Electrochemical Oxidation Treatment of Petroleum Refinery Effluent

Dhorgham Skban Ibrahim, P. Seethala Devi, N. Balasubramanian[*]

Abstract—An electrochemical oxidation process was carried out in a batch reactor for treating and upgrading petroleum refinery effluent, as a more adept option compared to the conventional methods, which consume more amounts of chemicals and produce large amounts of sludge. The electrochemical technology is regarded as a clean and powerful technology for the destruction of organic pollutants in water. The optimized electrooxidation conditions were current density 30 mA/cm^2, pH 8, supporting electrolyte 2 g/l, and treatment time 120 minutes. Under the optimal condition, the power consumption 69 kWh/kg, mass transfer coefficient 0.006164 cm/s, and COD removal efficiency 92 %, were estimated. FTIR analysis was also done to study the removal of pollutants by electrooxidation degradation. The result shows the applicability of electrochemical technology as an alternative for removing the pollutant generated in petroleum industries.

Index Terms— Electrochemical treatment; oil refinery; wastewater; FT-IR analysis; electrooxidation; petroleum; traditional treatment.

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1 INTRODUCTION

PETROLEUM refining is the physical, thermal, and chemical separation of crude oil into its major fractions that can be further processed through a series of separation and conversion steps into finished petroleum products. The products of crude oil like liquefied petroleum gas (LPG), gasoline, kerosene, aviation turbine fuels, diesel fuels, fuel oil, lubrication oils, petroleum waxes, and bitumen are very important in our daily lives and it is used in many industries. For the purpose of obtaining these products, the process requires the use of large quantities of water. About 80-90 percent of the water supplied to the petroleum refinery comes out as wastewater. The generated wastewater from petroleum refinery has polluting contents like free hydrocarbons, suspended solids, inorganic having high concentration of salts, phenol, benzene, sulphides, ammonia, and organic carbon [1, 2]. This wastewater tends to increase toxicity and creates the major environmental impact and taint the water, making them unsuitable for use.

The traditional treatment of the wastewater employed in the petroleum refineries typically involves a combination of primary, secondary and tertiary treatment processes. The stages of these processes can be seen in Figure 1.

The removal of petroleum contaminants to allowable global limits can be accomplished by means of well-known and accepted techniques such as electrochemical methods [3, 4], biodegradation [5, 6], membrane degradation [7], photo degradation [8], advanced oxidation processes [9, 10], fluidized bioreactor [11], and adsorption [12].

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However, the performance of any given separation technique will depend entirely on the condition of the wastewater mixture.
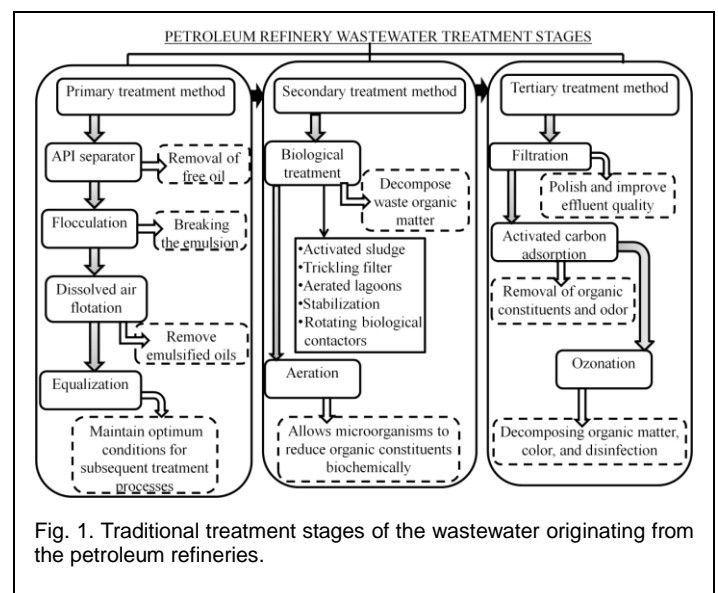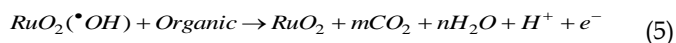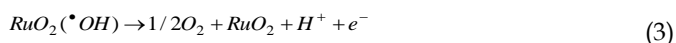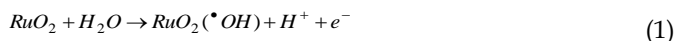

Fig. 1. Traditional treatment stages of the wastewater originating from the petroleum refineries.

The performance of electrochemical processes in mineralization of pollutants is established by the complex interaction of different parameters that may be optimized to obtain an effective and economical process.

The principal parameters that determine an electrochemical performance are: electrode potential; current density; current distribution; mass transport regime; cell design; electrolysis medium, and the electrode materials [13]. An electrochemical oxidation process was carried out in a batch reactor for treating and upgrading petroleum refinery effluent, as a more adept option compared to the conventional methods, which consume more amounts of chemicals and produce large amounts of sludge. The electrochemical technology is regarded as a clean and powerful technology for the destruction of organic pollutants in water. The optimized electrooxidation conditions were current density 30 mA/cm², pH 8, supporting electrolyte 2 g/l,

and treatment time 120 minutes. Under the optimal condition, the power consumption 69 kWh/kg, mass transfer coefficient 0.006164 cm/s, and COD removal efficiency 92 %, were estimated. FTIR analysis was also done to study the removal of pollutants by electrooxidation degradation. The result shows the applicability of electrochemical technology as an alternative for removing the pollutant generated in petroleum industries Equations 1 to 5 elucidate the electrode mechanism of oxygen evolution during the oxidation of wastewater [14].

$$RuO_2 + H_2O \rightarrow RuO_2(^\bullet OH) + H^+ + e^- \tag{1}$$

$$RuO_2(^\bullet OH) \rightarrow RuO_3 + H^+ + e^- \tag{2}$$

$$RuO_2(^\bullet OH) \rightarrow 1/2O_2 + RuO_2 + H^+ + e^- \tag{3}$$

$$RuO_3 \rightarrow 1/2O_2 + RuO_2 \tag{4}$$

$$RuO_2(^\bullet OH) + Organic \rightarrow RuO_2 + mCO_2 + nH_2O + H^+ + e^- \tag{5}$$

In this work, the electrooxidation process was applied to remove chemical oxygen demand (COD) from petroleum refinery wastewater using batch electrochemical reactor operated in a different conditions such as current density, pH, supporting electrolyte. Also, FTIR analysis was observed to study the functional group degradation of petroleum effluent.

2 MATERIAL AND METHODS

2.1 Characteristics of Refinery Effluent

The petroleum refinery effluent was taken from Chennai Petroleum Corporation Limited (CPCL) Chennai, India. The sample was collected from downstream of an API separator which effluents from this unit may still contain 400–500 mg/L of oil based on American Petroleum Institute design parameters [15]. The samples were preserved in frozen and then transferred for analyzed. The initial characteristics of the raw effluent are given in Table 1.

TABLE 1
THE INITIAL CHARACTERIZATION OF RAW EFFLUENT

Constituent	Value
pH	8
TS (ppm)	1465
TSS (ppm)	315
Phenol (ppm)	13.8
Sulfides (ppm)	16.8
COD (ppm)	480
BOD ppm	195
Oil and Grease (ppm)	94

2.2 Experimental Procedure and Setup

The experimental setup consists of a batch electrochemical reactor with the provisions for fixing the anode, cathode. The magnetic stirrer with stirrer bar was used and an opening for periodic removal of sample for analysis. The reactor was equipped with Ruthenium oxide coated Titanium as anode and stainless steel as the cathode with active surface area of 20 cm^2. The electrodes were fixed with an inter electrode distance of 2.5cm. A constant stirring speed was carried out at room temperature. A regulated power supply was used as D.C source (Metronic-305A). The electrolyte pH is measured using a digital pH meter (Roy Instrument- Model RI501A) and the electrolyte was adjusted using HCl or NaOH for appropriate experimental condition. Sodium chloride was added as supporting electrolyte. The samples are collected and analyzed for pollutant degradation for every 15 minutes of electrochemical treatment. The pollutant concentration is given in terms of Chemical oxygen demand (COD). COD was determined by the open reflux method. (FT-IR) analysis was applied to raw sample before treatment and after the treatment at optimal condition to study the effect of treatment on groups present in the sample. Figure 2. Shows the reactor set up.
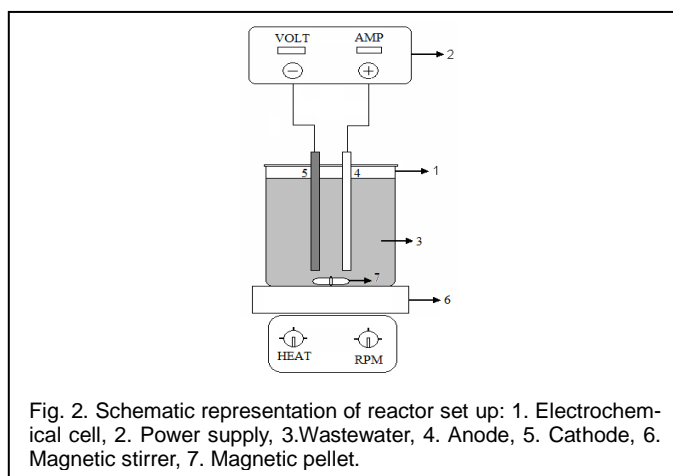

Fig. 2. Schematic representation of reactor set up: 1. Electrochemical cell, 2. Power supply, 3.Wastewater, 4. Anode, 5. Cathode, 6. Magnetic stirrer, 7. Magnetic pellet.

3 RESULTS AND DISCUSSION

3.1 Effect of Current Density

Figure 3 shows the variation of COD removal with respect to electrolysis time for various current densities. The percentage COD removal increased from 50 to 93 when the current density was increased from 6 to 35 mA/cm^2. Also the figure shows that the percentage removal of COD within the first 15 min range being 30-60% depending on applied current density, which may correspond to the loss of stability of the dispersion, whereas removal after this period was more related to the treatment process. The increasing in %COD removal above 30 mA/cm^2 was marginal; hence 30 mA/cm^2 was selected as optimal value.
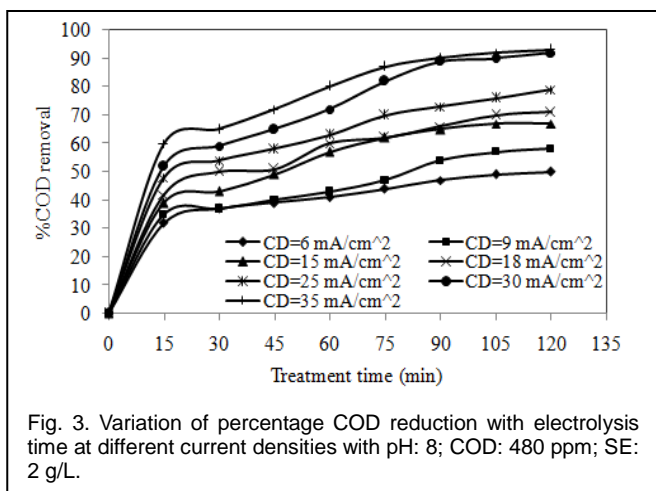
Fig. 3. Variation of percentage COD reduction with electrolysis time at different current densities with pH: 8; COD: 480 ppm; SE: 2 g/L.
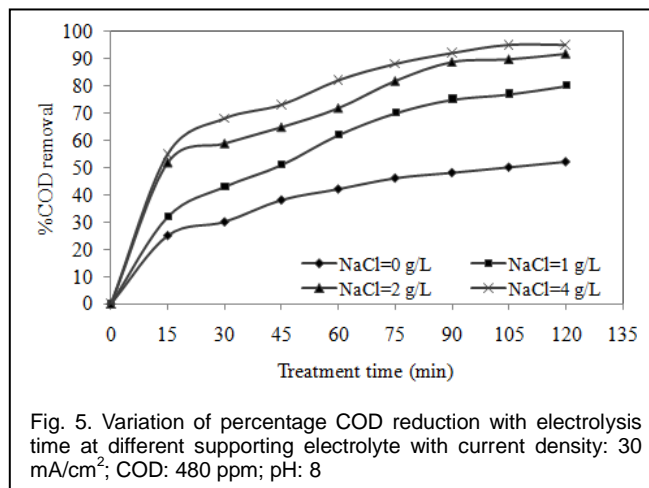

Fig. 5. Variation of percentage COD reduction with electrolysis time at different supporting electrolyte with current density: 30 mA/cm^2; COD: 480 ppm; pH: 8

3.2 Effect of pH

Figure 4 shows the effect of pH on percentage removal of COD. The percentage removal of COD changed from 70 to 93% as the pH changes from 4 to 10. The results show that the optimal pH was 8 (initial pH of the solution) for COD removal so the pH value without any adjustment was selected.
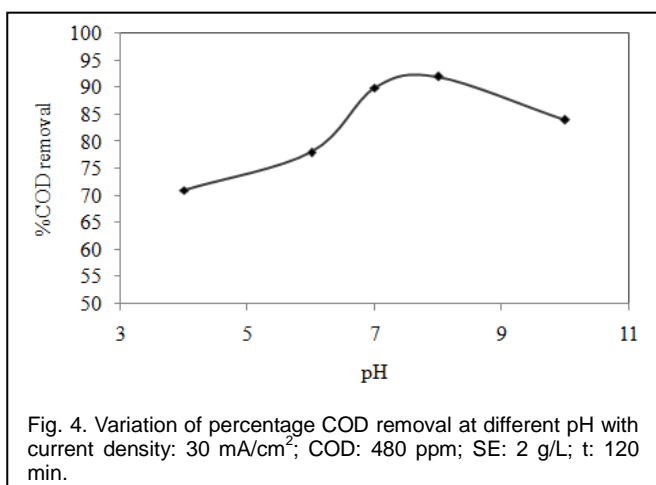

Fig. 4. Variation of percentage COD removal at different pH with current density: 30 mA/cm^2; COD: 480 ppm; SE: 2 g/L; t: 120 min.

3.3 Effect of Supporting Electrolyte

Figure 5 shows the effect of sodium chloride concentration on the percentage removal of COD. It was found that, as sodium chloride concentration increases from 0 to 4 g/L, the percentage of COD degradation was improved from 42 to 93%. It can be seen from the figure that the rate of COD removal increases as sodium chloride concentration increases up to 2 g/l and further increase (4 g/l) did not make significant improvement in pollutant removal, so the optimal sodium chloride concentration used to be 2 g/l.

3.4 Energy Consumption and Mass Transfer Coefficient

The mass transfer coefficient in an electrochemical batch reactor is [13]:

$$km = \frac{Vr}{Ae \cdot t} \ln\left(\frac{COD_o}{COD}\right) \qquad (6)$$

Where Vr is the volume of the reactor in (cm^3), Ae is the surface area of the electrode in (cm^2), t is the reaction time in (s), COD is COD concentration of the treated effluent in (mg/l), COD_o is an initial COD concentration of the effluent, and km is mass transfer coefficient in (cm/s).

The specific power consumption, (SPC) is the quantity of energy consumed in the process for a kg of COD to get digested. The term (in kWh/kg) can be obtained using the equation, [15]:

$$SPC = \frac{I_A \cdot V_A \cdot t}{V \cdot \Delta C \cdot 3600} \qquad (7)$$

where ΔC is the difference in COD values in (g/L), due to the treatment by passing I_A current in (A). V is the volume of effluent in (L), V_A represents the applied cell voltage in volts, and t is the electrooxidation time in (s).

Figure 6. shows the relation between specific power consumption and mass transfer condition with current density. The Specific power consumption and mass transfer coefficient increase with the increase in current density. The optimized current density was 30 mA/cm^2 due to high km and COD removal efficiency as shows in Table 2.
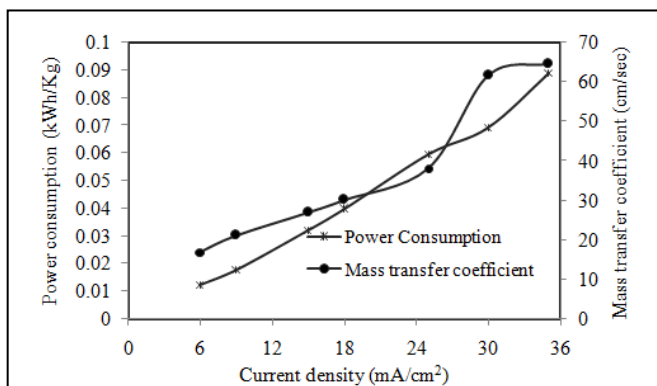
Fig. 6. Variation of power consumption and mass transfer coefficient at different current density.
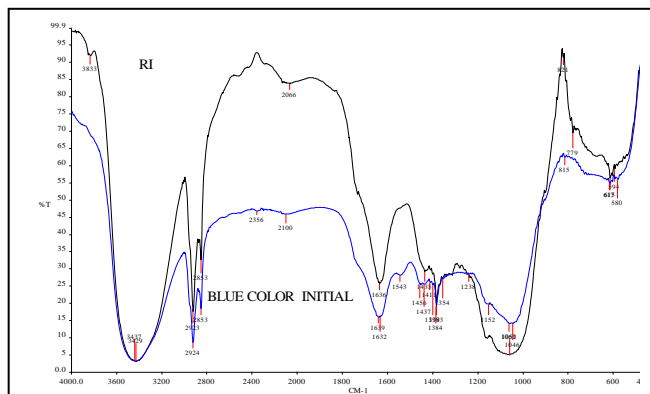

Fig. 7. FT-IR analysis of the raw and treated refinery wastewater at optimum conditions.

TABLE 2
EFFECT OF CURRENT DENSITY ON THE PERFORMANCE OF THE ELECTROCHEMICAL REACTOR, C_0: 480 MG/L, T: 120 MIN, SEC: 2 G/L, AE: 20 CM^2, V_R: 350 CC

CD (mA/cm^2)	Cell Voltage, (V)	% COD Removal, η	Power Consumption SPC, kW h/kg	K_m x10^4 cm/s
6	4.2	50	12	16.84
9	4.8	58	17.6	21.15
15	6	67	31.9	27.00
18	6.6	71	39.8	30.12
25	7.9	79	59.3	38.12
30	8.9	92	69	61.64
35	9.9	93	88.7	64.63

TABLE 3
FTIR- GROUP COMPONENTS AND PEAK VALUE

Range (cm^{-1})		Molecular motion	
Before Treatment	After Treatment	Before Treatment	After Treatment
3429	3437	N-H	N-H stretch
2924	2923	Symmetric stretching of C-N	OH stretching of the hydroxyl group
2100	2066	NH$_3$ stretching of amino amide	N-H stretch of amides
1639	1636	Stretch of secondary amide	NH bending
1456	1435	CH deformation of alkanes	C-H pla
617	615	Saturated Aliphatic and aromatic compounds.	The mineralization of aromatic rings

3.5 FTIR Analysis

Corresponding to the wave number and percentage transmittance, the groups present in the sample can be inferred as shown in Figure 7 and Table 3. Analysis of isolated samples informs about the distribution of functional group within the organic compound and provides a basis for comparison of compositional differences between isolates and among samples. Considerable reduction in intensity of peaks was noted after treatment when compared with raw effluent.

4 CONCLUSION

Electrochemical oxidation technology was carried out to remove pollutants from petroleum effluent using a Ti/RuO$_2$ anode in the batch electrochemical reactor. The present findings indicated that the degradation rate was affected by current density, pH, and supporting electrolyte during 120 minutes of electrochemical treatment. Strong electro-generated oxidants, such as $RuO_2(^\bullet OH)$ and $RuO_2(^\bullet OCl)$ formed by supporting electrolyte (NaCl), participating in the electrooxidation, therefore increasing the efficiency of the oxidation process. The optimum mass transfer coefficient was attained at current density 30 mA/cm². FTIR analysis conforms the removal of pollutants by electrooxidation from the effluent

ACKNOWLEDGMENT

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