



**DEVELOPMENT OF ELECTRO-CHEMICAL  
TREATMENT TO REMOVE THE TOTAL DISSOLVED  
SOLIDS AND ORGANIC CONTENT FROM  
KALEESUWARI REFINERIES SURFACE WATER**

**A PROJECT REPORT**

*Submitted by*

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*in partial fulfillment for the award of the degree of*

**BACHELOR OF TECHNOLOGY**

*in*

**CHEMICAL ENGINEERING**

**SRI VENKATESWARA COLLEGE OF ENGINEERING**

**(An Autonomous Institution; Affiliated to Anna University, Chennai -600 025)**

**ANNA UNIVERSITY :: CHENNAI 600 025**

**MAY 2020**

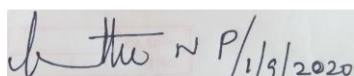
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**BONAFIDE CERTIFICATE**

Certified that this project report **“DEVELOPMENT OF ELECTROCHEMICAL TREATMENT TO REMOVE TOTAL DISSOLVED SOLIDS FROM KALEESUWARI REFINERIES SURFACE WATER”** is the bonafide work of **“YESWANTHKUMAR J, NITHEESH T. R., VAITHIYANATHAN P”** who carried out the project work under my supervision.



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**TO WHOM IT MAY CONCERN**

It is to certify that **Mr. Yeswanthkumar J , Mr. Nitheesh T.R. , Mr. Vaithiyanatham .P B.Tech**, Chemical Engineering, Sri Venkateswara College of Engineering have undergone project entitled “Development of Electrochemical treatment to remove total dissolved solids from Kaleesuwari refineries surface water” in the Department of Chemical Engineering, A.C Tech , Anna University , Chennai – 600025 from 02-01-2020 to 10-03-2020.

## LETTER OF CONSENT



23<sup>rd</sup> January 2020

To,

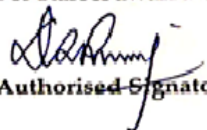
Head of Department,  
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This is to confirm that the following students from your college are permitted to do their B. Tech Chemical Engineering. Final Year Project work with effect from 23<sup>rd</sup> January 2020 to 30<sup>th</sup> April 2020 in our Organization under our guidance and support.

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Yours faithfully,

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## **ABSTRACT**

Water is the key component in several industrial operations like washing, heat transfer operations, steam generation etc... The quality of the water used, has adverse effects such as reduction in heat transfer rates, increase scale deposits, increase heat losses thereby reducing the boiler efficiency in steam generation and heat transfer operations. Among the various water treatment processes, Electrochemical technology has attracted much attention for its environmental compatibility, high removal efficiency, potential cost effectiveness and flexible in case of fluctuating waste water streams. The **KALEESUWARI REFINERIES LTD.**, uses multi-stage RO system to remove the dissolved solids from their surface water which used for steam generation in boiler. They have planned to implement other feasible techniques for further optimised system by reducing the number of stages without affecting the required water parameters to reduce the operating cost in purification process. Thus our research is to work on feasible electrochemical methods and to find the more optimised method for reducing the TDS, COD in the water used in the industry without affecting their quality requirements.

## ACKNOWLEDGEMENT

In the accomplishment of this project successfully, many people have bestowed upon us their blessings and the heart pledged support, this time we were utilizing to thank all the people who have been concerned with this project.

We would like to thank our college, Sri Venkateswara College of Engineering , Sri Kaleesuwari Refineries Ltd., and Anna University (AC Tech campus) for providing us all the facility that were required for the completion of project.

Practical knowledge on industries accounts more in learning process, on such a way we express our sincere thanks to **Sri Kaleesuwari Refineries Ltd.**, which offered us this project to enhance our knowledge in the field.

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We express our sincere thanks to **Dr. N. Balasubramanian (Professor, Chemical Engineering Department, AC Tech Campus, Anna University)** for his valuable attention to our work and insightful comments, which incited us to widen our research from various perspectives.

We wish to express our heartfelt thanks to our project coordinators **Dr. Nalinkanth V Ghone (Professor, Chemical Engineering Department, Sri**

**Venkateswara College of Engineering)** and **Dr. M. Yogesh Kumar (Associate Professor, Chemical Engineering Department, SVCE)** for their constructive criticism which helped us to make our project a remarkable success.

We feel to acknowledge our indebtedness and deep sense of gratitude to our supervisor **Dr. N.P. Kavitha (Assistant Professor, Department of Chemical Engineering, SVCE)** whose valuable guidance and kind supervision given to us throughout the course which shaped the present work as its show.

We would like to thank the research scholars of Electrochemical Engineering Laboratory in AC Tech Campus who have been there for us during the progress of the project.

Laboratory work can be a challenging task, but we were lucky to have our Chemical Engineering Department supporting staffs, who guided and instructed us patiently throughout this research work. Without their help with experiments and analytical equipment it would not have been possible to get the results presented here.

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## LIST OF SYMBOLS AND ABBREVIATION

EF	:	Electro-Fenton
EO	:	Electro-Oxidation
EC	:	Electrocoagulation
AOPs	:	Advanced oxidation process
Ppm	:	Parts per million
LPH	:	Litre per hour
TSS	:	Total Dissolved Solids
TDS	:	Total Suspended Solids
TS	:	Total Solids
COD	:	Chemical Oxygen Demand
BOD	:	Biological Oxygen Demand
UV	:	Ultraviolet Visible spectroscopy
GC	:	Gas Chromatography
DO	:	Dissolved oxygen
D <sub>0</sub>	:	DO in the diluted solution after preparation
D <sub>5</sub>	:	DO in the diluted solution after 5 days of incubation
B <sub>0</sub>	:	DO in the diluted seed sample after preparation
B <sub>5</sub>	:	DO in the diluted seed sample after 5 days of incubation
P	:	Decimal dilution factor
FAS	:	Ferrous ammonium sulphate
b	:	Volume of FAS consumed by blank sample
s	:	Volume of FAS consumed by given sample
N	:	Normality of FAS solution
rpm	:	Rotations per minute
OH <sup>-</sup>	:	Hydroxyl radicals

RO	:	Reverse Osmosis
CO <sub>2</sub>	:	Carbon di-oxide
Fe	:	Iron
Al	:	Aluminium
Am <sup>-2</sup>	:	Current density
mg L <sup>-1</sup>	:	milligram per litre
O <sub>3</sub>	:	Ozone

# **CHAPTER 1**

## **INTRODUCTION**

### **1.1 GENERAL**

Water is widely used in industry for various purposes such as heat exchange operations, steam generation , injection, washing etc. Impurities in water is due to the suspended and dissolved solids, chemical oxygen demand, biological oxygen demand present in it. Total dissolved solids is the total concentration of dissolved substances in water. The inorganic salts that are commonly found in water includes calcium, magnesium, potassium and sodium, which are all cations, and carbonates, nitrates, bicarbonates, chlorides and sulfates. Thus, this kind of water must be treated before entering the process to ensure its quality and properties to meet the specifications demanded by the industrial process. Total Dissolved Solids (TDS) are the impurities in boiler feed water that reduces the heat transfer rates, increase scale deposits, increase heat losses thereby reducing the boiler efficiency. As Boiler generates steam, any impurities which are in the boiler feed water and which do not boil off with the steam will concentrate in the boiler water. These solids will accumulate at control valves, heat exchangers and steam traps and causes water hardness, scale formation and staining. Careful control of TDS level together with attention to these other factors can ensure that the risks of foaming and carryover are minimized. The **KALEESUWARI REFINERIES LTD.**, uses multi-stage RO system to remove the dissolved solids from their surface water which used for steam generation in boiler. They have planned to implement other techniques for further optimised system by reducing the multi-stage RO system to double stage without affecting the required water parameters to reduce the operating cost in purification process. Thus our work is

to reduce the fouling inside the pipelines, boiler, heat exchangers by reducing the TDS, COD in the water used by the industry.

## **1.2 ELECTROCHEMICAL TREATMENT**

There are various methods to remove the TDS such as reverse osmosis, distillation, deionisation, electrochemical treatment. Reverse osmosis is one of the finest methods to remove TDS but it generates a waste stream which contains almost 15-25% of the feed flow with high salt concentration. Even this waste stream can be purified by electrochemical treatment and also electrochemical methods are cheaper compared to other processes. Industrial electrochemistry has undergone development towards cleaner processes and more environmentally friendly products, which is one of the strategies for purification of water and waste water. From the viewpoint of high efficiency and low resource consumption, **electrochemical technologies** can be used either as a pre-treatment step to increase the biodegradability of a pollutant or as an advanced treatment method further to reduce COD, TDS, colour in the water to achieve relevant effluent standards. Thus we planned to analyse their sample with the electrochemical methods namely electro-fenton, electro-oxidation, electrocoagulation and ozonation and to find the cost efficient method (Yujie et al., 2016).

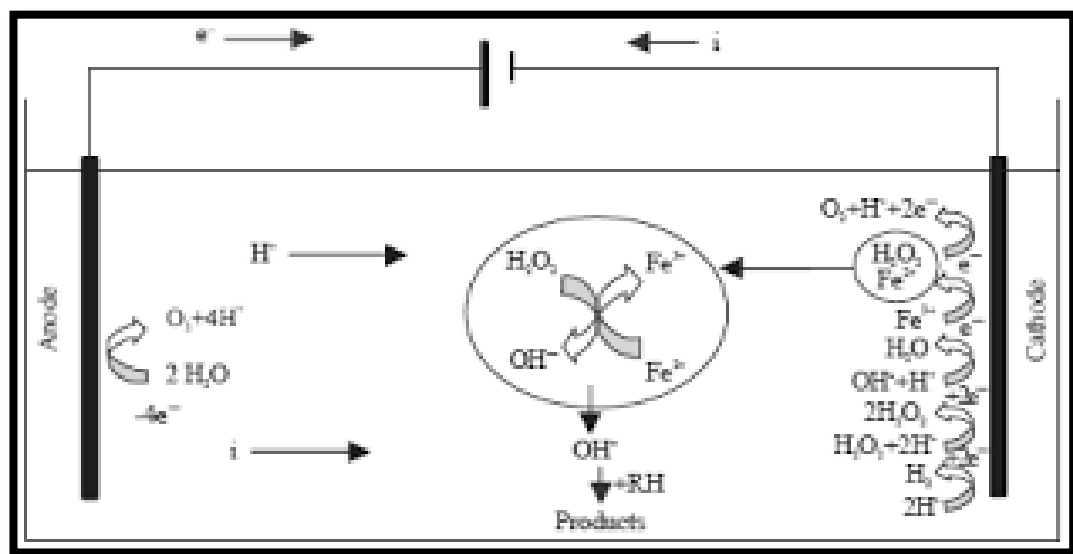
### **1.2.1 ELECTRO-FENTON**

In AOPs, oxidation using Fenton's reagent is one of the best effective, alternative, powerful and environmental friendly technique, this method is used for the degradation of a large number of hazardous and organic pollutants. Fenton reagent first named as fenton chemistry, fenton chemistry is the oxidation of organic substrate by Iron (II) and hydrogen peroxide.

EAOPs are eco – friendly methods and recent days it received more attention for water remediation. Electro – Fenton is the most popular process in EAOPs,



Electro – Fenton process is a promising technology for wastewater treatment process and its more economical, efficient, and environmental friendly for treatment and removal of organic matter compared to conventional technologies. This technology based on the continuous electro generation of  $\text{H}_2\text{O}_2$  at a suitable cathode by the reduction of dissolved oxygen or air along with the addition of an iron catalyst to the treated solution to produce oxidant (Pushpalatha et al,2017).



**Fig 1.2.1** Schematic representation of Electrofenton mechanism

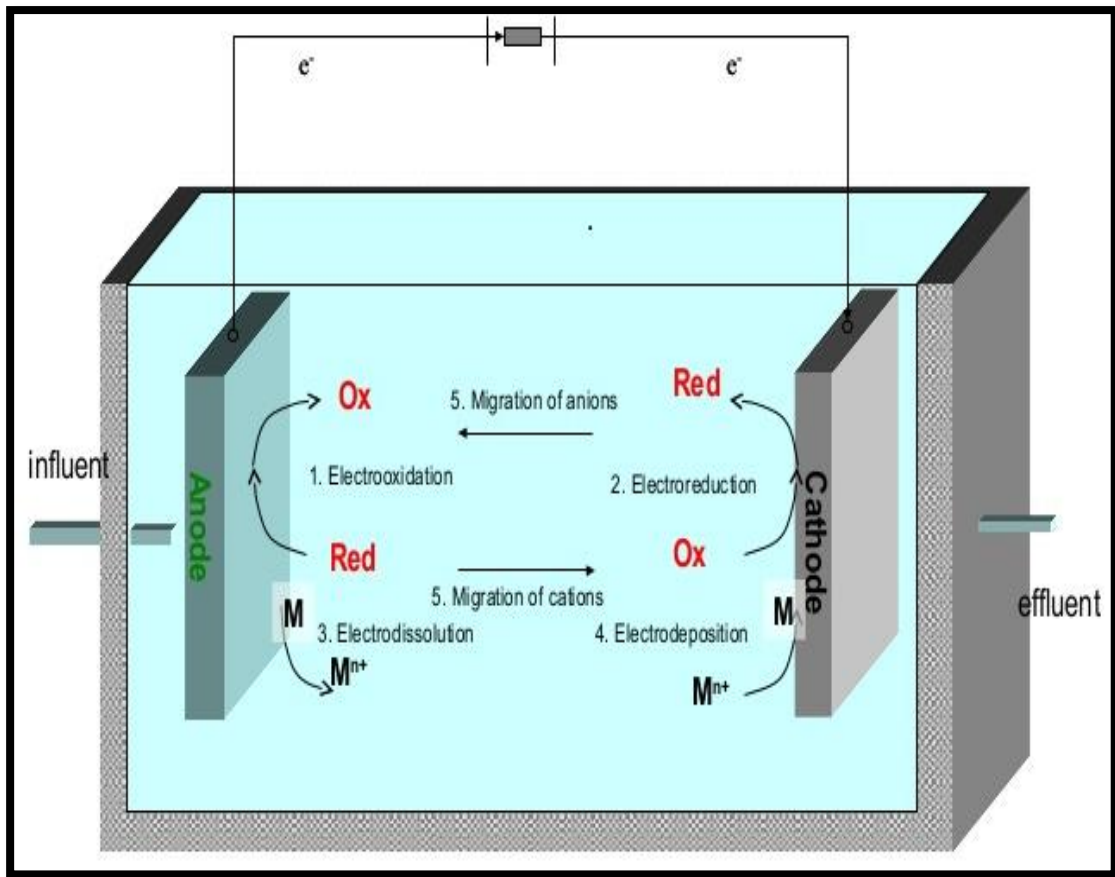
Electro – Fenton process solves some problems generated from conventional Fenton process, for example degradation of organic pollutants increase because of the continuous regeneration of  $\text{Fe}^{2+}$  at the cathode and  $\text{H}_2\text{O}_2$  is produce at onsite so that it avoids storage and transport problems. Electro-Fenton process includes

both electrochemical and Fenton treatment methods and each method are powerful and effective method for the treatment process (Huanqi He et al,2017). In electrofenton process, the pollutant removal is effective on pH 4 as the production of hydroxy radicals  $\text{OH}^\cdot$  is effective.

### **1.2.2 ELECTRO-OXIDATION**

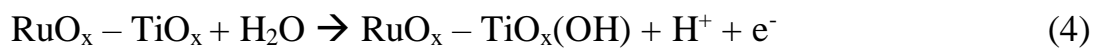
Electro-oxidation (EO), also known as anodic oxidation, is a technique used for wastewater treatment, mainly for industrial effluents, and is a type of advanced oxidation process (AOP). The most general layout comprises two electrodes operating as anode and cathode, connected to a power source. When an energy input and sufficient supporting electrode are provided to the system, strong oxidizing species are formed, which interact with the contaminants and degrade them. The refractory compounds are thus converted into reaction intermediates and, ultimately, into water and  $\text{CO}_2$  by complete mineralization (Mohan et al, 2007).

Electro-oxidation has recently grown in popularity thanks to its ease of set-up and effectiveness in treating harmful and recalcitrant organic pollutants, which are typically difficult to degrade with conventional wastewater remediation processes. Also, it does not require any external addition of chemicals (contrarily to other processes like in-situ chemical oxidation), as the required reactive species are generated at the anode surface.



**Fig 1.2.2** Schematic representation of Electro-oxidation mechanism

The reaction mechanism is as follows,

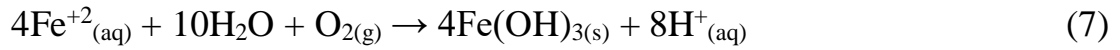


Electro-oxidation has been applied to treat a wide variety of harmful and non-biodegradable contaminants, including aromatics, pesticides, drugs and dyes. Due to its relatively high operating costs, it is often combined with other technologies, such as biological remediation (Yusuf *et al*, 2006).

### 1.2.3 ELECTROCOAGULATION

The electrocoagulation process operates on the principle that the cations produced electrolytically from iron and/or aluminum anodes which is responsible for the increasing of the coagulation of contaminants from an aqueous medium. Electrocoagulation operating conditions are mostly dependent on the chemistry of the aqueous medium, mainly conductivity and pH. Also other important characteristics are particle size, type of electrodes, retention time between plate, plate spacing and chemical constituent concentrations. The mainly operating principal is that the cations produced electrolytic from iron and/ or aluminium anodes enhance the coagulation of contaminants from an aqueous medium (Satish *et al*,2013). Electrophoretic motion tends to concentrate negatively charged particles in the region of the anode and positively charged particles in the region of the cathode. The consumable metal anodes are used to continuously produce polyvalent metal cations in the region of the anode. These cations neutralize the negative charge of the particles moved towards the anodes by production of polyvalent cations from the oxidation of the sacrificial anodes (Fe and Al) and the electrolysis gases like Hydrogen evolved at the anode and oxygen evolved at the cathode (Siddharth *et al*,2019). When current is passed through electrochemical reactor, it must overcome the equilibrium potential difference, anode over potential, cathode over potential and potential drop of the solution. The anode over potential includes the activation over potential and concentration potential, as well as the possible passive over potential resulted from the passive film at the anode surface, while the cathode over potential is principally composed of the activation over potential and concentration over potential. Generally, aluminium and iron are used as an electrode material in the electrocoagulation process (Shiv *et al*,2013). In case of iron as anode,

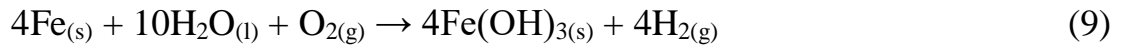
Anode:



Cathode:



Overall:

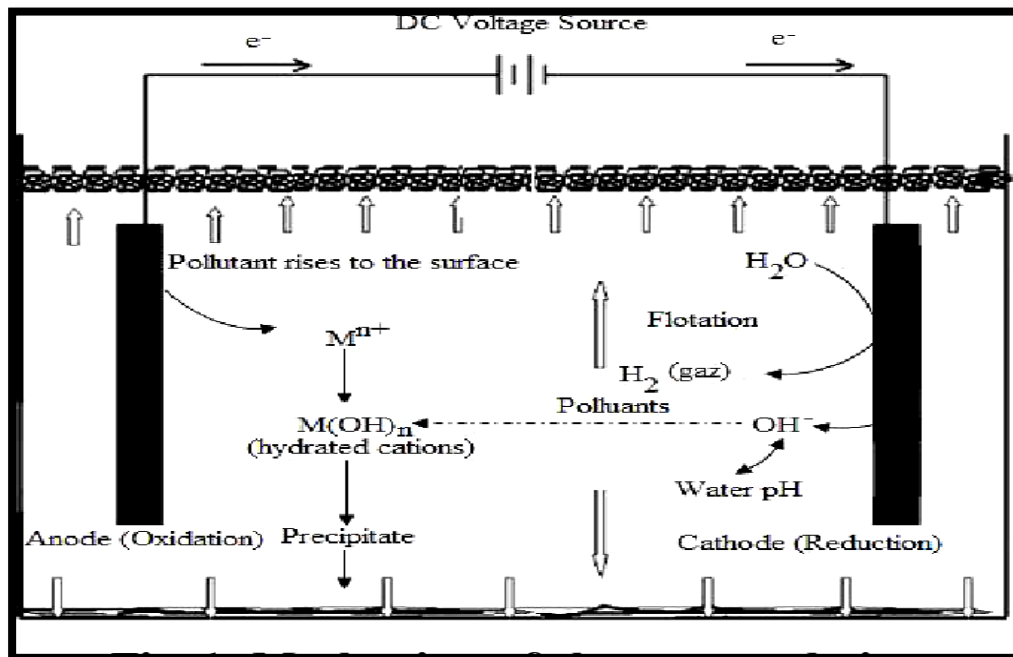


In case of aluminium as anode,

Anode:



Cathode:



**Fig 1.2.3** Schematic representation of Electrocoagulation mechanism

For the aluminium electrodes,  $\text{Al}^{3+}_{(\text{aq})}$  ions will immediately undergo further spontaneous reaction to generate corresponding hydroxides and polyhydroxides. Due to hydrolysis of  $\text{Al}^{3+}$ ,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Al}(\text{H}_2\text{O})(\text{OH})^{2+}$  generated. This hydrolysis products produced many monomeric and polymeric substance such as,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}(\text{OH})^{4+}$ ,  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  (Satish *et al*, 2013).

#### 1.2.4 OZONATION

Ozone is a form of oxygen ( $\text{O}_2$ ) with the molecular formula  $\text{O}_3$ . It forms when oxygen in the air is exposed to the discharge of a powerful electric current through air. In nature, it forms in the upper atmosphere when lightning passes through the air (Aji *et al*, 2019). Ozone oxidizes the iron, manganese, and sulfur in the water to form insoluble metal oxides or elemental sulfur. These insoluble particles are then removed by post-filtration. Organic particles and chemicals will be eliminated through either coagulation or chemical oxidation. Ozone is effective over a wide pH range and rapidly reacts with bacteria, viruses, and protozoans and has stronger germicidal properties than chlorination and also has a very strong oxidizing power with a short reaction time. The treatment process does not add chemicals to the water. Ozone can eliminate a wide variety of inorganic, organic and microbiological problems and taste and odor problems (Jefferson *et al*, 2019). The microbiological agents include bacteria, viruses, and protozoans.

#### 1.3 PROBLEM STATEMENT

The **KALEESUWARI REFINERIES LTD.**, uses multi-stage RO system to remove the dissolved solids from their surface water which used for steam generation in boiler. They have planned to implement other techniques for further optimised system by reducing the number of stages without affecting the required water parameters to reduce the operating cost in purification process. Thus our work is to work on other feasible methods and to find the more optimised method for reducing the TDS, COD in the water used in the industry without affecting

their quality requirements. Electrochemical technology has attracted much attention for its environmental compatibility, high removal efficiency, potential cost effectiveness and flexible in case of fluctuating waste water streams. Thus, we have decided to work on the electrochemical methods such as electro-fenton, electro-oxidation and electrocoagulation.

## CHAPTER 2

### 2.1 LITERATURE REVIEW

Many authors have conducted various electrochemical treatments on water to remove the organic pollutants. Some of them are listed below

**Kobyia *et al.* (2011)** have proposed the removal of arsenic from drinking water by electro-coagulation using Fe and Al electrodes. The electro-coagulation process was able to reduce the arsenic concentration to less than  $10\mu\text{gL}^{-1}$  and the reported optimum values of pH and current density for arsenic removal were 6.5 for Fe and 7 for Al and  $2.5\text{A m}^{-2}$ . The optimum operating time was 12.5min for Fe and 15min for Al. The operating costs at the optimum operating conditions were  $0.020\text{€m}^{-3}$  for Fe and  $0.017\text{€m}^{-3}$  for Al.

**Alaadin *et al.* (2011)** investigated the electro-coagulation treatment process for the removal of total suspended solids (TSS), biological oxygen demand (BOD) particulates from municipal water using stainless steel electrodes. The treatment was carried out in a capacity test beaker with stainless steel electrodes and two glass pyres tubes were also used as baffles for better stirring. The results concluded that the maximum removal efficiency 95.4% of total suspended solids occurred at 0.8A with a contact time of 5min. The highest BOD particulate removal was approximately 99% under the operating conditions 0.8A and 5min of contact.

**Rahman *et al.* (2012)** have proposed the electro-coagulation technique for the removal chemical oxygen demand (COD) using aluminum electrode. The experiments were performed in a two-electrode static electro-coagulation reactor with aluminum electrode. They reported that after several experiments the initial of COD of  $1050\text{ mg O}_2/\text{L}$  is reduced to  $166.67\text{ mg O}_2/\text{L}$  under sample pH itself.



Hence they have concluded that the maximum removal efficiency could be attained in the sample pH. The optimum internal electrode distance was found to be 2.5cm or 4cm under the operating conditions current density  $4\text{Acm}^{-2}$  and contact time 30min. The results presented allows us to believe that the electro-coagulation is cheaper and effective

**Abbas *et al.* (2019)** conducted experiment on the treatment of Saline water using electro-coagulation with combined electrical connections of electrode. The experiments were conducted in a batch reactor made of glass with upper cover of the reactor made of Plexiglas. The results concluded that the maximum removal of total dissolved solids (TDS),  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{SO}_4^{2-}$  were found to be 91%, 93%, 92% and 90% respectively. The achieved optimal conditions were current density  $2.0\text{mA/cm}^2$ , reaction time 80min, pH=8, temperature  $25^\circ\text{C}$ , inter electrode distance 1cm and stirrer speed 500rpm.

**Ahmed *et al.* (2008)** experimented the total dissolved solids removal by electrochemical ion exchange (EIX) process. This experiment was performed with Ruthenium oxide coated with titanium plates ( $\text{RuO}_2/\text{Ti}$ ) as anode and stainless steel as cathode. They were configured to remove both cations and anions from the system. They evaluated the removal of 3.25mM calcium chloride and calcium sulphate, and 2.6mM of magnesium sulfate at applied voltage of 5V and 7V and reported that 95% removal of cations and anions were observed at 5V within 7 hours of operation however 100% removal was achieved at 7.5V.

**Mohan *et al.* (2006)** experimented electrochemical oxidation of textile dye wastewater using  $\text{RuO}_2/\text{Ti}$  anode in batch electrochemical reactor. The authors reported more than 90% COD removal under optimum conditions pH 9, current density  $2\text{-}3\text{A/dm}^3$ . Later the authors (2007) attempted to reuse the electrochemically treated textile effluent for dyeing application and reported that

the electrochemically treated wastewater can be effectively reused for industrial application.

**Huanqi *et al.* (2017)** studied electro fenton process on water and waste water. The experiments were conducted in an electro fenton reactor under pH 2. They evaluated that the higher concentrations of  $\text{H}_2\text{O}_2$  could contribute in the increase of chemical oxygen demand (COD) values. They reported that 1 mg/L  $\text{H}_2\text{O}_2$  can contribute .27 mg/L COD. The COD removal efficiency rate was 89.2% at 250mA but the reduction value was dropped to 79.3% at 300mA. They observed that the electro fenton process was peak at current density 28.5mA/cm<sup>2</sup>. However higher current densities can show less removal time and higher degradation rate of COD up to a certain extent after that it tends to fall but there will be increase in energy consumption with decreased energy efficiency.

**Pushpalatha *et al.* (2008)** conducted fenton process on synthetic waste water. The set up consists of a Batch Plexiglas reactor with 1L capacity with iron and stainless steel plates as anode and cathode respectively to remove dissolved chromium in the aqueous solution. They reported that they have achieved 97% removal of dissolved chromium. The reactions were conducted at pH 2, Voltage 30V,  $\text{H}_2\text{O}_2$  50ml/L, time of reaction 25min.

**Aji *et al.* (2018)** studied the effects of pH and gas flow rate on ozone mass transfer. The experiments were conducted in a bubble column reactor. They reported that the effectiveness of ozonation process is affected by ozone gas mass transfer. Their research showed that the concentration of ozone is high at a flow rate of 4Lmin<sup>-1</sup> and at a pH ranging from 7-8.

**Faycal *et al.* (2017)** conducted a tertiary treatment process on waste water using electro fenton process. The experiment was conducted in a electrochemical cell consisting of two iron electrodes with 2cm gap and surface area of 28.5 cm<sup>2</sup> each. The report conveyed that COD removal efficiency of 75% and BOD

removal efficiency of 52% was obtained at pH 2.8. The report showed that the energy consumed for removing 1Kg of COD was 2.25KWh/kg COD after 180min and the treatment cost of 1m<sup>3</sup> of waste water was estimated to 17.331€/m<sup>3</sup>

**Umran *et al.* (2015)** treated waste water from paper mill using electro fenton process. The setup consists of a cylindrical iron reactor operated as cathode with 8 pedal blades acting as an anode and it was connected to a mechanical stirrer. They reported that the initial COD of 1200mg/L was reduced to 228mg/L with the removal efficiency of 81% at pH 2, current density 20mA/cm<sup>2</sup> with addition of 0.2M H<sub>2</sub>O<sub>2</sub>.

**Siddharth *et al.* (2019)** have designed a electro coagulation unit for the treatment of waste water from paper industry. The unit consists of two electrodes namely iron or aluminum as anode and stainless steel as cathode with 1.5cm apart of size 13mm x 80mm. Those electrodes were attached to rotor. The results showed that the removal efficiencies of 95% for color, 100% for odor, 95% for TSS, 49% for TDS and 71% for COD. The optimum parameters were RPM of electrodes 42-45, voltage 12V, pH 7-8 and current density 41.95A/m<sup>2</sup>.

**Yusuf *et al.* (2005)** experimented electrochemical oxidation of phenol in parallel plate reactor using ruthenium mixed metal oxide electrode. The process was conducted in a parallel plate reactor consisting of four compartments of volume 270ml each. Ruthenium treated titanium electrodes of size 3cm x 4cm was used as an anode. The report revealed that removal efficiency of 99.7% and 88.9% were achieved for the initial concentration of phenol of 200mg/L and COD of 480mg/L, under the operating conditions current density 15mA/cm<sup>2</sup>, pH same as the sample pH.

**Chaohai *et al.* (2016)** published an article regarding ozonation in water treatment. It conveyed that ozonation can disinfect microbes, bacteria, fungal

spores and antibiotic resistance genes. It can also reduce dissolved organic carbon levels in water streams, conventional chlorinated DPBs could be inhibited, and the non-biodegradable organic compounds in cooking waste water could be eliminated.

**Jefferson *et al.* (2016)** have conducted experiments in removing cyanide from waste water using ozonation techniques. The reports showed that the concentration of cyanide ions was reduced to 0.08mg/L from 400mg/L. The removal of 99.98% was achieved at pH=11 and addition of 10 mgH<sub>2</sub>O<sub>2</sub>/mgO<sub>3</sub>. The report also revealed that the reduction levels of COD and TOC were found to be 82.2% and 76.11% respectively.

**Shiv *et al.* (2013)** have researched on removal of chromium ions from electroplating industry effluent using electro coagulation process. The experiments were performed in a batch reactor of 300ml with iron as electrodes of sizes 120 x 32 x 1.5mm (length x breadth x thickness) and a magnetic stirrer. The results showed that 100% removal efficiency of Cr(IV) ions were obtained for an electrolysis time of 15min at a pH 4. However 100% removal of both Cr(III) and Cr(IV) ions were achieved at 45min. The optimum parameters reported are inter distance between the electrode 1.5cm, stirrer speed 200rpm, current density 100mA/cm<sup>2</sup> and electrolysis time 25min.

**Reza *et al.* (2018)** treated waste water from edible oil plant using electro fenton process. The experiments were conducted based on the standard apparatus as shown in literature (Davarnejad *et al.* (2014)). The results showed that the COD removal efficiency of 62.94% was achieved by reducing 822mg/L COD to 304.63mg/L at pH 3.03, current density 57mA/cm<sup>2</sup>, operating time of 87.33min and by adding 3.61M of H<sub>2</sub> O<sub>2</sub>/M of Fe<sup>2+</sup>.

**Saad *et al.* (2018)** investigated the performance of electro coagulation technique on the removal of TOC, TDS and turbidity from the surface water.

They studied the removal efficiencies of both aluminium and iron electrodes in a batch reactor. The reports concluded that removal efficiencies of aluminium electrode were 74%, 99.10%, 84% and for iron electrode the results were 64.8%, 98.3%, 78% for TOC, turbidity, TDS respectively.

**Rusdianasari *et al.* (2019)** studied the effectiveness of electro coagulation method in processing integrated waste water using stainless steel and aluminium electrodes. The experiments were performed in a electrolytic cell with two electrodes and a magnetic stirrer. They reported the removal efficiencies of 87.96% for COD, 52.98% for TSS, 88.96% for TDS using aluminium electrodes at 12V after 150min. And for iron electrodes the values were 88.43%, 57.5% and 80.27% for COD, TSS and TDS removal respectively after 150min. Based on the reports the current efficiency was about 78.91% for aluminium electrode and 81.25% for iron electrode.

## **2.2 OBJECTIVES**

### **2.2.1 MAIN OBJECTIVE**

- Development of an electrochemical pre-treatment method to remove the total dissolved solids and organic content from Kaleesuwari Refineries surface water.

### **2.2.2 SUB-OBJECTIVE**

- Optimisation of observed results of Electrofenton, Electrocoagulation, Electro-oxidation, ozonation.

## CHAPTER 3

### MATERIALS AND METHODOLOGY

#### 3.1 MATERIALS USED

The sample water to be treated was collected from the KALEESUWARI REFINERIES, which they use for steam generation. DC power supply (METRONICS-305A) was used for supplying power to the electrodes in the electrochemical setup. Magnetic stirrer (Remi Private limited) was used to stir the sample during the process. A COD digester was used to carry out reaction between the reagents at specific temperature in COD process. Four stoppered glass were used for BOD process. A pH meter was used to measure and change the pH of the sample as needed. Whatman filter paper NO.1 was used separate the suspended solids and the filtrate of the sample for TDS and TSS measurement. A hot air oven was used to dry the filter paper with suspended solids. An aerator 0.25LPH was used to supply oxygen production for the survival of microbes in the sample. An ozone generator of capacity 0-10 LPH used to produce ozone for ozonation process. Electrodes used were stainless steel as cathode and mild steel as anode for electrofenton process, stainless steel as cathode and aluminium/mild steel as anode for electrocoagulation process, ruthenium based titanium oxide for electro-oxidation process. All the chemicals used were hydrogen peroxide( $\text{H}_2\text{O}_2$ ), calcium chloride( $\text{CaCl}_2$ ), magnesium sulphate( $\text{MgSO}_4$ ), ferric chloride( $\text{FeCl}_3$ ), manganese sulphate( $\text{MnSO}_4$ ), ferrous ammonium sulphate (FAS), phenolphthalein. A digital TDS meter was used to measure the total dissolved solids. UV spectroscopy and Gas chromatography analysis were performed using the instruments (Thermo Scientific GENESYS 10S Vis & Thermo scientific TRACE 1300) to find the different chemicals present in the samples.

## **3.2 METHODOLOGY**

Water quality is generally measured in terms of Total solids [Total suspended solids + Total dissolved solids] , Chemical oxygen demand, Biological oxygen demand. The procedures to measure these parameters are as follows.

### **3.2.1 TOTAL SUSPENDED SOLIDS [TSS]**

Total suspended solids are the dry weight of suspended particles that are not dissolved in a sample of water that can be trapped by a filter using a filtration apparatus. TSS was measured by using the following procedure , The sample was collected in a HDPE 1L container and vacuum pump was connected to the side arm of the vacuum flask. The filter holder was placed on the top of the vacuum flask or a manifold could be used for increased number of simultaneous samples and higher efficiency. A Whattman filter paper was placed on the top of the filter holder. The wet filter paper was secured and seated and the funnel was secured to the base. The sample was filtered to the maximum within 10 mins using a suction vacuum pump and the pan along with initial weight from the label was noted. After completing filtration the paper was removed from the holder and kept in a oven set at  $104 \pm 1^{\circ}\text{C}$  for one hour. The filter paper was placed in a desiccator until they reached room temperature. The filter paper was weighed along with sample over it and TSS was calculated.

TSS can be calculated using the formula:

$$\text{TSS} = [(\text{dry weight of residue and filter}) - (\text{dry weight of filter medium})] / (1)$$

**Volume of sample**

### 3.2.2 TOTAL DISSOLVED SOLIDS [TDS]

Total dissolved solids represents the total concentration of dissolved solids includes all inorganic and organic substances present in a sample. Water quality levels can be tested using digital TDS ppm meter. The two principal methods of measuring TDS are Gravimetric analysis and conductivity. Gravimetric methods are the most accurate one which involves evaporating the filtrate and measuring the remaining mass of the residues left. Initial weight of a glass crucible was noted. The filtrate was collected in the glass crucible and kept in a furnace which was maintained at a temperature about 100-110°C. The final weight of the crucible after taken out from the furnace was noted. Difference between the initial and final weight of the crucible gives the TDS present in the sample. Even though this method is time consuming it is being used frequently for determining TDS. TDS was calculated by the formula,

$$\text{TDS} = \frac{[\text{Final weight of the crucible} - \text{Initial weight of the crucible}]}{\text{Volume of sample}} \quad (2)$$

Volume of sample

### 3.2.3 TOTAL SOLIDS [TS]

Total solids refers to the solids present in terms of both suspended and dissolved state. Total suspended solids refers to the suspended solids such as sand stones, macro particles, etc.. Total dissolved solids refers to the total concentration of dissolved substances in water. Total solids can be calculated as the sum of total suspended solids and total dissolved solids measured in the given sample.

$$\text{TS} = \text{total suspended solids}[\text{TSS}] + \text{total dissolved solids}[\text{TDS}] \quad (3)$$

### 3.2.4 BIOLOGICAL OXYGEN DEMAND [BOD]

BOD is the amount of dissolved oxygen needed by the aerobic biological organisms to break down organic material present in a given water sample at



certain temperature over a specific time period. The BOD value is mostly expressed in milligrams of oxygen consumed per litre of sample during 5 days of incubation at 20°C. Four 300mL glass stoppered BOD bottles were taken (two for the sample and two for the blank). 10mL of the sample were added to each of the two BOD bottles and the remaining quantity were filled with the dilution water without forming any air bubbles i.e. we have diluted the sample 30 times. 2ml of manganese sulfate was added to the BOD bottle carefully by inserting the pipette just below the surface of water. So that the formation of air bubbles can be avoided. 2 mL of alkali-iodide-azide reagent was added in the same manner. The bottle was closed and the sample was mixed by inverting many times. A brownish cloud was appeared in the solution as an indicator of the presence of Oxygen. The brown precipitate was allowed to settle out to the bottom. 2ml of Conc.H<sub>2</sub>SO<sub>4</sub> was added carefully without forming air bubbles. The bottle was closed and the solution was mixed well to dissolve the precipitate. The bottle was kept in BOD incubator at 20°C for 5 days of incubation. After incubation, the sample water was titrated with Sodium thiosulphate to a pale yellow color. Then 2ml of starch solution was added. So the sample turned blue in color. The titration was continued till the sample gets clear and the readings were noted. The concentration of dissolved oxygen in the sample was equivalent to the number of milliliters of titrant used. The same procedure was repeated for concordant values. The following formulae were used to calculate BOD:

$$\text{Unseeded BOD} = (D_0 - D_5) / P \quad (4)$$

$$\text{Seeded BOD} = [(D_0 - D_5) - (B_0 - B_5)F] / P \quad (5)$$

Where  $D_0$  is dissolved oxygen (DO) of the diluted solution after preparation (mg/L);  $D_5$  is the DO of the diluted solution after 5 days of incubation (mg/L);  $P$  is the decimal dilution factor;  $B_0$  is the DO of diluted seed sample after

preparation (mg/L);  $B_5$  is the DO of diluted seed sample after 5 days of incubation(mg/L);  $F$  is the ratio of seed volume in dilution solution to seed volume in BOD test onseed.

### 3.2.5 CHEMICAL OXYGEN DEMAND[COD]

COD is the measure of amount of oxygen that can be consumed by reactions in a measured solution. It is expressed in mass of oxygen consumed over volume of solution as (mg/L). The formula to calculate COD is

$$\text{COD} = \frac{8000 * (b - s) * N}{\text{Sample volume}} \quad (6)$$

where

$b$  is the volume of FAS consumed by blank

$s$  is the volume of FAS consumed by given sample

$N$  is the normality of FAS solution

A COD test can be used to quantify the amount of organics in water. 1.25 ml of the water sample was collected in a glass vial. COD acid is a mixture of silver sulphate and conc.sulphuric acid. 0.75 ml of potassium dichromate and 1.75 ml of COD acid were added in the same vial. The vial was closed and kept in the COD digester at temperature about 120°C for 2 hours. After 2 hours the vials were taken out and allowed to cool down to the room temperature. The cooled sample was titrated against ferrous ammonium sulphate(FAS) solution which was prepared by the ratio 3.98g of FAS in 100ml of water and 2ml of  $H_2SO_4$  using ferroin as indicator. The titration was stopped as the sample turned to reddish brown and the burette reading was noted.

**Table 3.2 Initial parameters of the Kaleesuwari refineries sample**

<b>SAMPLE</b>	<b>TDS</b>	<b>TSS</b>	<b>TS</b>	<b>COD</b>	<b>pH</b>
<b>1</b>	<b>2300</b>	<b>50</b>	<b>2350</b>	<b>640</b>	<b>7.5</b>
<b>2</b>	<b>2130</b>	<b>60</b>	<b>2190</b>	<b>576</b>	<b>7.2</b>

### **3.3 EXPERIMENTAL PROCEDURE**

On the basis of literature survey, we had planned to check out the electrochemical methods such as electrofenton, electro-oxidation, electrocoagulation and ozonation.

#### **3.3.1 ELECTROFENTON**

Electrofenton process is an advanced oxidation process which uses hydroxyl radicals[OH<sup>•</sup>] generated by the Fe-H<sub>2</sub>O<sub>2</sub> reaction to oxidize the organic and inorganic salts present in the sample. This method has the electrochemical setup of two cathodes(stainless steel), an anode(mild steel) separated at a distance of 1cm with the help of wooden clips was dipped in a 250ml beaker containing sample as electrolyte. The beaker and the electrodes were cleaned well to avoid contamination during the process. pH of the sample was measured and changed to pH 4 by adding respective acid/base. H<sub>2</sub>O<sub>2</sub> was added to the prepared sample solution in right proportion. Thus the sample solution along with the electrode setup was arranged in the beaker and the current supply to the electrodes was given with proper connections for 2 hours. For every time interval of 15 mins , 2ml of the reacted sample was collected for the TDS and COD measurement. The same procedure was repeated for different voltage supply and the optimized one was found out

### **3.3.2 ELECTRO-COAGULATION**

Electrocoagulation is one of the advanced oxidation processes in which the reduction of cathode hydrolyses the sample into hydrogen gas and hydroxyl groups. These hydroxyl groups neutralize the particulates by the formation of hydroxide complexes. As the reaction continues agglomerates are settled in the bottom which can be filtered. Thus, reducing the contaminants in the sample. This electrochemical setup consists of two electrodes namely iron / aluminium as an anode and stainless steel as a cathode with inter-electrode distance of 1cm, which is achieved with the help of wooden clips. This electrode system was dipped into a 250ml beaker containing sample as an electrolyte. The beaker and the electrodes were cleansed well to avoid contamination. The pH of the sample was tested and changed to 8 with the addition of respective acid and base,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . The electrochemical setup with a beaker and electrodes were connected to a DC supply for 2 hours. During the process, for every 2min the reacted sample was taken for the measurement of TDS and COD. This procedure was carried for different pH and current with iron as well as aluminium electrode to find the optimized one.

### **3.3.3 ELECTRO-OXIDATION**

Electro-oxidation is one of the advanced oxidation processes in which anodic oxidation is used to oxidize the dissolved organic and inorganic contaminants. This electrochemical cell consists of a stack cell with two Ruthenium coated Titanium oxide electrodes as anodes and one stainless steel electrode as cathode which is separated by a inter electrode distance of 1cm by wooden clips. This electrode system was dipped into the 250ml beaker holding sample as an electrolyte. The beaker and the stack cell were cleansed will in order to avoid contamination in the system. The pH of the sample measured and changed into 8 with the addition of respective acid and base,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . This setup was connected to a DC supply for 2 hours. For every 2min during the process the

reacted sample was taken for the measurement of TDS and COD. The same procedure was repeated with different pH and current to find the optimized parameters.

### **3.3.4 OZONATION**

In ozonation the most powerful oxidant ozone is infused into sample to disintegrate a wide range of microorganisms. In this process the ozone is produced with the use of energy by subjecting oxygen to high electric voltage. 100ml of sample was taken in a 250ml beaker which was cleansed to avoid contamination in the system. The pH of the sample was measured. And the ozone was infused into the sample at a flow rate of 4 LPH with proper working conditions. During the process, 2 ml of reacted sample was taken for every time interval of 15mins for 2 hours for the measurement of TDS and COD measurement. The same procedure was carried out for different pH and flow rates to find the optimized one.

## **3.4 CHARACTERIZATION TECHNIQUES**

### **3.4.1 Ultraviolet visible Spectroscopy (UV Spectroscopy)**

UV Spectroscopy refers to absorption or reflectance spectroscopy in part of the ultraviolet and full adjacent visible spectral regions, which means it, uses light in the visible region. The absorption in the visible range directly affects the perceived color of the chemicals involved. Using measurements of the whole UV Spectrum enables to monitor changes in wastewater concentration. With just one instrument nitrate, organic matter and suspended solids can be measured simultaneously. . UV spectroscopy and GC analysis were performed using instruments (Thermo Scientific GENESYS 10S Vis &Thermo Scientific TRACE 1300).

### **3.4.2 Gas Chromatography (GC)**

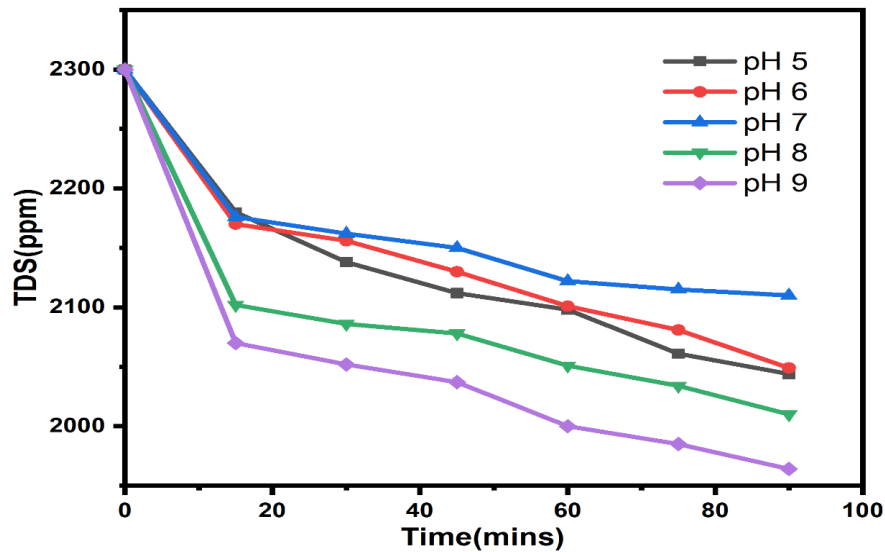
Gas Chromatography is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of mixture. In a GC analysis, a known volume of gaseous or liquid analyte is injected into entrance (head) of the column, usually using a micro syringe (or, solid phase micro extraction fibers, or a gas source switching system). As the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto the packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified (qualitatively) by the order in which they emerge (elute) from the column and by the retention time of the analyte in the column.

## CHAPTER 4

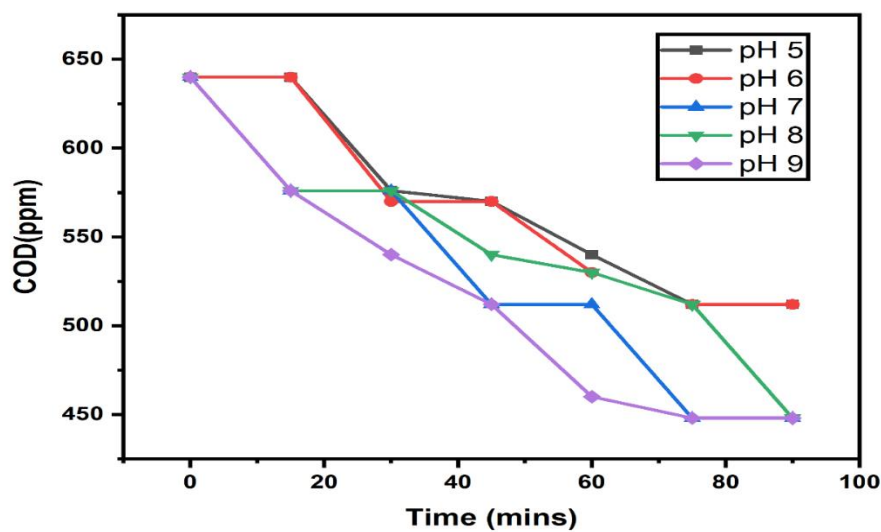
### 4. RESULTS AND DISCUSSION

#### 4.1 OPTIMISATION OF PARAMETERS IN OZONATION

##### 4.1.1 EFFECT OF pH



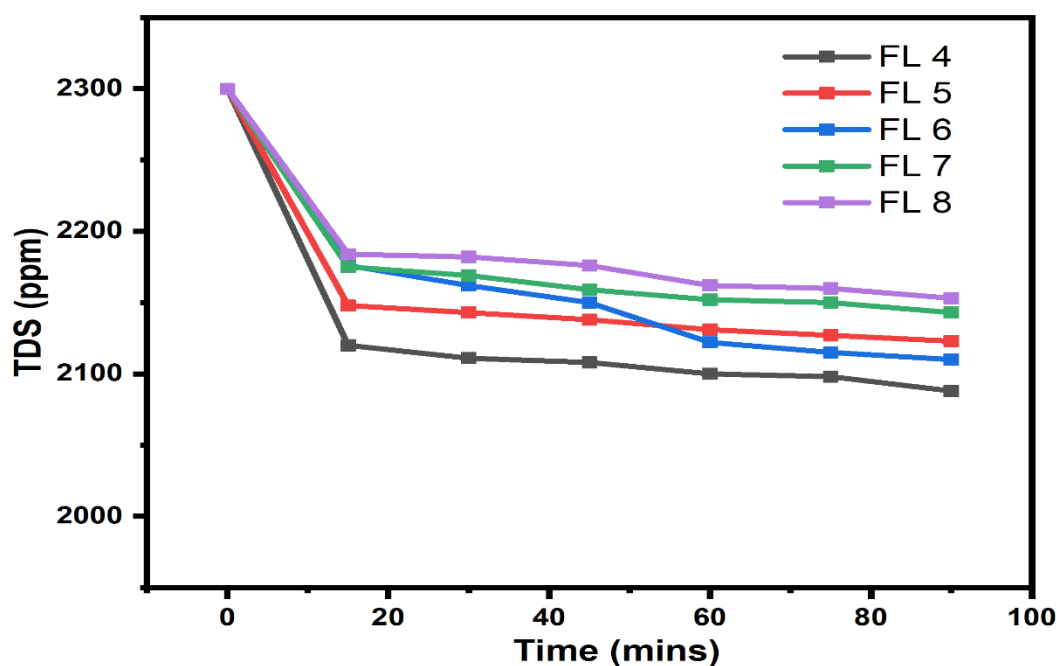
**Fig 4.1.1.a Effect of pH on TDS in ozonation, Conditions: pH 7, Flowrate 6LPH, Temperature 30°C.**



**Fig 4.1.1.b Effect of pH on COD in ozonation, Conditions: pH 7, Flowrate 6LPH, Temperature 30°C.**

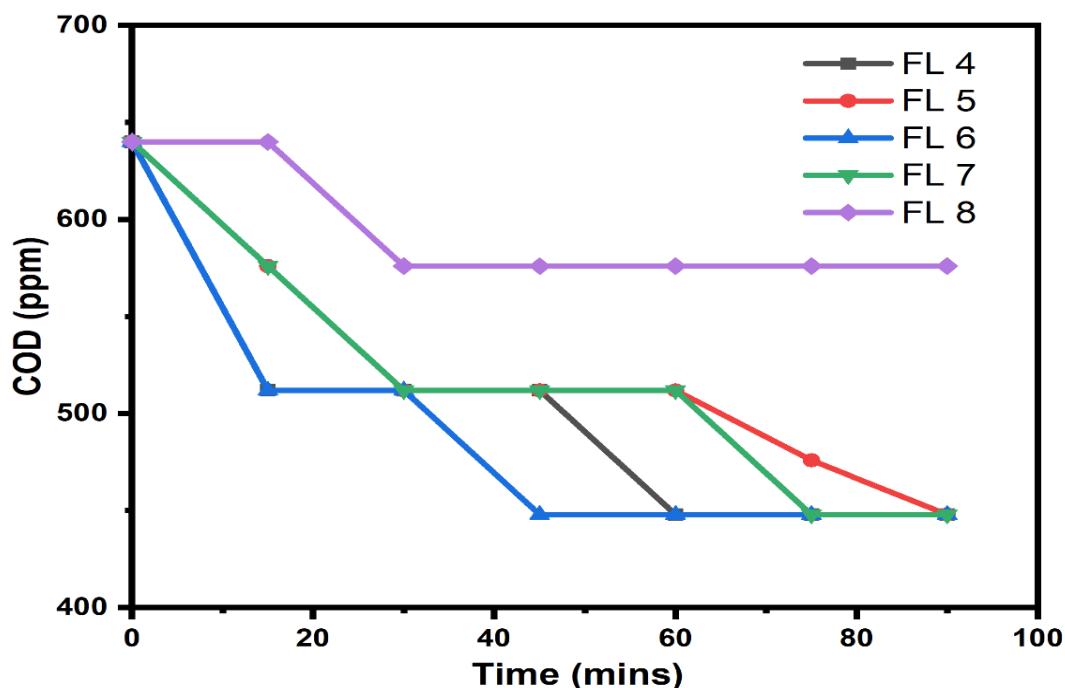
Ozonation, an AOP does not favour TDS reduction to the greater extent as ozone is a powerful-oxidative reagent. It is evident that only 30% TDS reduction takes place during ozonation process. This is because at higher pH the concentration of hydroxyl ions raises thus lowers the solubility of ozone in water which promotes the decomposition of ozone (Wang et al., 1999). The pH of the water is the most prominent parameter and the hydroxide ions initiates decomposition at the alkaline condition (Beltran, 2014). The result of this study shows that the dissolved ozone concentration decreases with an increase in pH, thus OH\* ions will provoke ozone decomposition into OH\* radicals (Gao et al., 2005, Lovato et al., 2009).

#### 4.1.2 EFFECT OF FLOWRATE



**Fig 4.1.2.a Effect of flowrate on TDS in ozonation, Condition: pH : 9 (optimised), Temperture : 30°C**





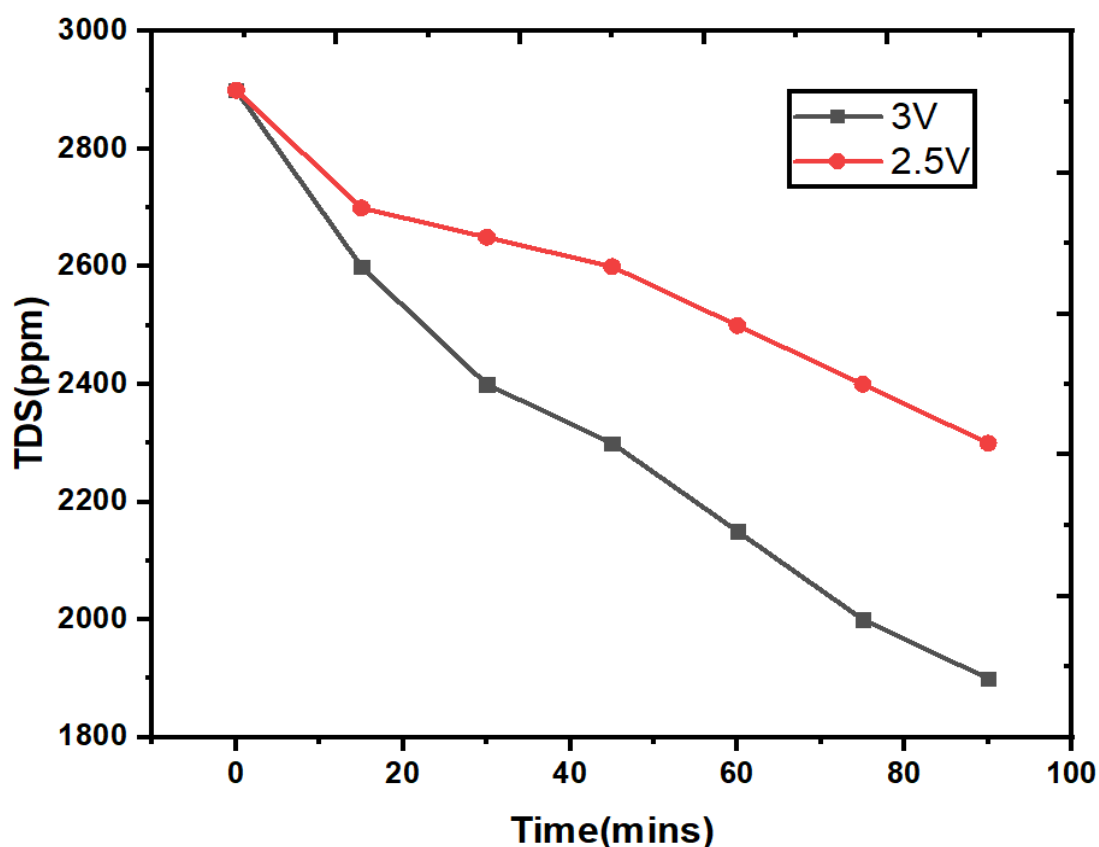
**Fig 4.1.2.b Effect of flowrate on COD in ozonation, Condition: pH : 9 (optimised), Temperature : 30°C**

The optimised pH was observed by keeping the flowrate constant. Now the optimised pH was maintained constant in the sample and the flowrate of ozone was varied 4 – 8 LPH to find the optimised flowrate. From fig 4.1.2.a, it was clear that COD and TDS were reduced on lower flowrate of ozone itself. Upon maintaining flowrate at 4 LPH it is found that the TDS reduction was 8.6% which is very minimal reduction due to the presence of heavy dissolved solids which cannot be broken in the process of ozonation. The ozone potential was not enough to break the dissolved solids in the water. The COD reduction percentage was 28.5% and the flowrate of 4 LPH was found to be optimised. In the process of passing ozone at 5, 6, 7 and 8 LPH the residence time of the ozone in the system was significantly decreased as the gas flow rates was increased. So, this shorter residence time decreases the dissolved ozone concentration and thus was not able to remove the organic and inorganic pollutants which is responsible for the

formation of biofilm on the membrane. The maximum ozone dissolved concentration was obtained at a gas flow rate of 4 LPH (Aji et al., 2018).

## 4.2 OPTIMISATION OF PARAMETERS IN ELECTROFENTON

### 4.2.1 EFFECT OF VOLTAGE

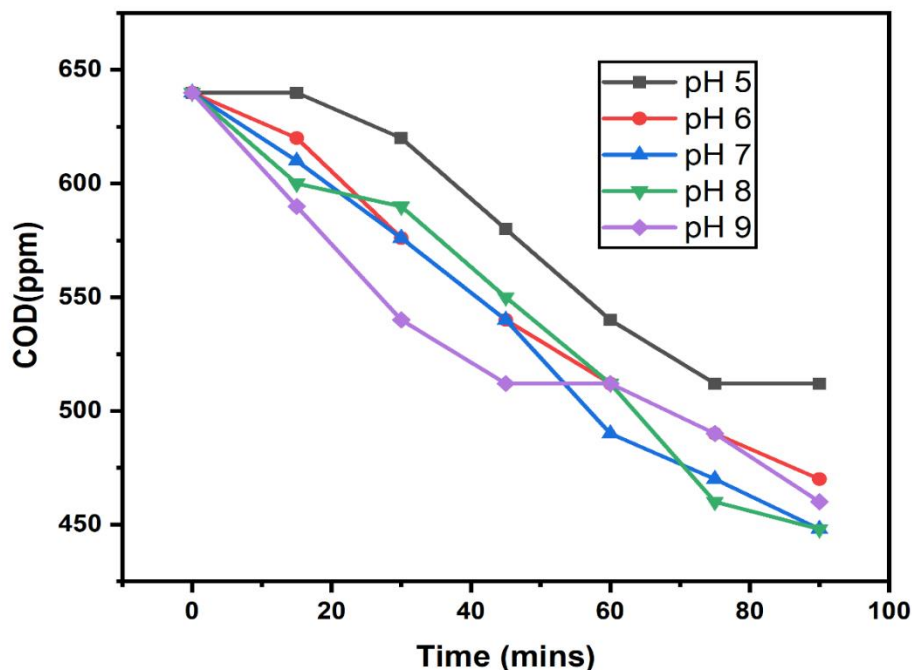


**Fig 4.2.1 Effect of voltage on TDS in Electro-fenton,** Condition: pH: 4, Temperature: 30°C, Speed of the stirrer: 500 rpm.

From the fig 4.2.1, on comparing the two voltage supply to electrofenton process, increasing the voltage decreases the TDS on constant pH(4) on the sample. It is because the voltage supply produces to some extent produces more hydroxyl radicals  $[OH^\cdot]$  by deionising hydrogen peroxide in the sample, which enhances the settlement of the dissolved solids by oxidation (Kavitha *et al*). The removal percentage for 3V was calculated as 35%.

## 4.3 OPTIMISATION OF PARAMETERS IN ELECTRO- OXIDATION

### 4.3.1 Effect of pH



**Fig 4.3.1 Effect of pH on COD in electro-oxidation,** Conditions: Voltage : 2V, Temperature 30°C, Stirrer speed : 500rpm

The voltage supply to electrodes was maintained constant at 2V and the pH was varied from 5 to 9 and the COD reduction was found to be 30.1% under optimised pH 7. This low reduction is due to the very less oxygen evolution with high oxygen evolution potential in acidic medium and vice versa in the basic medium in diffusion rate of organic pollutants towards anode.

## **CHAPTER 5**

### **CONCLUSION**

#### **5.1 SUMMARY**

Three electrochemical treatments were done for the surface water of Kaleesuwari Refineries Limited and the results obtained were mentioned below

- Ozonation-28.5% of COD reduction, 30% of TDS reduction
- Electro-Fenton-35% of TDS reduction and
- Electro-Oxidation-30.1% of COD removal, does not impact TDS much.

The removal efficiency obtained from the two electrochemical treatments for the surface water was around 30%.Ozonation process acts as a supporting process in removing the COD and TDS as its main purpose is to avoid the biofilm formation in the system. In future, if these electrochemical treatments were integrated with ozonation process, we could obtain high percentage of COD and TDS reduction.

#### **5.2 SCOPE & FUTURE OF THE WORK**

Developed a electrochemical treatment for Kaleesuwari Refineries Ltd., to remove TDS and COD from their surface water which was used for steam generation.

Various Electrochemical processes such as Adsorption, Electro Dialysis, Sand Filtration, Non Thermal Plasma process, Reverse Osmosis, Electro Coagulation and Membrane Technology could be adopted for the treatment of

surface water which will increase the removal of total dissolved solids and total organic contents.

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