Treatment of Tannery Wastewater by Electrocoagulation using Aluminium and Iron Electrodes

Kiran Kumar H S, Lokeshappa B, Mohammad Rizwan M R

Abstract—This Tannery industry is one of oldest industry the effluent is highly complex and characterized by high Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), suspended solids, dissolved solids, total solids, and color. Untreated Tannery wastewater when discharged directly into the water bodies or into open lands cause irreversible damage to environment. Electrocoagulation is one of the most important electrochemical treatment employed for industrial wastewater treatment to treat highly polluted industrial effluents which have high suspended and colloidal materials, BOD, COD in wastewater.

Electrocoagulation treatment is used in this study to study the removal efficiency of BOD, COD, Chromium (Cr) Total Dissolved Solids (TDS) and the effect of pH of tannery wastewater. The experiments were conducted using aluminum and iron as plane and punched electrodes. 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.

Keywords— Tannery wastewater; Electrocoagulation; Aluminum electrodes; iron electrodes; plane and punched electrodes; BOD; COD; TDS and Chromium.

I. INTRODUCTION

Tanning is claimed as the second oldest profession in the world. A total of 1800 million square feet of leather was produced per year from all the industries. India is the third largest producer of leather in the world, behind China and Italy [1]. In India the most of the tannery industries adopted inefficient and conventional production methods to produce leather. The waste water generated from these industries characterized by high BOD, COD, suspended solids, dissolved solids, color and strong odor. Inorganic chemicals such as chlorides and Chromium. [2]. This results for the generation of large amount of low biodegradable wastewater. Inefficient treatment of wastewater causes decreased use of raw materials and also cost for economy [3].

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Untreated wastewater if discharged to the stream, high inorganic solids cause hardness and high alkalinity in the waste leads to the formation of slimy layers on the streams. High BOD depletes the DO contents in the streams causes lack of oxygen to the aquatic life. High suspended solids increase the load to the treatment plants. Degradable matter leads to the propagation of pathogens. High chromium as carcinogenic to the human health. Untreated wastewater if discharge to the streams not only affects fish but also affects the health of the cattle and vegetative system along the shore line. It also leads to the pollution of soil, it affects the soil fertility alters soil pH, due to high organic contents it causes clogs to the soil and impair soil structure leads to soil degradation. [4].

Electro-chemical treatment of tannery wastewater has recently attracted great attention to researchers for its simplicity and ease of operation. When conventional physico chemical process fails to treat the polluted effluent efficiently, electrochemical methods such as electrocoagulation plays a prominent role in not only decreasing the pollutional load but also proves to be efficient in removal of pollutants, besides it is also proving that the byproducts obtained can be utilizable. The sludge can be utilized as a manure.

1.1 Impacts of Tannery Wastewater on Environment

Improper management and inadequate treatment technology create heavy pollutional load to the environment. 95% of the tannery industries are still adopted traditional treatment methods. Due to its unpleasant odor it creates unnecessary nuisance [5].

High inorganic solids cause hardness to the streams if untreated, high alkalinity in the waste leads to slimy layer formed to the streams. High BOD depletes the Dissolved Oxygen (DO) contents in the streams causes lack of oxygen to the aquatic life. High suspended solids increase the load to the treatment plants. Degradable matter leads to the propagation of pathogens. High chromium act as carcinogenic to the human health [6]. Untreated wastewater if discharge to the streams not only affects fish but also affects the health of the cattle and vegetative system along the shore line. It also leads to the pollution of soil, it affects the soil fertility alters soil pH, due to high organic contents it causes clogs to the soil and impair soil structure leads to Soil degradation [7].

People who are working in the industry environment cause severe skin irritation, respiratory disorders. Long term exposure to the waste leads to depression, headache, dizziness eye and skin irritation. The chromium act as a carcinogenic and causes cancer [8].

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1.2 Treatment of Tannery Wastewater

The different treatment methods adopted for tannery wastewater are shown in the Table 1

Table 1. Treatment Methods Available for Treatment of Tannery Waste Water

Pre-treatment	Mechanical screening, equalization
Primary treatment	Sulfide removal, Chromium removal from tanning effluents Physical-chemical treatment for BOD removal and neutralization
Secondary treatment	Biological treatment such as Activated sludge process, Lagooning
Tertiary treatment	Nitrification and denitrification, Electrochemical methods

1.3 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 [9].
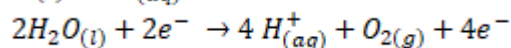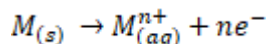
The process of coagulation of pollutants in the solution through various stages is listed below

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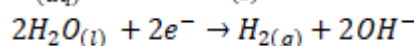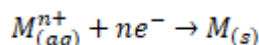
When a potential is applied from an external power source, the anode material undergoes oxidation, while cathode undergo reduction.

The electrochemical reactions with metal M as anode is summarized as follows [10].
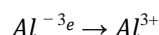
Reactions at anode:

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^-$$
$$2H_2O_{(l)} + 2e^- \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$$

Reactions at cathode:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$$
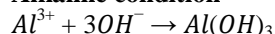$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-$$

When aluminum or iron electrodes were used the generated, Fe $(aq)^{3+}$ or Al $(aq)^{3+}$ ions will instantaneously undergo spontaneous reactions to produces the corresponding hydroxides and polyhydroxides. This hydroxide and poly hydroxide settle in the form of precipitate [11].

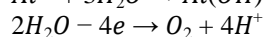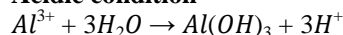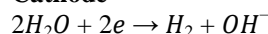Following reactions are carried out for aluminum electrodes:

Anode

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

Alkaline condition
$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$$

Acidic condition
$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$
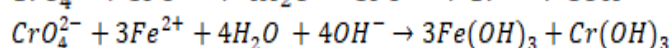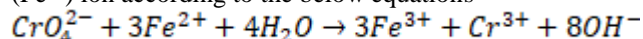$$2H_2O - 4e \rightarrow O_2 + 4H^+$$

Cathode
$$2H_2O + 2e \rightarrow H_2 + OH^-$$

Waste water containing Cr^{6+} (CrO_4) ions can be removed by the electrocoagulation using iron as the sacrificial anode. The ferrous ion (Fe^{2+}) generated by electro-oxidation of the iron (anode) can reduce Cr^{6+} to Cr^{3+} under alkaline conditions and is itself oxidized to ferric (Fe^{3+}) ion according to the below equations

$$CrO_4^{2-} + 3Fe^{2+} + 4H_2O \rightarrow 3Fe^{3+} + Cr^{3+} + 8OH^-$$
$$CrO_4^{2-} + 3Fe^{2+} + 4H_2O + 4OH^- \rightarrow 3Fe(OH)_3 + Cr(OH)_3$$

The Cr^{3+} (aq) ions are then precipitated as Cr (OH)$_3$(s) by raising the pH of the solution.

The mechanism of electrocoagulation was schematically shown in the Figure 1
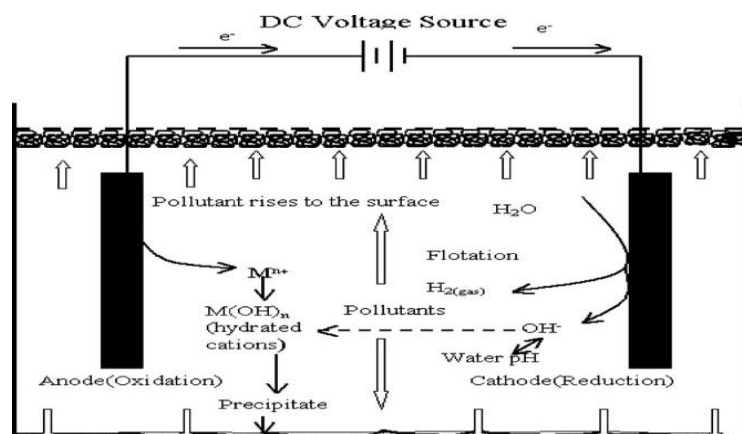

Figure 1. Schematic Diagram of a Bench-Scale Two-electrodes Electrocoagulation Cell

II. 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 6^0C 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 is determined using Standard Methods and are presented in Table 2.

Table 2. 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_5	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 I 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 2. shows the laboratory experimental set up of electro coagulation
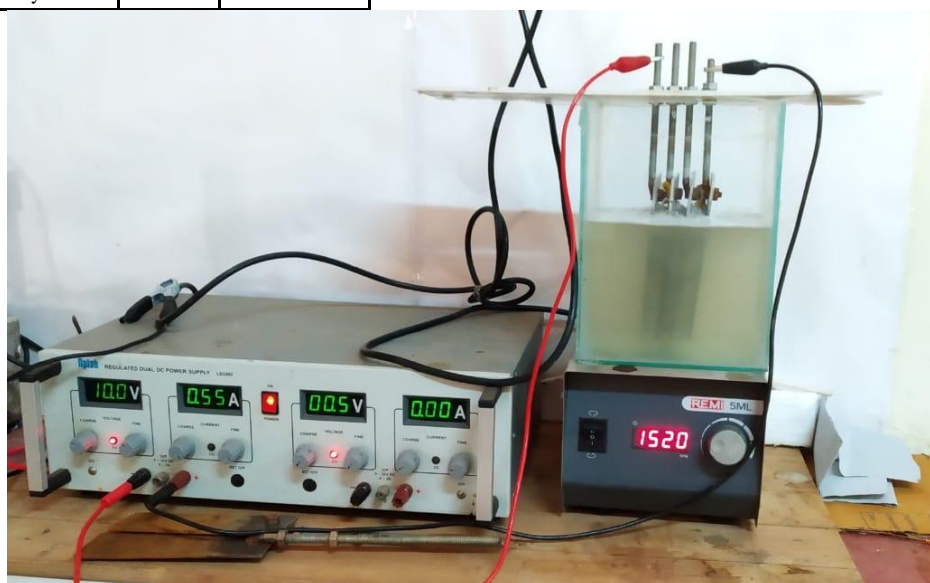

Figure 2. Laboratory Experimental Setup

2.3 Experimental procedure

The raw wastewater was diluted to 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 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 6^0C 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.

III. RESULTS AND DISCUSSIONS

3.1 Effects of pH on Removal Efficiency

The Figure 3.1 and Figure 3.2 represents the graphs plotted to study the effect of pH in removal efficiencies of various parameters such as TDS, BOD, COD and Chromium. The graphs reveal that all the parameters show highest removal efficiency for pH 8 for 1 cm punched aluminium electrodes. It was observed that at pH 7, 93.02% of COD removal efficiency was found. As the pH increases the removal efficiency also increases. The graph shows removal efficiency of 98.62% for aluminum and 96.59% for iron was found to be at pH 8. And as the pH increase to pH 9, the removal efficiency decreases in both the cases to 96.44% and 92.61% for aluminum and iron respectively due to the dissolution of aluminium and

iron electrodes was found to be maximum at pH 8.

Lower removal efficiency at pH 9 is due to the predominance of an ineffecient adsorbant (monomeric $Al(OH)_4^-$ anion) under alkaline conditions. At higher pH values, deposits on the anode surface lead to an increasing ohmic drop (because of the inert, little conducting layer formed) and to an increase in the electrical consumption.
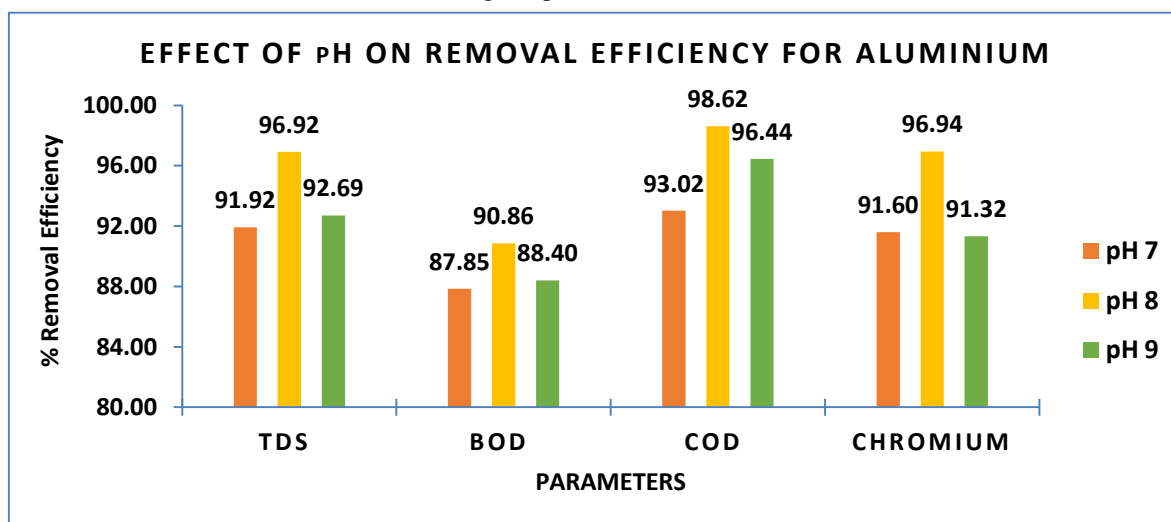
EFFECT OF pH ON REMOVAL EFFICIENCY FOR ALUMINIUM

Figure 3.1 Effect of pH on Removal Efficiency for Aluminium Electrodes

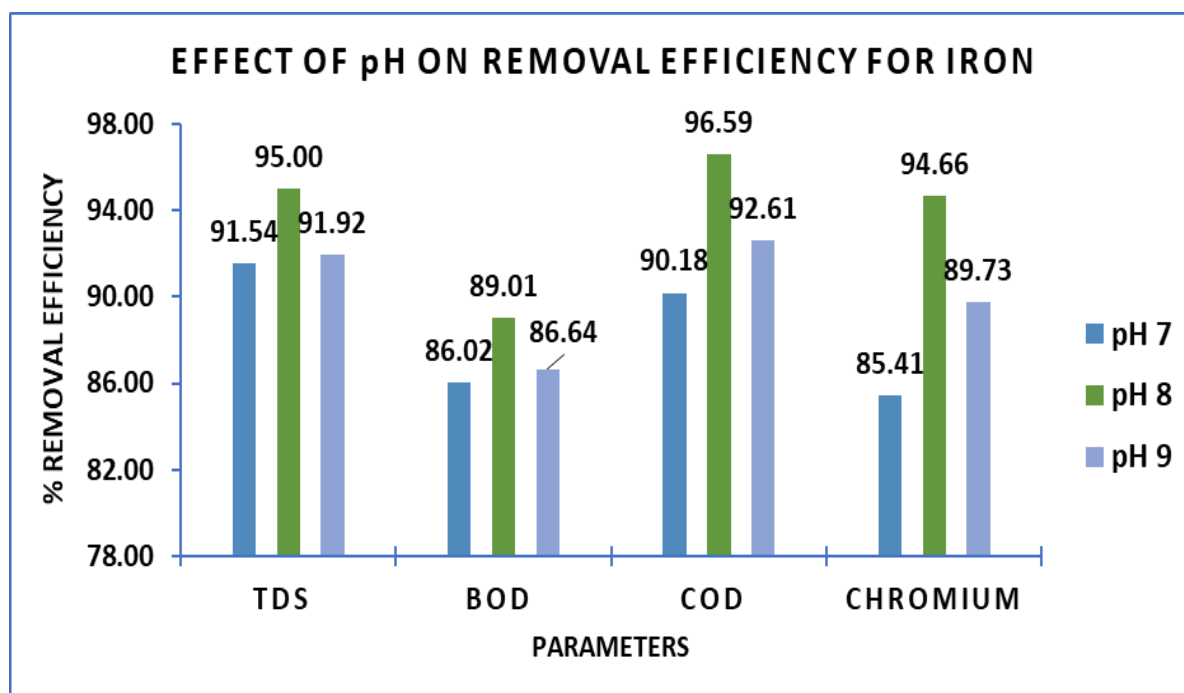**EFFECT OF pH ON REMOVAL EFFICIENCY FOR IRON**

Figure 3.2 Effect of pH on Removal Efficiency for Iron Electrodes

3.2 Effects of Voltage on Removal Efficiency

The Figure 3.3 and 3.4 were plotted to study the effect of voltage on removal efficiencies of TDS, BOD, COD and Chromium. It was observed that at 10V, 93.46% of COD removal efficiency was found. As the voltage increases the removal efficiency also increases. The graph shows removal efficiency of 98.62% for aluminum and 96.59% for iron was found to be at 20V this is due to the fact that as the electrode potential increases the number of coagulant ions and, consequently, pollutant recovery rate increases. On the other hand, voltage density determines the speed and the amount of hydroxyl ion produced. The higher the hydroxyl ion production rate and, the greater the removal efficiency.
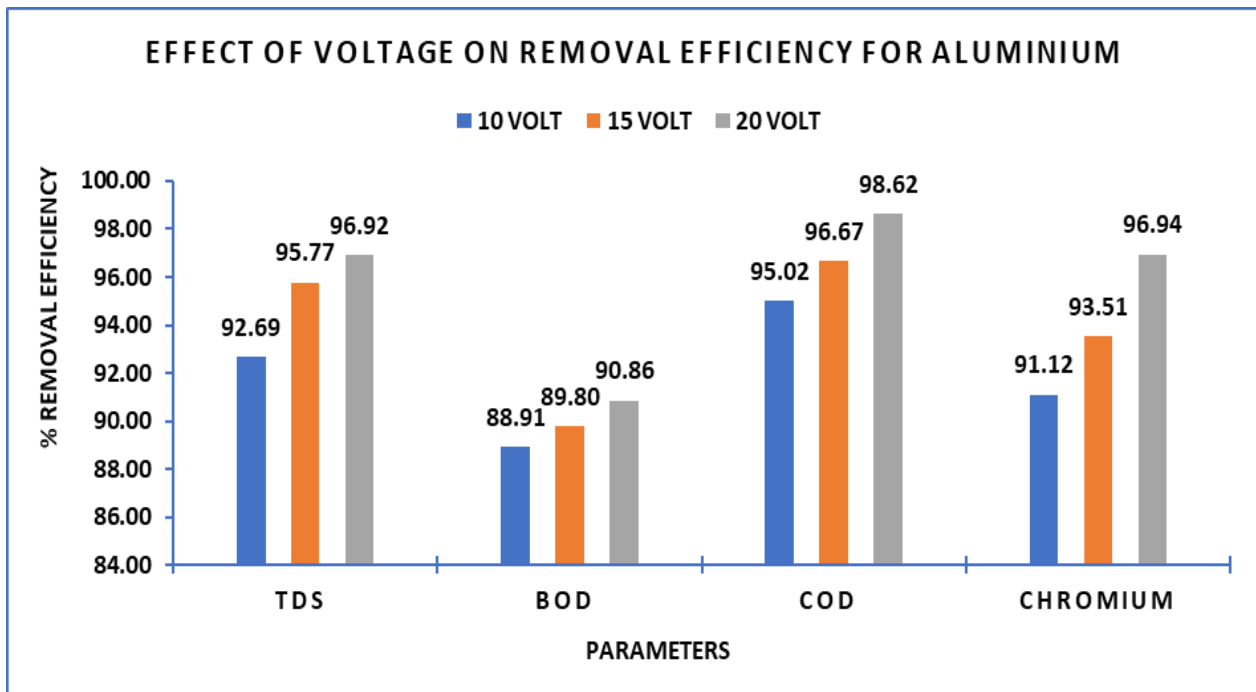
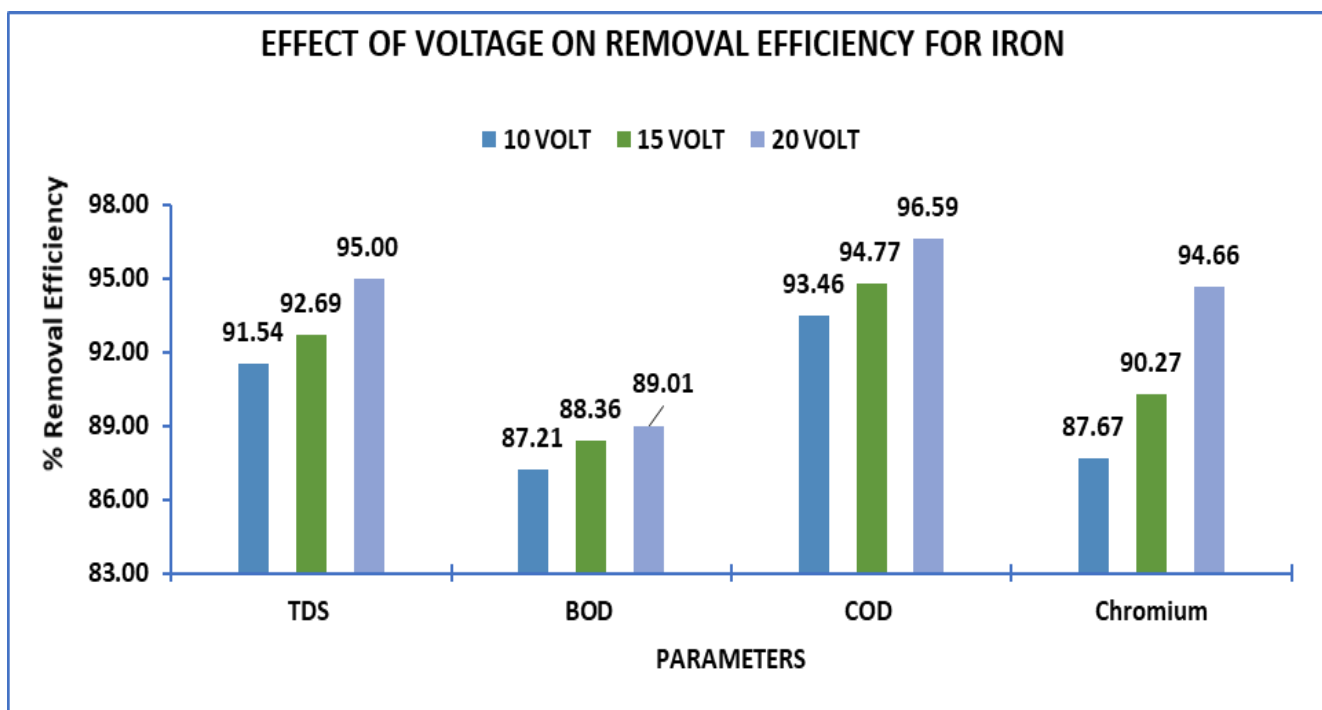**Figure 3.3 Effect of Voltage on Removal Efficiency for Aluminium Electrodes**

Figure 3.4 Effect of Voltage on Removal Efficiency for Iron Electrodes

3.3 Effects of Electrolysis Time on Removal Efficiency

The Figure 3.5 and 3.6 were plotted to study the effect of electrolysis time on removal efficiencies of TDS, BOD, COD and Chromium. It was observed that at 30 minutes of electrolysis time, 95.61% of COD removal efficiency was found. As the electrolysis time increases the removal efficiency also increases. The graph shows removal efficiency of 98.62% for aluminum and 96.59% for iron was found to be at 90 minutes of electrolysis time, As the electrolysis time increases the concentration of specific pollutants influences the stability of the passive layer of an electrode, this leads to the deposition of cations (pollutants) and sludge particles on the surface of electrode material and the formation of oxide layer which inhibits the dissolution of metal and thus causes a reduction in the yield of electrode with prolonged electrolysis time, thereby simultaneously removal efficiency also decreases as the electrolysis time increases.
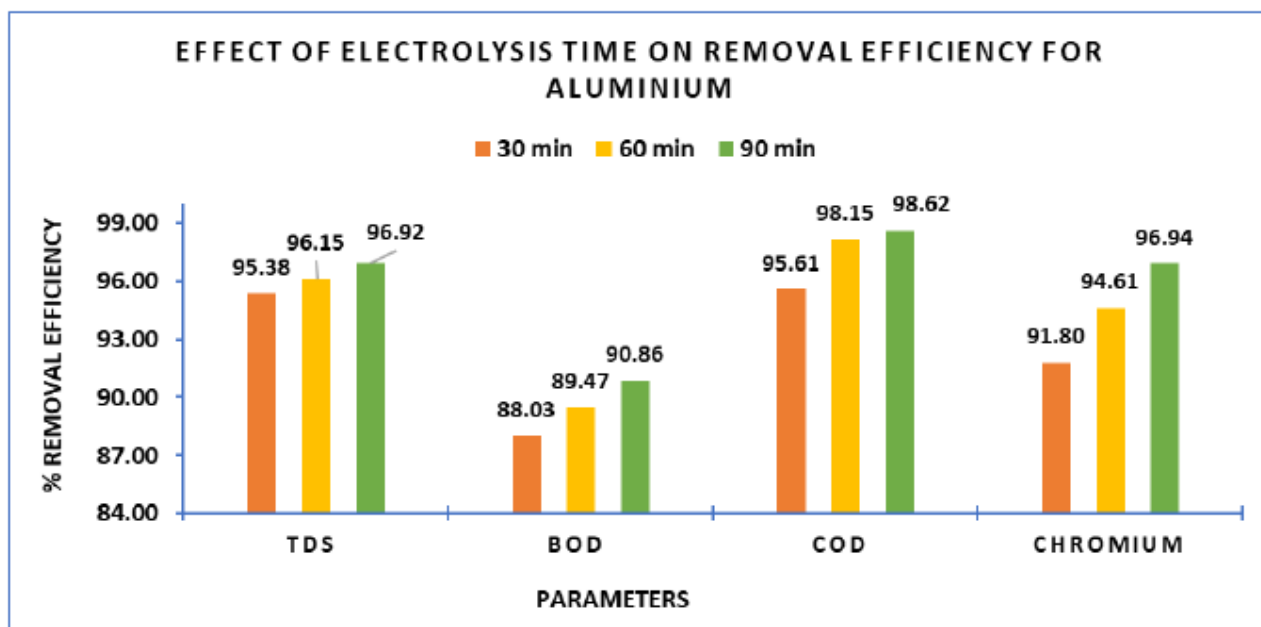
Figure 3.5 Effect of Electrolysis Time on Removal Efficiency for Aluminium Electrodes
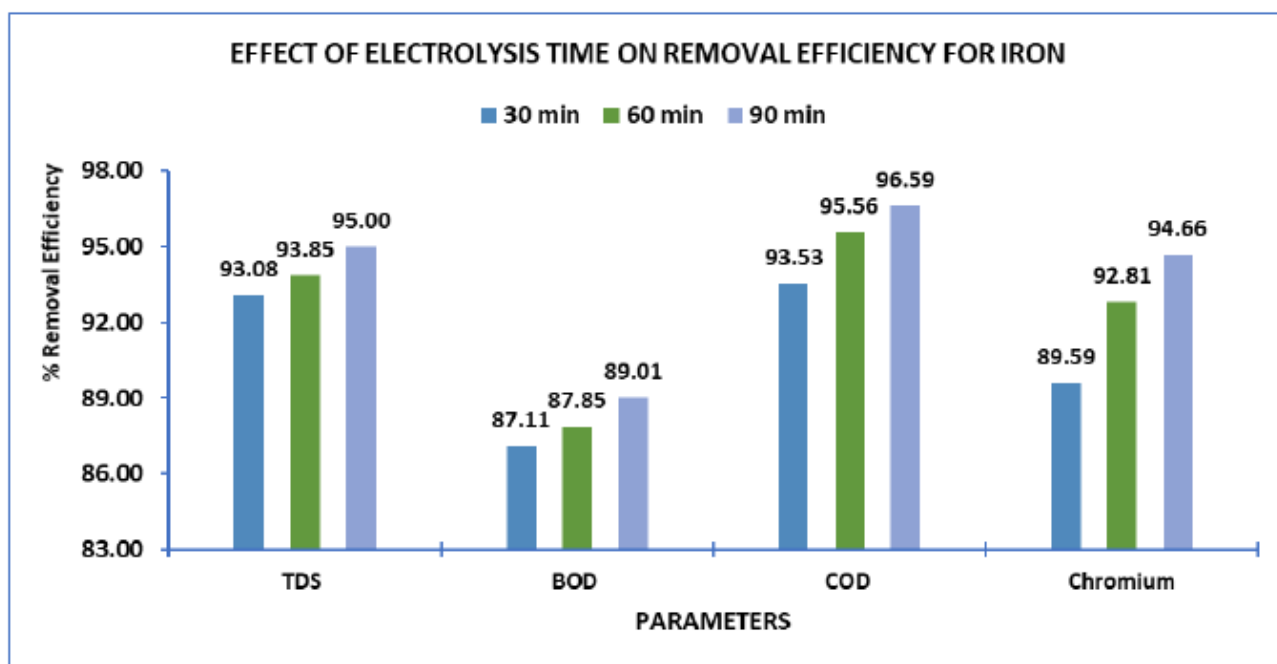

Figure 3.6 Effect of Electrolysis Time on Removal Efficiency for Iron Electrodes

3.4 Effects of Electrode Distance on Removal Efficiency

The Figure 3.7 and 3.8 were plotted to study the effect of electrode distance on removal efficiencies of TDS, BOD, COD and Chromium. It was observed that at 1cm of electrode distance, 98.62% of COD removal efficiency was found. As the electrode distance increases the removal efficiency decreases. The graph shows removal efficiency of 96.92% and 94.54% at 1.5cm and 2cm electrode distance for punched aluminum electrodes and 96.59%, 94.13%, and 90.48% for punched iron electrodes respectively, as the distance increases the faradaic yield and the potential difference between the electrodes decreases. Consequently, the amount of metal getting dissolved into the solution is reduced. Another possible reason for the higher recovery efficiency at lower inter-electrode distance is that, low inter-electrode distances result in an electric field with high potential gradient and low resistance to motion of ions. This results in a faster formation of aluminum hydroxide $Al(OH)_3$ and $Fe(OH)_3$ species and in faster collision of electrode cations with that of the pollutants in the solution.
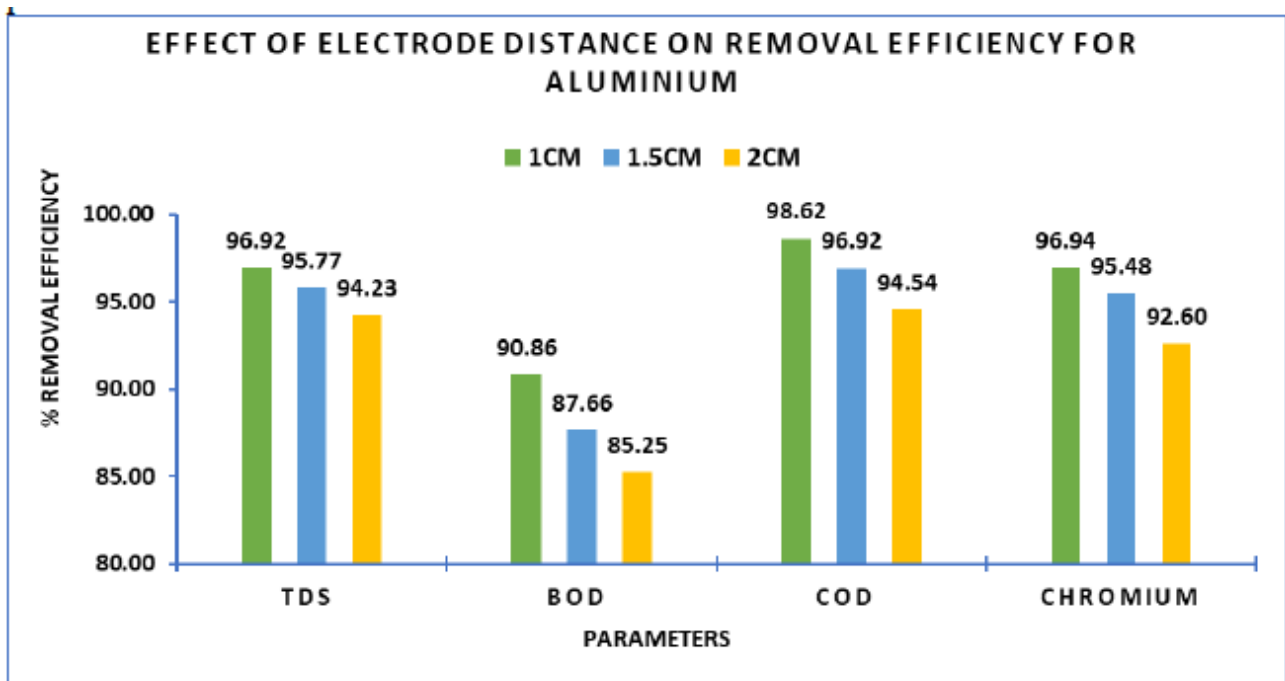
Figure 3.7 Effect of Electrode Distance on Removal Efficiency for Aluminium Electrodes
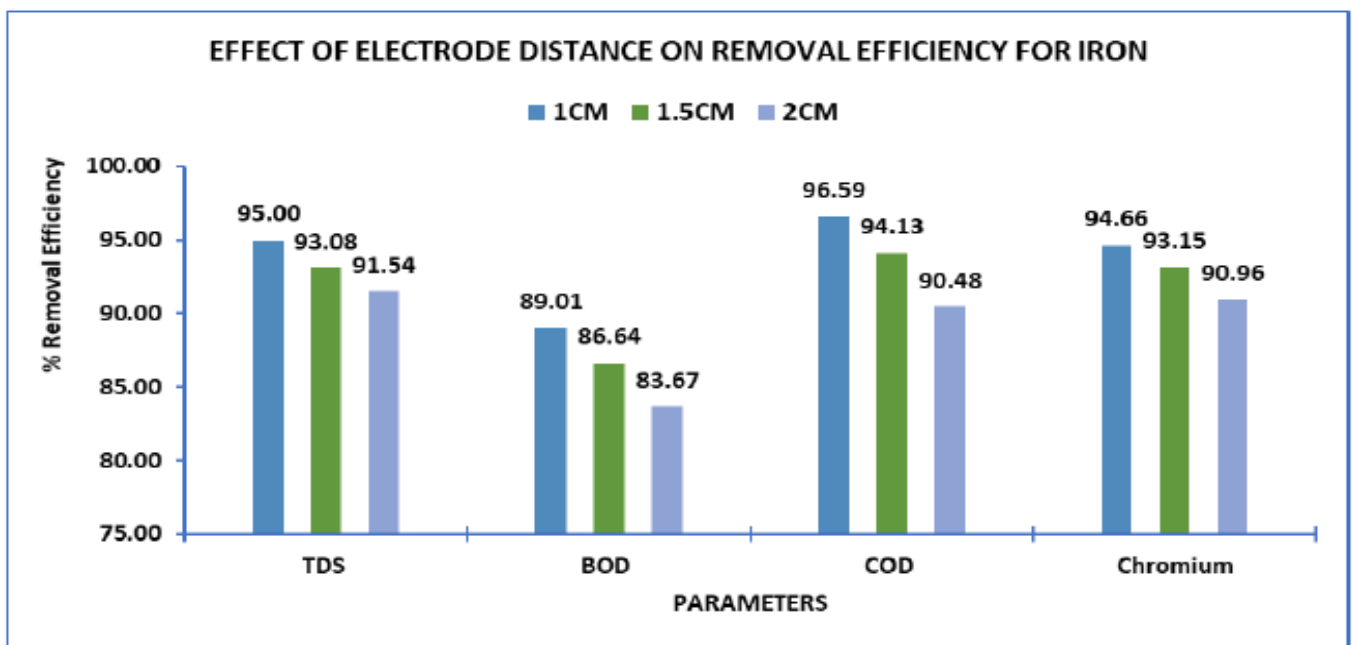

Figure 3.8 Effect of Electrode Distance on Removal Efficiency for Iron Electrodes

3.5 Effects of Electrode Shape on Removal Efficiency

The Figure 3.9 and 3.10 were plotted to study the effect of electrode shape on removal efficiencies of TDS, BOD, COD and Chromium. It was observed that for plane aluminium and iron electrodes, 96.21% 94.77% of COD removal efficiency was found respectively. For punched aluminium and iron electrodes, 98.62% 96.59% of COD removal efficiency was found respectively. The shape of the electrodes affects the performance of the electrocoagulation. The punched electrodes provide greater surface area than the plane, as the electron density would be highest at the sharp edges, more electron accumulate at the holes and edges. These electrons carry more current and subsequently more reaction occur in the solution results in higher efficiency.

The electric field intensity at the edge of punched holes type electrodes is higher than at plane type electrode resulting in an increase in the discharge current at punched type electrode. Electric field intensity at the edge of punched holes type electrodes is higher (1.2 times) than at plane type electrode. More electron accumulate at the holes and edges, these electrons carry more current and subsequently more reactions occur in the solution results in higher efficiency thus, resulting in an increase in the discharge current at punched type electrodes.
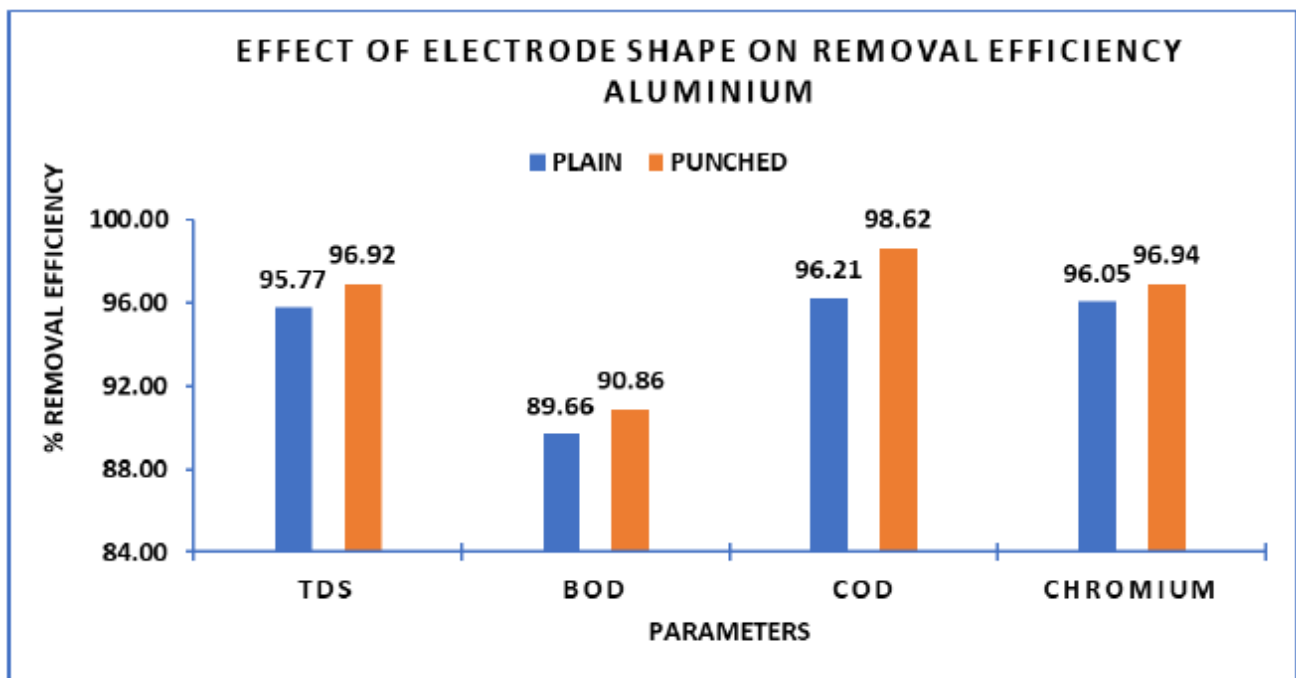
EFFECT OF ELECTRODE SHAPE ON REMOVAL EFFICIENCY ALUMINIUM

■ PLAIN ■ PUNCHED

Parameter	PLAIN	PUNCHED
TDS	95.77	96.92
BOD	89.66	90.86
COD	96.21	98.62
CHROMIUM	96.05	96.94

Figure 3.9 Effect of Electrode Shape on Removal Efficiency for Aluminium Electrodes

EFFECT OF ELECTRODE SHAPE ON REMOVAL EFFICIENCY IRON

■ PLAIN ■ PUNCHED

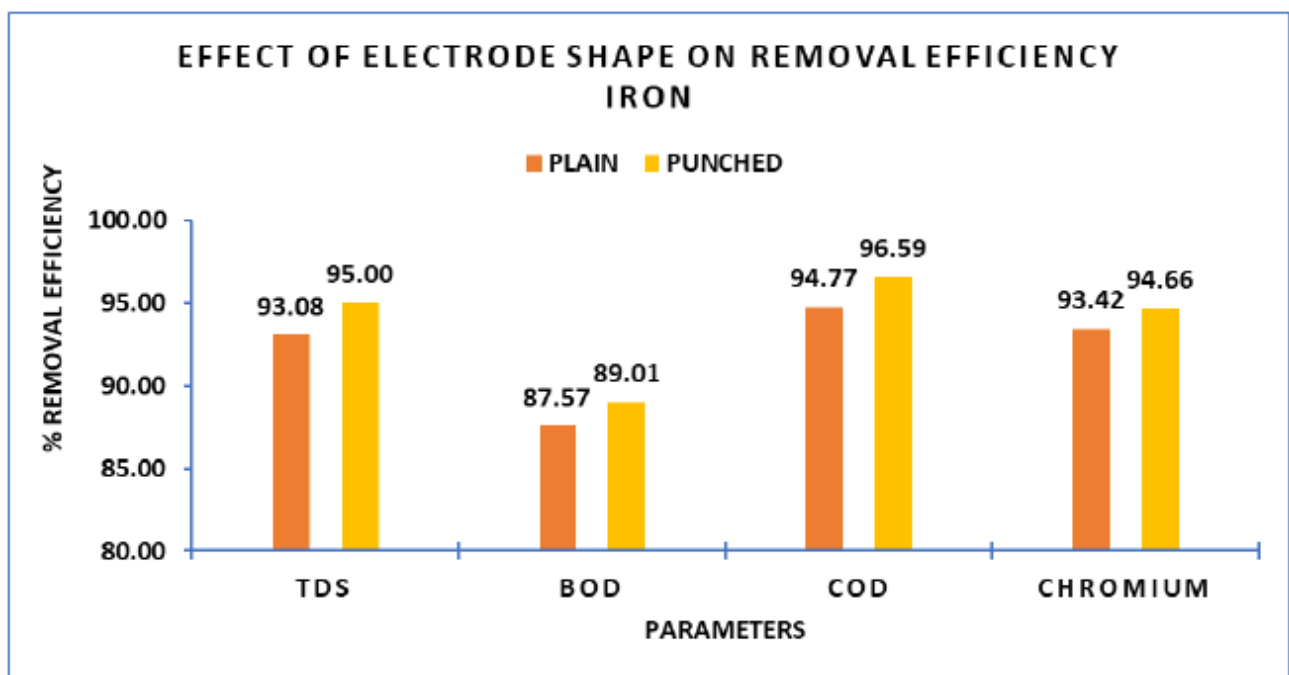| Parameter	PLAIN	PUNCHED
TDS	93.08	95.00
BOD	87.57	89.01
COD	94.77	96.59
CHROMIUM	93.42	94.66

Figure 3.10 Effect of Electrode shape on Removal Efficiency for Iron Electrodes

3.6 Effects of Electrode Material on Removal Efficiency

The Figure 3.11 represents the graph plotted to study the effect of electrode material in removal efficiencies of various parameters such as TDS, BOD, COD and Chromium. The graphs reveal that all the parameters show highest removal efficiency for aluminum electrodes compared to iron.

The electrode material has a significant effect on the removal efficiency of the pollutants. The better performance of aluminum electrodes in comparison to iron is because iron hydroxides are relatively inefficient coagulants compared to aluminum hydroxides coupled to a higher faradaic yield with aluminum electrodes.
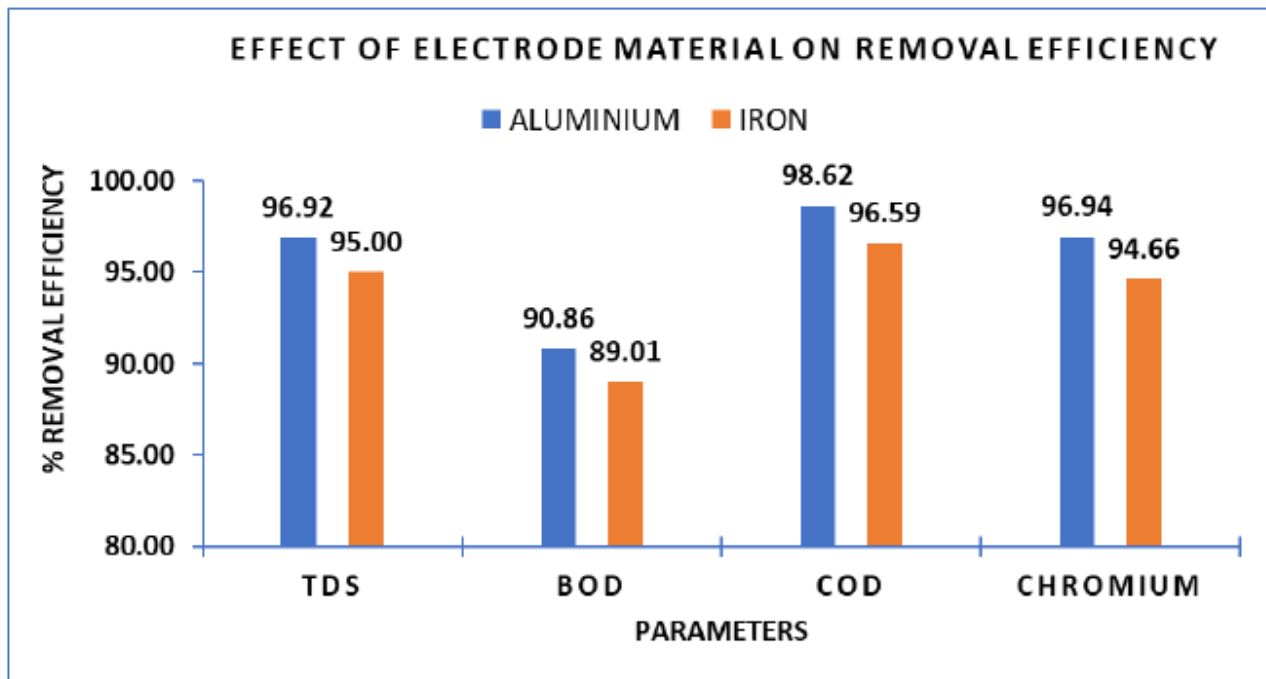
Figure 3.11 Effect of Electrode Material on Removal Efficiency

IV.   CONCLUSIONS

Based on the above finding the following conclusion are drawn

- The optimum condition for the removal of TDS, BOD, COD and Chromium from the tannery wastewater using aluminium and iron electrode was found to be at pH of 8, voltage 20V, electrolysis time 90min, electrode distance of 1cm for punched electrodes.

- It was observed that, the removal efficiency of all the parameters increased with increase in the pH of the solution, time, voltage. Whereas the efficiency increases with decrease in electrode distance for both aluminium and iron electrodes.

- Increase in pH was observed during the electrolysis process as the aluminium and iron electrodes get more dissolution. The alkaline pH of 8 is best suited for the maximum removal efficiency

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