

# A Comparative Study of Peroxi-coagulation and Peroxi- photo coagulation Methods for Treatment of Petrochemical RO Reject: Optimization and Kinetic Study

Vishal Kumar Sandhwar<sup>1</sup>, Shivendu Saxena<sup>2</sup>, Rohit Lade<sup>3</sup>, Diksha Saxena<sup>4</sup>, BasheshwarPrasad<sup>5</sup>

<sup>1</sup> Department of Chemical Engineering, Parul Institute of Technology, Parul University  
Vadodara- 391760, Gujarat, India

vishal.sandhwar8850@paruluniversity.ac.in

<sup>2</sup> Department of Chemical Engineering, Parul Institute of Technology, Parul University  
Vadodara- 391760, Gujarat, India

shivendu.saxena8938@paruluniversity.ac.in

<sup>3</sup> Department of Chemical Engineering, Parul Institute of Technology, Parul University  
Vadodara- 391760, Gujarat, India

rohit.lade8921@paruluniversity.ac.in

<sup>4</sup> Department of Chemical Engineering, Parul Institute of Technology, Parul University  
Vadodara- 391760, Gujarat, India

diksha.saxena8882@paruluniversity.ac.in

<sup>5</sup> Department of Chemical Engineering, Indian Institute of Technology Roorkee,  
Roorkee-247667, Uttarakhand, India,

bashefch@iitr.ac.in

**Abstract:** This study elucidates a comparative study of peroxi-coagulation and peroxi- photo -coagulation methods for the reduction of total dissolved solids from petrochemical reverse osmosis (RO) reject. All experiments were done in a batch reactor incorporating an iron anode and a graphite cathode, whereas the solution was also irradiated with UV light during peroxi- photo-coagulation process. Independent parameters such as pH, current density, electrode gap, and electrolysis time were optimized by Central Composite Design of Design Expert Software was applied for peroxi coagulation process and optimum operating conditions obtained. Peroxi- photo-coagulation treatment was performed at the same optimum conditions obtained during peroxi coagulation treatment. The present study reveals that photo peroxi coagulation process was found more efficient than peroxi coagulation process in order to get maximum removal of total dissolved solids from RO reject. Maximum removal of total dissolved solids was attained 63.19% during photo peroxi coagulation treatment and 52.78% during peroxi coagulation treatment at optimum operating conditions. Kinetic study was performed at optimum operating conditions and 2nd order kinetic model was best fitted to describe the removal rate.

**Keywords:** Peroxi-coagulation, Photo peroxi-coagulation, Total dissolved solid, Central composite design, Kinetic analysis

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## I. INTRODUCTION

Reverse osmosis (RO) is usually used for the treatment of brackish and industrial water containing high total dissolved solids (TDS). Even though RO is one of the most efficient techniques, but it generates large quantities of concentrated brine which needs for further treatment before its use or discharge especially, when the plants are located inland [1]. The ferrous ions ( $\text{Fe}^{2+}$ ) and cannot be further concentrated by RO due to high osmotic pressure and is therefore it is necessary to get an effective technique to treat RO reject wastewater containing hazardous dissolved solids. Since past few years, electrochemical processes have attracted more attention than other conventional techniques for treatment of different types of wastewater containing toxic pollutants. Due to have several properties viz. high efficiency, economic, automation, less sludge generation, effective wastewater treatment technique. Among various electrochemical techniques, Peroxi-coagulation (PC) process is one of the most efficient method for wastewater treatment. In this process, generation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and discharge especially, when the plants are located inland [1]. The ferrous ions ( $\text{Fe}^{2+}$ ) takes place electrochemically during concentrate containing dissolved solids is also known as reject treatment. Here the probability of reaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  is quite high due to simultaneous generation of both the Fenton's reagents (i.e.  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$ ) [2]. Main reactions of this process are summarized as below.

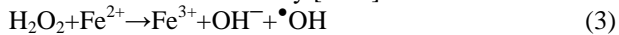
At anode

$$\text{Fe}_{(s)} \rightarrow \text{Fe}_{(aq)}^{2+} + 2e^- \quad (1)$$

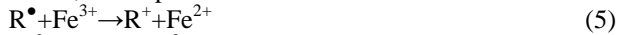
At cathode



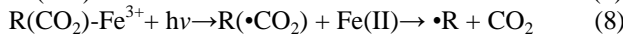
After production of Fenton's reagents during treatment, formation of hydroxyl radicals ( $\bullet OH$ ) takes place via Fenton's reaction chemistry [9-11] as discussed below



where, RH is pollutant



In Peroxi-photo-coagulation (PPC) method, efficiency of PC process can be improved by using visible light illumination (UV) which favors higher production rate of  $\bullet OH$  from the photoreduction of  $Fe(OH)_2$  and the photodecomposition of complexes from  $Fe^{3+}$  reactions [3] as discussed below.



The present study attempted to examine the possibility of TDS removal from petrochemical RO reject by peroxi-coagulation and combined peroxi-coagulation & UV process known as photo-peroxi coagulation. The influence of various process variables such as initial pH, current density, electrode gap and electrolysis time were optimized by Response Surface Methodology (RSM) to get maximum TDS removal. The performance of both electrochemical processes was compared on the basis of removal efficiency and kinetics.

## II. MATERIALS AND METHODS

### A. Chemicals

All chemicals used in the study were of analytical grade.

Sodium hydroxide, Sulfuric acid and other chemicals were supplied by Ranbaxy Fine Chemical Limited, New Delhi, India.

### B. Source of wastewater

RO reject wastewater was collected from the effluent treatment plant (ETP) of petrochemical complex in northern India. RO reject was stored in a deep freezer (at 4 °C) and used for experiments without any dilution.

### C. Wastewater analysis

RO reject was analyzed for various physico-chemical parameters such as pH, total dissolved solids (TDS), conductivity etc. by using standard methods [4]. All samples and reagents were kept at 4 °C to prevent biodegradation and microorganism's growth. Initial pH, TDS and conductivity of RO reject were 6.5, 3629 mg/L and 4860 mmho/cm respectively. Percentage removal of TDS was calculated as follows.

$$\% \text{ Removal of TDS} = \frac{T_i - T_f}{T_i} \times 100 \quad [9]$$

Where,  $T_i$ - initial TDS,  $T_f$ - final TDS

## III. TREATMENT PROCEDURE

Entire treatments were performed in a open rectangular batch cell. Iron anode and graphite cathode were used as electrodes during PC and PPC treatments. Effective electrode area was 131.2 cm<sup>2</sup>. Fig.1. indicates the schematic diagram for PC and PPC treatments. Electrodes were cleaned by H<sub>2</sub>SO<sub>4</sub> (5% v/v) and subsequently washed with water after each run. During PC treatment, air was bubbled continuously through fish aerator to saturate the solution with oxygen till the end of experiments.

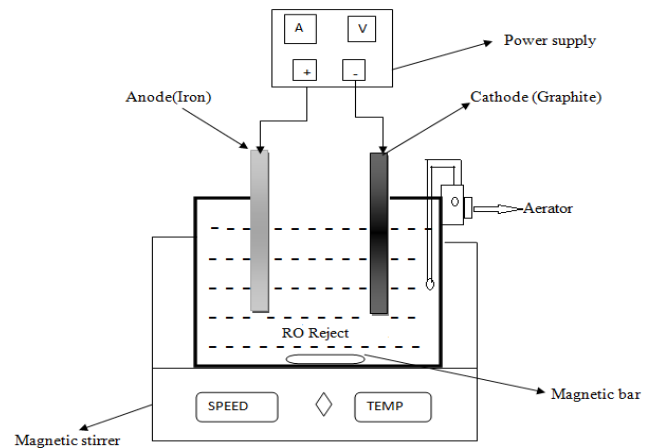


Fig.1. Schematic diagram of experimental set up

Optimization of process variables viz. pH: (1-5), current density (CD): (76-230 A/m<sup>2</sup>), electrode gap: (1-3 cm) and time: (20-100 min) in PC treatment was studied to get maximum removal of TDS. Optimization of process variables viz. pH: (1-5), current density (CD): (76-230 A/m<sup>2</sup>), electrode gap: (1-3 cm) and time: (20-100 min) in PC treatment was studied to get maximum removal of TDS. In PPC treatment, the optimum operating conditions maintained were similar to that of PC treatment but in addition, the reaction contents were exposed to UV irradiation. For PPC process, irradiation (254 nm) was carried out with a 12-W low pressure mercury lamp as a UV light source, which was put above the batch cell. The distance between solution and UV source was constant in all experiments. The operating parameters ranges for PC process are shown in Table 1.

TABLE 1  
OPERATING PARAMETERS AND THEIR LEVELS OBTAINED FOR PC PROCESS

Levels	Central Composite Design characteristics			
	Parameter (Range)			
	X <sub>1</sub> pH (1-5)	X <sub>2</sub> CD (A/m <sup>2</sup> ) (76→230)	X <sub>3</sub> Electrode gap (cm) (1→5)	X <sub>4</sub> Time (min) (20→100)
-2(-α)	1	76.00	1.0	20
-1	2	114.50	1.5	40
0	3	153.00	2.0	60
+1	4	191.50	2.5	80
+2(α)	5	230.00	3.0	100

## IV. RESULTS AND DISCUSSION

### A. Influence of pH, current density, electrode gap and time on TDS removal during PC treatment

During PC treatment, effect of pH (1-5), CD (76-230 A/m<sup>2</sup>), electrode gap (1-3 cm) and time (20-100 min) was investigated for TDS removal as shown in Fig. 2 (a & b). In PC, process formation of Fenton's reagents (Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>) takes place. At iron anode, Fe<sup>2+</sup> ions are generated and at graphite cathode, H<sub>2</sub>O<sub>2</sub> is generated by continuous air bubbling through fish aerator. Formation of hydroxyl

radicals ( $\bullet\text{OH}$ ) take place at acidic pH when  $\text{H}_2\text{O}_2$  is catalyzed by  $\text{Fe}^{2+}$  ions, favor more removal as shown in Eq. [1] and [2]. Removal efficiency was higher at low pH due to the joint effect of  $\text{Fe}^{2+}$  ions (which neutralize the charges of colloidal particles present in solution and reduce their solubility) and hydroxyl radicals. At optimum pH 3.3, maximum removal was observed as shown in Figs. 2 (a) and decrease in removal efficiency was found beyond this optimum pH value. This is because of the fact that, instead of generation of hydroxyl radicals, decomposition of  $\text{H}_2\text{O}_2$  into oxygen and water occurs at high pH and formation of oxonium ions ( $\text{H}_3\text{O}_2^+$ ) takes place at low pH resulting lower removal [5]. Moreover, current density and electrolysis time are the most effective operating variables in electrochemical treatment. According to Faraday's law of electrolysis, concentration of  $\text{Fe}^{2+}$  depends on CD and time according to following equation;

$$C_{\text{Fe}} = \frac{MIt}{ZFV} \quad (10)$$

where  $C_{\text{Fe}}$ , M, I, t, Z, F and V are theoretical concentration  $\text{Fe}^{2+}$  (g/m<sup>3</sup>), molecular weight of iron (g/mol), electric current, time, chemical equivalence, Faraday's constant (96,487 C/mol) and volume of reactor (m<sup>3</sup>) respectively [6]. Increase in charge loading with increase of CD and time favor increase in removal efficiencies. With increase of CD and time, extent of anodic dissolution of iron increases, resulting in more amount of  $\text{Fe}^{2+}$  ions and  $\text{Fe}(\text{OH})_{\text{n(s)}}$ . Moreover, increasing  $\text{Fe}^{2+}$  concentration could enhance the rate of production of  $\bullet\text{OH}$  radicals resulting higher removal. Figs. 2 (a& b) shows that TDS removal increases with CD and time up to optimum value (CD- 166.3 A/m<sup>2</sup>& time-58.23 min) and decrease in removals was observed beyond these optimum values which may be due to the inefficacy of electrodes due to corrosion or the consumption of more amount of charges through side reactions. During electrochemical treatment, it is required to keep the electrodes at optimum distance. TDS removal increases with electrode gap up to an optimum value due to the slower movement of produced ions favor more opportunity to aggregate and produce flocs. Fig. 2 (b) shows the influence of electrode gap (1-3) and observed an optimum electrode gap value (2 cm). Beyond this optimum distance, a decrease in removal efficiency was found which is because of the weaker interaction of flocs and pollutants [7]. Lower electrode distance results short circuit due to high current density between electrodes [8]. Enhancement in solid and fluid transfer was observed during very short inter electrode distance, resulting in accumulation of solid particles and bubbles on electrodes and consequent higher electrical resistance [9]. Maximum TDS removal was observed 52.78% at optimum operating conditions as mentioned in Table 1.

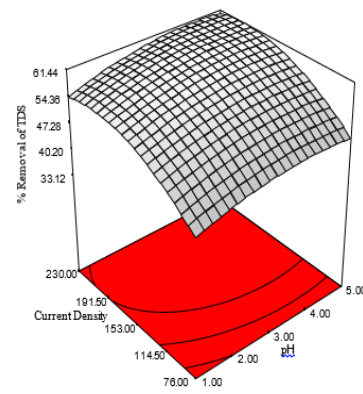
**B. Optimization**

Various experiments were performed using statistically designed experiments to study the effect of operating variables such as pH, CD, electrode gap and time on maximum TDS removal. Table 2 shows optimum operating conditions with experimental as well as CCD predicted results during PC treatments. Closeness between

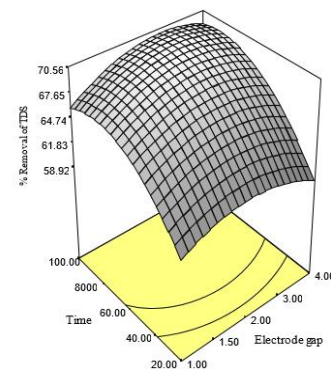
experimental and CCD predicted results represents an effective CCD model.

TABLE 2  
CCD PREDICTED OPTIMUM OPERATING CONDITIONS AND THEIR EXPERIMENTAL AND CCD RESULTS DURING PC PROCESS

	pH	CD (A/m <sup>2</sup> )	Electrode gap (cm)	Time (min)	% Removal of TDS	
					CCD (Pre.)	Test Run
PC	3.2	151.54	2	61.81	58.11	52.78



2 (a)



2 (b)

Fig.2. Effect of pH, CD, time and electrode gap on removal of TDS during PC treatment

**C. Influence of pH, current density, electrode gap and time on TDS removal during PPC treatment**

PPC treatment was performed at optimum operating conditions obtained during PPC treatment but in addition,

the reaction contents were exposed to UV light source. The contents were mixed thoroughly using a magnetic stirrer. Maximum TDS removal was observed 63.19% at optimum operating conditions as mentioned in Table 2. The removal efficiency of PPC process was improved by using UV light illumination. This is due to the higher production rate of •OH from the photodecomposition of complexes from Fe<sup>3+</sup> reactions and photo-reduction of Fe(OH)<sup>2+</sup> as discussed earlier.

### V. KINETIC STUDY

The removal kinetic during PC & PPC treatments at optimum parametric conditions as mentioned in Table 2 were studied as shown in Figures 3 (a) and (b). To compare kinetics during PC and PPC treatments first order and second order kinetic model were used to find best fit reaction order. 1<sup>st</sup> order and 2<sup>nd</sup> kinetic models are represented as;

$$\text{For } 1^{\text{st}} \text{ order: } \frac{-d(T)}{dt} = k_1(T_t) \text{ or } \ln \frac{T_0}{T_t} = k_1 t \quad (11)$$

$$\text{For } 2^{\text{nd}} \text{ order: } \frac{-d(T_t)}{dt} = k_2(T_t)^2 \text{ or } \frac{1}{T_t} - \frac{1}{T_0} = k_2 t \quad (12)$$

where, T- concentration of TDS, T<sub>0</sub>= TDS at t = 0 and T<sub>t</sub>= TDS at t = t, k<sub>1</sub>- 1<sup>st</sup> order rate constant, k<sub>2</sub>- 2<sup>nd</sup> order rate constant, and t- time (in sec). Figs 3 (a) and (b) indicates 1<sup>st</sup> & 2<sup>nd</sup> order plots for PC & PPC treatments. Higher rate constants (k) values indicates higher degradation rate, hence from the observed results it can be concluded that between PC & PPC treatments. In the present study, TDS removal during PC & PPC treatment favors 2<sup>nd</sup> order rate kinetics due to high R<sup>2</sup> value as shown in Figures.

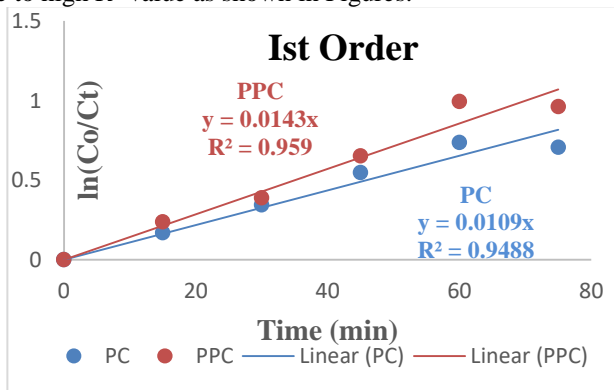


Fig.3 (a). First order reaction rate plots for PC and PPC processes at optimum operating conditions

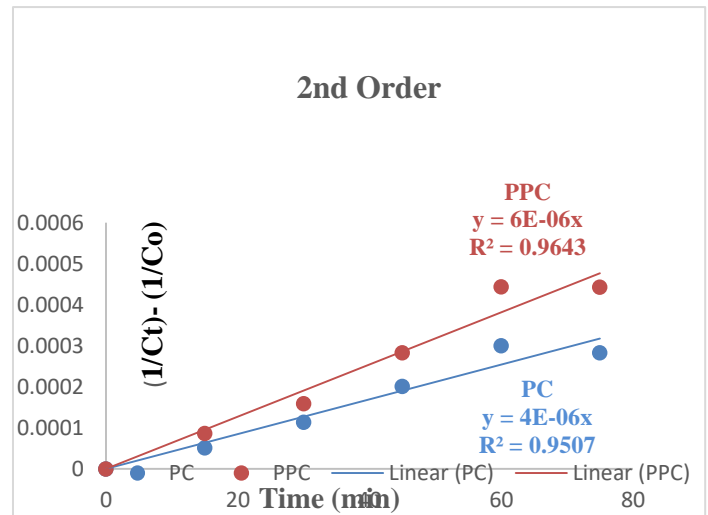


Fig 3. (b) Second order reaction rate plots for PC and PPC processes at optimum operating conditions

### VI. CONCLUSIONS

The performance of peroxi-coagulation and peroxi-photo-coagulation processes on the removal of TDS was studied and their performance was compared. Based on the results, it can be concluded that the removal of TDS is strongly dependent on solution pH, current density, electrode gap and electrolysis time during both electrochemical treatments. The optimum pH of 3.2, current density of 151.54 A/m<sup>2</sup> electrode distance of 2 cm, electrolysis time of 61.81 minutes were observed to obtain maximum TDS removal (63.19%) during photo-peroxi-coagulation treatment and 52.78% during peroxi-coagulation treatment. Closeness of experimental and CCD predicted results shows a high efficiency of CCD model. From the kinetic analysis, the reaction order for the both the processes were found to be second order. The rate constant values at optimum operating conditions were found to be 6 × 10<sup>-6</sup> and 4 × 10<sup>-6</sup> for peroxi-coagulation and photo-peroxi-coagulation processes respectively.

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AUTHOR PROFILE

	<p><b>Dr. Vishal Kumar Sandhwar</b> Assistant Professor, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India Specialization: Chemical Engineering Experience: 2.5 years 7 SCI publications B.Tech., M.Tech., Ph.D. in Chemical Engineering</p>
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	<p><b>Dr. Shivendu Saxena</b> Assistant Professor, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India. Specialization: Chemical Engineering Experience:3 years 4 SCI publications B.Tech., M.Tech., Ph.D. in Chemical Engineering</p>
	<p><b>Dr. Rohit Lade</b> Assistant Professor, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India. Specialization: Chemical Engineering Experience:1.5 years 5 SCI publications B.Tech., M.Tech., Ph.D. in Chemical Engineering</p>
	<p><b>Diksha Saxena</b> Assistant Professor, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India. Specialization: Chemical Engineering Experience:2 years 1 SCI publication B.Tech., M.Tech. in Chemical Engineering</p>
	<p><b>Dr. Basheshwar Prasad</b> Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee-247667, Uttarakhand, India, Experience:38 years 58 SCI publications</p>