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# Optimizations of Electro-Oxidation Process for the Treatment of Petrochemical RO Reject Using Response Surface Methodology

**Vishal Kumar Sandhwar[1], Diksha Saxena[2], and Shivendu Saxena[3]**

1,2,3 Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, Gujarat, India.

Correspondence should be addressed to Vishal Kumar Sandhwar; vishal.sandhwar8850@paruluniversity.ac.in



**ABSTRACT**: Even though Reverse Osmosis (RO) is one of the greatest prominent and effective techniques for the waste water treatment, but it also generates large amount of concentrated brine known as RO reject. The present work aimed to achieve maximum efficiency as well as optimal conditions for the treatments of petro-chemical RO reject by electro-oxidation process using graphite electrodes. The Response of the Surface Methodology under Central Composites Design was utilized to examine the effects of various independent parameters likes reaction time, pH, current density as well as electrode distance on the removal efficiency. The maximum total dissolved solid (TDS) removal was obtained 51.16% at optimum situation. 1st as well as 2nd orders kinetic model were fitted to described the finest kinetic model for TDS removal. The effectiveness of electro-oxidation therapy in removing TDS was studied. During EO treatment, TDS removal was found to be substantially influenced by solution reaction time, pH, current density, and electrode gap.

**KEYWORDS**: Electro-oxidation, Kinetic Analysis, Reverse Osmosis (RO), Response Surface Methodology, Total Dissolved Solid.

## I. INTRODUCTION

Reverse osmosis (RO) is a highly efficient and eco-friendly membrane separation process to treat wide range of dissolved solids present in the aqueous solution. During RO treatment, approximately 50–80% of water is obtained as permeate [1] and rest of the amount 20 to 30 percent formed as RO rejects or also known concentrates as well as can't be further treated by the RO method because of high osmotic pressure. Huge amount of wastewater is generated during production of various petrochemical products such as High Density Polyethylene (HDPE), Mono Ethylene Glycol (MEG), Para xylene (PX), Purified Terephalic Acid (PTA) etc.[1], [2]. In some of petrochemical plants, RO efficiently treats generated wastewater but at the same time large quantity of RO reject forms having very high total dissolved solid (TDS) which need to be further treatment. Therefore, it is essential to treat RO reject or concentrate through an efficient treatment technique before its use or open discharge. Moreover, several conventional treatment techniques such as coagulation, flocculation, adsorption, advanced oxidation technologies, has been developed for the effective treatments of contaminants or pollutants from concentrate stream[3]–[7].

Because they are efficient, cost-effective, and environmentally friendly, electrochemical approaches have shown significant promise for replacing or supplementing existing procedures. In the treatment of RO reject, electrochemical oxidation offers various benefits over other methods. For sample, it may be uses on RO concentrates stream with the reasonable to higher salinity, which promotes strong electric conduction as well as also minimises the amount of energy used [8]. Few studies have been reported for the treatment of RO rejects of different wastewaters such as textile, pharmaceutical etc. by different electrochemical methods [9]. The present study revealed the option of removal of TDS from petrochemical RO reject by electro-oxidation (EO) method using graphite electrodes. EO is an effective wastewater treatment technique where degradation takes place with the help of numerous oxidants likes hydrogen peroxide (H2O2), nascent oxygen, free chlorine as well as radicals. EO process occurs either as indirect EO method using electrochemically produced strong oxidants like hypochlorite/chlorine and H2O2 or as direct EO method in which oxidation takes place by physically adsorbed "active oxygen" [10]. EO utilizing the graphite's electrodes takes place through combinations of indirect oxidations of in-situ generated oxidizing agents as well as direct oxidation at anode surface [11]. Further, an efficient optimization tool known as Response Surface Methodology was utilized to examine the effects of various independent parameters likes reaction time, pH, and current density as well as electrolyte concentrations to get maximum TDS removal.

Distillery wasted wash is treated using a variety of ways before being disposed of on land or in the ocean. Physical techniques for removing organic matter from wastewater have been used, but they have a number of drawbacks, including poor removal effectiveness and high cost. Because of the methane retrieval in anaerobic stage of the treatments, bio methanation has achieved widespread acceptance among the many approaches for the treatments of distillery wasted wash. According to reports, biological treatment reduces BOD by 60 to 85 percent, however a significant proportion of resistant organic pollutants remains in the effluent release. The electrochemical treatment techniques (EC) is a popular alternative treatment method that offers various benefits over

traditional treatment methods, including ease of automation, maximum elimination efficiency, shorter reduced sludge creation, treatment times, as well as low operating costs. In this electrochemical treatment technique, a great deal of study was done on several electro oxidation procedures. It is possible to remove or convert contaminants into simpler forms likes carbon dioxide as well as water with the use of electro oxidation technology. Direct oxidation and indirect oxidation are the two kinds of oxidation processes that might take place. Anode electrochemical production of stronger oxidants likes hypochlorite as well as hydrogen peroxide, as well as the production of chlorine and the production of hydroxyl ions, are all possible in the indirect oxidation process. All of the oxidants are produced on-site and put to use immediately. According to the process of indirect electrochemical oxidation, water is electrolyzed by anodic catalysis, resulting in the formation of a hydroxyl radical.

## II. LITERATURE REVIEW

Wamda Faisal Elmobarak et al.[12] discussed the Advanced Oxidation Procedures for treatment of Petroleum Refinery Waste-water. The petroleum business the fastest-growing sectors, and it is expected to expand even faster in the next years. The petroleum refining industry is being pushed to employ green techniques and industrial wastewater treatment as a result of current environmental initiatives and worldwide demands for greener approaches. Among the toxins present in wastewater from the petroleum industry include petroleum hydro carbons, phenol, oil as well as grease, sulphides, ammonia, and different organic composite, to name a few. All of these compounds may be found in very complex forms in discharged water from the petroleum industry, which poses a serious threat to human health and the environment. Water treatment systems used in traditional refineries are plagued by a variety of faults, counting lower efficiency, higher capital and working costs, as well as a sensitivity to lower bio-degradability as well as toxicity. When it comes to wastewater treatment, one of the most often employed methods in petroleum refineries is the advanced oxidation procedure. The purpose of this research is to examine how advanced optical processing (AOP) technologies are presently being utilised to clean wastewater from the petroleum industry. In addition to photo-Fenton procedures and Fenton, H2O2 and UV, ozonation, photocatalysis, as well as biological procedures are all employed to treat petroleum effluent as part of AOP technology. According to the findings of this research, the treatments efficiency are strongly dependent on the kind of AOP utilised, the physicals in addition to chemical characteristics of the target pollutants, and the operating conditions. In addition to AOP treatment, other processes such as hydroxyl radical oxidation have been documented to occur, which are thought to contribute to the reduction of pollutants in the treated drinking water supply. The primary focus of this study is on recent achievements in AOP treatment of the petroleum effluents, which are the topic of the majority of the research. According to the results of the study, gaps in the scientific literature have also been found, as well as viable research pathways for analysing the influence of various technology in the treatment of the petroleum waste-water. The findings of the study also suggest that.

Sridhar et al. [13] explained the Reverse osmosis treatment of composite industrial effluent. As a well-established method in the fields of water desalination and sewage treatment, reverse osmosis (RO) is expected to see significant use in the near future, particularly in the action of complicated combinations of manufacturing effluents, according to the International Water Association. By the spiral wound thin-film composites (TFC) polyamide cell wall in conjunction with a spiral scar TFC polyamide membrane, researchers investigated the potential of RO for treating a fibreglass effluents, which comprised of a mixtures of the waste waters from bulk drug as well as pharmaceutical manufacturers. It was discovered that raising the feed pressure and feed concentrations improved separation performance, and this was shown by the fact that increasing the input pressure resulted in improved separation performance. Using appropriate flow rates and water recovery, it was feasible to achieve high rejection of dissolved solids (98 percent), biochemical oxygen demand (BOD), and carbon dioxide, as well as practically total colour removal with very little colour transfer. Throughout the course of this investigation, a time-dependent study was performed to assess the impact of concentration polarisation and contamination on the flow and rejection rates. It is proposed that an aerobic approach be used for the treatment of composite effluent, rather than a RO membrane process, in order to save costs. Verma et al. [1] explained the Coagulation and flocculation of petrochemical effluent, as well as sludge properties. Pretreatment processes for pure terephthalic acid (PTA) wastewater treatment were explored in this work. The impacts of coagulation and flocculation were investigated as a pretreatment procedure for PTA wastewater treatment. Investigations were carried out on the effects of a range of inorganic as well as organic coagulants over treatment of waste water collected from an effluent treatment plant's flow equalisation tank. The results were published in the journal Water Research. There were additional investigations into the sludge's settling and filtration capabilities, which were completed. In the jar testing, it was discovered that an iron chloride dose of 3000mgl-1 at pH 5.6 offered the most effective treatment for effluent. The COD of the effluent was decreased by 75.5 percent when the system was working at peak efficiency. According to the results of gravimetric filtration trials, the filtering capabilities of treated wastewater were increased with the addition of cationic polyacrylamide (175 mgl-1) to ferric chloride coagulation, while the cake resistance was lowered in particular. Transmission electron microscopy and energy dispersive spectroscopy were utilised by the researchers to get a better knowledge of the chemistry and structure of the sludge under investigation. That conclusion was backed by the experiments, which validated what the thermal analysis had shown about the sludges: according to the findings of the present research, sludge oxidation is a three-step process. Researchers determined that the oxidation process was definitely a two-step process as a consequence of the addition of C-PAA to the ferric chloride coagulation system.

## III. DISCUSSION

### *A. Chemicals Used*

Ranbaxy Fine Chemical Limited, in New Delhi, India, as well as the Mumbai-based Loba Chemical Pvt. Ltd., provided the analytical-grade chemicals utilised in the whole investigation.

### *B. Wastewater collection and characterization*

RO refuse from a petrochemical complex in northern India was collected from the effluent treatment plant (ETP) of the complex. Entire pre-treatment characterizations were performed using standard methods prescribed by APHA (APHA, 1912). Initial TDS was found 3750 mg/L. Removal efficiency was calculated as follows.

$$\% \text{ Removal of TDS} = \frac{T_i - T_f}{T} \times 100 \quad (1)$$

Where, Ti- initial TDS, Tf- final TDS

### *C. Experimental*

The complete series of tests was carried out in an exposed rectangular shape batch reactor. While treating patients, graphite electrodes with an actual electrode area of 131.20 cm square were employed as both anode and cathode, with the anode having a larger effective electrode area. In the Figure 1 depicts a representation depiction of experimental setup for the purpose of illustration.

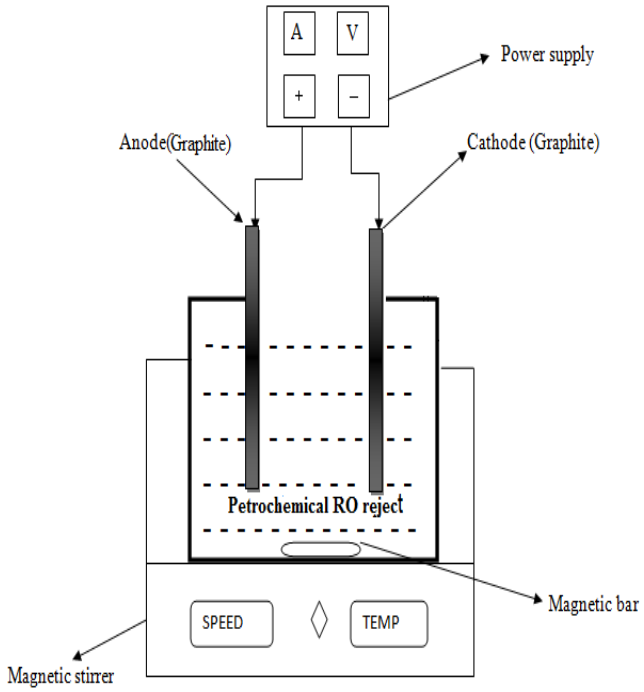


Figure 1: Illustrating the Schematic representation of the experimental setup.

Electrodes were cleaned with H2SO4 (5 percent v/v) after each set of experiments and then washed with water. Optimization of independent parameter likes reaction times (20-100 min), pH (1-9), the current density (CD) (60.961-182.88 A/m2), as well as electrode gap (1 to 5 cm) were investigated in order to achieve the greatest possible TDS removal during EO treatment. Table 1 illustrates the variation of operational parameter that may be used during EO therapy.

Table 1: Functioning parameters as well as their levels got for EO treatment

| Levels | Parameter Range | | | |
|---|---|---|---|---|
| | X1 | X2 | X3 | X4 |
| | Time (min) (20→100) | pH (1 to 9) | CD (A/m2) (60.96→182.88) | Electrode gap (cm) (1→5) |
| -2(-α) | 20 | 1 | 60.96 | 1 |
| -1 | 40 | 3 | 91.44 | 2 |
| 0 | 60 | 5 | 121.92 | 3 |
| +1 | 80 | 7 | 152.40 | 4 |
| +2(α) | 100 | 9 | 182.88 | 5 |

### *D. Effects of the pH, CD, Reaction Time, as well as Electrode Gaps on TDS Removals*

During the EO treatment process, oxidants like hydrogen peroxide, nascent oxygen, free chlorine (Cl, ClO), as well as hydroxyl radicals (OH●) play a critical part in the process. At low pH, generation of strong oxidants like HOCl and ●OH occurs rapidly [14] results higher removal. The creation of chlorate through oxidation of the free chlorines and the formation of perchlorate through the combination of HOCl and hypochlorite leads in a reduced elimination rate at neutral pH. When the pH is high, hypochlorite ions are responsible for the elimination. Figure 2 (a) shows that TDS removal increases with increasing pH, and that once the pH reaches the optimal value of 5.32, it begins to decrease. During EO therapy, the reaction time and current density (CD) are critical metrics to monitor. We noticed that the impacton density of the current and response time on TDS removal is depicted in Figures 2 (a) and 2 (b), respectively, and that TDS removal rises continuously with current density and time. As current density increases, the creation of electrons and H2O2 by catholic reduction of molecular oxygen is enhanced, resulting in more elimination. It was discovered that, beyond the ideal conditions shown in Table 1, removal efficiencies begin to decline as a result of the scavenging impact on the available substrate.

●OH radicals by excess amount of H2O2.

$$H2O2 + \bullet OH \rightarrow HO2\bullet + H2O \quad (2)$$

Influence of electrode distance was also studied as shown in Figure 2 (a). The optimum distance was found 4 cm. Based on the literatures, it can be said that there is a chance of higher electrical resistance due to accumulation of solid particles between electrodes results lower removal [15]. Because of the existence of a high current density between the electrodes, a short circuit may also occur when the electrodes are separated by a small distance. After a certain distance between electrodes, the removal of TDS begins to rise. This is because to the slower movements of formed ions, which allows for more opportunities for them to combine as well as form flocs. Efficiency decreases when the electrode spacing is increased above the optimal value, owing to weaker interactions between contaminants and flocs.

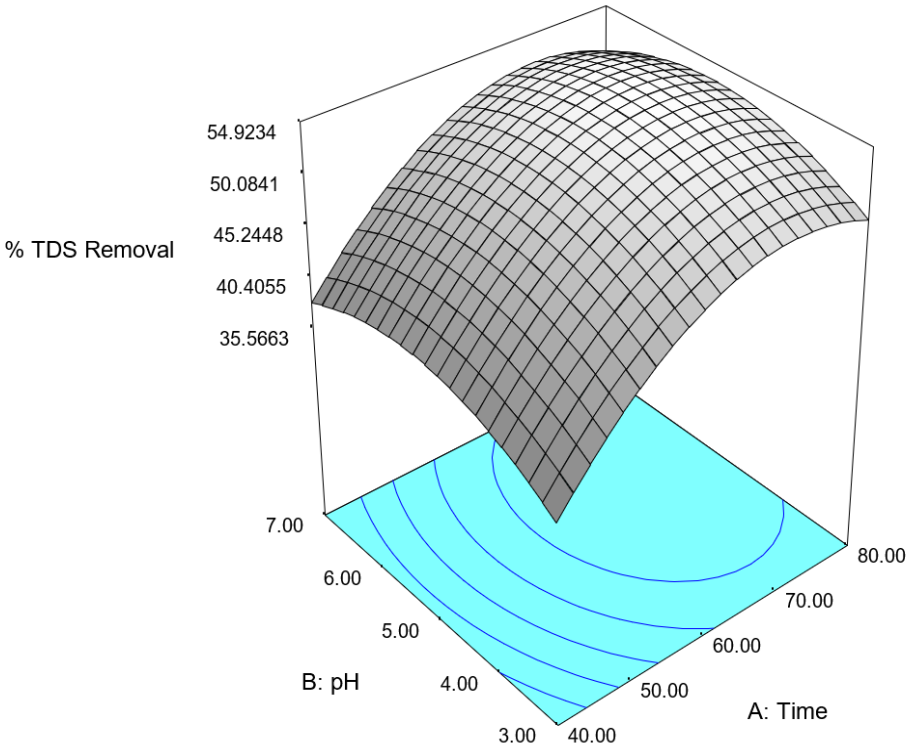


Figure 2 (a): Illustrating the Influence of electrode

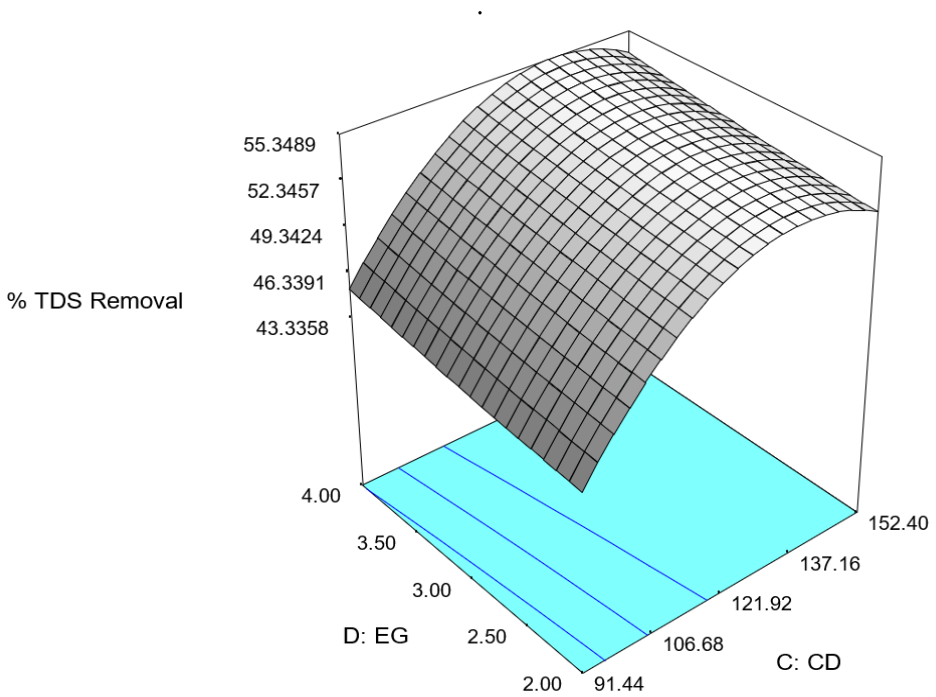


Figure 2 (b): Illustrates the Influences of current density and reaction time on TDS Removal.

***E. Optimization***

A total of thirty tests were passed out based of the Central Composite Design (CCD) projected set of operating parameters to investigate the effect of operating factors such as CD, reaction time, pH, and electrode gaps on the maximum elimination of trivalent cations (TDS). Optimal variable circumstances with CCD predicted and experimental data are shown in Table 2, which also demonstrates an effective CCD model.

Table 2: The optimal operating conditions predicted by CCD, as well as the findings obtained experimentally and forecasted by CCD.

| | Time (min) | pH | CD ($A/m^2$) | Electrode gaps (cm) | % Removal of TDS | |
|---|---|---|---|---|---|---|
| | | | | | CCD (Pre.) | Test Run |
| **EO** | 72.03 | 5.32 | 139.55 | 4 | 57.69 | 51.16 |

***F. Study about Kinetic***

Figures 3 (a) and 3 (b) show the results of the kinetic experiments conducted during EO treatments under the optimal parametric settings listed in Table 2. (b). the First as well as second order kinetic models were utilised to determine the response sequence that was most closely aligned with reality.

For 1st order: $\frac{-d\,(T)}{dt} = k_1(T_t)$ or $\ln\frac{T_o}{T_t} = k_1 t$ (3)

For 2n order: $\frac{-d\,(T_t)}{dt} = k_2(T_t)^2$ or $\frac{1}{T_t} - \frac{1}{T_o} = k_2 t$ (4)

where, T- TDS value, To= TDS at t = 0 in addition to Tt= TDS at t = t, $k_1$- Rates constant for 1st order, $k_2$- Rate constant for 2nd order and t- time TDS elimination during EO treatments at optimal circumstances is shown in Figure 3 (a) and (b), which are 1st and 2nd order plots, respectively. Higher rate constants (k) values suggest a faster degradation rates; hence, based on the observed data, it can be resolved that TDS removal favours 2nd orders rate kinetics owing to the higher R2 values, as seen in Figures 3 (a) as well as 3 (b).

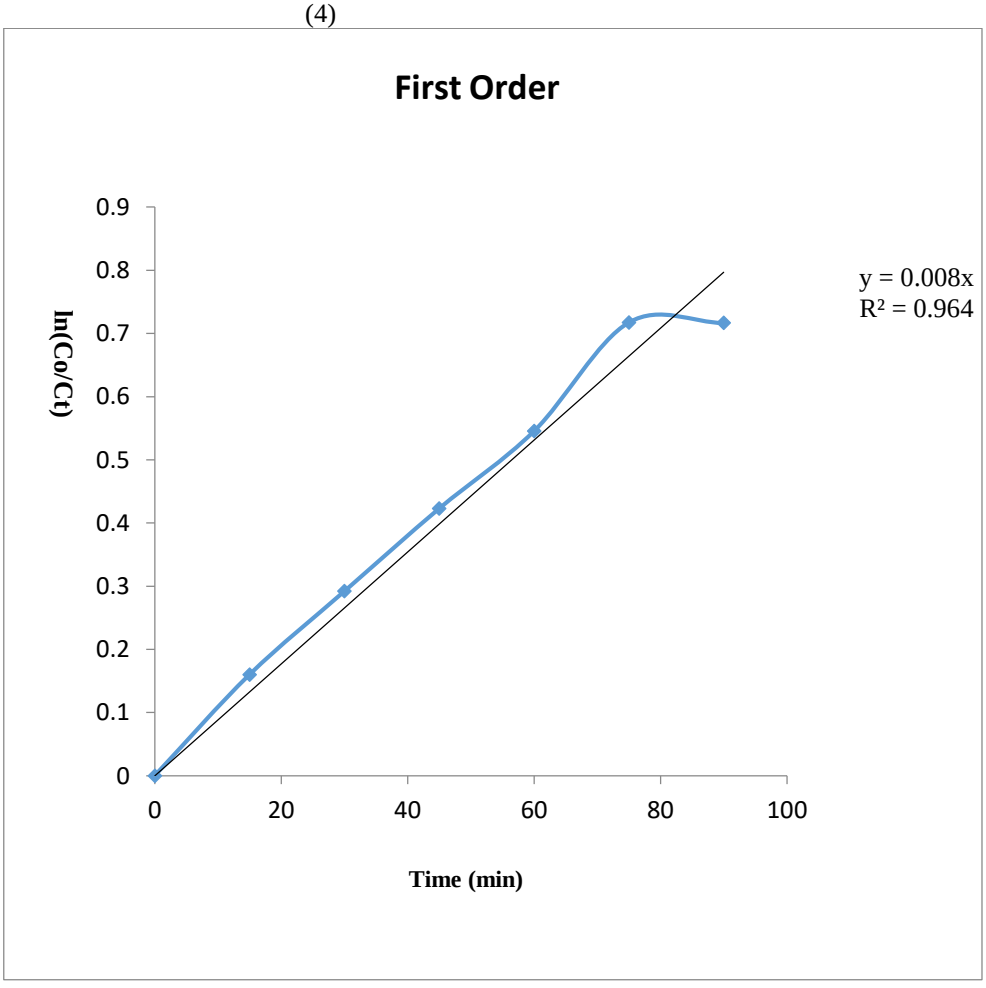


Figure 3 (a): Represents 1st order plots for removal of TDS during EO treatments at optimum conditions

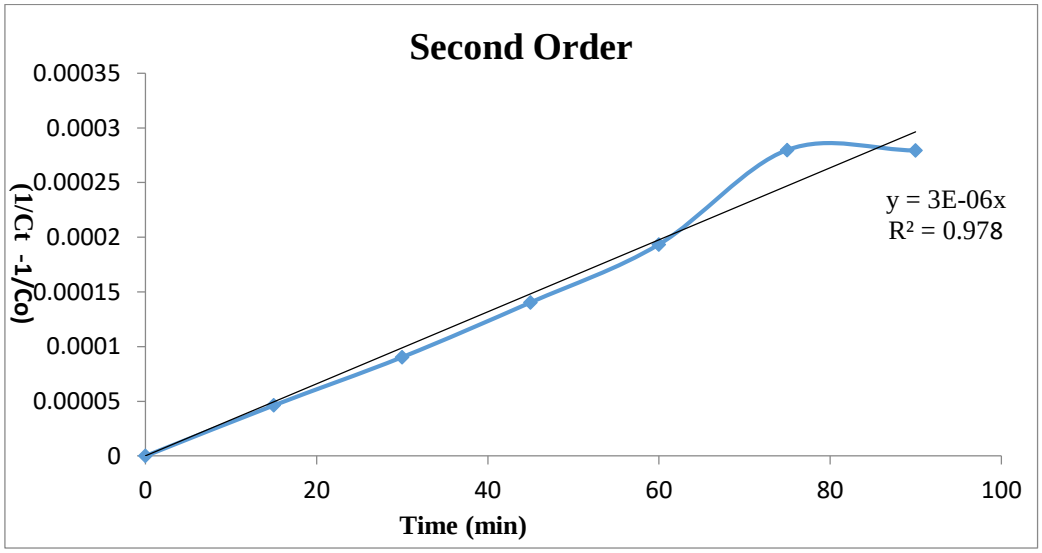


Figure 3 (b): Represents second order plots for removal of TDS during EO treatments at optimum conditions.

## IV. CONCLUSION

The study evaluated the effectiveness of electro-oxidation therapy for the elimination of TDS from water. During EO treatment, it was exposed that the removal of TDS is extremely needy on the solution reaction time, pH, current density, and electrode gap of the solution. It was possible to achieve the maximum TDS removal of 51.16 percent under optimal circumstances, which included pH 5.32, current density 139.55 A/m2, reaction period 72.03 min, and electrode gap of 2 cm. The comparison of experimental and CCD projected results demonstrates that the CCD model is efficient. The elimination of TDS favours the second order kinetic model.

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