COD removal increases with increasing current density. The minimum current density used for COD removal gave the residual COD value well below the permissible limit as shown in the Table 3 and Figure 10.

This is ascribed to the fact that at high current density, the extent of anodic dissolution of aluminum increases, resulting in a greater amount of precipitate for the removal of pollutants. Moreover, bubble generation rate increases, bubble size decreases, greater upward flux and hence faster removal of arsenic can be seen with increasing current density. These effects are both beneficial for high pollutant/ COD removal by H_2 flotation. Similar result was observed by Adhoum and Monser study.

Table 3: Effect of current density on COD removal

Sr. No	Time(minute)	Residual COD (mg/l) at 9.25 mA/cm^2	Residual COD (mg/l) at 11.88 mA/cm^2	Residual COD (mg/l) at 14.53 mA/cm^2
1	0	1360	1360	1360
2	15	1160	1120	1080
3	30	920	880	840
4	45	740	680	600
5	60	480	440	440
6	75	200	320	240
7	90	180	160	120

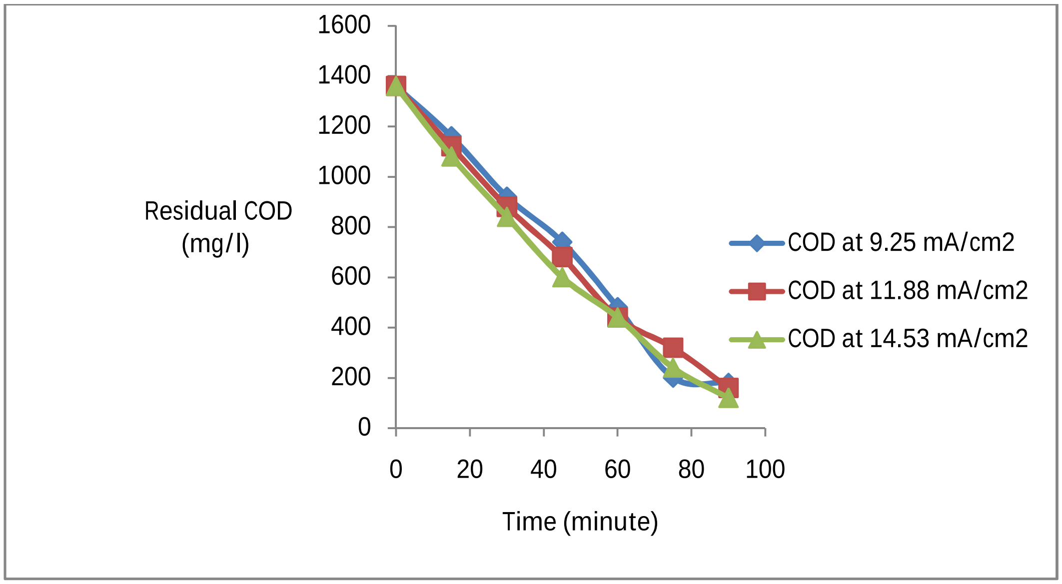


Figure 10: Effect of current density on COD removal.

5.4 Kinetics of dye removal by electro-coagulation process

Different set of experiment were performed with for current density varying from 9.25-14.53 mA/cm^2, inter electrodes distance was kept at 1 cm.

The rate of removal can be represented by a first order kinetics, i.e.

$$-dC/dt = kC$$

Which when integrated gives the relation as

$$C(t)/ C_0 = \exp(-kt)$$

So a plot of $\ln(C(t)/ C_0)$ against t should give a straight line for a particular current density. Fig. 11 is such a plot. The kinetics constant for different current densities (3.5A, 4.5 A and 5.5 A) are 0.021 min^{-1}, 0.0203min^{-1} and 0.0221 min^{-1} respectively. The kinetic rate constant for COD removal was found to be maximum for current density of 14.53 mA/cm^2 (at 5.5A).

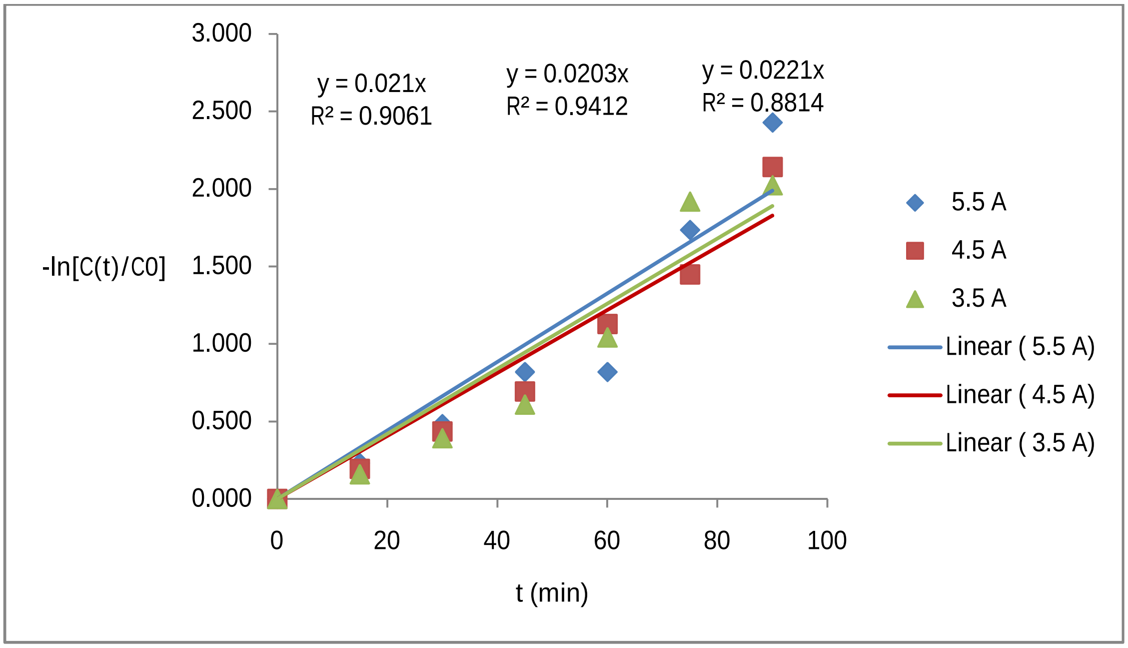


Figure 11: Kinetics of dye removal by electro-coagulation process

5.5 COD removal by oxidation with H_2O_2

Effectiveness of oxidation process was used for the COD removal with different oxidant (H_2O_2) dose. The results are given in Table 4

Table 4: COD removal with time for different oxidant doses

Sr.No.	Time (minute)	Residual COD with 1ml/l dose of H_2O_2	Residual COD with 1.5 ml/l dose of H_2O_2
1	0	1200	1100
2	15	1080	540
3	30	840	420
4	45	520	260
5	60	280	180
6	75	120	120
7	90	120	60

5.6 Effect of H_2O_2 dose on COD removal in combined EC and Oxidation process

Different amount of hydrogen peroxide dose was added in to the EC cell, its effect were observed with the residual COD amount, initial pH was adjusted at 6 for the each run and the EC time for the experiment was 90 minute along with the 30 minute of settling time. The results are presented in Table 5 and Figure 12.

The comparison of COD removal by EC alone and with EC and oxidation combined shows that the COD removal efficiency increased from 87% to 97% with 1.5 ml/l of H_2O_2 dose and from 87% to 94% with 1.0 ml/l of H_2O_2 dose. This increased COD removal results due the formation of hydroxyl radicals. Also, the treatment time decreased from 90 min to 60 min in case of combined process.

Table 5: COD removal in combined EC and Oxidation process

Sr.No.	Time (minute)	Residual COD with 1ml/l of H_2O_2 dose	Residual COD with 1.5 ml/l Of H_2O_2 dose
1	0	1080	920
2	15	920	540
3	30	680	384
4	45	280	120
5	60	160	40
6	75	80	40
7	90	80	40

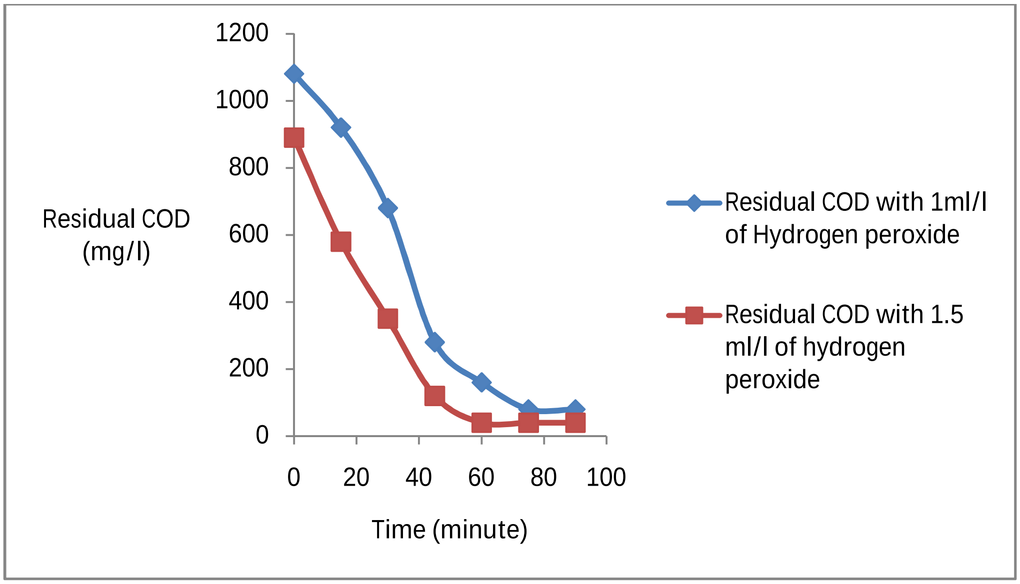


Figure 12: COD removal in combined EC and Oxidation process

CHAPTER 6

CONCLUSIONS

Based on the present work the following conclusions can be drawn:

- pH of 6 was found to be most appropriate for COD removal from the tested synthetic dye-water sample by EC.
- With EC time pH of the sample increases by about 1unit.
- Better COD removal was observed with increasing current density. It was found that for current density equal to 14.53 mA/cm^2 (with 5.5 A current) with four electrodes gave better result as compared to 9.25 and 11.88 mA/cm^2.
- The kinetics constant for different current densities (3.5A, 4.5 A and 5.5 A) are 0.021 min^{-1}, 0.0203min^{-1} and 0.0221 min^{-1} respectively.
- In the combined process (EC + oxidation) the COD removal efficiency increased from 87% to 97% with 1.5 ml/l of H_2O_2 dose and from 87% to 94% with 1.0 ml/l of H_2O_2 dose as compared to the EC process alone.
- In the combined process the treatment time decreased from 75 min to 45 min to bring the effluent COD within the permissible limit.

CHAPTER-7

FUTURE SCOPE AND RECOMMENDATIONS

- It was observed that sludge was not easily settled by gravity. Therefore sludge separation method should be further studied.
- For treatment of dye wastewater from dyeing stage by electro-coagulation process the cost effectiveness analysis should be investigated and compared with other treatment method.
- The following batch scale results should be used in pilot plant to use this technique in to the industrial application economically.

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