PERFORMANCE EVALUATION OF ELECTRO-COAGULATION IN REMOVAL OF CRYSTAL VIOLET DYE

Submitted in partial fulfilment of the requirements of the degree of Bachelor of Engineering

by

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CERTIFICATE

This is to certify that the project entitled "Performance Evaluation of Electrocoagulation in Removal of Crystal Violet Dye*"* is a bonafide work of Shaikh Kafil Sabir (13CES51), Khan Sohail Akram (13CES27), Khan Rizwan Aslam (13CES24), Mohammed Shafique (13CES31) submitted to the University of Mumbai in partial fulfilment of the requirement for the award of the degree of "Bachelor of Engineering" in Department of Civil Engineering.

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PROJECT REPORT APPROVAL FOR B. E.

This project report entitled "Performance Evaluation of Electro-Coagulation in Removal of Crystal Violet Dye" by Shaikh Kafil Sabir (13CES51), Khan Sohail Akram (13CES27), Khan Rizwan Aslam (13CES24), Mohammed Shafique (13CES31) approved for the degree of "Bachelor of Engineering" in "Department of Civil Engineering".

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DECLARATION

I declare that this written submission represents my ideas in my own words and where others ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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ABSTRACT

In this study, we evaluate the performance of Electrocoagulation for the colour removal of crystal violet dye from synthetic wastewater. An electrocoagulation batch reactor study was conducted using aluminium plate as electrode and regulated DC power supply as a power source. In this study, important operational parameter like current density, initial dye concentration, inter-electrode distance and quantity of electrolyte (NaCl) that affects the crystal violet removal were varied. Various experiments were carried out to obtain the optimum experimental condition for efficient removal of crystal violet dye concentration. The decolourisation study showed that 99.85 % colour removal achieved at initial concentration of 120 mg/L with the current density of 14.23 mA/cm² at 1 cm spacing between electrodes after 20 minutes of operation time (electrolysis time) added with 10 ppm NaCl.

Keywords:- Electrocoagulation , crystal violet dye, current density, Decolourisation. .

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ABBREVIATION NOTATION AND NOMENCLATURE

- EC Electrocoagulation
- IS Inter Electrode Spacing
- OP Operation Time
- mg/L Milligram per litre
- ppm Parts per million
- CD Current density
- UV Ultra violet

Chapter 1

Introduction

1.1 Introduction

One of the major challenges facing mankind is to provide clean water to a vast population around the world. Therefore reuse of water has become an absolute necessity. The textile industry consumes large quantities of water for manufacturing and cleaning and discharge effluents contain mainly strong dyes and toxic compounds. Dyes are made to give colors which should be resistant to oxidizing and reducing agents. This property of Dye makes the waste water highly inert in conventional treatment methods. Thus there is a requirement of cheap and effective method of purifying and cleaning of waste water before discharging into any water body.

A literature survey shows that the EC is alternates which simple and efficient method for the treatment of many dyes and waste water. Electro-coagulation is not a new technology. Treatment of waste water by EC has been practiced for most of $20th$ century. It is primarily used to treat effluent from paper and pulp industry, mining etc. It is effective in removing suspended solids, dye, heavy metals, breaking of emulsion, etc.

Different technological approaches like; adsorption, coagulation, biological treatment, advanced oxidation process, UV treatment, ozone treatment, membrane separation technologies, etc. All the processes with certain limitation, in the application. Adsorption and coagulation can be time consuming methods. Biological methods also suffer due to toxicity of dye. However, additions of chemicals in this process increase the secondary pollutants in discharge. In membrane filtration technique (Nano-filtration or reverse osmosis) flux decline is common problem, which makes the process inefficient. Electrocoagulation offers some distinct advantages over existing process such as ambient operability conditions, no threat of secondary pollution due to the absence of any extra chemicals.

1.2 Coagulation and Electro-Coagulation

Coagulation is a phenomenon in which charged particles in colloidal suspension are neutralized, followed by sedimentation. Aluminium and iron salts are commonly used coagulants. The coagulant is added in the form of suitable chemical substance like Alum $[A_2(SO_4)_3.18H_2O]$ in conventional methods which has been widely used for ages for waste water treatment . It is generally accepted that coagulation is brought about primarily by the reduction of the net charge to a point where the colloidal particles are stabilised by electrostatic repulsion, can approach closely enough for van der waal's forces to hold them together and allow aggregation.

Figure 1.1 Coagulation Mechanism

1.2.1 Electro-Coagulation

The theory of EC has been discussed by various researchers. It is generally accepted that the EC process involves three successive stages:

- (a) formation of coagulants by electrolytic oxidation of the 'sacrificial electrode';
- (b) destabilization of the contaminants, particulate suspension, and breaking of emulsions;
- (c) 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:

- 1. Compression of the diffuse double-layer around the charged species, which is achieved by the interactions of ions generated by dissolution of the sacrificial electrode, due to passage of current through the solution.
- 2. Charge neutralization of the ionic species present in wastewater, which is caused by the counter ions, produced by the electrochemical dissolution of the sacrificial electrode. These counter ions reduce the electrostatic interparticle repulsion sufficiently so that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
- 3. Floc formation, and the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles that have been complexed.

Figure 1.2 Electrocoagulation Mechanism

In electrocoagulation process, an applied potential generates the coagulant species as the sacrificial aluminium (or ferric) anode dissolves, while hydrogen is simultaneously evolved at the cathode. Coagulant species do help in the aggregation of the suspended particles followed by the precipitation and adsorption of dissolved contaminants accordingly. Different electrodes have been reported in the literature like carbon , mild steel , graphite, titanium , iron and aluminium. But Iron and aluminium have been reported to be effective and successful in pollutant removal at favourable operating conditions. In this work, aluminium has been selected as electrode material. The electrode reactions are summarized as follows:

Anode:

$$
Al \Rightarrow Al^{3+} + 3e \tag{1}
$$

Cathode:

$$
3H_2O + 3e \Rightarrow \frac{3}{2}H_2 + 3OH^-
$$
 (2)

Flotation is the dominant pollutant removal path for high operating currents, while sedimentation is dominant at lower currents. The shift is due to the insufficient bubble concentration at low currents to remove the aggregated material, hence allowing sedimentation to dominate [5]. At sufficiently high anodic potential, secondary reactions may also occur, such as direct oxidation of organic compounds and of Cl ions present in wastewater: the chlorine produced is a strong oxidizing agent which can oxidize some organic compounds. On the other hand, the cathode may be chemically attacked by OH- ions generated during H2 evolution, especially at high pH values 2

$$
2Al + 6H_2O + 2OH^- \Rightarrow 2Al(OH)_4^- + 3H_2 \tag{3}
$$

Two major interaction mechanisms are being considered in recent years: precipitation and adsorption, each one has been proposed for a separate pH range. Flocculation in the low pH range is explained as precipitation while the higher pH range (>6.5) as adsorption. Al^3 and OH-ions generated by electrode reactions (1) and (2) react to form various monomeric species such as Al $(OH)^{2+}$, Al $(OH)^{+}_{2}$, Al₂ $(OH)^{4+}_{2}$, Al $(OH)^{-}_{4}$ and polymeric species such as $\text{Al}_{6}\text{(OH)}_{15}^{3+}$, $\text{Al}_{7}\text{(OH)}_{17}^{4+}$, $\text{Al}_{8}\text{(OH)}_{20}^{4+}$, $\text{Al}_{13}\text{O}_{4}\text{(OH)}_{24}^{7+}$, $\text{Al}_{13}\text{(OH)}_{34}^{5+}$, which transform finally into Al $(OH)_{3(S)}$ according to complex precipitation kinetics:

$$
Al^{3+} + 3H_2O \Rightarrow Al(OH)_3 + 3H^+ \tag{4}
$$

Freshly formed amorphous Al $(OH)_{3(S)}$ occurs "sweep flocs" having large surface areas. These flocs are active in rapid adsorption of soluble organic compounds and trapping of colloidal particles and are easily separated from aqueous medium by sedimentation or H_2 flotation. These flocks polymerizes as:

$$
nAl(OH)_3 \Rightarrow Al_n(OH)_{3n}[1]. \tag{5}
$$

1.3 Other Colour Removing Techniques

Adsorption system: Resin separation, Ion exchange, Activated alumina, Activated carbon.

Figure 1.3 Adsorption

Precipitation system: Coagulation with trivalent metal salts, Lime, poly-electrolytes.

Figure 1.4 Coagulation Process

Membrane system:-Reverse osmosis, Ultra-Filtration

Figure 1.5 Membrane Filtration Process

1.4 Crystal Violet Dye

Crystal violet is a type of dye which is used in textile, pulp and paper industry for manufacturing, dying and printing purpose. When crystal violet dye dissolves in water it forms blue-violet colour with an absorbance maximum at 582 nm. The colour of the dye depends on the acidity of the solution. At a pH of 1.0, the dye is green with absorption maxima at 420 nm , while in a strongly acidic solution (pH of −1), the dye is yellow with an absorption maximum at 420 nm.

1.5 Aim and Objectives

1.5.1 Aim

To reduce the concentration of crystal violet dye from textile synthetic waste water to an extent which water can be recycle.

1.5.2 Objective

- 1. To study the colour removal efficiency of crystal violet dye using electrocoagulation technique
- 2. To investigate the decolourisation efficacy with various current density
- 3. To optimize the electrocoagulation process for different initial dye concentration
- 4. To study electrocoagulation process with respect to various dose of electrolyte (NaCl)
- 5. To optimize the electrocoagulation with respect to inter electrode spacing

Chapter 2

Literature Review

Umran Tezcan Un & Ersin Aytac (2011) This study was designed to treatment of textile waste water using the electro-coagulation process. In this system two type of flow regimes are used semi-continuous flow regime. have been altered to investigate the effects of COD & dye stuff removal. In this study the COD removal & dye removal achieve a greater value . The inlet COD concentration was 1953 mg/l was reduced to 30 mg/l at current density of 20 mA/cm2 and retention time of 60min. The dye removal was about 93% thus the experiment shows great potential to treat the textile waste water.

Ashock Kumar Chopra and Arun kumar Chopra (2013):- A study was conducted for the removal of Turbidity, COD, and BOD from secondary treated sewage water through electrolytic batch mode experiments with DC power supply (12V) foe 30min with combinations of different metals. The different surface area (40, 80, 120 and 160 cm) and distance between electrode (2.5-10cm) were studied. The effective treated water is obtained with combination of Al-Fe with max removal efficiency of turbidity (81.51%), COD (74.36%) and BOD (70.86%) and combination of Fe-Al with efficiency of (71.11%), (64.95%) and (61.87%) respectively. The Al-Fe electrode combination had lower energy consumption as compared to Fe-Al combination. They showed that Al-Fe electrode combination is more effective as well as economic where Al is sacrificial electrode with electrode area of 160cm at short distance of 2.5cm between the electrodes in a 5 litre reactor.

M.Yousuf A. Mullah et al.(2000):-They showed the science and application of electrocoagulation. Their explained the various advantages and disadvantages of EC. Description of technology had been showed like electrode in parallel and series connection. Alternate current and direct current electrocoagulation had explain. Hybrid process can be used for a maximum efficient treatment. They concluded that eletro-coagulation can applied successfully to contaminated water. Explanation of reaction occurs in the process of aluminium and iron as an electrode had given process avoids the use of chemicals and then is no problem of neutralising excess chemicals.

D.Zerrouki et al.(2014):-The treatment solution on synthetic dyes used in the textile industry of Draa Ben Knedda/Tizi Ouzou, Algeria by electro-coagulation. The standard dyes Red solophenyl 4GE, Blue Thio Bezathren R, Cibacron Blue Turquoise & GR and Black Diamix Rxne brlonging to four classes widely used in textile industry. By using aluminium electrodes in electro-coagulation in a batch mode has prevent its efficiency for the treatment of these dyes with current density of $34mA/cm²$ and an electrolysis time of 1 hour to get 87 to 97% efficiency in the removal of dye with an amount of aluminium dissolved from 1.5 to 1 kg to remove 2.5 kg of dye.

Edris Bazrafshan et al.(2014) investigated the efficiency of electro-coagulation process using aluminium electrodes in basic red 18 dye removal from aqueous solution. The maximum efficiency of dye removal which was obtained in voltage of 50V, reaction time 60min, initial concentration 50mg/L , conductivity 3000s/cm and pH 7 was equal to 97.7%.

Mehnet kobya et al.(2003) investigated treatment of textile waste waters by electrocoagulation using iron and of aluminium electrode, which was mainly focused on removal of COD & turbidity removal . The results showed that iron is superior to aluminium as sacrificial electrode material, from COD removal & energy consumption points. The results also revealed that use of iron and aluminium as sacrificial electrode in treatment was found to be pH dependent.

Vinodha S.et al. (2012) investigated the decolourisation efficiency of textile waste waters by electro-coagulation process for a CLB Red reactive dye using iron electrodes. The results showed that the colour removal is dependent on current density and the process time. Electrocoagulation process was found be an efficient, safe and reliable method for the treatment of textile waste water.

Sachin K. Patil et al. (2001) Reviewed various techniques used in treating textile & dye waste waters such as:- i) Coagulation ii)Enhanced coagulation iii)Adsorption iv)Chemical oxidation v)Biological methods vi)Innovative methods and electro-coagulation and found out that physico-chemical method produces more sludge, involves high cost and lower efficiency. He stated that electro-coagulation process, compare to the traditional conventional coagulation process was superior by considering advantages of electro-coagulation process over above technique (Mollah, Schennach, Parga J.P., Cocke, 2001).

Vinodha S and Jegathambal P (2012) reviewed various techniques for Decolourisation of textile waste waters and found that conventional method i.e. Biological & volume of sludge. They also stated that electro-coagulation technique has been recently proving to evade most of the problems also being economically attractive & clean technology.

MOH Faiqun Ni'am et al. (2007): The removal of COD and turbidity from waste water by EC using iron (Fe) electrode material was investigated. They studied the effect of various parameter like pH, current density and operating time for higher removal efficiency. They made waste water from milk powder with initial COD of 1140 mg/L and turbidity of 491 NTU. Current density was varied from 3.51 to 5.62 mA/sq.cm and operating time of 30 to 50 minutes. The experimental results also show that the electro-coagulation can neutralize pH of waste water. They conducted experiment in cylindrical glass cell (Volume 2000mL) of 50mm distance between the electrodes. They get the maximum removal efficiencies of COD and turbidity of 72.28% and 96.74% respectively at 5.62 mA/sq.cm.

Ajjam et al.(2012): Electro-coagulation technique is widely used in textile industry located in Al-Hilla-Iraq by using batch wise mode. The parameters such as current density, total suspension removal, turbidity, COD were studied. It was found that the application of 12 mA/sq.cm provided 69.2% removal in turbidity, 62.5% removal in COD and 54.3% removal in TSS. While the application of 20mA/sq.cm show 90.1% removal in turbidity, 85.2% removal in COD and 83.1% removal in TSS. Within 60 minutes of electro-coagulation treatment with an inter-electrode distance of 5cm.The contaminants treated waste water such as **BOD**, COD, TDS, TSS, Turbidity, Nitrates, Chloride, Total hardness, Total Sulphate, Electrical Conductivity are within allowable limits for waste water reuse.

Neha Tyagi et al. (2013): This study investigates the influence of operating parameters on COD and Colour removals from a dye bath effluent using electro-coagulation. Generally the

treatment of waste water is carried out in batch processes. But looking to large quantities of waste water continuous flow regime offer the better solution. The operational parameters such as current density, Detention time and time of electrolysis were optimized. The weight of sacrificial anode was calculated under optimum condition. The size of electrode plate is (5cm*5cm*0.5cm,124 sq.cm)kept constant for all experiments. The results show almost 76% of COD removal and 95% of colour removed. The pH was observed to be 9 and detention period of 20 minutes and current density of 14-17 mA/sq.cm.

M.Kashefialasl et al. (2006): The removal of pollutants from effluents by electro-coagulation has become an attractive method in recent years. The electrode which is use to remove the pollutants is iron electrode. Generally the effect of electrolyte concentration depends on initial pH, Current density, electrode area, inter electrode distance. Iron hydroxpolymeric species forms at the earlier stage of the operation efficiency remove dye molecule by adsorption and precipitation and there by trap the colloidal particle and make solid liquid separation during flotation stage. The stages of electro-coagulation must be optimized to design economically feasible EC process. As the current density increase from 32 to 127.8 A/sq.cm it increase efficiency of the colour removal from 21 to 83.5% because when current increase ion production at anode and cathode increase. During electrolysis the positive electrode undergoes anodic reaction while negative electrode undergoes cathodic reaction. The released ions neutralize the particle charge and there by initiate coagulation.

D.Ghos et al. (2008) investigated the removal efficiency of crystal violet dye (CI 4255) by electrocoagulation. The results showed that 99.75% of crystal violet was decolourised for initial concentration of 100 mg/l with the current density 1112.5 A/m² and 99% of COD reduction with electrolysis time as 60min using Aluminium electrode.

Summary

From literature review we conclude the following advantages of electrocoagulation;

- 1. EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running.
- 2. Wastewater treated by EC gives palatable, clear, colourless and odourless water.
- 3. Sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low sludge producing technique.
- 4. 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.
- 5. EC produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
- 6. The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
- 7. 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.
- 8. 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.
- 9. The electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring less maintenance.
- 10. 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.

Chapter 3

Materials and Methodology

3.1 Introduction

The dye used in this study was crystal violet dye which is strong and toxic and we observed the removal of crystal violet dye from solution. We will obtain the characteristics of crystal violet dye like its concentration before and after treatment. We will study the effect of electrocoagulation parameters in the removal of crystal violet dye like electrode material, voltage, current density, electrode spacing, etc. For maximum efficiency we will optimise the parameters by varying the one parameter and kept other parameter constant . we obtain the optimum values of operational parameters.

3.2 Materials

In this section we have discussed about the materials used for conducting decolourisation experiments

3.2.1 Crystal Violet Dye

crystal violet is a well known dye being used for various purposes: a biological stain, a dermatological agent, a veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus etc. It is also extensively used in textile dying and paper printing. It is a mutagen and mitotic poison [1-3]. Because of its low cost, its effectiveness as an antifungal agent for commercial poultry feed, and its ready availability, the general public may be exposed to the dye and its metabolites through the consumption of treated poultry products. Therefore, there are both environmental and human health concerns regarding the bioaccumulation of gentian and leucogentian violet.

Figure 3.1 Molecular Structure of Crystal Violet

Properties of crystal violet dye:

- Chemical formula: $C_{25}H_{30}CIN_3$
- Molar mass: 407.99 g/mol
- Melting point: 205° C (401 °F; 478 K)

Figure 3.2 Crystal Violet Stock Solution

The different colours are a result of the different charged states of the dye molecule. In the yellow form, all three nitrogen atoms carry a positive charge, of which two are protonated, while the green colour corresponds to a form of the dye with two of the nitrogen atoms positively charged. At neutral pH, both extra protons are lost to the solution, leaving only one of the nitrogen atoms positive charged. The pKa's for the loss of the two protons are approximately 1.15 and 1.8.

In alkaline solutions, nucleophilic hydroxyl ions attack the electrophilic central carbon to produce the colourless triphenylmethanol or carbinol form of the dye. Some triphenylmethanol is also formed under very acidic conditions when the positive charges on the nitrogen atoms lead to an enhancement of the electrophilic character of the central carbon, which allows the nucleophilic attack by water molecules. This effect produces a slight fading of the yellow colour.

3.2.2 Experiment Setup

Dimensions of Tank

Material:-Acrylic fiber

Length : 26 cm, Width : 8.5 cm, height: 8.5 cm, Volume:-2000 cm3

Figure 3.3 Electrocoagulation Tank

Figure 3.4 Schematic Diagram of Electrocoagulation Unit

Electrode

Material Used: Aluminium, length : 6 cm, thickness: 0.5 cm, height : 7.5 cm

Surface area : 22.5 cm^2 , number of plates: 8, Efective area : $5.8 \text{ cm}^*5.3 \text{ cm}^* \text{ cm}^*8 = 28.8 \text{ cm}^2$

Figure 3.5 Electrode Plates

Power: Regulated Dc Power Supply

Figure 3.6 Regulated DC Power Supply

Complete Experimental Setup

Figure 3.7 Experimental Setup

3.2.3 Chemicals Used

1) Sodium Chloride (NaCl):-

 Sodium chloride is an electrolyte is used to increase the conductivity of the solution because pure water is non-conductive in nature. When we apply the potential difference to the solution of dye there is more resistance because of less conductive nature of solution which consumes more energy to achieve desired current density. So to decrease the resistance and to increase the current density at low potential difference, different dose (2,4,6,8 and 10 mg/L) of sodium chloride is carried out.

Textile effluent have a broad variation in ionic strength due to the chemical substances added at a high concentration from dyeing and finishing processes in the textile industry. The greater ionic strength will generally cause an increase in current density at the same cell voltage, or the cell voltage decreases with increasing effluent conductivity at constant current density. Therefore, it is necessary to investigate the effect of effluent conductivity on electrocoagulation in terms of dye removal. The conductivity of solution depends both on the type and concentration of electrolyte.

2) **Hydrochloric Acid (HCl):-**

 Hydrochloric acid of 98% concentrated is used to clean the electrode plates which is get coated with hydroxide and decrease the efficiency of the electrode. Therefore by diluting it by ratio 1:10 in 1 litre of water and plates are dipped in acid solution after every experiment for 10 minutes to remove the greasy material and dye from the plates. Tank is also washed by this solution to remove the dye and then washed by tap water.

3) Ethyl Alcohol (C₂H₅OH):-

Ethyl alcohol is used to remove the dye from the glassware (measuring jar, pipette, cuvette, etc). Crystal violet dye is strong and once any glassware get in contact with this, it is not get easily removed by water.

3.3 Methodology

3.3.1 Experimental Method

A measured quantity $(1.2 \times 10^{-3} \text{ m}^3)$ of solution of crystal violet dye was made at different concentration by using distilled water. All the runs were performed at room temperature (27°C) and stirring speed of 200 rpm on magnetic stirrer. In each run solution was placed in electrochemical cell and eight monopole electrodes of aluminium sheets of effective surface area of 245.92 cm^2 was hang on the tank. The gap between the anode and cathode was varied from 0.5 cm to 2 cm. The solutions were prepared at different concentrations of NaCl to increase the conductivity. The assembly was connected to regulated dc power supply as shown in Figure 3.7. The current density was adjusted to desired value and the operation was started. After the experiment the power was switched off and the electrodes were dismantled. The treated dye sample was collected at different time interval and was centrifuge at 2000 rpm as shown in Figure 3.8. Dye concentration was determined by using visible spectrophotometer at 582 nm as shown in Figure 3.9 . Before each run the electrodes were washed with HCL solution of dilution 1:10 for 10 minutes to remove surface grease. After each run the used anode and cathode plate was interchanged for effective utilization of electrode.

Figure 3.8 Centrifuge

3.3.2 Analytical Method

The spectrum of crystal violet and its change during electrocoagulation was recorded using digital visible spectrophotometer as shown in Figure 3.9. The characteristics peak of crystal violet was observed at 582 nm. The standard method was followed in order to determine concentration of the dye in effluents.

Figure 3.9 Spectrophotometer

The standard curve was made by preparing samples of different concentration 1 to 4 ppm solution as shown in Figure 3.10. The absorbance were recorded given by spectrophotometer for each concentration and the scatter graph was plot (concentration v/s absorbance) and we get the linear equation (R2=0.9953). From this equation we get the concentration of effluent at different interval.

Figure 3.10 Calibration Curve

3.3.3 Optimization of Electrocoagulation for Various Operating Parameters

Operating Conditions:-

The chosen parameter in experiment were current density, initial dye concentration, dose of electrolyte (NaCl), interelectrode spacing and operating time. All the conditions are given in Table 3.1.

Parameters	Units	Values
Current density	mA/cm ²	4.06, 8.13, 12.20, 14.23
Crystal violet concentration	mg/L	50, 80, 100, 120
Dose of electrolyte (NaCl)	mg/L	2, 4, 6, 8, 10
Inter electrode spacing	$\rm cm$	0.5, 1.0, 1.5, 2.0
Time of operation	minutes	30

Table 3.1 Operation Condition

Optimization

For optimization we vary one parameter by keeping constant other parameter as shown in the flow chart given below. In optimization we observe the variation of parameter like

3.4 Experiment Plan

Aim of our experiment was to study the effectiveness of electrocoagulation process thus we started optimizing the current density, operation time, dose of electrolyte, interelectrode spacing and initial concentration. The optimisation was as follows:

step:01 (*optimization of current density*)- We kept operation time, dose of electrolyte, inter electrode spacing, initial concentration constant and started varying current density and voltage, which was optimised.

step:02 (*optimisation of reaction time*)-From step 01 we kept current density, volt and settling time (not optimised yet) constant and started varying reaction time, which was optimised.

step:03 (*optimisation of electrode spacing*)-From step 01,02,03 all the parameter was kept constant and started varying spacing between electrode, which was optimised.

step:04 (*finding the effectiveness of experiment for different concentration*)-From step 01,02,03,04 all the parameter was kept constant and maximum efficiency was found for a particular concentration of dye.

Step 2

Step 3

Step 4

Chapter 4

Result and Conclusion

4.1 Standard curve

The standard curve was discussed in standard method of chapter-3 (Methodology). In order to determine the concentration of effluent at different intervals standard curve is required. The standard curve is plot by taking absorbance of different concentration from 1 to 4 ppm solution in spectrophotometer at 582 nm wavelength.

The scatter graph was plotted by concentration v/s absorbance and we put the regression typelinear, we get the line equation with ($R^2=0.9953$) coefficient of determination for computing the correlation. Using the equation of line we had determine the concentration of effluents.

4.2 Effect of Current Density

During electrolysis, the positive electrode undergoes anodic reaction (loss of electron) while cathodic reaction (gain of electron) occurs on negative electrode, this rate of reaction is directly proportional to applied current. The current density not only determines the coagulant dosage rate but also the bubble production rate, size and the flocs growth which can influence the treatment efficiency of the electrocoagulation

The effect of C.D on the removal of dye was evaluated by carried out various experiments by keeping other parameters constant, viz $(NaCl)=10$ mg/l, t=20 min, crystal violet dye concentration= 20 ppm, but with different current densities.

It is obvious that the operation cost increases when the current density increases. On the other hand, at a higher current density higher removal efficiency was observed at a shorter electrolysis time. As shown in the Figure 4.2 to Figure 4.10, there is sharp decrease in concentration due to fresh electrodes surfaces initially but the concentration reduction is achieved further as the time progresses with more generation of aluminium hydroxides for coagulation of the particles.

Sr.no	Time (min)	Final concentration (mg/L)	% Colour removal
		20.0	$0.0\,$
2		17.4	12.9
3		15.7	21.5
		14.2	28.9
		13.2	34.2
		12.0	40.1
	$\mathbf{12}$	11.0	44.8
	14	10.9	45.7
	16	10.6	

Table 4.2 Colour removal efficiency at CD= 4.06 mA/cm2

(Initial conc. = 20 ppm, $NaCl = 10$ ppm, $IS = 1$ cm)

Figure 4.1 Effect of Current density at 4.06 mA/cm2 on percentage colour removal

Figure 4.2 Effect of Current density at 4.06 mA/cm2 on concentration reduction

Time (min)	Final	% Colour
	concentration	removal
	(mg/L)	
	20	
$\overline{2}$	16.7	16.37
	14.6	26.94
6	12.9	35.1
8	11.2	43.9
10	9.81	50.9
12	9.17	54
14	8.24	58.7
16	7.95	60.21

Table 4.3 Colour removal efficiency at CD=8.13 mA/cm2

(Initial conc.= 20 ppm, $NaCl = 10$ ppm, $IS = 1$ cm)

Figure 4.3 Effect of Current density at 8.13 mA/cm2 on percentage colour removal

Figure 4.4 Effect of Current density at 8.13 mA/cm2 on concentration reduction

Sr.no	Time (min)	Final	% Colour
		concentration	removal
		(mg/L)	
		20.0	0.0
$\overline{2}$	$\overline{2}$	15.5	22.5
3		12.7	36.3
	6	10.5	47.7
5	8	7.5	62.4
6	10	5.1	74.3
	12	3.0	84.8
8	14	1.8	91.2
9	16	0.1	99.6
	$(T_{11}, T_{22}, T_{12}, T_{13}, T_{14}, T_{15}, T_{16}, T_{17}, T_{18}, T_{19}, T_{10}, T_{10}, T_{11}, T_{12}, T_{13}, T_{14}, T_{15}, T_{16}, T_{17}, T_{18}, T_{19}, T_{10}, T_{10}, T_{11}, T_{12}, T_{13}, T_{14}, T_{15}, T_{16}, T_{17}, T_{18}, T_{19}, T_{10}, T_{10}, T_{11}, T_{12}, T_{13}, T_{14}, T_{15}, T_{16}, T_{17}, T_{18}, T_{19}, T_{10},$ $20 - 11$	$10 - 10$	$1 - \ldots$

Table 4.4 Colour removal efficiency at CD= 12.19 mA/cm2

(Initial conc.= 20ppm, NaCl = 10ppm, $IS = 1cm$)

Figure 4.5 Effect of Current density at 12.19 mA/cm2 on percentage colour removal

Figure 4.6 Effect of Current density at 12.19 mA/cm2 on concentration reduction

Sr.no	Time	Final concentration	% Colour
	(min)	(mg/L)	removal
		20.0	0.0
$\overline{2}$	$\overline{2}$	14.1	29.3
3		10.3	48.6
4	6	7.1	64.5
5	8	2.8	86.1
6	10	0.4	97.9
7	12	0.0	99.9
8	14	0.0	100.0
q	16	0.0	100.0

Table 4.5 Colour removal efficiency at CD= 14.23 mA/cm2

(Initial conc= 20 ppm, $NaCl = 10$ ppm, $IS = 1cm$)

Figure 4.7 Effect of Current density at 14.23 mA/cm2 on percentage colour removal

Figure 4.8 Effect of Current density at 14.23 mA/cm2 on concentration reduction

Figure 4.9 Effect of various Current density on percentage colour removal

Figure 4.10 Effect of various Current density on concentration reduction

As shown in Figure 4.1 to Figure 4.10, an increase in the C.D from 4.06 to 14.23 mA/cm² yields an increase in the efficiency of colour removal from 50 to 99.5% & more because when the C.D Increases, the efficiency of ion production on the anode increases. Therefore, there is an increase in floc production, increasing the coagulation efficiency.

For a solution with a dye concentration up-to 120ppm, the optimum C.D was 14.23mA/cm² (3.5 Ampere) with colour removal efficiency greater than 99.5%.

Figure 4.11 Effect of Current density with time on colour removal

4.3 Effect of Dose of Electrolyte (NaCl)

The increase of conductivity by the addition of sodium chloride is known to reduce the voltage between the electrodes at a constant current density, due increase in the conductivity of the solution. The energy consumption, which is proportional to the voltage applied between the electrodes should decrease.

Sr.no	Time (min)	Final concentration	% Colour
		(mg/L)	removal
		8.0	
		6.9	30
		6.2	38
		5.8	42

Table 4.6 Colour removal efficiency at NaCl = 2 ppm

 $(CD = 14.23$ mA/cm², Initial conc. = 10 ppm, IS= 1 cm)

Figure 4.12 Effect of electrolyte dose (NaCl) at 2 ppm on percentage colour removal

Figure 4.13 Effect of electrolyte dose (NaCl) at 2 ppm on concentration reduction

Sr.no	Time (min)	Final	% Colour
		concentration	removal
		(mg/L)	
		10.0	
		7.6	24
		6.1	39
		4.9	51
		4.1	59
		3.8	

Table 4.7 Colour removal efficiency at NaCl = 4ppm

 $(CD = 14.23$ mA/cm², Initial conc. = 10 ppm, IS= 1 cm)

Figure 4.14 Effect of electrolyte dose (NaCl) at 4 ppm on percentage colour removal

Figure 4.15 Effect of electrolyte dose (NaCl) at 4 ppm on concentration reduction

Time (min)	Final	% Colour
	concentration	removal
	(mg/L)	
	10.0	
	7.1	29
	5.8	42
	4.2	58
	3.2	68
10	2.1	79
		$2 - \cdots$

Table 4.8 Colour removal efficiency at NaCl = 6ppm

 $(CD = 14.23 \text{ mA/cm}^2$, Initial conc. = 10 ppm, IS= 1 cm)

Figure 4.16 Effect of electrolyte dose (NaCl) at 6 ppm on percentage colour removal

Figure 4.17 Effect of electrolyte dose (NaCl) at 6 ppm on concentration reduction

Sr.no	Time (min)	Final	% Colour
		concentration	removal
		(mg/L)	
		10.0	
		6.5	35
		4.8	52
	6	3.4	66
		1.6	84
	10		89

Table 4.9 Colour removal efficiency at NaCl = 8ppm

 $(CD = 14.23$ mA/cm², Initial conc. = 10 ppm, IS= 1 cm)

Figure 4.18 Effect of electrolyte dose (NaCl) at 8 ppm on percentage colour removal

Figure 4.19 Effect of electrolyte dose (NaCl) at 8 ppm on concentration reduction

Sr.no	Time (min)	Final	% Colour
		concentration	removal
		(mg/L)	
		10.0	
		5.9	
		3.7	63
		1.8	82
		0.3	
	10		

Table 4.10 Colour removal efficiency at NaCl = 10ppm

 $(CD = 14.23 \text{ mA/cm}^2$, Initial conc. = 10 ppm, IS= 1 cm)

Figure 4.20 Effect of electrolyte dose (NaCl) at 10 ppm on percentage colour removal

Figure 4.21 Effect of electrolyte dose (NaCl) at 10 ppm on concentration reduction

Figure 4.22 Effect of various electrolyte dose on percentage colour removal

Figure 4.23 Effect of various electrolyte dose on concentration reduction

Furthermore solution conductivity affects the current efficiency, voltage and consumption of electrical energy in EC process. Typically NaCl was used to obtain the conductivity. Hence a set of experiments was performed using 2 to 10 ppm NaCl concentration at 2 ampere (i.e. $8.132mA/cm²$, initial dye concentration 10ppm.

As can be seen from fig x, dye removal efficiency was increase with increase of solution conductivity. On the other hand, as the NaCl increases from 2 to 10 ppm (Figure 4.12 to Figure 4.23) the removal efficiency increases from 40 to 99.5%.

Figure 4.24 Effect of electrolyte dose with time on colour removal

4.4) Effect of Inter Electrode Distance

The set up of electrode assembly is very important for required effective surface area of electrode and inter electrode distance. With the increase of inter electrode distance IR resistance increases which increases the cell voltage and adversely affect the dye removal.

Sr.no	Inter-electrode Spacing (m)	% Colour removal	IR drop (V)
	0.005	99	5.69
	0.01	97	11.38
	0.015	90	17.07
	1.02		22.77

Table 4.11 Colour removal efficiency at various inter-electrode distance

Figure 4.25 Effect of Inter-electrode on percentage colour removal

Figure 4.26 Effect of Inter-electrode spacing vs IR drop

Variation of percentage removal of dye and IR drop with inter electrode distance is shown in Figure 4.25 at 20 min RT, initial concentration of 100 mg/l, a current density of 14.23 mA/cm² and NaCl concentration of 10 mg/l.

The Figure 4.26 shows that, as the inter-electrode distance decreases, the resistance encountered for current flow in a solution medium is lower that facilitates the electrolytic process for enhanced the removal.

The optimum inter electrode distance was selected as 1cm from graph x, because at 0.5 cm inter electrode distance the removal efficiency was not much altered thus the cost minimization will also be achieved.

Figure 4.27 Effect of Inter electrode distance with time on colour removal

4.5) Effect of Initial Dye Concentration

To determine influence of initial dye concentration, different initial concentration in the range of 50 to 120ppm were treated at 20min, C.D=14.23mA/cm2 (3.5 Ampere), inter-electrode distance of 1cm and NaCl of 10 ppm.

Sr.no	Time (min)	Final	% Colour	
		concentration	removal	
		(mg/L)		
		50.0	0.0	
$\overline{2}$	$\overline{2}$	23.9	52.3	
3	4	2.2	95.6	
	6	0.4	99.2	
5	8	0.1	99.9	
6	10	0.1	99.9	
7	12	0.1	99.7	
8	14	0.1	99.7	
9	16	50.0	0.0	
	$(CD = 14.23$ mA/cm ² , NaCl = 10 ppm, IS = 1cm)			

Table 4.12 Colour removal efficiency at Initial conc. = 50ppm

Figure 4.28 Effect of dye concentration at 50 ppm on percentage colour removal

Figure 4.29 Effect of dye concentration at 50 ppm on concentration reduction

Time (min)	Final	% Colour
	concentration	removal
	(mg/L)	
	80.0	0.0
2	34.8	56.5
	12.4	84.5
6	1.5	98.1
8	0.4	99.5
10	0.2	99.7
12	0.1	99.9
14	0.1	99.9
	$\sqrt{2}$	\sim 2 λ τ \sim 1 $1102 \pm l$ $10 \quad \text{or} \quad 1 \quad \text{or}$

Table 4.13 Colour removal efficiency at Initial conc. = 80 ppm

 $(CD = 14.23 \text{ mA/cm}^2$, NaCl = 10ppm, IS = 1cm)

Figure 4.30 Effect of dye concentration at 80 ppm on percentage colour removal

Figure 4.31 Effect of dye concentration at 80 ppm on concentration reduction

Sr.no	Time (min)	Final concentration	% Colour
		(mg/L)	removal
		100.0	0.0
2		60.0	40.1
		34.3	65.7
		23.3	76.7
		6.9	93.1
	10	0.2	99.8
	12	0.2	99.8
	14	0.2 ┑ _____	99.8

Table 4.14 Colour removal efficiency at Initial conc. = 100 ppm

 $(CD = 14.23 \text{ mA/cm}^2$, NaCl = 10ppm, IS = 1cm)

Figure 4.32 Effect of dye concentration at 100 ppm on percentage colour removal

Figure 4.33 Effect of dye concentration at 100 ppm on concentration reduction

Sr.no	Time (min)	Final concentration	% Colour removal	
		(mg/L)		
		120.0	0.0	
2	ി	77.8	35.2	
\mathcal{R}		48.6	59.5	
		29.2	75.7	
5		14.1	88.3	
	10	1.5	98.7	
	12	0.4	99.7	
	14	0.4	99.7	
2.37.01 1.4.22 $\sqrt{2}$ λ / \sim $T \cap 1$ \sim				

Table 4.15 Colour removal efficiency at Initial conc. = 120 ppm

 $(CD = 14.23 \text{ mA/cm}^2$, NaCl = 10ppm, IS = 1 cm)

Figure 4.34 Effect of dye concentration at 120 ppm on percentage colour removal

Figure 4.35 Effect of dye concentration at 120 ppm on concentration reduction

Figure 4.36 Effect of various initial concentration of dye on percentage colour removal

Figure 4.37 Effect of various initial concentration of dye on concentration reduction

Figure 4.28 to Figure 4.37 that when dye concentration increased from 10 to 120 ppm, removal efficiency decreases (In time sense, i.e. it took 12 min for 50ppm and 20min for 120ppm).

Efficiency decreased because the adsorption capacity of flocs is limited and specific amount of flocs is able to adsorb specific amount of dye molecules. So, with increasing of dye concentration amount of produced flocs is insufficient to adsorb all dye molecules therefore dye removal decreases.

Figure 4.38 Effect of various initial concentration of dye with time on colour removal

Table 4.16 Optimum Experimental Condition

Figure 4.39 Colour comparison with dye treated water and tab water (from right)

4.6) Cost Estimation

Operating cost is one of the most important parameter in the EC process because it effects the application of any method of wastewater treatment. The operating cost includes material (mainly electrodes) cost, electrical energy cost, labour, maintenance, and other costs. The latter costs items are largely independent of the electrode material. Thus, in this study the operating cost was calculated with electrodes and electrical energy costs. So both energy and electrode consumption costs are taken into account as major cost items. Calculation of operating cost is expressed as:

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Operating Cost = X Energy consumption + Y Electrode consumption
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...where Energy consumption and Electrode consumption are consumption quantities per m3 of treated wastewater. Unit prices, X and Y, given for Indian market, May 2017, are: electrical energy price 5.0 Rs/kWh, electrode material price 123.65 Rs/kg of aluminium.

Calculation Of Energy Consumption Is Expressed as:

According to Faraday's Law:

Energy consumption =
$$
\frac{(V \times I \times t)}{v}
$$

...where Energy consumption, V, I, t, and v are energy consumption (kWh/m3), V is voltage (volt), I is current (Ampere), t is EC time (s) and v is volume of treated wastewater (m^3) .

Thus Energy consumption $=\frac{(40 \times 3.5 \times 1200)}{(0.0012)} = 38.88$ *kWh/m3.*

Therefore Energy consumption cost = 38.88×*5.0 = 194.44 Rs/m3 of water.*

Calculation Of Electrode Material Consumption and Charge Loading (Al aq):

According to Faraday's Law:

Charge loading = $(I \times T)/(F \times v)$

Electrode consumption = $(I \times t \times M)$ *w* $/(z \times F \times v)$

...where F is Faraday's constant (96,485 C/mol), M w is the molar mass of aluminium (26.98 g/mol), and z is the number of electron transfer (z Al:3).

Therefore, Charge loading = $\frac{(3.5 \times 20 \times 60)}{(0.6405 \times 0.0012)}$ (96,485×0.0012) *= 36.275 Faradays/m3.*

 $Electrode consumption = \frac{(3.5 \times 20 \times 60 \times 26.98)}{(3 \times 96,485 \times .0012)} = 0.3262 kgAl/m3.$

Therefore the Electrode consumption cost = $0.3262 \times 123.65 = 40.33$ *Rs/m3 of water.*

Thus the Operating cost as 235 Rs/m3 of water under the optimum operating conditions was evaluated.

Chapter 5

Conclusion

Electro-coagulation is one the effective technique used to remove crystal violet dye from synthetic wastewater. The effects of various operational parameters on crystal violet dye removal efficiency were investigated. The results showed that the removal efficiency was enhanced with the increase in current density from 8.13 mA/cm² to 14.23 mA/cm². It was found that the proper electrolysis time was 20 min for the removal of 99.85%.

Degradation efficiency was decrease when the initial dye concentrations increased from 10 ppm to 120 ppm (In time sense, i.e. it took 12 minutes for 50 ppm and 20 min for 120 ppm). Operating costs for the treatment of crystal violet dye using EC were evaluated for 100% operating condition (235 Rs/m^3).

The conductivity of the solution changes with the time during EC treatment. To avoid this problem NaCl (10 ppm) was used. Operating time and current density exhibit similar effects on the process performances and the operating cost.

Since the complete dye degradation was achieved by electrocoagulation treatment thus the treated effluent can be reused for textile industry itself.

FUTURE SCOPE OF THE WORK

It has been proven that electrocoagulation technique is very useful in degradation strong industrial dyes like crystal violet blue.

However the setup can be upgrade to pilot study to scale up which can beneficial to industry.

In this study we have used aluminium metal as an electrode, in future other metals like iron electrodes can be used. Also combination may give better results.

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