

Model Analysis for the Treatment of Tannery Wastewater by Electrocoagulation using Aluminium and Iron Electrodes

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Abstract - The electro-coagulation treatment using aluminium and iron electrodes was studied for the removal of organic and inorganic pollutants from the tannery wastewater. A linear regression model was applied in order to obtain optimal values of the variables. The electro-coagulation (EC) process efficiency was based on the biochemical oxygen demand (BOD), chemical oxygen demand (COD) and Chromium. Linear regression model has confirmed the predicted model by the experimental design within a 95% confidence level. The reactor working conditions sets to pH of 7, 8 and 9 voltage was set to 10, 15 and 20 volts electrode distance was set to 1cm, 1.5cm and 2cm electrolysis time in the range 30, 60 and 90 min and electrodes were fabricated to two shapes plane and punched were proved to be optimum parameters to achieve highest removal efficiency of organic and inorganic pollutants concentrations. An appreciable improvement in BOD, COD and Chromium removal efficiency was obtained for electro-coagulation treatment.

When aluminum Plane and punched electrodes were used the optimum removal efficiency for plain electrodes was found to be BOD-89.66%, COD-96.21%, Cr-96.05% and TDS-95.77% for punched electrodes BOD-90.86%, COD-98.62%, Cr-96.94% and TDS-96.92% and for iron plane electrodes BOD-87.57%, COD-94.77%, Cr-93.42% and TDS-93.08% for iron punched electrodes BOD-89.01%, 96.59%, Cr-94.66% and TDS-95.0% at pH of 9, Voltage 20V, for electrode distance of 1cm and 90 minutes electrolysis duration. The Electrocoagulation treatment has proved to be economical and efficient method for the treatment of tannery wastewater rather than chemical coagulation.

Key Words: Tannery wastewater; Electrocoagulation; Regression analysis model; Aluminum; iron; plain and punched electrodes; BOD; COD; and Chromium.

1. INTRODUCTION

India is the third largest leather producer in the world, behind China and Italy. The Indian leather industry is a large player in the global market, and a major source of foreign exchange revenues. A total of 1800 million square feet of leather was produced per year from all the industries. The technique of tanning is one that converts the protein of the rawhide or pores and skin into a non-putrefied strong material is referred to as leather [1]. The chemical substances used in tanning technique are lime, sodium carbonate, sodium bicarbonate, chrome sulphate, fats liquors, vegetable oils and dyes. Other chemical substances

like zinc chloride and mercuric chloride is used as disinfectants, bleaching powder and sodium fluoride is used to prevent skin and hides from putrefaction. Hence the tannery effluent characterized by its strong Colour, excessive COD, high pH, and high dissolved solids. [2] There are two varieties of tanning vegetable tanning and chrome tanning are commonly practiced. Vegetable tanning is not often used due to its excessive contaminated load and much less treatability in nature. Moreover, vegetable tanned leather having its own properties and physical nature but biodegradable in nature. Presently more than 90% of world wide produces 18 billion Sq feet of leather. is through chrome tanning technique. Around 15 industrial nations were importing 85% of the leather and cow hide items, in fact all these industrialized nations which are in Asia. China alone was contributing 54% of leather and its concerned items. [3]. India placed as third largest producer of leather, after the china and Italy. Chromium sulphate used extensively in tanning procedure. Hides tanned with chromium salts have a good mechanical resistance, and wonderful dyeing suitability and a higher hydro thermic resistance in preference to vegetable tanning. Only a small quantity of the chromium salts used in the tanning method react with the skins. Remaining salts within the tanning exhaust bath and they're sooner or later dispatched to a depuration plant where the chromium salts emerge as within the sludge. [4]. Considering the huge amount and the low biodegradability of chemicals were inside the tannery processing cycle. Tannery wastewater represents a serious. Therefore the development and improvement of treatment techniques for these effluents is extraordinarily essential to protect the soil and human life. Tannery effluent is conventionally treated by way adopting various physico-chemical and biological methods. The Conventional method of treatment is frequently insufficient for complete removal of pollutant in tannery industry. Convention coagulant having drawback increases the sludge production. Hence the electro coagulation is better solution decrease the sludge in tannery waste water. [5]

1.1 Impacts of Tannery Wastewater on Environment

Large quantities of sewage and solid waste generated during leather production are generated by the tannery industry. No less than 30 kg of chemicals per ton of hides are added in the tanning process. When tannery effluent released into water bodies, it modifies water's physical, chemical and biological features and decreases dissolved oxygen, increases

alkalinity, suspended solids and sulfides that are damaging to fish and other aquatic life. Tannery wastewater includes chromium and pathogens of fecal origin and toxic in nature, the tannery waste includes several dangerous heavy metals such as Cr, Cu, Zn, Pb and Cd, which pose a significant health and environmental risk. The tannery effluent release into the water system damages the gills of fish leads to fish mortality, and also cause diseases, infertility and birth defects in human beings. It also causes various cancers in animal through food chain. In humans, according to how it is absorbed, chromium creates various ailments cancer. Chromium were inhaled, it acts as a carcinogenic and pulmonary irritant it impacts the upper respiratory tract, obstructs airways, and increases the lung, nasal, or sinus cancer. If dry, cracked and scaled skin causes unprotected handling and contact with tannery wastewater, the erosive ulcerations is known as "chrome holes." The untreated waste water discharge into water bodies not only effect aquatic life it also effect cattle and vegetative system. It also leads to the pollution of soil, it affects the soil fertility alters soil pH, due to high organic contents it cause clogs to the soil and impair soil structure leads to Soil degradation. [6]

1.2 Theory of Electrocoagulation

The process of applying electric current in to an aqueous medium in an electrochemical cell using electrode is called electrocoagulation. The principle of electrocoagulation process depends on, responses of water contaminants to a strong electric fields and electrically induced oxidation and reduction reactions. Electrocoagulation utilizes direct current to remove undesirable contaminants by chemical reactions and precipitation. The different types of electrodes used in this process are Aluminum, Zinc, Copper, Iron [7].

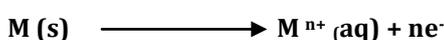
The process of coagulation of pollutants in the solution through various stages is listed below

1. Electrolytic oxidation takes place at the anode (Sacrificial electrode) results in the formation of coagulants.
2. Weakening of the pollutants, particulate suspension and breaking of emulsions.
3. Adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or floatation.

When a potential is applied from an external power source, the anode material undergoes oxidation, while cathode undergo reduction.

The electrochemical reactions with metal M as anode is summarized as follows:

Reactions at anode:



Reactions at cathode:

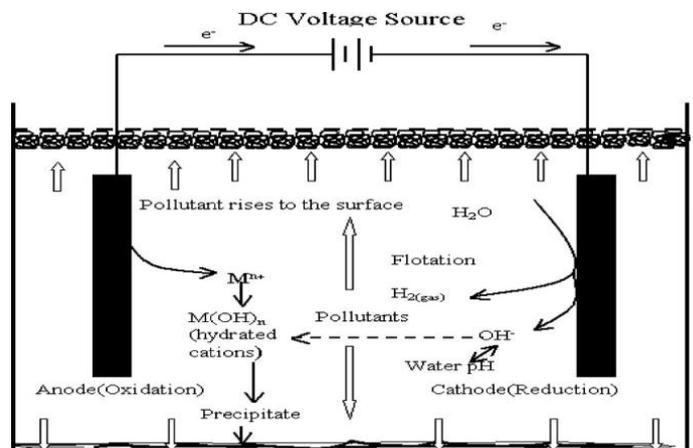
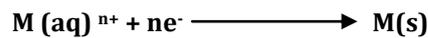


Figure 1.1 Schematic Diagram of A Bench-Scale Two-Electrode Electrocoagulation Cell

2. Materials and Methods

2.1 Materials

The sample to be studied was collected from a common effluent treatment plant at the Vanitec tannery wastewater treatment plant, Tamil nadu. The sample was collected according to the standards. The sample was preserved at 60C and brings it to the laboratory at standard condition before analysis. The aluminium and iron plane and punched electrodes of dimension 15cm x 5cm x 0.2cm were used for the experimentation and a glass container as an electrochemical cell with a working capacity of 2 liters. The composition of the tannery wastewater are determined using Standard Methods and are presented in Table 2.1

Table 2.1 Initial Characteristics of Raw Tannery Wastewater

Sl no	Parameter	Unit	Values
1	Color		Brown
2	Temperature	°C	24 ⁰
3	pH	-	8.4
4	Turbidity	NTU	727
5	TDS	Ppm	26000
6	EC	S/m	38806
7	BOD	mg/L	2156
8	COD	mg/L	6100
9	Chromium	mg/L	14.6

2.2. Experimental Setup

For the batch electro coagulation studies, the reactor was designed and fabricated using glass material with the total working volume, of 2 liter and with the dimensions of 22cm x 11cm x 10cm. The electro coagulation unit consists of four

monopolar electrodes connected in series. The DC power supply of 0-30V and 0-2A was used as the power supply to the system. Plane and punched aluminium and iron electrodes having dimensions of 15cm x 5cm x 0.2 cm. The distance between the electrodes were kept 1cm, 1.5cm and 2cm to study and evaluate optimum distance. One set of electrodes were punched with a 5mm diameter holes and a total of 5 numbers of holes were made. The below figure shows the laboratory experimental set up of electro coagulation.



Figure 2.1 Laboratory Experimental Setup

2.3 Experimental procedure

The raw wastewater was diluted to 1 in 10 dilution before analysis. The monopolar electrodes were arranged in series and connected to a 0-30V and 0-2A DC power supply. Four numbers of electrodes were arranged in series, the end electrodes were connected to positive and negative terminals and the inner electrodes remains unconnected and acts as sacrificial electrodes. A constant gap of 1cm, 1.5cm and 2cm was kept between the electrodes. The glass container was filled with 2 liters diluted wastewater and the initial pH was adjusted to 7, 8 and 9 to determine the optimum pH. The voltage in the DC power supply was adjusted to 10V, 15V and 20V to evaluate the optimum voltage. The electrolysis was carried out for 90 minutes and the samples were taken at an interval of 30 minutes. The collected sample was filtered with the whatman's filter paper and simultaneously the pH and TDS were measured. The filtered sample was preserved in a 60 ml polythene bottle with tight lid in a refrigerator at below 60C to test other parameters. The BOD is measured using DO calculations, COD and chromium test were conducted later by instrumental methods. HACH 2700 Spectrophotometer of was used to analyze the parameters.

2.4 Analysis using Regression Model

Multiple linear regression is a statistical technique to model the relationship between one dependent variable and two or more independent variables by fitting the data set into a linear equation. The difference between simple linear regression and multiple linear regression: Simple linear regression only has one predictor [8].

Multiple linear regression has two or more predictors. The design of response surface factors is created by inserting the low and high values of the independent variables or response factors in the tabulation. The design includes four different factors pH, Applied Voltage Electrode distance and Electrolysis duration [9]. The design factors are indicated by two levels low levels (-1) and the high levels (+1) code. In this experimental design codes are given by,

- Codes for pH, low level value (-1) is coded for pH 7, middle value (0) is coded for pH 8 and high-level value (+1) is coded for pH 9.
- Codes for Applied Voltage, low level value (-1) is coded for 10 V, middle value (0) is coded for 15V and high-level value (+1) is coded for 20V.
- Codes for Electrode distance, low level value (-1) is coded for 1cm, middle value (0) is coded for 1.5 cm and high-level value (+1) is coded for 2 cm.
- Codes for Electrolysis duration, low level value (-1) is coded for 30 mins, middle value (0) is coded for 60 mins and high-level value (+1) is coded for 90 mins.

3. RESULT AND DISCUSSION

3.1 Regression analysis for BOD

3.1.1 Regression Analysis for Aluminum: BOD versus pH, Voltage, Distance, Duration

The regression equation for aluminium plane is as shown below.

$$\text{BOD} = 83.80 + 0.931 \text{ pH} + 0.0667 \text{ Voltage} - 6.473 \text{ Distance} + 0.0239 \text{ Duration}$$

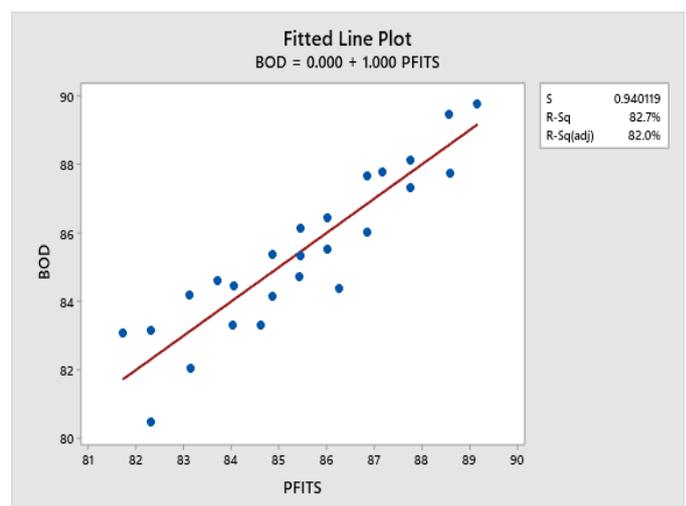


Figure 3.1 Scatterplot of The BOD Together With Least Square Line For Plane Aluminum

The Figure 3.1 represents the fitted line plot for the BOD with respect to PFITS, the value standard error S is 1.15 shows very low error and it is described as the average distance of the values of the PFITS from the removal efficiency of BOD is about 1.15%. The value of the R square for the best fit is 81.3% this shows that the model is precised.

The regression equation for punched aluminium is as shown below.

$$\text{BOD} = 87.06 + 0.420 \text{ pH} + 0.0823 \text{ Voltage} - 5.462 \text{ Distance} + 0.03308 \text{ Duration}$$

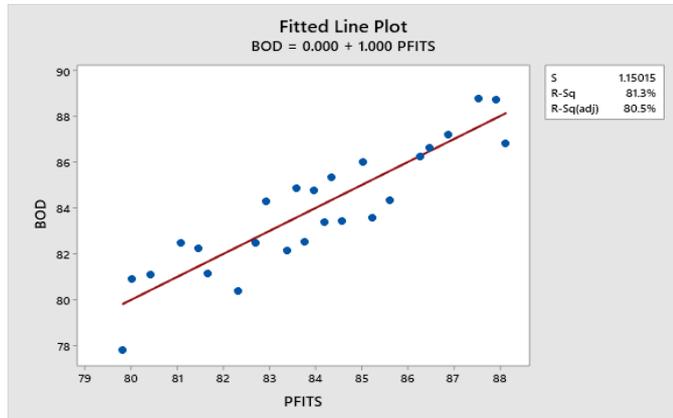


Figure 3.2 Scatterplot of The BOD Versus PFITS Together With Least Square Line For Punched Aluminum

The Figure 3.2 represents the Regression line plot for the BOD with respect to PFITS, the value of standard error S is 0.94 shows very low error and it is described as the average distance of the values of the PFITS from the removal efficiency of BOD is about 0.94%. The value of the R square for the best fit is 82.7% this shows that the model is more accurately fits.

The scatterplot graph in both the case shows nearly equal values but, the standard error S is lower and the value of R-square is larger in punched aluminum electrodes as compared to plane electrodes, this clarifies that punched electrodes can have better removal efficiency.

3.1.2 Regression Analysis for Iron: BOD versus pH, Voltage, Distance, Duration

The regression equation for plane iron is as shown below.

$$\text{BOD} = 70.39 + 1.817 \text{ pH} + 0.200 \text{ Voltage} - 6.29 \text{ Distance} + 0.0450 \text{ Duration}$$

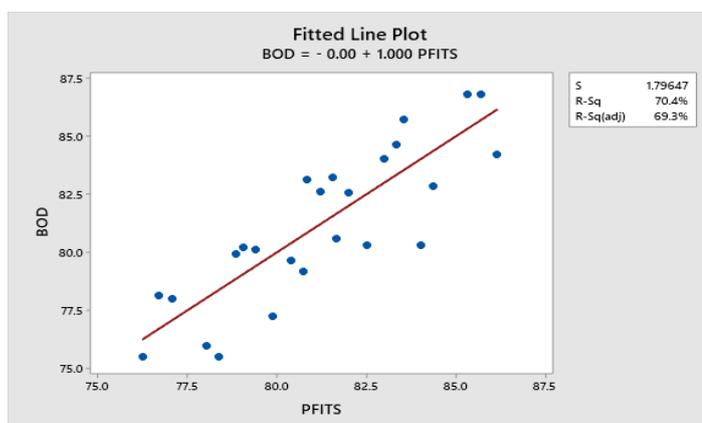


Figure 3.3 Scatterplot of The BOD Versus PFITS Together With Least Square Line For Plane Iron Electrodes

The Figure 3.3 represents the Regression line plot for the BOD with respect to PFITS, the value of standard error S is 1.79 shows the standard error is slightly greater than the standard error for aluminum electrodes for the BOD analysis. And it is described as the average distance of the values of the PFITS from the Regression line for the removal efficiency of BOD is about 1.79%. The value of the R square for the best fit is 70.4%.

The regression equation for punched iron is as shown below.

$$\text{BOD} = 77.64 + 1.250 \text{ pH} + 0.1490 \text{ Voltage} - 6.090 \text{ Distance} + 0.0387 \text{ Duration}$$

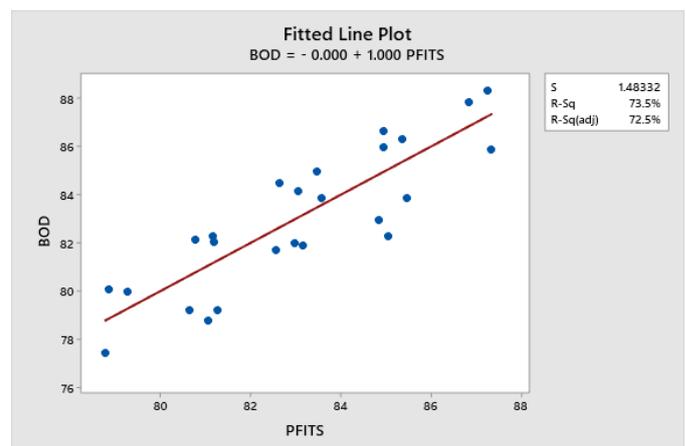


Figure 3.4 Scatterplot of The BOD Versus PFITS Together With Least Square Line For Punched Iron Electrodes

The Figure 3.4 represents the Regression line plot for the BOD with respect to PFITS, the value of standard error S is 1.48. The value is lesser than the value obtained for plane iron electrodes. The value of the R square for the best fit is 73.5% this shows that the model shows better results than plane electrodes.

The scatterplot graph in both the case shows that the standard error is lower for aluminum electrodes when compared to iron electrodes and the value of R-square is larger in aluminum electrodes as compared to iron electrodes, this clarifies that aluminum electrodes are more significant in producing their effect in electrocoagulation in both experimental and model analysis.

3.2 Regression Analysis for COD

3.2.1 Regression Analysis for Aluminum: COD versus pH, Voltage, Distance, Duration

The regression equation for aluminum plane is as shown below.

$$\text{COD} = 77.64 + 2.212 \text{ pH} + 0.1583 \text{ Voltage} - 6.073 \text{ Distance} + 0.0305 \text{ Duration}$$

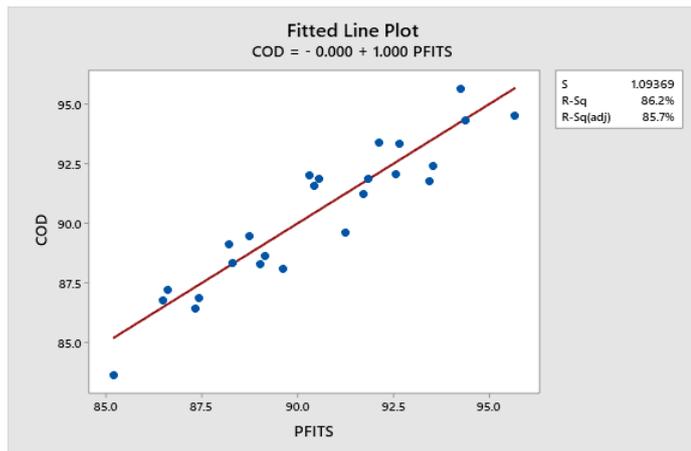


Figure 3.5 Scatterplot of The COD Together With Least Square Line For Plane Aluminum

The Figure 3.5 represents the Regression line plot for the COD with respect to PFITS, from the graph it can be seen that the scatterplots are aligned linearly with respect to the regression line, the value of standard error S is 1.09 shows the standard error is less. And it is described as the average distance of the values of the PFITS from the Regression line for the removal efficiency of COD is about 1.09%. The value of the R square for the best fit is 86.2%.

The regression equation for punched aluminum is as shown below

$$\text{COD} = 74.42 + 2.305 \text{ pH} + 0.2562 \text{ Voltage} - 4.185 \text{ Distance} + 0.0378 \text{ Duration}$$

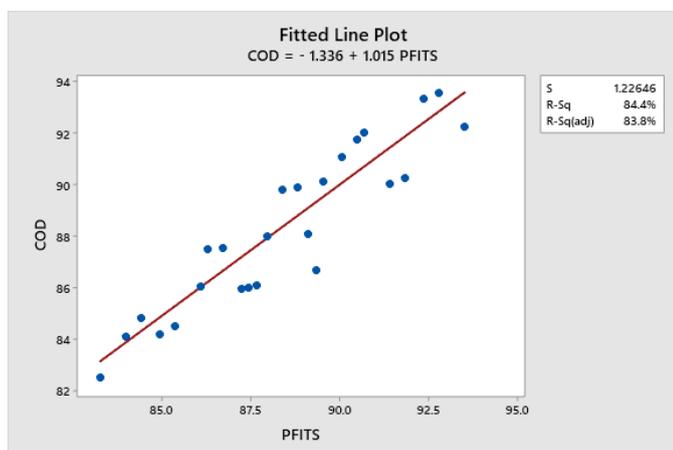


Figure 3.6 Scatterplot of The COD Versus PFITS Together With Least Square Line For Punched Aluminum

The Figure 3.6 represents the Regression line plot for the COD with respect to PFITS, the value of standard error S is 1.29 shows very low error and it is described as the average distance of the values of the PFITS from the removal efficiency of COD is about 1.29%. The value of the R square for the best fit is 78.2% this shows that the model is more accurately fits.

3.2.2 Regression Analysis for Iron: COD versus pH, Voltage, Distance, Duration

The regression equation for plane iron is as shown below.

$$\text{COD} = 74.12 + 2.236 \text{ pH} + 0.1620 \text{ Voltage} - 6.042 \text{ Distance} + 0.0496 \text{ Duration}$$

The Figure 3.7 represents the Regression line plot for the COD with respect to PFITS, the value of standard error S is 1.22 shows the standard error is smaller than the standard error for iron electrodes for the BOD analysis. And it is described as the average distance of the values of the PFITS from the Regression line for the removal efficiency of COD is about 1.22%. The value of the R square for the best fit is 84.4%. Here the R value obtained is much greater than the value obtained for BOD analysis when the same electrodes were used.

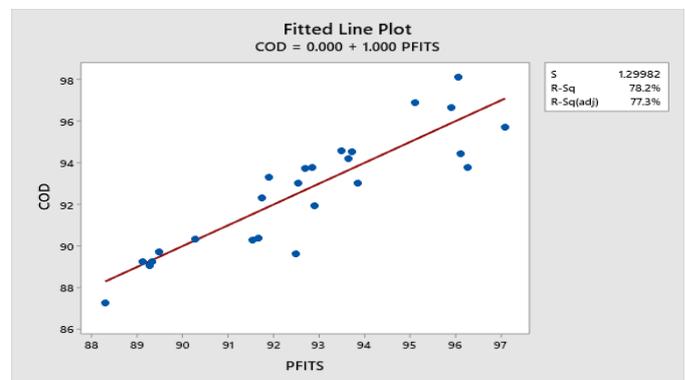


Figure 3.7 Scatterplot of The COD Versus PFITS Together With Least Square Line For Plane Iron Electrodes.

The regression equation for punched iron electrodes is as shown below.

$$\text{COD} = 79.45 + 1.679 \text{ pH} + 0.2007 \text{ Voltage} - 5.745 \text{ Distance} + 0.0411 \text{ Duration}$$

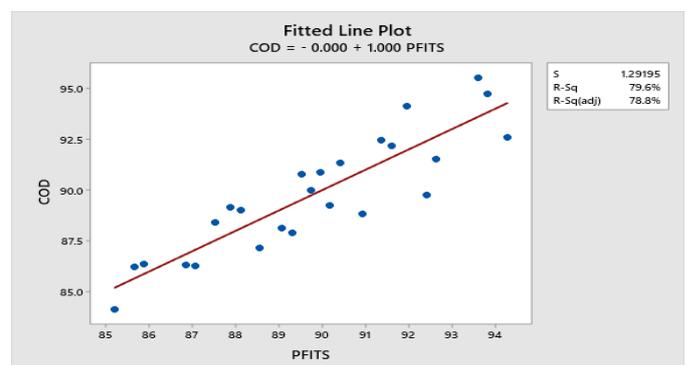


Figure 3.8 Scatterplot of The COD Versus PFITS Together With Least Square Line For Punched Iron Electrodes.

The below Figure 3.8 represents the Regression line plot for the COD with respect to PFITS, the value of standard error S is 1.29. The value is almost same as the value obtained for plane iron electrodes. The value of the R square for the best fit is 79.6% this shows that the model shows better results than plane electrodes.

The scatterplot graph in both the case shows that the standard error is lower for aluminum electrodes when compared to iron electrodes and the value of R-square is larger in aluminum electrodes as compared to iron electrodes, this clarifies that aluminum electrodes are more significant in producing their effect in electrocoagulation in both experimental and model analysis.

3.3 Regression Analysis for Chromium

3.3.1 Regression Analysis for Aluminum: Chromium versus pH, Voltage, Distance, Duration

The regression equation for aluminum plane is as shown below.

$$\text{Chromium} = 55.57 + 3.147 \text{ pH} + 0.543 \text{ Voltage} - 6.59 \text{ Distance} + 0.1014 \text{ Duration}$$

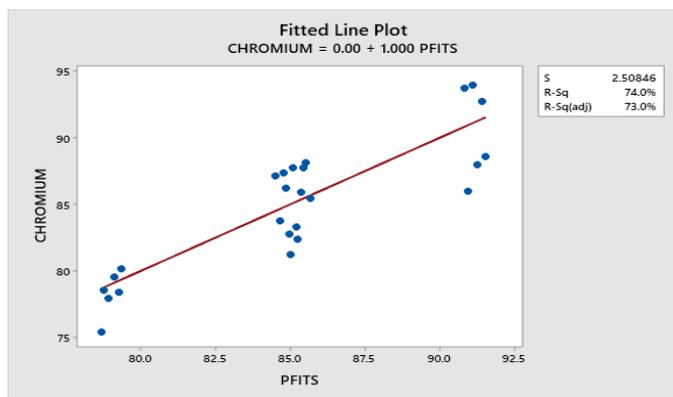


Figure 3.9 Scatterplot of The Chromium Together With Least Square Line For Plane Aluminum

The Figure 3.9 represents the Regression line plot for the Chromium with respect to PFITS, the value of standard error S is 2.50 shows very large error as compared to BOD and COD The value of the R square for the best fit is 74.0% this shows that the model is moderately fits.

The regression equation for punched aluminum is as shown below

$$\text{Chromium} = 54.02 + 3.278 \text{ pH} + 0.527 \text{ Voltage} - 4.90 \text{ Distance} + 0.1014 \text{ Duration}$$

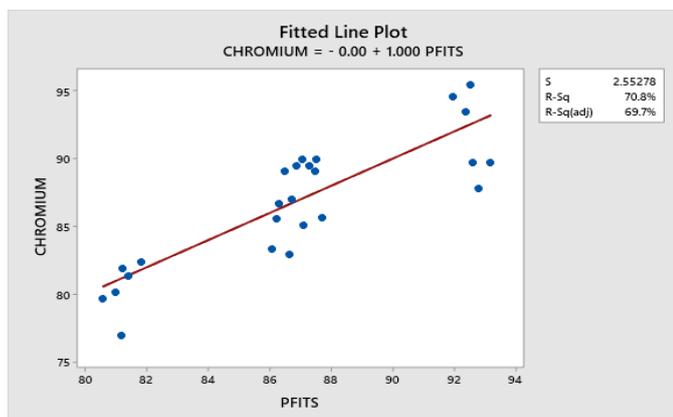


Figure 3.10 Scatterplot of The Chromium Versus PFITS Together With Least Square Line For Punched Aluminum.

The Figure 3.10 represents the Regression line plot for the Chromium with respect to PFITS, the value of standard error S is 2.52 shows same error as in the previous scatterplot graph for chromium when plane electrodes were used. and it is described as the average distance of the values of the PFITS from the removal efficiency of Chromium is about 2.52%. The value of the R square for the best fit is 70.8% the value is still lesser than the value obtained for plane electrodes.

3.3.2 Regression Analysis for Iron: Chromium versus pH, Voltage, Distance, Duration

The regression equation for plane iron electrodes is as shown below.

$$\text{Chromium} = 63.30 + 2.522 \text{ pH} + 0.453 \text{ Voltage} - 8.66 \text{ Distance} + 0.0735 \text{ Duration}$$

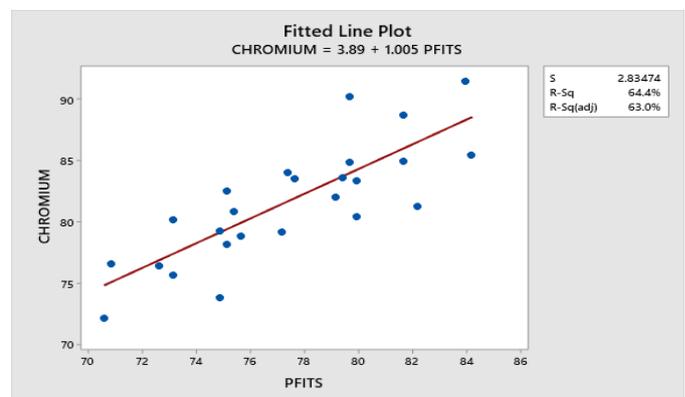


Figure 3.11 Scatterplot of the Chromium versus PFITS together with least square line for plane iron electrodes

The Figure 3.11 represents the Regression line plot for the Chromium with respect to PFITS, the value of standard error S is 2.83 shows the standard error is greater than all the errors obtained till now. The scatterplots were also scattered from the regression line so that the R square value obtained is low as 64.4%

The regression equation for punched iron electrodes is as shown below

$$\text{Chromium} = 60.62 + 2.529 \text{ pH} + 0.490 \text{ Voltage} - 4.99 \text{ Distance} + 0.0706 \text{ Duration}$$

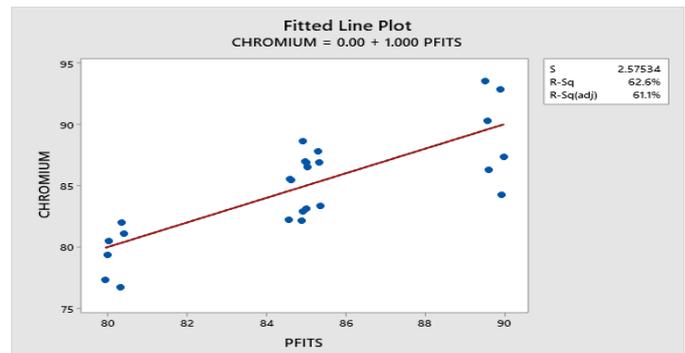


Figure 3.12 Scatterplot of The Chromium Versus PFITS Together With Least Square Line For Punched Iron Electrodes

The Figure 3.12 represents the Regression line plot for the chromium with respect to PFITS, the value of standard error S is 2.57 this value also shows greater demarcation compared to all other previous graphs. The value of the R square for the best fit is 62.6% this shows that the model shows less significant compare to all other models.

3.4 Validation of Regression Equations

To validate the above obtained regression equations, we compare the theoretical and experimental values obtained during the experiment and the comparison is tabulated in the Table 3.1

Table 3.1 Comparison of Theoretical And Experiment Values For Different Parameters To Validate Regression Equations

Electrodes arrangement	Parameters	pH	Voltage (V)	Distance (cm)	Duration (min)	Theoretical Value	Experiment Value
Aluminium Plane	COD	7	10	1	30	89.55	88.16
					60	90.46	89.08
					90	91.38	89.85
					30	90.34	88.90
					60	91.26	89.59
					90	92.17	90.79
					30	91.13	89.98
					60	92.05	90.33
					90	92.96	90.77
Aluminium Punched	BOD	8	10	1.5	30	84.46	84.04
					60	85.25	85.03
					90	86.46	86.03
					30	84.79	84.45
					60	86.13	85.45
					90	87.38	86.44
					30	85.39	84.87
					60	86.64	85.86
					90	87.66	86.85
Iron Punched	Chromium	9	10	2	30	78.77	75.41
					60	81.30	77.62
					90	82.81	79.82
					30	76.78	77.68
					60	78.84	79.88
					90	79.45	82.09
					30	75.55	79.94
					60	78.42	82.15
					90	80.62	84.35

5. Conclusions

Based on the above findings the following conclusion are drawn

- The scatterplot graphs for BOD and COD with aluminum and iron electrodes shows that the standard error is lower for aluminum electrodes compared to iron electrodes.
- Aluminum electrodes are more significant in producing their effect in electrocoagulation in both experimental and model analysis.
- The Regression model for all the cases for BOD, COD and chromium, it was observed that the model for COD is best fit, BOD seems to be nearly best fit with slight variations and chromium model shows poor scatterplot alignment with respect to the regression line as the S values and R square values obtained for chromium is differ compare to other parameters.

- The behavior of regression equations may be hypothetical which might be the reason for slight deviations in theoretical and experimented values.
- From the table 3.1 it can be concluded that the theoretical and experimented values are nearer which concludes that regression equations are valid.

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