TREATMENT OF CUTTING OIL EMULSION BY ELECTRO-OXIDATION PROCESS

M.Tech. Dissertation

Submitted in the partial fulfillment of the requirement for the award of degree of

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by

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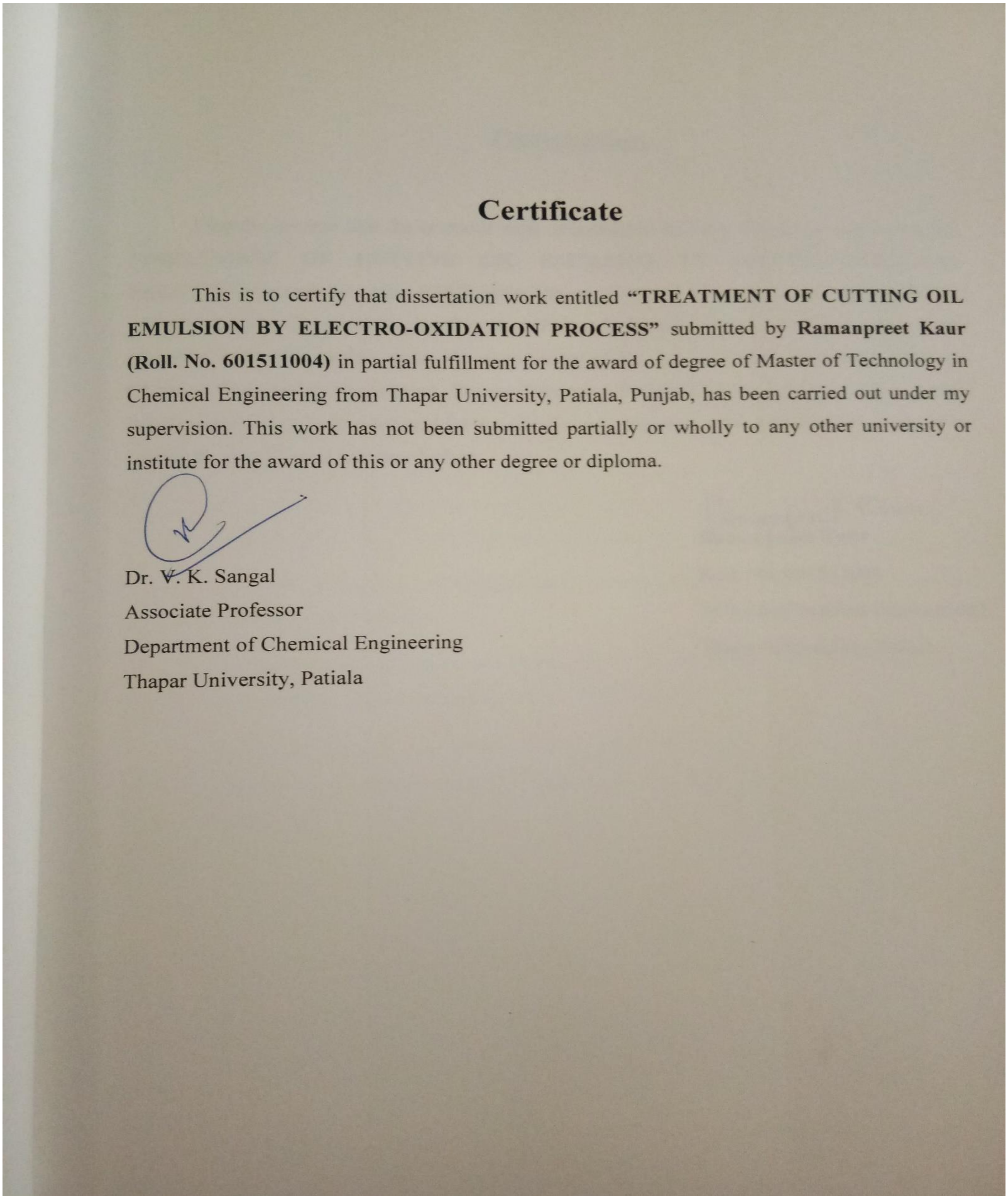

Certificate

This is to certify that dissertation work entitled **“TREATMENT OF CUTTING OIL EMULSION BY ELECTRO-OXIDATION PROCESS”** submitted by **Ramanpreet Kaur (Roll. No. 601511004)** in partial fulfillment for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, Punjab, has been carried out under my supervision. This work has not been submitted partially or wholly to any other university or institute for the award of this or any other degree or diploma.

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Declaration

I hereby declare that the research work presented in M.Tech dissertation report entitled **"TREATMENT OF CUTTING OIL EMULSION BY ELECTRO-OXIDATION PROCESS"** by me in the partial fulfillment of the requirements for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, Punjab, is an authentic record of my work carried under the supervision of Dr. V. K. Sangal, Associate Professor, Chemical Engineering Department, Thapar University, Patiala. Further, I declare that no part of this dissertation has been submitted for the award of any degree or other qualification, in any other university or published any time before.

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Abstract

Wastewaters comprising oil-in-water (O/W) emulsions are generated in many industrial processes such as food processing, petroleum refining, petrochemical and metal finishing industries. A large amount of waste oil water emulsion is thus generated in this fashion worldwide every year by various industries.

In the present study, demulsification of soluble oil-emulsion was done by electro-oxidation (EO) using a Ti/RuO_2 in batch and continuous mode. The effect of pH, current, flow-rate and electrolysis time on the removal efficiencies of demulsification process was examined. Box behnken design (BBD) under response surface methodology (RSM) was used to optimize the selected process parameters. The BBD model fits very well with the experimental data. The R^2 value for percentages removal efficiencies of oil, turbidity, COD and energy consumption were 0.9833, 0.9894, 0.9976, and 0.9913 in batch mode respectively, 0.9535, 0.9858, 0.9819, 0.9849 and 0.9781 for oil, turbidity, COD, energy consumption and mass transfer coefficient in continuous mode respectively.

The optimum pH, current and electrolysis time were found to be 7.23, 0.50 A, and 99 min and elapsed time, flow-rate and current was 170 min, 2.2 cc/min and 1.11 A for batch and continuous modes, respectively. The experimental values oil, turbidity and COD removal at optimized conditions are found to be 98.83 %, 99.90% and 94.93% for batch process and 92.90%, 98.99% and 91.36% for continuous process, respectively. Mass transfer coefficient for continuous process found to be 0.658 (m/hr). Minimum energy consumption for batch and continuous process are 2.833 (KWh/m^3) and 19.57 (KWh/m^3).

Keywords: Electro-oxidation; oil-water emulsion; pH; cutting oil; RSM.

Contents

Chapter :1 Introduction **Page no.**

List of Figures

List of Tables

Nomenclature

Abbreviations

WMCFs	Waste metal cutting fluid
COD	Chemical oxygen demand
TOC	Total organic carbon
EO	Electro-oxidation
EC	Electrochemical
ECP	Electrochemical process
MINAS	Minimal national standard
COD	Chemical oxygen demand
RSM	Response surface methodology
BBD	Box Behnken Design

Chapter-1

INTRODUCTION

1.1 General

The use of the cutting oil was firstly described in 1894 by F. Taylor who observed without reducing tool life by applying large volumes of water in the cutting area, cutting speed would be increased up to 33 % (Avila et al., 2001). The cutting fluids called as soluble oils are extensively used in metallurgical industries, such as metal rolling, cutting operations, metal forming, drilling and metal working operations/ mechanical operations of machining and grinding of metal surfaces reduce the friction between the mechanical and metal surfaces. Soluble oil water emulsions such as a mixture of cutting oil and water forms a whitish fluid, these emulsion provide a lubricant and coolant for different metal-working operations. Various types of the cutting fluid such as soluble oil, synthetic oils and semi synthetic oils used in the metal cutting operations (Patel et al., 2016). They including up to 15% of mineral oils and combination of vegetables and animal oil, mineral oils. Some additives, emulsion stabilizers, corrosion inhibitors and anti-degradation agent also added to improve its life, resistance to bacterial growth and low corrosion capacity (Kobya et al., 2008 and Cheng et al., 2008).

The temperature of oil water emulsion is usually maintained in the range of 40 to 90 ^{0}C, due to heat removal from the metal surface. The cost of the cutting oil is high, after use a solid particles are removed from the fluid, they are reused in the metal working operations. Due to the prolonged use and exposure of environmental conditions, oil emulsion losing effectiveness and properties, thus yielding a waste oil emulsion which generally high in COD and turbidity. Therefore, the o/w emulsion is replaced periodically (Demirbas et al., 2017). So, it must be treated before discharge into the drainage, the environmental regulatory agencies must conform a discharge standards for the treated waste water. In India, the Ministry of Environment and Forests has set the standards of 10 mg^{-l} and 20 mg^{-l} of oil/grease concentration for the discharge of wastewaters in land surface waters and public sewers, respectively, under the Environment (Protection) Act, 1986. The numerous resources of oil waste water (Patterson 1985) was illustrated in Table 1.1

Table 1.1 Resources of oily waste water

Manufacturing process	Oil concentration (mg/ *l*)
Petroleum refining	20- 4000
Car washing	50-2000
Metal handling and finishing	100-20000
Copper wire drawing	1000-10000
Food processing industries	500-14000
Aircraft maintenance	500-1500
Paint manufacturing	1000-2000
Cleaning bilge water	30-2000
Edible oil refining	4000-6000
Wool scouring	1500-12500
Leather processing	200-40000
Aluminum rolling	5000-50000

1.2 Oil water emulsion

An emulsion is a homogenous combination of two or more immiscible liquid phases, such as oil and water, in which the liquids are mutually insoluble. In water chemistry, two types of emulsions are usually found, oil water emulsions (oil emulsified in water or O/W emulsions) and waste oil emulsions (water emulsified in oil or W/O emulsions). Various types of emulsion categories as showed in Table 1.2. In an O/W emulsion the oil precipitations were spread in a continual water phase (>30% water), and in a water-in oil (W/O) emulsion an uninterrupted oil phase (<25% water), respectively (Coca et al., 2011).

The stability of the emulsions in the thermodynamic conditions was did not change, and they can change these stability only in particular ranges of composition, pressure, and temperature. There are three leading interaction energies (forces) within emulsions droplets was a Vander Waals attraction, electrostatic repulsion and Brownian diffusion (motion). The Vander Waals attraction is induced the attraction between two or more molecules of oil droplets that are very close to each other. The Brownian motion was the indiscriminate motion of colloidal between suspended particles in a liquid or gas, affected by collisions with molecules of the surrounding oil emulsion droplets. The colloids particles were small enough to be affected by random molecular collisions and rapidly settled to the bottom of the vessel, the some distributing droplets approach the interface. Electrostatic forces are an attraction or repulsion between the different elements and based on their electrical charges surrounding particles and droplets.

Table 1.2 Emulsion categories

Free (floating) emulsion	Dispersed emulsion	Emulsified emulsion	Dissolved emulsion
Immiscible in water, rise quickly to the water surface under quiescent conditions	It is an array of fine droplets stabilized by their electrical charges	It has a similar distribution as dispersed oil, but it stability was enhanced by surfactants.	The oil is not present as visible droplets, but truly dissolved chemically or dispersed extremely fine droplets.
≥ 150 μm	20-150 μm	≤ 20 μm	≤ 5 μm

1.3 Stabilization and Surface Charge

The oil water emulsion are very stable because of certain additional forces i.e. Brownian motion and electrostatic forces. Brownian motion is a random motion of particles due to the continuous collusion of phase molecules with the dispersion phase molecules of the oil emulsion. Due to these collusions small movements of dispersed phase particles, the small redistributing oil droplets reaches to the interface.

Electrostatic stability rises as an effect of the electrical double layer encompassing each droplet as shown in Figure 1.1. This avoids the nearly approach of one droplet to another. Most oil particulates suspended in water take on a net negative charge. Phase changes can emerge from the particular adsorption of potential determining elements, at the interphase separation of ionic species, core atomic imperfections into the solid phase, or other reasons. This surface change was counterweigh by dissimilar charged ions in the liquids adjacent to the solid-liquid integrate. This fixed cationic layer is in turn neutralized by a diffuse layer of anions assembled inside it.

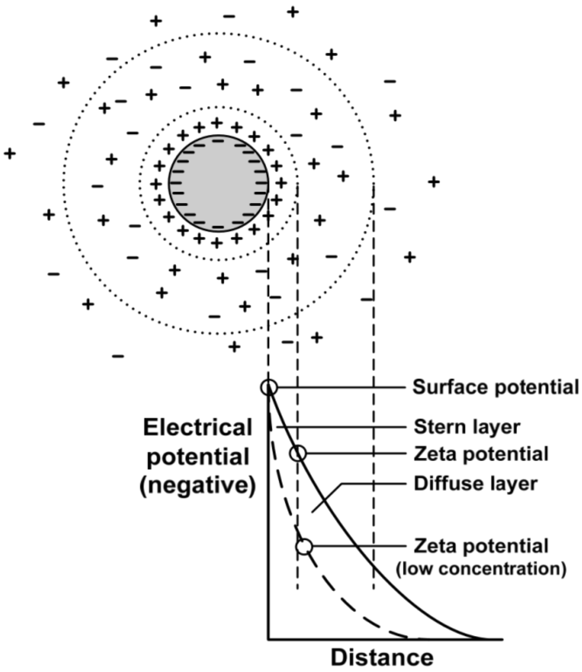


Figure 1.1 Electrical double layer and Zeta potential

Figure 1.2 is a representation of an electrical double film based on the Gouy-Chapman model. Outside this fixed layer was diffuse surface of ions whose attentiveness is described by Boltzman distribution. A surface of fixed, approximately immobilized ions nearby to the negatively charged surface decreases the surface probable to the stern potential.

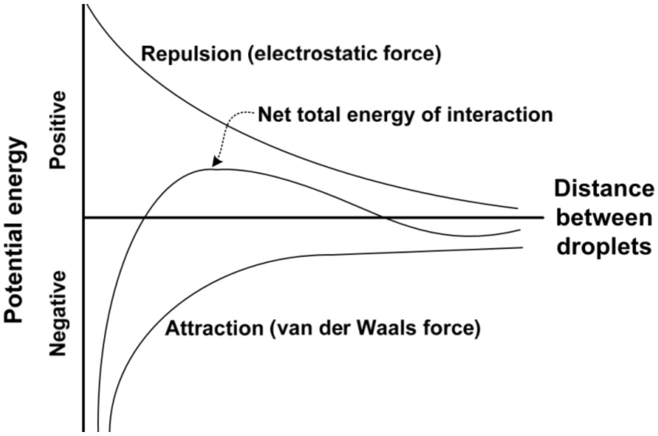


Figure 1.2 Interaction between oil droplets by potential energy

Since each molecule has an electrostatic charge of the similar polarity, at longer distances they initially repulse each other. However, as the distance between them decreases, short-range Vander-Waals universal forces are also considerable. These forces appear from interrelating, induced atomic and stable dipoles essential dispersion forces.

1.4 Cutting Oil

Cutting oils was a combination of a mineral oil (40-60 wt %), germicides (20-60 wt %), coupling agents, additives and emulsifiers. In cutting oil emulsion generally water content varies between (3-60 %). In the oil contaminated waters generally contain 15-20 % of oil emulsions, minerals oils, combinations of vegetable, mineral or animal oils.

1.5 Usages and characteristic of cutting oil

Cutting fluids have two major utilization are: cooling and lubrication. The primary function of the cutting oils was to diminish abrasion and adhesion at low cutting rate by lubrication and providing the cooling effects to cool the tools and work segment at high cutting rate and temperature. The grinding method creates a significant quantity of heat began by the undefined cutting situations prevailing about high relative rate between crushing roll or work piece, as well as effective cooling from the cutting fluid.

1.6 Characterization of ecological factors

The effects of cutting fluid on living environment, mechanical operations, machine parts and mankind explained by their ecological parameters. These cutting oil must still be resistant at the contact temperature avoiding at a working point i.e they must not yet have reached their melting point and after use, it become a hazardous waste. Depending on mode of disposal, it resulting a ground, water and/or air pollution.

1.7 Classification of cutting oil

1.7.1 Oil-based cutting fluids

Cutting oils was a mixture of different sorts of oil, i.e vegetables, animal and mineral. Mineral oils were the considerable verities caused by their appropriate lubricating features. These cutting solutions generally containing some extracts oil improve their utilization. For example, the nature of the oil based cutting fluid the characteristics of inorganic oils and paraffinic oils were generally improved by the insertion of fatty lubricant, supreme pressure additives, aura, polar additives and thickness modifier.

1.7.2 Synthetic cutting fluids

The oil which was produced from extracts of chemicals and make weaker by adding water and independent from mineral oil and other oils. Synthetics cutting fluid improve water ease, confrontation, lubrication, corrosion resistance and mixing by expansion of organic and inorganic chemicals in the oil. These fluid generates clear solutions and giving great perceivably for cutting operation.

1.7.3 Semi-synthetic cutting fluids

Semi-synthetic cutting oils providing further lubrication than the synthetic oils by increasing the mineral oil concentration between 10 to 50 %. The emulsion of these fluids having diluted mineral oil with water by some extracts to decreased the extent of oil elements making it gives more efficient lubricant. The benefits, limitations, and utilization of cutting oil types as illustrated in Table 1.3 and Table 1.4 respectively.

Table 1.3 Benefits and limitations of cutting fluid type (Patel et al., 2016)

Category of cutting fluid	Benefits	Limitations
Straight oil	Excellent lubrication and corrosion resistance	forming smog or smoke, limited to low-rate, Low temperature cooling and fire hazard
Soluble oils	Good lubrication and cooling	Corrosion resistance problems, highly bacterial growth, and evaporation losses
Semi synthetics	Good cooling, rust control and microbial control	Solidity is pretentious by stiffness of water, and simply polluted by other device solutions, easy to ready
Synthetics	Excellent cooling, bacterial control, fire-resistant, good deterioration control, reduced haziness and fizzing	Poor lubrication and easily contaminated

Table 1.4 Utilizations of cutting fluids (Patel et al., 2016)

Nature of oil	Occurrence	Service	Dilution
Oil based cutting oil	Oily, wastes	Dense material, anti-rust retardation.	Not Required
Emulsifiable oils	whitish color	Cooling and lubrication, corrosion retardation.	Yes, 2-3%
Semi-synthetic oils	Transparent	Cooling and lower lubrication than aqueous Oils	Yes, 1-3%
Synthetic Oils	Transparent	Magnificent coolant, insignificant lubricant	Yes, 1-5%

1.8 Minimal national standards (MINAS) for industrial effluents

The Central Pollution Control Board (CPCB), Delhi, under powers vested in it through the water (Prevention and control of pollution) Act, 1974, has prescribed effluent standards for various quality parameters. For oil and greases, the standard limit is 10 mg/*l* as shown in Table 1.5. Taking in to account the treatability of the effluent from the technical feasibility point of view, the cost of treatment and cost burden that can be boomed by industry, CPCB has noticed industry specific MINAS. The MINAS will be binding for all industrial units throughout the country

Table 1.5 Effluent Criteria for Industries. Sources: CPCB book

Parameter		Oil and grease
Limit for disposal to sewers		10 mg/*l*
Limit for disposal to open drains	Flow = 25 KLD	0.25 Kg/day
	Flow > 25 KLD	10 mg/*l*
Limits for disposal on land		10 mg/*l*

1.9 Effects of oil effluent on water bodies

Oils excrete into the water bodies/on soils causes adverse effects on the atmosphere, human health and water treatment process appeared in Table 1.6. Oil present in the waste process water also creates an issue.

Table 1.6 Impact of oil-discharged contaminants

Impact on atmosphere	Impact on human health	Impact on Industries manufacturing processes
1) Free oil obstructs the penetration of sunlight in river water distracting aquatic life and restricts natural cleansing of water in rivers or lakes	1) Consumption of untreated chemically emulsified oil disposed in river causes several health risks like cancer.	1) Oil contaminated water causes foaming, priming, over heating of tubes, as a result less amount of heat exchange, also creating a problem in stream production and cooling
2) Adverse odour from oily waste was a nuisance	2) Bathing in contaminated oily water causes skin cancer.	2) Emulsified oils can obstruct filters and ion exchange beds, reduces efficiency of filtration.
3) Oil waste water may coat the gills of fish and reduces the oxygen transfer makes fatal for them	3) Fish affected by toxic oils, if consumers can cause nausea and vomiting	3) In biological treatment the oil layer attached to the microorganisms forming barrier to oxygen and nutrient transfer to biomass and decreases the treatment efficiency.

1.10 Treatment of oil water emulsions

Conventional waste water treatment methods and their drawback:-

- ➢ Biological treatment
- Aerobic biological treatment
- Anaerobic biological treatment
- ➢ Physio-chemical techniques
- Chemical coagulation
- Electrochemical treatment
- Adsorption
- Membrane filtration
- Advanced oxidation process

Various conventional treatment methods have revealed either limited success or high energy consumption. The coagulation treatment process formed huge amount of sludge and poses a problem of sludge disposal, and treatment waste water was contaminated by added coagulants and contribute secondary pollution. Membrane was very costly and has drawback of the potential membrane. Adsorption process was very time consuming and costly treatment method with low efficiency. Primary, secondary and tertiary treatments for oil emulsion as shown in Table 1.7. Nevertheless, these process were not accomplished of eliminating all hazardous elements from effluents or formed a huge volume of toxic mud.

Table 1.7 Treatment categories of oil water emulsions

Primary analysis	Secondary analysis	Tertiary analysis
Removal of floating oil from dispersed blended and dissolved fractions, oil wet solids.	Breaking of oil water emulsion to remove dispersed oil.	Removal of dispersed soluble oil fractions.
Utilize sedimentation, flotation and centrifuge related technique.	Utilizes chemical treatment and filter coalescence or other techniques.	Utilizes ultrafiltration, biological treatment and carbon adsorption or other techniques.

1.11 Oil water separation technology

1.11.1 Gravity separation

Gravity settling is simplest and cheapest method for treating oily waste water. Because of the density difference, by gravity forces the water was settle down through oil. When forces (gravitational and drag) are became equal, then from Stoke's law a constant velocity computed,

$$v = \frac{\left(1.78 \times 10^{-6}\right) \Delta y_{ow} d^2}{\mu_0}$$

Where

d = the water droplet diameter, μm

v = the water droplet downward velocity, ft/sec

$\Delta\gamma_{ow}$ = the specific gravity difference among the oil and water

μ_o = oil dynamic viscosity , cp

The water droplet size was greater, than its downward rate is high i.e., the higher the drops, takes lesser time to settle at the bottom, and thus the easier it was to treat the oil. The density difference between the water droplet and the oil, if the downward velocity was greater than separation was easier. It is effortless to process the oil at low and high temperatures. The effectiveness of the gravity separator depend upon the hydraulic design and time period for taken for the treatment of oily waste. Longer retention time generally increase separation efficiency.

1.11.2 Filtration

Filtrating process have been applied for the removal of emulsified from the water streams. The effectiveness of oil removal by filtration which is based on adsorption of the oil onto clarifying material induced coalescence and growth of oil droplets and droplet size. In which the oily waste water passes through a filter bed for removal of the droplets, the clean waste water was collected at the filter outlet.

1.11.3 Air flotation

Separation of oil droplets and light solids by introducing the fine air bubbles into the waste water. There are mainly two sorts of the air flotation such as:

Induced air flotation was a course which is liquid and air separated by mechanical blended to induce bubble development in the liquid.

Dissolved air flotation (DAF) in which compacted air was utilized to pressurize the oily waste water that was disintegrated in the liquid. When the pressure was reduced very fine gas bubbles were formed into the solution.

1.11.4 Carbon Adsorption

This process was not much use in the free oil expulsion but still, it is in practice. Which wastewater was further treated to avoid the coating and clogging of activated carbon with free oil.

1.11.5 Chemical coagulation

Chemical treatment utilized for the elimination of suspended or colloidal oil. Chemical coagulation has been utilized for dissolving the metals parts and also biological species from aqueous streamlet, thus allowing their evacuation through filtration or sedimentation, lime, alum, and furthermore polymers chemical coagulants utilized. The main disadvantage of this course are, obtained in excess quantities of mud which is large bound content present those reduce the rate of filtration.

1.12 Electrochemical Technologies

Electrochemical techniques were rather straight and simple which can degrade numerous hazardous contaminates entirely before they influence into the water. Electrochemical techniques are very effective for treatment of the effluents, have been applying appropriately to treat different wastewaters, industrial waste water, food industry effluent and heavy metal containing effluents. Electrochemical technologies, involved such electrochemical coagulation (EC), electro-oxidation (EO) and electrochemical flotation (EF). These strategies were examined underneath:-

1.12.1 Electroflotation

Electro-flotation was a simple method tiny bubbles of hydrogen and oxygen gases was prompted from water electrolysis. These bubbles support to contaminants float to the surface of water body. Consequently, the electrochemical reactions at the anode and cathode were oxygen and hydrogen evolution reactions, respectively.

1.12.2 Electrocoagulation

Electrocoagulation process also called an electrofloculation process includes in which the formation of coagulants in situ by dissolving electrically either aluminum or iron ions from respectively aluminum or iron electrodes. Hydrogen gas was discharged from the cathode and metals ions generation take place at the anode. The hydrogen gas would besides help to float the flocculated elements out of the water. The electrodes can be organized in a mono-polar or bi-polar mode.

1.12.3 Electro-oxidation

Electrochemical oxidation of wastewater is a complex phenomenon. Electrical energy was utilized to generate an oxidant, which oxidize the contaminants present in the wastewater. In direct oxidation in which hydroxyl radicals generated on surface of anode and indirect process in which the oxidants such as chlorine, hypochlorite and hypo-chlorous acid or hydrogen peroxide/ozone were generated at electrodes. The electro-oxidation process for treatment of the waste water is subdivided into the two sub-categories.

- Indirect anodic oxidation (organics are demolished at the surface of the electrode)
- Direct oxidation (a mediator was electrochemically generated to carry out oxidation)

1.13 Electro-oxidation process

1.13.1 Introduction of the technology

Study on the treatment of wastewater by electro-oxidation was explored in 19's century. Predominantly the exploration work was focused on the different types of the electrodes on the oxidizing efficiency the treatment of contaminants, electrochemical stability of the electrode material, factor influencing the process performance, performance of the anodic materials and kinetic of the contaminants degradation. Electro-oxidation process in which contaminants are degraded or oxidized and converted into carbon dioxide and water. With the impact of the electrochemical technologies, the cost of the treatment was decreased. Because of a high efficiency, easily maintained, operating under normal temperature and pressure, it has the consideration of the researchers. The electro-oxidation process for treatment of the waste water is subdivided into the two categories

1.13.2 Indirect electro-oxidation

Indirect electrochemical, Organic pollutants were oxidized by electrochemically generated oxidants during the electrolysis. The chloro-oxidant CI_2, HOCI and CIO^- and hydrogen peroxide are generated at anode (Xue et al., 2011). At anode, in the presence of chloro-oxidant species (CI_2, HOCI and CIO^-), sodium chloride are generated (Chen 2004) via following reaction 1.1-1.6:-

$$2CI^- \rightarrow CI_2 + 2e^- \tag{1.1}$$

$$CI_2 + H_2O \rightarrow HOCI + HCI \tag{1.2}$$

$$HOCI \rightarrow H^+ + OCI^- \tag{1.3}$$

$$O \rightarrow O_2 + H^+ + e^- \tag{1.4}$$

$$2 \cdot OH \rightarrow H_2O_2 \tag{1.5}$$

$$\cdot OH + \ H_2O_2 \rightarrow HO_2 + H_2O \tag{1.6}$$

Depending upon the pH, the type of chloro-oxidant is generated. At highly acidic medium the chloride ions were found ($pH<3$) and OCl^- was the predominant species for $pH\geq7$. At $3<pH<5$ HOCI was found to dominate, having maximum oxidation ability between all chlorine species. At basic medium, the ClO_3^- and ClO_4^- ions were also formed. During the oxidation mediated by these chloro-oxidant species, the possibility of formation of chlorinated organic compounds, which are reported to be toxic. Also, H_2O_2 and O_3 may produce through following reaction equation 1.7-1.8:-

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1.7}$$

$$4\,H_2O + 2O_2 \rightarrow O_3 + 2H^+ \ + 2e^- \tag{1.8}$$

Excluding these mediators, ·OCl free radicals, nascent oxygen and free chlorine and were formed in electrolytic oxidation and mediate the oxidation of organics (Kumar et al., 2016 and Cong et al., 2016).

1.13.3 Direct anodic oxidation

In electro-oxidation contaminations were directly oxidized on surface of anode with forming physically adsorbed "active oxygen" (adsorbed hydroxyl radicals, ·OH) or chemisorbed "active oxygen" (oxygen in the oxide lattice, MO_{X+1}). This process is generally called anodic oxidation or direct oxidation. Interestingly, electrochemical degradation results water and CO_2, no additional purification being necessary (Huitle et al., 2006 and Sarkka et al., 2015). However, the feasibility of this process based upon the formation of chemically or physically adsorbed hydroxyl radicals, oxygen advancement reaction and nature of the anodic material.

$$M + H_2O \rightarrow M(HO\cdot) + H^+ + e^- \qquad (1.9)$$

The mechanism for the electrochemical oxidation of organics, depends upon oxygen evolution reaction in aqueous fluid media (Bashir et al., 2009). In active electrodes, there is a strong connections among the electrode (M) and the hydroxyl radicals (·OH). Adsorbed hydroxyl radicals may interface with the anode, forming a so called higher oxide MO as appeared in (Equation 1.10)

$$M\,(\cdot OH) \rightarrow MO + H^+ + e^- \qquad (1.10)$$

In active electrodes for the oxidation of organics, the redox couple MO/M exhibitions as a mediator (Equation 1.11). This reaction was compares with the subordinate reaction of oxygen evolution, which was formed caused of chemical deterioration of the higher oxide as appeared in (Equation 1.12)

$$MO + R \rightarrow M + RO \qquad (1.11)$$

$$MO \rightarrow M + \frac{1}{2}O_2 \qquad (1.12)$$

For a non-active electrode, poor connections exist among the hydroxyl radical and the electrode surface. From equation 1.13, the oxidation of organics was mediated by hydroxyl.

$$M(HO\cdot) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \qquad (1.13)$$

In the Equation 1.13, R was fraction of an organic element, which required one oxygen atom to be completely transformed into CO_2 (Ganzenko et al., 2014). This reaction compares with the subordinate reaction of hydroxyl radicals to oxygen except any contribution of the anode surface (Equation 1.14):

$$M(HO\cdot) \rightarrow M + \frac{1}{2}O_2 + H^+ + e^- \tag{1.14}$$

1.13.4 Typical reactor design

The easiest electro-oxidation reactor configuration was the bipolar electrolysis cell. Additionally plane anodes, the round and hollow electrodes can be utilized. In electrochemical oxidation, reactor configuration was to keep up mass exchange rates as the main reactions that happen on the electrode surface. For bio-electro reactor, at surface of the cathode a thin layer of biofilm was immobilized. It was observed to be equipped for oxidation, when separate microorganisms are immobilized on the anode.

Generally classified into two electrodes, was two dimensional and three dimensional and both types of categorized into static and movable electrodes. The static parallel and cylindrical electrode cell was utilized in current investigations of waste-waters by electro-oxidation. The utilization of movable electrodes leads to expanded estimations of the mass-transfer coefficient because of turbulence advancement.

1.13.5 Electrode types

- Doped SnO_2 electrodes: Doped SnO_2 exhibit moderate resistivity, great stability, a high potential for O_2 evolution reaction and viable contaminants expulsion. The conductivity of SnO_2 electrodes was low (Brain 2014). The most recognized dopant was Sb, SnO_2 electrodes promote complete organic compound oxidation.
- PbO_2 electrodes: was mostly investigated anode electrode for electro-oxidation. PbO_2 electrodes were prepared polarized metal lead in H_2SO_4 solutions or by electrochemically coating of PbO_2 on Ti material (Chen 2004). Later studies examined PbO_2 and doped-PbO_2 anodes on a variety of compounds. PbO_2 electrodes are comparatively inexpensive and viable in oxidizing of contaminants.
- Doped and sub-stoichiometric TiO_2. TiO_2 was able to encourage the mechanical stability. Ti/RuO_2 electrodes arranged longer lifetime and higher electrochemical active region.
- Boron-doped diamond electrodes. The most promising and broadly contemplated electrode for electro-oxidation advanced oxidation process was BDD. BBD electrodes have very low capacitance and resistance to anodic corrosion.
- Pt electrodes demonstration very poor capacities in anodic oxidation of organic substances.

1.13.6 Advantages of the electro-oxidation

Electro-oxidation degradation of waste water treatment have several advantages as compared to the others technologies are following:-

- It can be easy to operate at room temperature and atmospheric pressure.
- It is a clean technique, consumption of chemicals was avoided, so there was no issue of degradation of overabundance chemicals and no probability of secondary contamination generated by addition of chemical compounds at high concentration as when treatment of waste water by coagulation.
- No moving parts and requires less maintenance.
- Electrolytic process is easily controlled by varying the applied voltage and current density.
- High efficiency for degradation the smallest colloidal substances due to the applying electrical field.
- Very less amount of sludge producing in this techniques. Sludge formed by electrochemical technique tends to be easiest to settable and de-water.
- No generation of the secondary pollutant.

Chapter-2

LITERATURE REVIEW

For the treatment of cutting oil emulsion various types of treatment technologies are available in literature. In this chapter, review of literature on the treatment technologies for oily wastewater is presented. Some general studies were given below:

General studies

Sokovic et al. (2001) studied about the ecological parameters and its machinability parameters effected by cutting fluid. This paper deals with the production process considering ecological norms based on the quality factors of the fluids. The economical cutting speed of the tools was increased by using a cutting fluid and it usually improves the effectiveness of the machined material or cutting tools. Through introducing the new cutting fluids with quantifiable presentation characteristics have been accomplished using a tapping test to satisfy the requirement of the environment safety act. The main objective of this study was obtained to suitable combinations of cutting fluid from point of view of improving the machinability parameters for cutting speeds.

Portela et al. (2001) studied the supercritical water oxidation (SCWO) to reduce a wide range of wastes and kinetic study of a complex effluent. But there are few literature available on the SCWO to treatment of oily wastes water and kinetics study have been found. The modified generalized model was efficient to predicting accurately the practical conversion attained Treatment of cutting fluids in a uninterrupted flow system operated at a suitable temperature conditions by SCWO. A generalized kinetic study of the cutting fluid, and developing a model to presenting the evolution of the SCWO process in terms of TOC and acetic acid. Due to its toxicity and stability, CO_2 has been found in almost all reactions at very high concentrations.

Portela et al. (2001) studied about the degradation of cutting oil waste water by hydrothermal oxidation. Hydrothermal oxidation was mainly a two forms, is wet air oxidation (WAO) and supercritical water oxidation (SCWO). Supercritical water oxidation was more efficient as compare to the wet air oxidation. For oily waste water, SCWO was a more efficient techniques as estimate to WAO process since operating at very high temperatures are usually more than 500 ºC. But this type of technique used of particular circumstances leads to main drawbacks in the commercialization of the technique.

In a consistent stream system, both oxidation has been tried to treat cutting oil wastes at high temperature. Hydrogen peroxide use as a source of oxygen and free radicals by initiating it which the reactor with or without prior thermal deterioration, respectively.

Organic material was effortlessly oxidized in each cases determining higher than 90% TOC diminishment in less than 10 seconds at very high temperature. The oxidation process enhanced at low temperature by using the promoters Activation energies was calculated for normal and promoted oxidation processes.

Talbi et al. (2009) studied the treatment of oily pollutant effluent based on phase separation applications using two aqueous phase extraction techniques. This paper deals with the two commercial ethylate fatty alcohol surfactants are used to treating a dissolving and dispersed organic contaminants from cutting oil waste materials, to define the problems due to cutting oils suspensions destabilization as well as cloud point removal techniques concurrently.

Earlier extraction test, the impact of cutting oil extracts on water–surfactant schemes studied by phase diagrams drawn from binary water or surfactants systems. In this study it examined the effects of pH of the solution, temperature, addition of sodium sulphate on oil extraction technique.

Minerals oils and additives can be concentrated and degradation simultaneously. Therefore, dissolved contaminants can be easily separated by using a two phase extraction method.

Jamaly at al. (2015) studied about the recently developed treatment methods of the oily waste water such as electrochemical and hybrid technologies, destabilization of emulsion by using zeolites and other minerals, membrane separation, filtration and using a bio-surfactants for removing the contaminants present in which the waste water were organic or inorganics pollutants, oily waste water, lubricants and grease. In this study oil removal efficiency of wastewater treatment affecting by applying a current. This methodology to oily wastewater remediation offers technical background for upcoming work, which will be expected at decreasing the unfortunate effect of the ejection of oil waste water into the atmosphere.

Milic at al. (2015) studied about the microfiltration of cutting oil emulsion improved by electro-coagulation (EC). The object of this pretreatment was to determine microfiltration execution regarding oil removal and flux decay by applying the minimum time as possible for electro-coagulation by using Al electrodes and flat sheet renewed cellulose film was used in microfiltration. The investigations were done at different concentrations of the oil emulsion. The effects of electrocoagulation time on zeta potential and usual droplet size evaluated by distribution drop size and zeta potential. He found that at all oil emulsions concentration, maximum 10 min time for electrocoagulation made the normal size of oil particles more than the normal size of the pores in microfiltration and significantly reducing pore clogging and permanent fouling.

Rios et al. (1998) studied about the destabilization of cutting oil emulsion using inorganic, $CaCl_2$ and $AlCl_3$ as coagulants were stated. The main aim of this investigation, to determine the effects of stability of different oil emulsions on the electrolytes. A preliminary step to break down the oil emulsion for ultrafiltration, to reducing the membrane fouling. Demulsification of oil emulsion was determined at a temperature less than 80 ºC. The turbidity of the emulsion was directly related to the concentration of the oil emulsion. The breakdown emulsion was trailed by turbidity measurements. Droplet size distribution was investigated by photon correlation spectroscopy and the impact of $CaCl_2$ on the droplet size was reported. The addition in size of the droplets later the expansion of the electrolyte displayed that the coalescence in an aggregate occurs instantaneously. The impact of electrolyte concentration and ionic charge on the zeta capability of dissolvable oils was also reported. It approaches to study oil droplet size distribution and zeta potential was investigates and impact of the various types of electrolytes was also examined.

Several investigations have been worked on the treatment of cutting oil emulsion as shown in Table 2.1 and Table 2.2

Table 2.1 Number of studies carried out for the treatment of a soluble metal waste fluid with different processes

Treatment processes	Operating conditions	Removal efficiency	Reference
Adsorption	Adsorbents used powdered activated carbon, bentonite and deposited carbon. Initial oil concentration 600 ppm to 1210 ppm	For bentonite oil removal =98.32 % For PAC oil removal= 93.54 % For DC oil removal =54.1 %	Okiel et al. (2011)
Aerobic process	COD = 13,500 mg/*l* (with polymer) 9980 mg/*l* (without polymer) Air flow = 200 *l*/min, Temperature = 28^{0}C, hydraulic retention time= 21 days	COD= 48.14 % (with polymer) COD= 29.85 % (without polymer)	Connolly et al. (2006)
Ultrafiltration	Pressure range = 0.05-0.30 MPa temperature= 298 K time = 3 hr , COD= 346 mg/dm^{3} TDS=3770 mg/dm^{3}	COD removal=93.2 % TDS removal =95.2 %	Karakuski et al. (1995)
Micro-filtration	COD=12 000 -73 800 mg/*l* oil and grease= 13 690 and 19 794 mg/*l*	COD = 75.5 to 90.3% Oil and grease =97.2% to 99.7%	Sohoemann et al. (2007)
Hydro-thermal oxidation	Initial COD = 2202 mg/*l*, operating temperature= 600^{0}C	Oil Removal = 98.8% COD Removal = 97.4%	Portela et al. (2001)
Sono-fenton process	pH= 7.4, conductivity= 2.75 µs/cm, turbidity= 1356 NTU, COD=3051 mg/*l*, TDS=183 mg/*l*	COD= 91.31 %	Painmanakul et al. (2013)
Distillation	COD=66,150 mg/*l*, TOC=17,680 mg/*l*, pH=8.8 optimum conditions : 70 mm Hg, T= 150 ^{0}C	Oil removal = 90 %	Canizares et al. (2004)
Vacuum evaporation	COD=31,840 mg/*l*, turbidity=9120 NTU, conductivity=965 µS/cm, temperature= 180 ^{0}C	COD removal= 99.5 %	Gutirerrez et al. (2007)
Combined demulsification + reserves osmosis	pH=6.4, oil concentration= 36000 mg/*l*, NTU= 23018 , COD= 156759 mg/*l* for demulsification : dosage = 0.1 % (w/v), operating time= 30-50 min, temperature = 80-85 ^{0}C for Reverse osmosis: operating time = 20 hr, driving pressure= 3.6 MPa, temperature= 35-40^{0}C	For demulsification: COD= 94.85 %, NTU=97.05 , oil =100% For reserve osmosis: COD=99.95%, NTU=100%,oil= 100%	Zhang et al. (2008)

Table 2.2 The Studies for the soluble oil emulsion waste-water treatment by electro-coagulation process

Treatment processes	**Operating conditions**	**Removal efficiency**	**Reference**
Electro-coagulation	Al and Fe electrodes are used for the treatment of MCF Initial COD 17315 mg/*l* and TOC 3155 mg/*l*	For Al : COD= 93% TOC=78% For Fe : COD= 92% TOC=82%	Kobya et al. (2008)
Electro-coagulation	COD=10,036 mgO_2/*l*, turbidity = 26400 NTU, pH=8.63	COD=91 %, Turbidity=99%	Bensadok et al. (2008)
Electro-coagulation	Oil concentration = 9600 mg/*l*, turbidity=2960 NTU, pH = 6.5,conductivity = 4.32 mS/cm, temperature = 20 ^{0}C, i = 3.5 A, time = 3 hr	Oil = 99 %	Sangal et al. (2013)
Electro-coagulation	pH=6.60,conductivity=1.85 mS/cm, COD=17,312 mg/*l*, Turbidity=15,350 NTU,TOC=3155 mg/*l*	For Al: COD=93% TOC=83% Turbidity=99.8% For Fe : COD=93.5 TOC=85.2% Turbidity=99.9%	Kobya et al. (2011)
Electro-coagulation	pH=8.65, COD=62300 mg O_2/*l* , turbidity= 29700 NTU, conductivity=1121 µs/cm	COD=88.44% Turbidity=98.5%	Tir and Mastefa et al. (2008)

Electro-oxidation method

In this section, literature on the electrochemical treatment technologies for the treatment of oily wastewater by electro-oxidation process is presented.

Al-Malack et al. (2013) studied about the treatment of synthetic petroleum refinery wastewater in a continuous electrochemical process by using stainless steel electrodes as an anode. The synthetic wastewater prepared in tap water having a conductivity of 5,000 µ ohm/cm. Different operational conditions were investigated at optimal conditions, optimal current density was to be 30 mA cm^{-2} with 20 min for degradation. The sequences of experiments showed that total dissolved solids (1,300 mg/*l*) in tap water formed a substantial interfering in removal of phenol in a refinery waste water. Although, removal efficiency was 99% for turbidity, while oil was underneath the minimum detection limit for treated samples was 1.4 mg/*l.*

Ibrahim et al. (2013) investigated about the treatment of oil refinery effluent by electrochemical oxidation prepare in a batch reactor for as a more skilled choice contrasted with the customary strategies, which devour huge amount of chemicals and deliver a lot of slime. The electrochemical innovation was viewed as a spotless and intense innovation for the obliteration of natural contaminations in water. At enhanced conditions the reactions for electro-oxidation handle were present thickness 30 mA/cm^2, pH 8, supporting electrolyte 2 g/*l*, and maximum treatment time 120 minutes observed to be the power consumption 69 kWh/kg, mass exchange coefficient 0.006164 cm/s, and COD removal efficiency 92 %, were assessed and FTIR investigation was additionally done to think about the expulsion of toxins. The outcome demonstrates the relevance of electrochemical innovation as an option for expelling the toxin produced in oil ventures.

Yavuz et al. (2010) studied about the treatment of oil refinery wastewater (PRW) by using a boron-doped diamond anode (BDD), coordinated by utilizing ruthenium blended metal oxide cathode, and electro-fenton and electrocoagulation by utilizing iron electrodes were explored. The outcomes acquired from electrochemical techniques were contrasted with each other. Complete phenol and COD evacuation can be accomplished in all electrochemical technique, with the exception of electrocoagulation, gave that electrolysis time is delayed. The most productive technique was the electro-fenton handle taken after by the electrochemical oxidation utilizing BDD anode. Phenol removal of more than 90% was accomplished in 6 min of electrolysis and COD removal of 75.71% was come to after 9 min of electrolysis in electro-fenton. Electrocoagulation was observed to be ineffectual for the treatment of PRW.

Canizarse et al. (2007) in this work, olive-oil industrial waste water treatment by three advanced oxidation processes (AOP) have been investigates: electro-oxidation, ozonation and fenton oxidation it contains a COD of nearly 3000 mg dm^{-3}. Electro-oxidation permitted accomplishing the entire mineralization of the waste with high current efficiencies. Both the procedures could treat the wastes, but they acquired altogether different outcomes as far as effectiveness and mineralization. This affirms other than the hydroxyl radical interceded oxidation, CDEO joins other imperative oxidation procedures, for example, the direct electro-oxidation on the electrode surface and the oxidation interfered by other electrochemically formed compounds produced on this cathode.

Candido et al. (2013) investigated about the treatment of industrial effluents by electrochemical technologies (EC). EC was an alternative to conventional techniques because of its applications, such as environmental compatibility, efficiency and process stability. In this approach, the electrochemical treatment of waste water from an oil refinery was performed utilizing a parallel-plate electrochemical reactor with Ti/RuO_2 and carbon steel as an anode and cathodes respectively. The utilization of roundabout oxidants with this innovation was vital to quicken the procedure and it can likewise trade off the execution of the terminals through consumption forms, predominantly because of varieties in the pH. The outcomes exhibited that the electrochemical treatment turned out to be successful for expelling pollutants and diminishing the chemical oxygen demand in the oil refinery polluted water. In this study, the indirect oxidant concentration directly affected pH of the electrolysis and the formation of chloramine.

Gotsi et al. (2005) studied about the electrochemical oxidation of olive oil waste waters using a Ti-Ta-Pt-Ir anode electrodes are investigated. Batch runs were conducted electrolytic cell with voltage vary between 5V to 9V, NaC*l* concentrations vary among 1% to 4%, desired recirculation rates and at different COD. The degradation of COD increased as well increases in voltage, NaC*l* concentration and recirculation also effected the degradation process. Approximately, maximum 60 min required for the complete degradation of phenol and decolonization.

The energy consumption per unit mass of COD removal usually lower at high initial concentrations and/or reduced in basic medium. Nevertheless, toxicity enhanced because to the generation of organ chlorinated by-products in reaction proceed as detected by GC/MS analysis.

A single study has been reported on the treatment of cutting oil emulsion by electro-oxidation was discussed below:

Bates and Taylor (2003) studied about the destruction of cutting fluid by electrochemical oxidation by utilizing diamond coated electrodes. The oxidation of cutting oil was carried out by applying a constant current to the electrolysis of oil emulsion, comparable to 30 mA per cm^2 of the anode surface. The organic material removal was 90 to 99% in a basic pH suspension of the cutting fluid. A further experiment confirmed that the oxidation could be sustained throughout periodic addition of oil to the electrochemical cell.

It was initiate that the hydraulic oil would not form a steady mixture and isolated from the electrolyte, efficiently eliminating it from the active range around the electrodes; as an impact the hydraulic oil resisted oxidation.

2.1 RESEARCH GAP

The research reported in the open literature for cutting oil emulsion treatment by EO method explains the treatment efficiencies:

- Oil removal is important parameter during the treatment of cutting oil, but in literature it is not considered by electro-oxidation process.
- No one considered the effect of pH, current, electrolysis time on the removal efficiency of COD, turbidity and oil in a single study.
- There is insufficient literature available on the treatment of cutting oil by EO process using dimensionally stable electrodes.
- To study the energy consumption as a response in view of operating cost is lacking in literature.
- The relation of mass transfer coefficient with flow rate in continuous mode was a lacuna of literature.

2.2 Objective

In the present study, electro-oxidation process (EOP) is applied for the treatment of soluble cutting oil emulsion using a Ti/RuO_2 electrodes in batch and continuous mode. The following objective have been proposed for this study:

- To study the feasibility of batch and continuous process for the treatment of cutting oil emulsion by electro-oxidation.
- To study the effects of operational parameter such as pH, current (i) and time (t) on oil removal efficiency (%), turbidity removal efficiency (%), COD removal efficiency (%) and energy consumption for batch electro oxidation process using dimensionally stable Ti/RuO_2 electrodes.
- To study the effects of operational parameter such as current (i), elapsed time (t) and flow rate (Q) oil removal efficiency (%), turbidity removal efficiency (%), COD removal efficiency (%), energy consumption and mass transfer coefficient for continuous electro-oxidation process, at optimum batch pH using dimensionally stable Ti/RuO_2 electrodes.
- Optimized the operational parameters for the treatment of cutting oil emulsion in batch and continuous mode.

Chapter-3

MATERIAL AND METHOD

3.0 General

This chapter reports explanation of materials and experiments methods adopted during the electro-oxidation (EO) of soluble cutting oil waste water. The experimental detail includes experimental set up, preparation of oil emulsion and experimental procedure during the soluble cutting oil emulsion by EO have been explained in detail.

3.1 Material and method

3.1.1 Reactor

A laboratory scale electrochemical cell was fabricated by a Plexiglas with a dimension of (12 cm length × 12 cm width× 12 cm depth) having a working volume of 1.5 liter.

3.1.2 Electrodes

Ti/RuO_2 and stainless steel electrodes are chosen as an anode and cathode (85 mm× 100 mm× 1.5 mm thick) respectively. The spacing between two electrodes was maintained constant to 1 cm during the experiment. To maintain a fixed inter-electrode distance by non-conducting wire was used as the electrode separation. Ti/RuO_2 electrodes purchased from Titanium Tantalum Products Limited, Chennai, India and cost of electrodes were 78.015 U$. Cleaning of the electrode before and after the experiment was done by ordinary detergent and using a diluted HC*l* solution followed by washing with water for perfect cleaning.

3.1.3 Preparation of the sample

Cutting oil emulsion was used as the waste water for present study. Ultra-cut oil is general purpose soluble cutting oil marketed by M/S Shield lubricant & specialties Pvt Ltd. The characteristics of cutting oil and emulsion are as given in Table 3.1. The mixing of cutting oil emulsion by mechanical stirrer for a few minutes shown in Figure 3.1. Oil was used in present study as it is widely used by metal working as a coolant and cutting operation with steel, ferrous and non-ferrous alloys.

Figure 3.1 Mixing of the cutting oil

Table 3.1 Characterization of ultra-cut cutting fluid and oil emulsion

Appearance of concentrate	Reddish fluid
Appearance of emulsion	Milky
pH	9.4 to 10.66
Odor	Mild
Density at 20 ^{0}C	0.94 g/cm^3
pH of emulsion	6.8
Oil concentration	8775 mg/*l*
Turbidity of emulsion	4032 NTU

3.1.4 Instrument Analysis

The electrodes are connected with a digital power supply (Crown DC regulated power supply; 0-30 V/15 A DIGITECH, Roorkee, model 4818A10) to apply the potential between the electrodes. A digital turbidity meter HACH 2100Q Portable turbidity meter Cat. No. 2100Q01 was used for the measurement of turbidity of cutting oil emulsion. The pH was measured using an Orion 5star bench top pH meter, Thermo Electron Corporation. The oil concentration of the cutting oil emulsion was determined by procedure given in the Bureau of Indian Standards Code – IS: 2488 part I (33). The COD analysis was conducted by the procedure described in standard method for examination of water and wastewater, APHA 1998. The energy consumption (KWh/m^3) and mass transfer coefficient (m/hr) k_M (Korbahti et al., 2009) during the EOP was calculated by following equations

$$\text{Energy Consumption} = \frac{i \times v \times t}{1000} \tag{3.1}$$

Where, i = current, v = voltage and t = treatment time

$$K_M = \frac{COD_{fraction} \times V_R}{(1 - COD_{fraction}) \times A_{electrode} \times \tau_{RT}} \tag{3.2}$$

Where, V_R = volume of the reactor; $A_{electrode}$ = Area of the electrode; τ_{RT} = Retention time

3.2 Experimental procedure for Batch process

The step by step procedure of conducting the experiments in the present study was following:

1. The sample solution was prepared as required. Cutting oil was diluted with the tap water at required oil concentration and stirred for a few minutes. The mixture formed a uniform milky color emulsion.
2. Before start the experiments adjust the pH of the emulsion to the required value with 0.1M NaOH or 0.1M HC*l* and requisite amount of NaCl as electrolyte was added.
3. The initial turbidity was measured with digital turbidity meter.
4. Before each experiment, the electrode was cleaned with sand paper to remove scale and the cleaned with a hydrofluoric acid and nitric acid.
5. Ti/RuO_2 and stainless steel are chosen for electrode as a (anode/cathode) and electrodes are situated 1 cm apart from each other. The schematic and laboratory scale experimental set up shown in Figure 3.2 and 3.3 respectively.
6. Cutting oil water emulsion filled into the reactor at required working volume. Electrodes are fully submerged into the reactor yielding an effective removal efficiency and the current was distributed by the controlled DC power supply. The voltage is applied between the pairs of anode and cathode connected in parallel by DC power supply.
7. A magnetic stirring at 250 rpm is maintained for all experimental runs is used to agitate the sample.
8. Sample is drawn after fixed interval of time for further analysis.
9. At the completion of the test, the electrodes was eroded carefully with water for exclusion of any solid elements on the electrodes sides, than dried out.

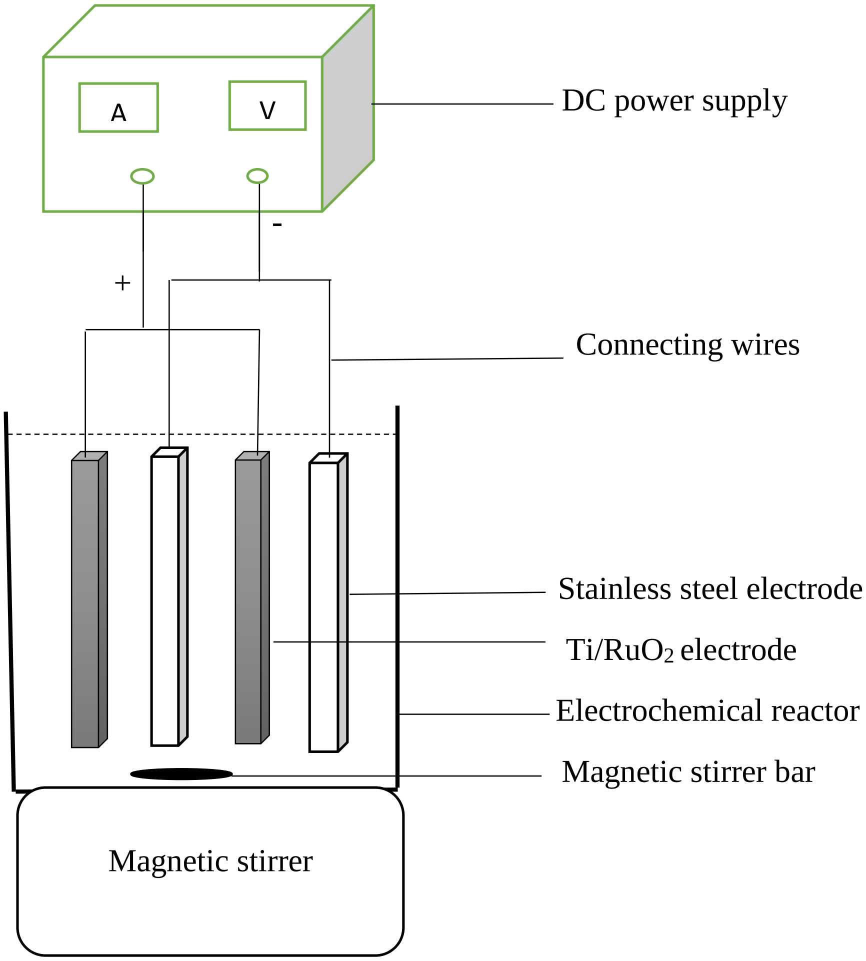


Figure 3.2 Schematic diagram of experimental setup for batch process

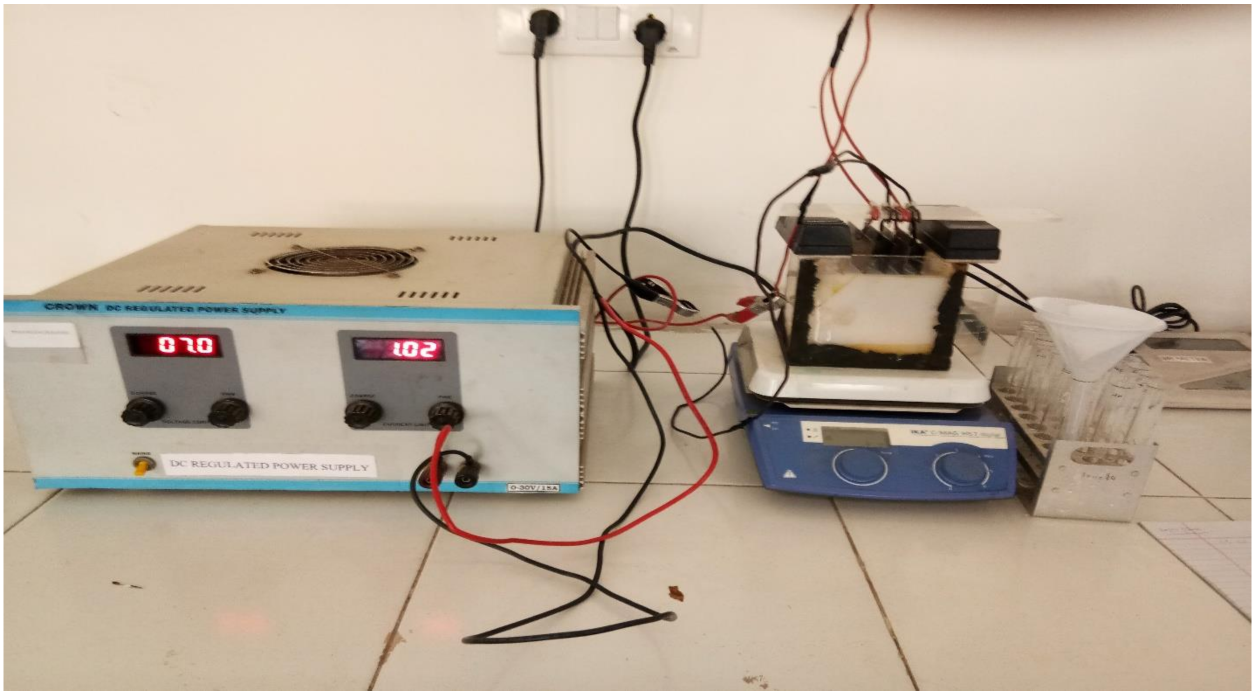


Figure 3.3 Laboratory scale batch electro-oxidation system

3.3 Experiment procedure for Continuous Process

The step by step procedure of conducting the experiments in continuous mode is outlined as under:

1. Cutting oil was assorted by the tap water for the required oil concentration mechanical stirring for a few minute. The mixture formed a uniform milky color.
2. The initial turbidity was measured with digital turbidity meter.
3. The oil water emulsion pH was determined by a digital pH meter and its pH adjusted with the required value of 0.1 N HC*l* or NaOH.
4. The emulsion was pumped in the continuous reactor with the support of a peristaltic pump with required flow rate as shown in Figure 3.4 and 3.5. The level of the emulsion was maintained constant. The voltage was applied between the pairs of electrodes DC power supply.
5. Magnetic stir was used to agitate the sample at 250 rpm.
6. Sample was drawn after fixed interval of time for further analysis.

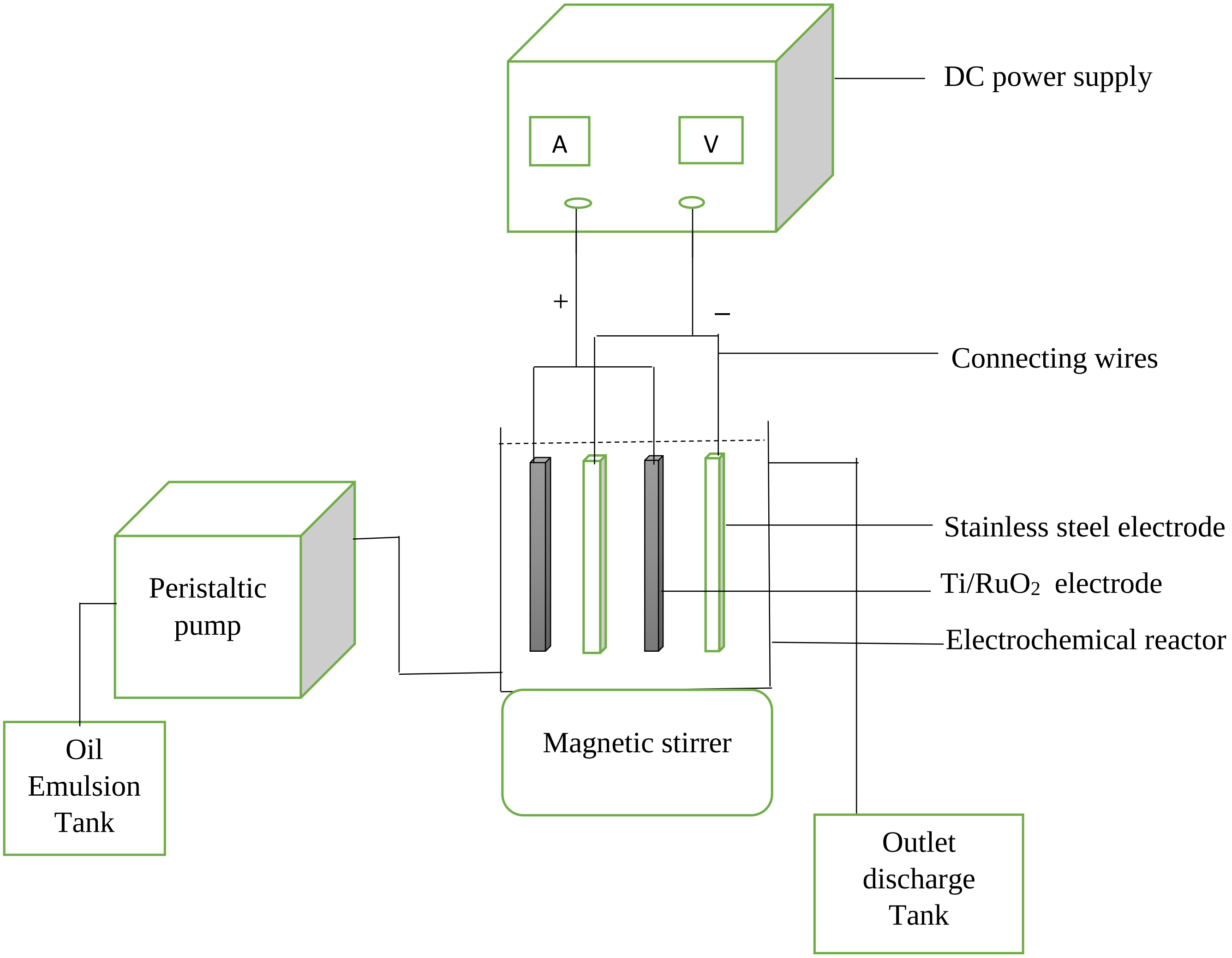


Figure 3.4 Schematic diagram of experimental setup for continuous process

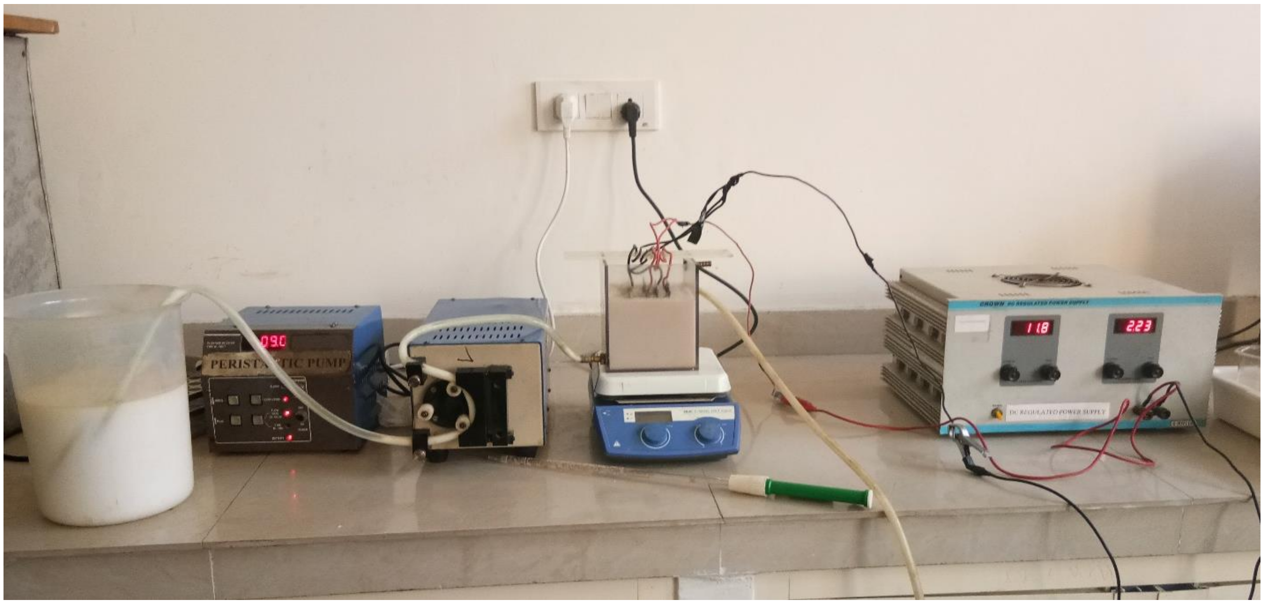


Figure 3.5 Laboratory scale continuous process

3.5 RSM Optimization

The response surface methodology (RSM) was a mixture mathematical and statistical techniques. Response of operational parameters concern was influenced by several variables and its major objective was to optimize this response commonly used for improving and optimizing processes and also useful in solving the problems of modeling analysis. It can be used to estimate the comparative significance of various affecting parameters between complex interactions. RSM was used for fitting a quadratic surface and to analyze the interactions among the parameters.

RSM was an effective device for improving the method and providing more comprehensive explanation and measureable valuation of the treatment method, when a mixture of various independent parameters and their interactions results desired responses.

The objective of design of experiment was the chosen of the points where the response should be investigates. Usually, these mathematical representations were polynomials with an unidentified structure, so the corresponding experiments were designed individually for each specific problem. The purpose was to identify the design parameters that have large impacts for further investigation.

3.5.1 Box-Behnken Design

Box-Behnken Designs (BBD) was a combination of rotatable or approximately rotatable second-order designs based on three-level inadequate factorial designs (Ferreira et al., 2007). In this design, augmented by process parameters were at the mediums of edges of the method space as shown in Figure 3.5 and axial points to allow calculation of the tuning parameters of a second-order model.

The number of design experiments (M) desired for the expansion of BBD was defined as M= 2K (K − 1) + C_0, where K is number of factors and C_o was the number of central points. In Box-Behnken designs, a block of samples corresponding to a two levels factorial design was repeated over different sets of parameters. The BBD was slightly more effective than the other design (central composite, doehlert matrix and three-level full factorial design) and it did not contain mixtures for which all features were at the same time maximum or lowest levels. So these designs were suitable in eluding experiments completed under critical circumstances, for which insufficient results might occur. The type full or fractional, the size of the factorial, and the number of blocks which was calculated from the number of operational parameters and it was chosen so that the design meets, accurately or approximately, the standard of ratability.

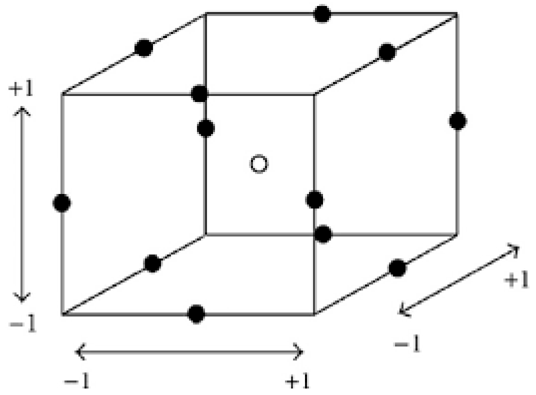


Figure 3.6 Box-Behnkn Design for three factors

Second order polynomial equation was useful to predicted the chosen response as a function of independent parameters and the interaction among them

The BBD was suitable design for fitting the second order model.

$$\mathrm{T} = \eta_o + \sum_{i=1}^{k} \eta_i \varphi_i + \sum_{\substack{i=1\\+e}}^{k} \eta_{ii} \varphi_i^2 + \sum_{i<j}^{K} \sum_{j=1}^{k} \eta_{ij}\, \varphi_i\, \varphi_j$$

Where T is the predicted dependent variable, η_o is a constant, $\eta_i$is the linear effect of φ_i , η_{ii} is the linear interaction between $\varphi_i$and φ_j , η_{ij} is the quadratic effect of interactions between

φ_i and φ_j and e is the statistical error. Estimation of graphical analysis of the data to achieve the interference among the process operating parameters and the responses by analysis of variance (ANOVA). Model terms are estimated by the P value (probability) with 95% confidence level.

The quality of the fit polynomial model was represented by the coefficient of determination R^2, and its statistical importance was determined by the Fisher F test in the similar program.

3.5.2 Multi-response optimization

In present study, there are four responses for batch process and five responses for continuous mode, therefore, multi-response methods optimization by desirability approach was convenient to improve the electro-oxidation process. All the desirability is united to form a complex desirability function which exchanges a multi-response into a one single response. The desirability function is maximum used method for the optimization of several response processes. One-sided desirability d_i is given by:

$$d_i = \left\{ \begin{matrix} 0 \\ \left[\dfrac{Y_i - Y_{i-\min}}{Y_{i-\max} - Y_{i-\min}} \right]^n \\ 1 \end{matrix} \right\}$$

if $Y_i \leq Y_{i\text{-}min}$,

if $Y_{i\text{-}min} < Y_i < Y_{i\text{-}max}$,

if $Y_i \geq Y_{i\text{-}max}$

Where, Y_i is response value, $Y_{i\text{-}min}$ and $Y_{i\text{-}max}$ is minimum and maximum adequate values of response i and n is a weight and a positive constant, used to studied scale of desirability. In multi-response process optimization, the desirability value vary between 0 and 1 for each response of desirability function transforms (Sangal et al., 2013). The individual desirability functions are combined in order to obtain the overall desirability D, as follow:

$$D = (d_1 \times d_2 \times d_3 \ldots\ldots\ldots\ldots.)^{\frac{1}{k}}$$

Where, $0 \leq D \leq 1$ and k is the number of responses.

If all the characteristics approaches their desired results, the desirability d_i is 1 for all i. Subsequently, the entire desirability was also 1. If some one of the process parameters did not reach its desired value than desirability was below 1. If some one of the responses cannot meet the quality desires, the total desirability was zero.

Chapter-4

RESULT AND DISCUSSION

4.0 Result and Discussion

4.0.1 Experimental design for batch process

The software Design Expert (Design Expert 6.0.8) was useful for the statistical design of experiments and data analysis. The three operational parameters pH, current (*i*), and time (*t*), were optimized. Their range were given in Table 4.1. The parametric ranges were chosen by preliminary experiments pH 3-11, current 0.25- 2.25 A, and time 10–120 min for the EO process using Ti/RuO_2 and oil removal efficiency % (T_{B1}), turbidity removal efficiency % (T_{B2}), COD removal efficiency % (T_{B3}) and energy consumption (T_{B4}) was taken as responses, in order to obtain optimum pH, *i* and *t* for batch process to achieve highest removal for the treatment of cutting oil emulsion using the EO process. The most suitable design to conduct such 3- level set of experiments was the 17-trial set of Box-Behnken design (BBD) combined with RSM shown in Table 4.2.

Table 4.1 Process parameters and coded ranges for batch mode

			Range of actual and coded variables		
Factor	Variables	Units	-1	0	+1
A	pH	-	3	5.5	11
B	Current	A	0.25	1.125	2.25
C	Time	Minute	10	60	120

Table 4.2 The Design of experiments using BBD method for batch process

Experiment no.	**pH**	**Current A (*i*)**	**Time Min (*t*)**	**Oil Removal % (T_{B1})**	**Turbidity Removal % (T_{B2})**	**COD Removal % (T_{B3})**	**Energy consumption (KWh/m^3) (T_{B4})**
1	3	2.25	65	99.82	99.93	90.43	10.23
2	7	2.25	120	99.96	99.89	99.51	18
3	7	2.25	10	21.78	58.11	47.72	2.92
4	7	0.25	10	18.54	17.34	23.53	0.22
5	3	1.25	120	99.5	99.34	98.39	10.5
6	7	0.25	120	96.1	93.08	93.03	2.4
7	7	1.25	65	86.81	89.98	95.91	3.79
8	3	0.25	65	85.17	82.68	73.65	1.13
9	11	1.25	10	40.86	39.04	34.64	1.27
10	7	1.25	65	99.81	99.93	97.03	5.68
11	3	1.25	10	25	43.48	36.63	1.27
12	7	1.25	65	99.01	99.90	94.13	5.68
13	7	1.25	65	98.81	99.98	95.91	5.68
14	11	0.25	65	87.86	85.71	75.86	0.64
15	7	1.25	65	99.81	99.9	94.13	5.68
16	11	1.25	120	99.56	99.72	92.27	9.83
17	11	2.25	65	99.81	99.84	92.11	11.21

The final quadratic equations in terms of coded factors for oil removal efficiency % (T_{B1}), % turbidity removal efficiency % (T_{B2}), COD removal efficiency % (T_{B3}) and energy consumption (T_4) are given below. Final equations in terms of coded factors are given below:

$$T_{B1} = + 96.85 +2.33A+ 4.21B+36.12C+1.72A^2 -5.41B^2 -32.35C^2- 0.6AB - 3.95 AC + 0.15BC \quad \textbf{(4.1)}$$

$$T_{B2} = + 97.94 - 0.14A+ 9.87B+ 29.26C - 1.30A^2 - 4.59B^2 -26.24C^2- 0.78AB + 1.20AC - 8.49BC \quad \textbf{(4.2)}$$

$$T_{B3} = + 95.42- 0.53A +7.96B +30.09C - 6.44A^2 - 5.97B - 23.5C^2 - 0.13AB -1.03AC - 4.43BC \quad \textbf{(4.3)}$$

$$T_{B4} = + 5.31– 0.022A + 4.75B + 4.38C + 0.17A^2 + 0.33B^2 + 0.25C^2+0.37AB– 0.17AC +3.23 BC \quad \textbf{(4.4)}$$

In mathematical equations, first-order effects on operational parameters A, B and C, interaction effects (AB, AC, BC), and second-order effects (A^2, B^2 and C^2).

4.0.2 Statistical Analysis

In the present study, the relationship between three operating parameters (pH, *i* and *t*) and four process responses T_{B1}, $T_{B2,}$ T_{B3} and T_{B4} for the EO process using Ti/RuO_2 as a anode and stainless steel (SS) electrodes as anode was analyzed using RSM.

Table 4.3 Regression coefficients for the responses in batch mode

Response	R^2	Adj R^2	SD	CV	PRESS	F value	Prob>F	AP
% Oil removal	0.983	0.961	6.09	7.62	2325.37	45.82	<0.0001	18.20
% Turbidity removal	0.989	0.975	4.11	4.96	748.50	72.45	<0.0001	26.44
% COD removal	0.997	0.994	1.91	2.43	316.36	324.36	<0.0001	51.83
Energy consumption (KWh/m^3)	0.991	0.980	0.69	12.15	11.42	88.58	<0.0001	34.61

SD standard deviation, CV coefficient of variance, PRESS predicted residual error sum of squares, AP adequate precision, and P probability of error.

The regression coefficients for response parameters were shown in Table 4.3. Only statistically significant terms are included in the model. The P value <0.01 indicates that the model was considered to be insignificant. Values of Probability>F value was less than 0.05 which shows that the model terms were significant (Vasseghian 2015). The F value for batch process T_{B1}, T_{B2}, T_{B3} and T_{B4} are 45.82, 72.45, 324.36 and 88.58 respectively, showed that the model was significant. A high R^2 value, which was close to 1, has a reasonable agreement with adjusted R^2. In the present study, R^2 values were 0.983, 0.989, 0.997 and 0.991 for T_{B1}, T_{B2}, T_{B3} and T_{B4} respectively. The coefficient of variance (CV) as the ratio of the standard error of estimate to the mean value of the experimental response is a measurement of reproducibility of the model. C.V for T_{B1}, T_{B2}, T_{B3} and T_{B4} removal was found to be 7.62, 4.96, 2.43 and 12.15 respectively. Adequate precision (AP) showed that the ranges of the predicted results at the design points to the average prediction error. Ratios of CV>4 shows that adequate model was desirable. The AP (adequate precision) values for T_{B1}, T_{B2}, T_{B3} and T_{B4} were 18.20, 26.44, 51.93 and 31.61 which indicate an adequate signal.

In order to decide about the adequacy of various models, sequential model sum of square and model summary statistics were tested and result are given in Table 4.4, Table 4.5, Table 4.6 and Table 4.7 for responses T_{B1}, T_{B2}, T_{B3} and T_{B4} respectively. Sequential model sum of squares that quadratic model best fits the experiment data for responses T_{B1}, T_{B2} and T_{B3} and 2F1 for T_{B4}. Cubic model was found to be aliased for all the process responses.

Table 4.4 Sequential model sum of square for oil removal efficiency % in batch mode

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	1.085E+005	1	1.085E+005			
Linear	10621.00	3	3540.33	9.31	0.0015	
2F1	64.33	3	21.44	0.044	0.9870	
Quadratic	4619.22	3	1539.74	41.49	<0.0001	Suggested
Cubic	132.95	3	44.32	1.40	0.3658	Aliased
Residual	126.83	4	31.71			
Total	1.241E+005	17	7298.71			

Table 4.5 Sequential model Sum of Square for turbidity removal efficiency % in batch mode

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	1.66E+005	1	1.66E+005			
Linear	7627.50	3	2542.50	9.44	0.0014	
2F1	296.56	3	98.85	0.31	0.8190	
Quadratic	3088.17	3	1029.39	60.95	< 0.0001	Suggested
Cubic	39.05	3	13.02	0.66	0.6194	Aliased
Residual	79.17	4	19.79			
Total	1.277E+005	17	7513.01			

Table 4.6 Sequential model Sum for COD removal efficiency % in batch mode

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	1.048E+005	1	1.048E+005			
Linear	7750.30	3	2583.43	11.46	0.0006	
2F1	82.75	3	27.58	0.097	0.9600	
Quadratic	2821.29	3	940.43	257.67	< 0.0001	Suggested
Cubic	19.15	3	6.38	3.99	0.1073	Aliased
Residual	6.40	4	1.60			
Total	1.155E+005	17	6793.99			

Table 4.7 Sequential model for energy consumption in batch mode

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	544.54	1	544.54			
Linear	333.51	3	111.17	31.09	< 0.0001	
2F1	42.25	3	14.08	33.22	< 0.0001	Suggested
Quadratic	0.93	3	0.31	0.66	0.6039	
Cubic	0.43	3	0.14	0.20	0.8908	Aliased
Residual	2.87	4	0.72			
Total	924.54	17	54.38			

Table 4.8 Analysis of the variance for oil removal efficiency % in batch mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	15304.55	9	1700.51	45.82	<0.0001	
pH	43.25	1	43.25	1.17	0.3162	
Current	141.96	1	141.96	3.83	0.0914	
Time	10435.79	1	10435.79	281.20	<0.0001	Highly significant
pH^2	12.53	1	12.53	0.34	0.5794	
$Current^2$	123.23	1	123.23	3.32	0.1112	
$time^2$	4405.05	1	4405.05	118.70	<0.0001	
pH × current	1.82	1	1.82	0.049	0.8309	
pH × time	62.41	1	62.41	1.68	0.2358	
Current × time	0.096	1	0.096	2.589E-003	0.9608	
Residual	259.78	7	37.11			
Lack of fit	132.95	3	44.32	1.40	0.3658	
Pure error	126.83	4	31.71			
Cur total	15564.33	16				

Table 4.9 Analysis of the variance for turbidity removal efficiency % in batch mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	11012.23	9	1223.58	72.45	<0.0001	
pH	0.16	1	0.16	9.285E-003	0.9259	
Current	779.34	1	779.34	46.15	0.0003	
Time	6848.01	1	6848.01	405.49	<0.0001	Highly significant
pH^2	7.16	1	7.16	0.42	0.5358	
$Current^2$	88.86	1	88.86	5.26	0.0555	
$time^2$	2898.88	1	2898.88	171.65	<0.0001	
pH × current	2.43	1	2.43	0.14	0.7155	
pH × time	5.81	1	5.81	0.34	0.5760	
Current × time	288.32	1	288.32	17.07	0.0044	
Residual	118.22	7	16.89			
Lack of fit	39.05	3	13.02	0.66	0.6194	
Pure error	79.17	4	19.79			
Cur total	11130.45	16				

Table 4.10 Analysis of the variance for COD removal efficiency % in batch mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	10654.34	9	1183.82	324.36	<0.0001	
pH	2.23	1	2.23	0.61	0.4604	
Current	507.21	1	507.21	138.97	<0.0001	Highly significant
Time	7240.86	1	7240.86	1983.96	<0.0001	Highly significant
pH^2	174.48	1	174.48	47.81	0.0002	
$Current^2$	150.18	1	150.18	41.15	0.0004	
$time^2$	2325.71	1	2325.71	637.23	<0.0001	
pH × current	0.070	1	0.070	0.019	0.8936	
pH × time	4.26	1	4.26	1.17	0.3156	
Current × time	78.41	1	78.41	21.48	0.0024	
Residual	25.55	7	3.65			
Lack of fit	19.15	3	6.38	3.99	0.1073	
Pure error	6.40	4	1.60			
Cur total	10679.88	16				

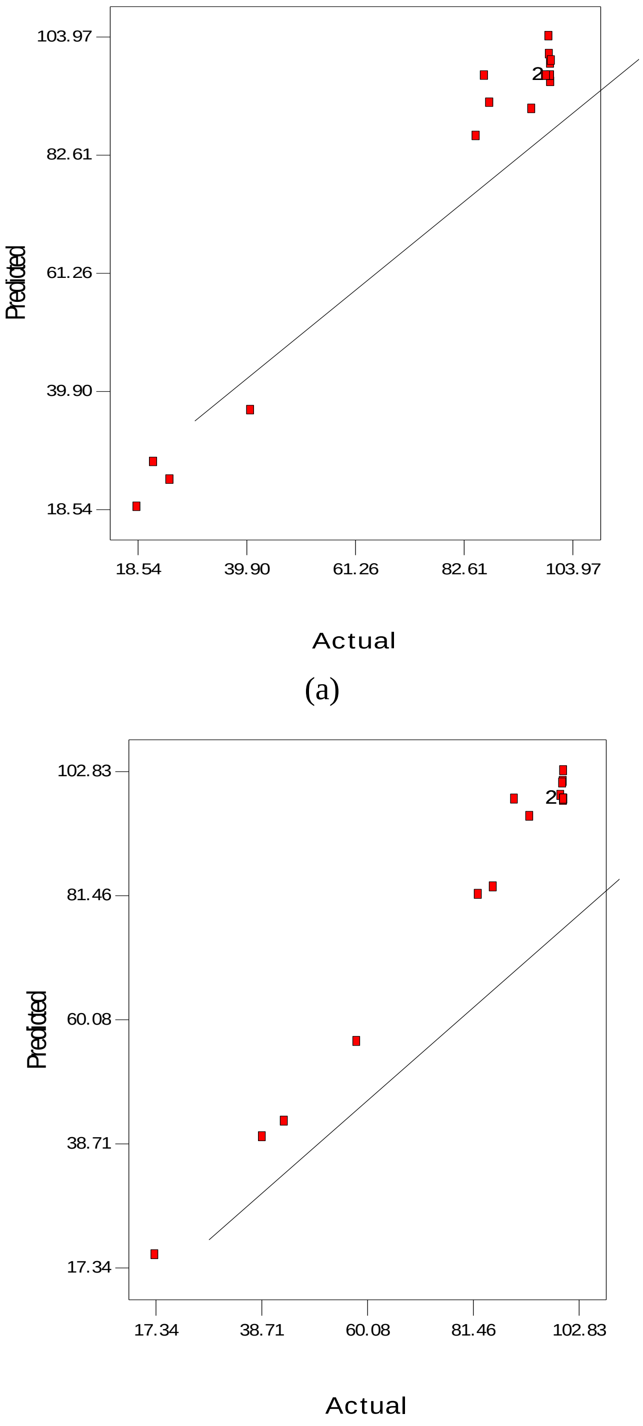
Table 4.11 Analysis of the variance for energy consumption in batch mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	376.69	9	41.85	88.58	<0.0001	
pH	4.032E-003	1	4.032E-003	8.533E-003	0.9290	
Current	180.14	1	180.14	381.24	<0.0001	Highly significant
time	153.37	1	153.37	324.58	<0.0001	Highly significant
pH^2	0.12	1	0.12	0.25	0.6316	
$Current^2$	0.47	1	0.47	0.99	0.3529	
$time^2$	0.26	1	0.26	0.54	0.4861	
pH × current	0.53	1	0.53	1.13	0.3228	
pH × time	0.11	1	0.11	0.24	0.6424	
Current × time	41.60	1	41.60	88.05	<0.0001	
Residual	3.31	7	0.47			
Lack of fit	0.43	3	0.14	0.20	0.8908	
Pure error	2.87	4	0.72			
Cur total	380	16				

Significant model terms were desired to obtain a good fit in a particular model. The response model shows as Table 4.8 and 4.9 that time was highly significant parameters for oil removal efficiency (%) and turbidity removal efficiency (%). For COD removal efficiency (%) and energy consumption, current and time were highly significant parameters respectively as shown in Table 4.10 and 4.11.

The actual and the predicted results for the responses T_{B1}, $T_{B2,}$ T_{B3} and T_{B4} by EO process are shown in Figures 4.1 and 4.2.

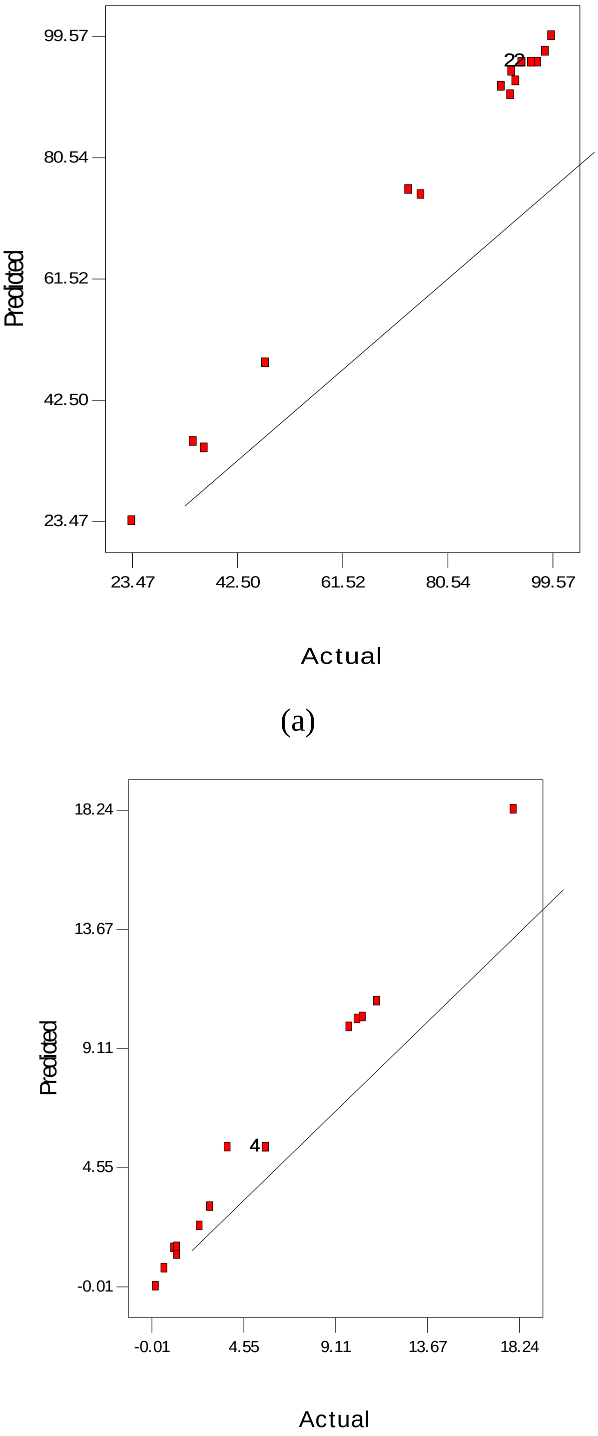
Actual values were the determined by experimental results and the predicted values were determined from the model. When the data points lie nearby to the diagonal line and the established model was adequate for the prediction of each process response.



(a)

(b)

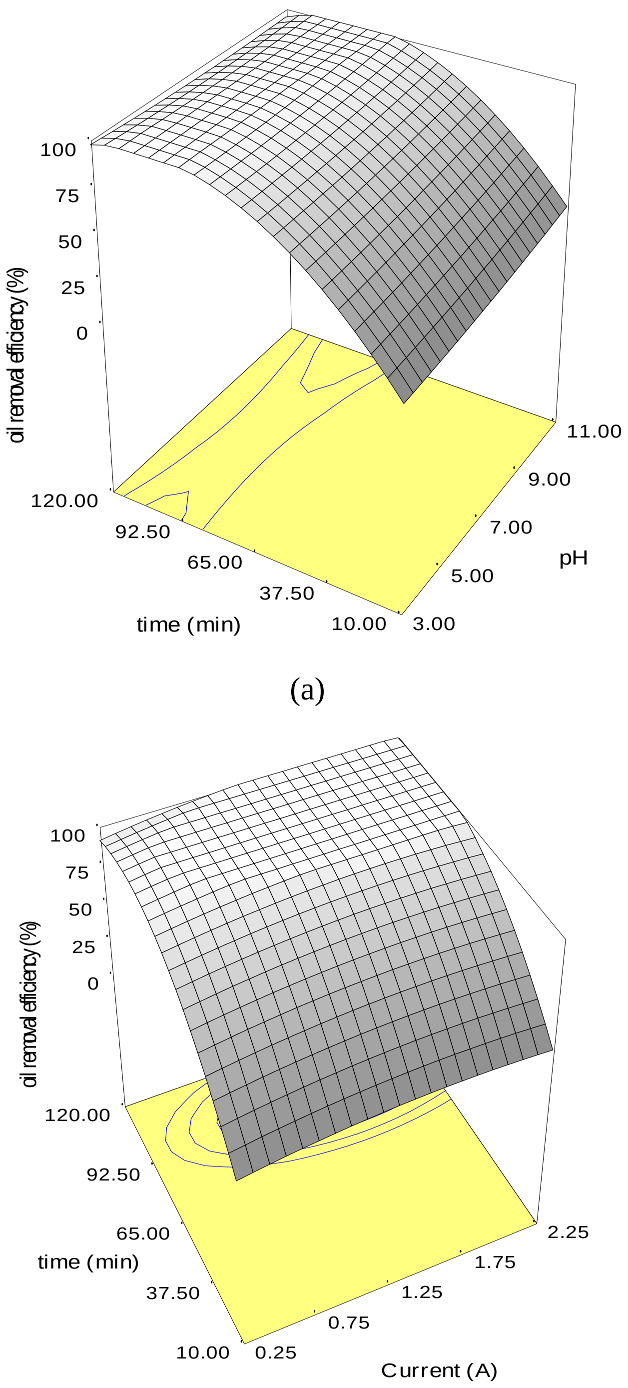
Figure 4.1 Comparison of predicted result with actual results (a) oil removal efficiency (%) and (b) turbidity removal efficiency (%) in batch mode



(a)

(b)

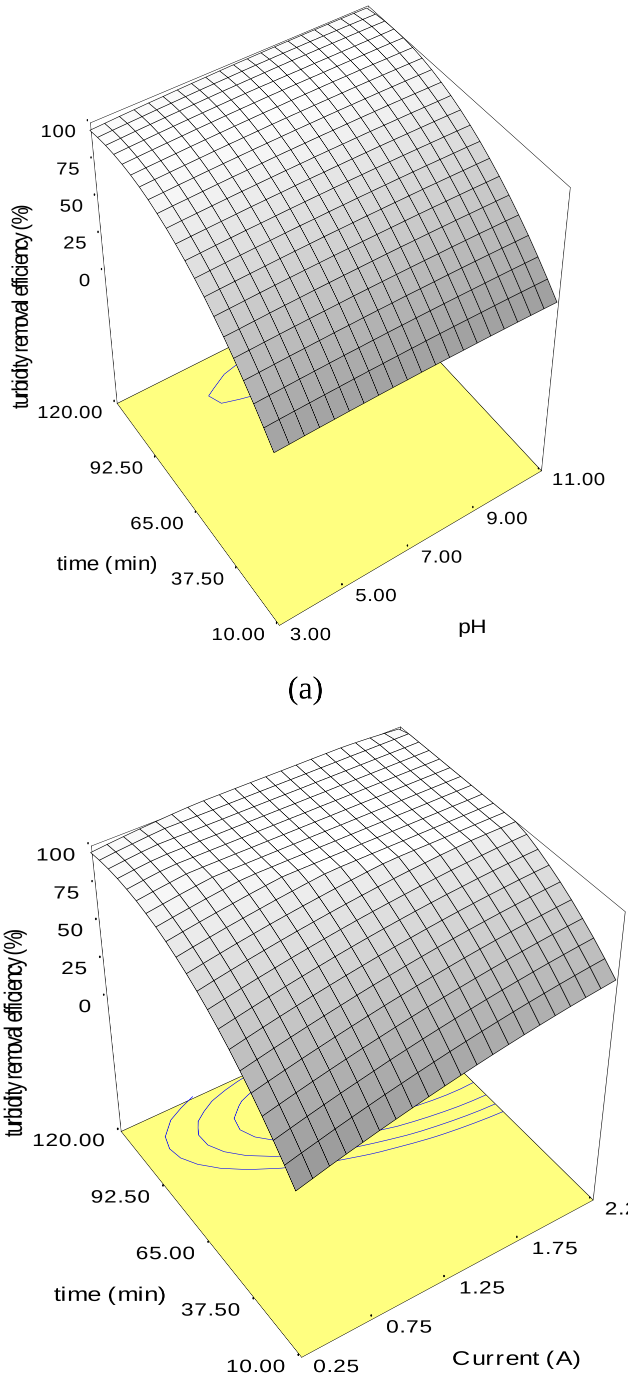
Figure 4.2 Comparison of predicted result with actual result (a) COD removal efficiency (%) and (b) energy consumption in batch mode



(a)

(b)

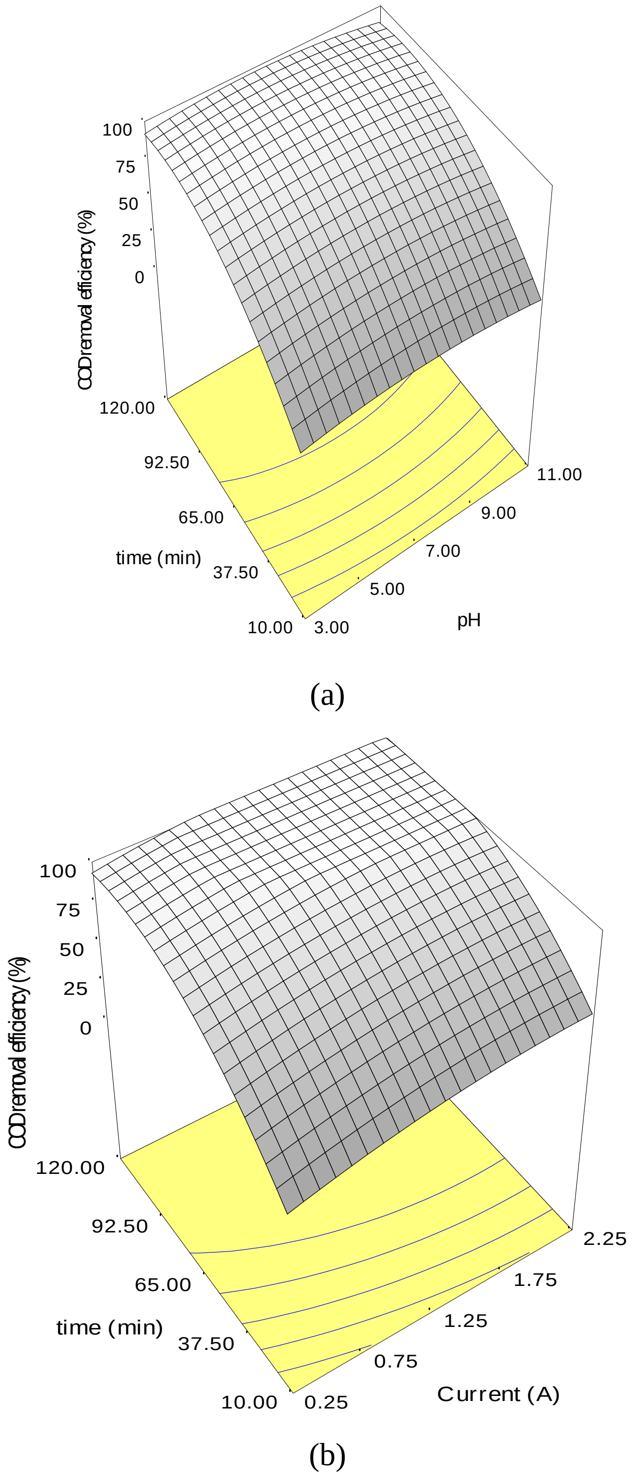
Figure 4.3 3D response surface graph for the treatment of cutting oil emulsion by electro-oxidation process with combined effect of (a) time– pH and (b) time–current for batch process on percentage of oil removal efficiency



(a)

(b)

Figure 4.4 3D response surface graphs for the treatment of cutting oil emulsion by electro-oxidation process with combined effect of (a) time–pH and (b) time–current for batch process on percentage of turbidity removal



(a)

(b)

Figure 4.5 3D response surface graphs for the treatment of cutting oil emulsion by electro-oxidation process with combined effect of (a) time–pH and (b) time–current for batch process on percentage of COD removal efficiency

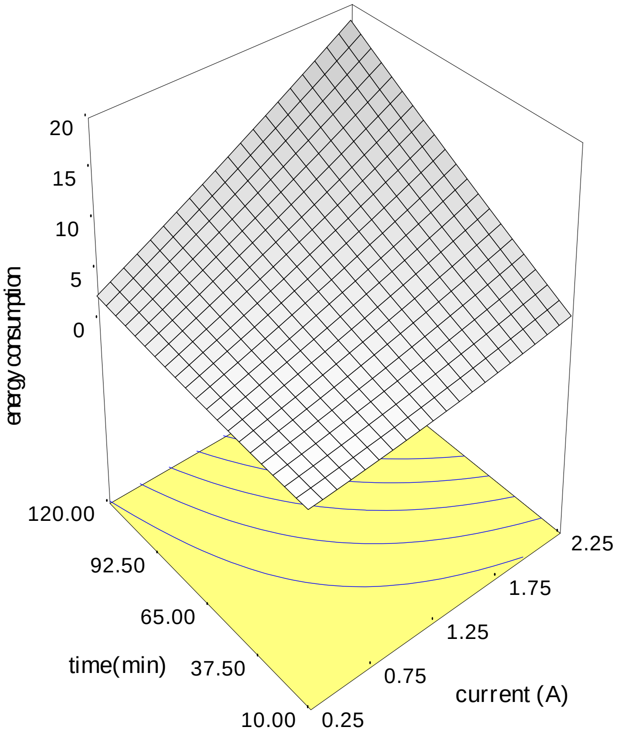


Figure 4.6 3D response surface graphs for treatment of cutting oil emulsion by electro-oxidation process with combined effect of time–current for batch process on energy consumption

4.0.3 Effect of variables on removal efficiencies

To considering the effects of various parameters i.e pH, *i* and *t* on responses T_{B1}, T_{B2}, T_{B3} and T_{B4} for batch process for the treatment of soluble cutting oil, three dimensional response surface graphs obtained from RSM were studied. The effect of *t* and pH on T_{B1} is observed in Figure 4.5a, it was clearly seen the effect of pH on T_{B1} is marginal, it can increases with the increases in t =10 to≈ 72.50 min but it is nearly maximum at 99.24 min, after that T_{B1} is the constant. Figure 4.5b shows the effects of *t* and *i* on the T_{B1}, it can be concluded that with increase in *i* w.r.t *t* increases T_{B1}. It is increased from *i* value at 0.25 to 0.5 beyond i = 0.5A, it is nearly constant at higher value of *t*. Higher *t* value is required to form steady state degradation.

Figure 4.6. a and b shows the effect of T_{B2} with *t*, pH and *i* and shows marginal effect on the T_{B2} w.r.t *t*. T_{B2} is slightly greater at the neutral pH. Higher *i* shows constant effect on the T_{B2} at the higher *t* values. T_{B2} is constant nearly at *t* value ≈95 to 120 min.

Figure 4.7 a and b show the effect of *t* with pH and *i* on degradation of T_{B3} is slightly higher at the neutral pH but if considered basic and acidic medium, it is slightly low in basic medium. T_{B3} is increased at all *i* values with increases in *t* and it becomes constant at higher *i* and *t* values. The effect of *t* and *i* on T_{B4} has direct relation with *i.* when *i* value increases T_{B4} is increased with increase in *t* value shown in Figure 4.8.

For treatment of soluble cutting oil both the treatment processes i.e. direct and indirect oxidation appears to be responsible. Direct oxidation method of treatment of soluble cutting oil at anode containing the adsorption of formed ·OH radicals in the oxide lattice of anode and subsequent oxidation of oil. At extremely acidic medium increasing *i* value up to ≈1.25A, the generation and adsorption rate of ·OH radicals are high at anode. It seems that direct oxidation is prominent in the treatment process because treatment efficiency is highest at neutral pH (Huitle-Martinez and Ferro 2006).

Simultaneously, generated H_2O_2 and HO_2 (Equation 1.5 and 1.6) indirectly oxidize the organics and also increasing the rate of chloro-oxidant species HOCI in the bulk solution, which dominates over all chloro-oxidant species (Cl_2, HOCl and ClO^-) in the extremely acidic medium by increasing the *i*, which indirectly oxidize the emulsion (Jung et al., 2016). But in extremely basic medium adsorption of ·OH radicals in the anode oxide lattice was reduced due to the increase in *i*. These generated ·OH radicals are transformed into lower oxidation potential oxidants such as H_2O_2 and HO_2 (Pletecher and Walsh 1993). Therefore degradation in basic medium is slightly low as compare to acidic.

4.0.4 Optimization analysis

In this study, electro-oxidation treatment of soluble cutting oil emulsion was optimized for responses T_{B1}, T_{B2} and T_{B3} to be maximized while T_{B4} to be minimized. Table 4.12 shows the optimum values of response. Desirability function approaches was used to get the maximum T_{B1}, T_{B2} and T_{B3} while minimum T_{B4} simultaneously. Optimum condition for batch process of treatment oil emulsion was to be pH 7.23, current 0.50 (A), and time 99.24 (min) which produced overall desirability 0.962.

Table 4.12 Optimum conditions for electro-oxidation process of cutting oil emulsion

Variables	Optimum Value
pH	7.23
i	0.50 A
t	99.24 min

Constraints applied for optimization of electro-oxidation process for cutting oil emulsion in batch mode shown in Table 4.13.

Table 4.13 Constraints applied for optimization of electro-oxidation process for cutting oil emulsion in batch mode

Variables	Goal	Lower Limit	Upper Limit
pH	Is in range	3	11
i (A)	Is in range	0.25	2.25
t (min)	Is in range	10	120
Oil Removal Efficiency (%)	Maximize	18.54	99.96
Turbidity Removal Efficiency (%)	Maximize	17.34	99.98
COD Removal Efficiency (%)	Maximize	23.53	99.51
Energy Consumption (KWh/m^3)	Minimize	0.225	18

Optimum condition for electro-oxidation of soluble cutting oil emulsion was experimentally verified. The experimental response values for T_{B1}, T_{B2}, T_{B3} and T_{B4} were 100%, 99.97%, 97.63% and 3.27 KWh/m^3 respectively. In order to confirm the result found by optimization, four confirmation experiments were conducted with the optimized set of operational parameters. The predicted value of response T_{B1}, T_{B2}, T_{B3} and T_{B4} were found to be 98.83%, 99.96%, 94.52 and 2.833 KWh/m^3 respectively, which was very close to predicted result.

Comparison between the predicted and experimental values of responses at optimum conditions is shown in Table 4.14

Table 4.14 Comparison between predicted and experimental values of response at optimum condition

Response	Predicted	Experimental
% oil removal efficiency	100%	98.83
% turbidity removal efficiency	99.97	99.90
% COD removal efficiency	97.63	94.03
Energy consumption (KWh/m^3)	3.2707	2.833

4.1 Continuous process

In earlier investigations, batch experiments conducted for electro-oxidation process using a Ti/RuO$_2$ as anode electrode was an efficient process for treatment of the cutting oil emulsion. Although, on a large scale waste water in the industrial area, the treatment process must be experiments was conducted in continuous mode. Therefore, a set of experiments was designed and conducted to efficiency of the electro-oxidation process for the treatment of the cutting oil emulsion.

4.1.1 Experimental design for continuous process

The three operating variables elapsed time (*t*), flow rate (*Q*), current *(i)* are optimized by using software Design Expert (Design Expert 6.0.8) for the statistical design of experiments and mathematical data analysis. The parametric ranges are chosen by preliminary experiments elapsed time 10–180 min, flow rate 2-16 cc/min, and current 0.25- 2.25 A for the EO process using Ti/RuO$_2$. Their operational parameters and range were given in Table 4.15. Five dependent parameters are analyzed as responses oil removal efficiency (%) T_{C1}, turbidity removal efficiency (%) T_{C2}, COD removal efficiency (%) T_{C3}, energy consumption (KWh/m^3) T_{C4} and mass transfer coefficient (m/hr) T_{C5} in order to obtain optimum elapsed time, flow rate and current, to achieve highest removal for the treatment of cutting oil emulsion using the EO process. Full factorial design of the experiments used for electro-oxidation of cutting oil emulsion as shown in Table 4.16

Table 4.15 Process operating parameters and their ranges for continuous mode

			Range of actual and coded variables		
Factor	Variables	Units	-1	0	+1
A	Time	Minute	10	95	180
B	Flow rate	cc/min	2	9	16
C	Current	A	0.25	1.25	2.25

Table 4.16 The Design of the experiment by using BBD method for continuous process

Experiment no	Time min (t)	Flow rate Q cc/min (Q)	Current A (i)	Oil removal (%) (T_{C1})	Turbidity removal (%) (T_{C2})	COD removal (%) (T_{C3})	Energy consumption (kWh/m^3) (T_{C4})	Mass transfer coefficient (m/hr) (T_{C5})
1.	95	9	1.25	62.27	66.27	41.38	10.28	0.07
2.	95	9	1.25	38.17	64.75	31.88	10.16	0.07
3.	95	9	1.25	59.66	62.72	42.88	14.46	0.07
4.	95	16	2.25	31.24	56.53	24.82	26.71	0.004
5.	95	9	1.25	38.17	68.55	35.78	8.90	0.07
6.	10	16	1.25	1.51	3.28	3.7	2.23	0.001
7.	95	2	2.25	88.55	97	78.68	12.69	0.43
8.	95	9	1.25	55.27	72.4	48.78	10.71	0.07
9.	10	9	0.25	2.01	2.14	0.5	5.56	0.0005
10.	95	2	0.25	63.38	88.71	62.54	3.11	0.26
11.	180	16	1.25	72.14	70.08	78.56	30.65	0.23
12.	180	2	1.25	95.79	95.29	91.36	25.78	0.51
13.	180	9	2.25	80.56	69.02	59.13	52.03	0.09
14.	10	9	2.25	5.13	13.48	2.81	2.97	0.07
15.	10	2	1.25	43.87	43.61	32.69	2.57	0.37
16.	180	9	0.25	60.82	72.28	79.41	5.96	0.21
17.	95	16	9.25	36.42	37.67	54.26	3.06	0.08

The final quadratics equations in terms of coded for oil removal efficiency % (T_{C1}), turbidity removal efficiency % (T_{C2}), COD removal efficiency % (T_{C3}), energy consumption (T_4) and mass transfer coefficient (T_{C5}).

$$T_{C1} = + 50.71 + 32.10\,A - 18.79\,B + 5.36C - 7.57A^2 + 10.19B^2 - 6.00C^2 + 4.68AB + 4.15AC - 7.59\,BC \tag{4.5}$$

$$T_{C2} = + 66.92 + 30.52A - 19.63B + 4.40C - 22.30A^2 + 8.45B^2 - 5.39C^2 + 3.78AB - 3.65AC + 2.64\,BC \tag{4.6}$$

$$T_{C3} = + 40.14 + 33.60A - 12.99B - 3.91C - 4.09A^2 + 15.53B^2 - 0.59 + 4.05AB - 5.65AC - 11.40\,BC \tag{4.7}$$

$$T_{C4} = + 10.91 + 12.64A + 2.31B + 9.60C + 4.79A^2 - 0.40B^2 + 0.89C^2 + 1.31AB + 12.15AC + 3.52\,BC \tag{4.8}$$

$$T_{C5} = + 1.13 + 2.31A - 1.55B - 0.40C + 1.03A^2 + 1.35B^2 - 0.071C^2 - 0.55AB - 0.50AC - 0.45BC \tag{4.9}$$

Table 4.17 Regression coefficients of the responses in continuous mode

Response	R^2	Adj R^2	SD	CV	PRESS	F value	Prob>F	AP
% oil removal	0.953	0.89	9.33	18.99	1814.51	15.94	0.0007	14.22
% turbidity removal	0.985	0.96	5.24	9.05	2266.79	53.94	<0.0001	24.98
% COD removal	0.981	0.95	5.68	12.55	1144.72	42.28	<0.0001	21.57
Energy consumption (KWh/m^3)	0.984	0.96	2.48	18.50	433.08	50.81	<0.0001	26.52
Mass transfer coefficient (m/hr)	0.978	0.95	0.50	22.70	10.78	34.75	<0.0001	21.39

SD standard deviation, CV coefficient of variance, PRESS predicted residual error sum of squares, AP adequate precision, and P probability of error.

4.1.2 Statistical analysis

In present work the BBD was applied to determine the combined impacts of operational parameters in continuous process. Regression coefficients of the responses for the continuous process as illustrated in Table 4.17.

F-statistics and p-value employed for statistical testing of various models to predict the desired model. Probability values for all the responses in continuous mode were found less than 0.01 and the quadratic model was suggested by statistical analysis. The F value for continuous process T_{C1}, T_{C2}, T_{C3}, T_{C4} and T_{C5} were 15.94, 53.94, 42.28, 50.81 and 34.75 respectively. In the present study R^2 values for continuous process T_{C1}, T_{C2}, T_{C3}, T_{C4} and T_{C5} were 0.9535, 0.985, 0.981, 0.984 and 0.978 respectively. The coefficient of variance (C.V) and adj-R^2 value were estimated to determine the model adequacy. C.V for continuous process T_{C1}, T_{C2}, T_{C3}, T_{C4} and T_{C5} were 18.99, 9.05, 12.55, 18.50 and 22.70 respectively. Adequate precision (AP) showed the range of the predicted results at the design points to the normal prediction error. AP for continuous process T_{C1}, T_{C2}, T_{C3}, T_{C4} and T_{C5} were 14.22, 24.98, 21.57, 26.52 and 21.39 respectively. The AP measures the signal-to-noise ratio (S/N), with a ration greater than 4 being desirable.

Ratios of CV>4 showed that adequate model was desirable. In order to decide about the adequacy of various models, sequential model sum of square and model summary statistics were tested and result are given in Table 4.18, Table 4.19, Table 4.20, Table 4.21 and Table 4.22 for responses T_{C1}, T_{C2}, T_{C3},T_{C4} and T_{C5} respectively. Sequential model sum of squares that quadratic model best fits the experiment data for responses T_{C2}, T_{C3}, T_{C4}, T_{C5} and linear for T_{C1}. Cubic model was found to be aliased for all the responses.

Table 4.18 Sequential Sum of Squares for oil removal efficiency (%) in continuous mode

Source	Sum of Squares	DF	Mean Squares	F Value	Prob >F	
Mean	41009.31	1	41009.31			
Linear	11295.16	3	3765.05	27.38	< 0.0001	Suggested
2F1	386.85	3	128.95	0.92	0.4657	
Quadratic	791.98	3	263.99	3.04	0.1024	
Cubic	59.79	3	19.93	0.15	0.9276	Aliased
Residual	549.03	4	137.26			
Total	54092.12	17				

Table 4.19 Sequential Sum of Squares for turbidity removal efficiency (%) in continuous mode

Source	Sum of Squares	DF	Mean Squares	F Value	Prob >F	
Mean	56918.04	1	56918.04			
Linear	10690.00	3	3563.33	16.50	0.0001	
2F1	138.37	3	46.12	0.17	0.9124	
Quadratic	2477.67	3	825.89	30.13	0.0002	Suggested
Cubic	136.24	3	45.41	3.27	0.1414	Aliased
Residual	55.61	4	13.90			
Total	70415.93	17	4142.11			

Table 4.20 Sequential Sum of Squares for % COD removal efficiency (%) in continuous mode

Source	Sum of Squares	DF	Mean Squares	F Value	Prob >F	
Mean	34800.42	1	34800.42			
Linear	10501.40	3	3500.47	22.77	< 0.0001	
2F1	712.49	3	237.50	1.85	0.2024	
Quadratic	1060.01	3	353.34	10.95	0.0049	Suggested
Cubic	54.85	3	18.28	0.43	0.7443	Aliased
Residual	170.93	4	42.73			
Total	47300.10	17	2782.36			

Table 4.21 Sequential Sum of Squares for energy consumption in continuous mode

Source	Sum of Squares	DF	Mean Squares	F Value	Prob >F	
Mean	3050	1	3050.86			
Linear	2059.12	3	686.37	11.26	0.0006	
2F1	647.28	3	215.76	14.85	0.0005	
Quadratic	102.34	3	34.11	5.55	0.0288	Suggested
Cubic	25.34	3	8.45	1.91	0.2688	Aliased
Residual	17.65	4	4.41			
Total	5902.60	17	347.21			

Table 4.22 Sequential Sum of Squares for mass transfer coefficient in continuous mode

Source	Sum of Squares	DF	Mean Squares	F Value	Prob >F	
Mean	83.55	1	83.55			
Linear	63	3	21	15.53	0.001	
2F1	3.09	3	1.03	0.71	0.5667	
Quadratic	12.70	3	4.23	16.62	0.0014	Suggested
Cubic	0.57	3	0.19	0.63	0.6344	Aliased
Residual	1.21	4	0.30			
Total	164.13	17	9.65			

Table 4.23 Analysis of variance for oil removal efficiency (%) in continuous mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	12473.99	9	1386.00	15.94	0.0007	
Elapsed time	8242.64	1	8242.64	94.77	<0.0001	Highly significant
Flow rate	2823.01	1	2823.01	32.46	0.0007	
Current	229.52	1	229.52	2.64	0.1483	
Elapsed time^2	241.54	1	241.54	2.78	0.1396	
Flow rate^2	437.51	1	437.51	5.03	0.0598	
Current^2	151.78	1	151.78	1.75	0.2280	
Elapsed time × flow rate	87.52	1	87.52	1.01	0.3492	
Elapse time × current	69.06	1	69.06	0.79	0.4025	
Flow rate× current	230.28	1	230.28	2.65	0.1477	
Residual	608.82	7	86.97			
Lack of fit	59.79	3	19.93	0.150	0.9276	
Pure error	549.03	4	137.26			
Cur total	13082.82	16				

Table 4.24 Analysis of the variance for turbidity removal efficiency (%) in continuous mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	13306.04	9	1478.43	53.94	<0.0001	
Elapsed time	7451.76	1	7351.76	271.88	<0.0001	Highly significant
Flow rate	3083.09	1	3083.09	112.49	<0.0001	Highly significant
Current	155.14	1	155.14	5.66	0.0489	
Elapsed time^2	2093.71	1	2093.71	76.39	<0.0001	
Flow rate^2	300.52	1	300.52	10.96	0.0129	
Current^2	122.18	1	122.18	4.46	0.0726	
Elapsed time × flow rate	57.15	1	57.15	2.09	0.1919	
Elapse time × current	53.29	1	53.29	1.94	0.2059	
Flow rate× current	27.93	1	27.93	1.02	0.3464	
Residual	191.86	7	27.41			
Lack of fit	136.24	3	45.41	3.27	0.1414	
Pure error	55.61	4	13.90			
Cur total	13497.89	16				

Table 4.25 Analysis of the variance for COD removal efficiency (%) in continuous mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	12273.90	9	1363.77	42.28	<0.0001	
Elapsed time	9028.99	1	9028.99	279.93	<0.0001	Highly significant
Flow rate	1350.18	1	1350.18	41.86	0.0003	
Current	122.23	1	122.23	3.79	0.0926	
Elapsed time^2	70.35	1	70.35	2.18	0.1832	
Flow rate^2	1014.84	1	1014.84	31.46	0.0008	
Current^2	1.47	1	1.47	0.045	0.8373	
Elapsed time × flow rate	65.53	1	65.53	2.03	0.1971	
Elapse time × current	127.58	1	127.58	3.96	0.0870	
Flow rate× current	519.38	1	519.38	16.10	0.0051	
Residual	225.78	7	32.25			
Lack of fit	54.85	3	18.28	0.43	0.7443	
Pure error	170.93	4	42.73			
Cur total	12499.69	16				

Table 4.26 Analysis of the variance for energy consumption in continuous mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	2808.74	9	312.08	50.81	<0.0001	
Elapsed time	1278.64	1	1278.64	208.16	<0.0001	Highly significant
Flow rate	42.57	1	42.57	6.93	0.0338	
Current	737.91	1	737.91	120.13	<0.0001	Highly significant
Elapsed time^2	96.78	1	96.78	15.76	0.0054	
Flow rate^2	0.66	1	0.66	0.11	0.7527	
Current^2	3.35	1	3.35	0.55	0.4841	
Elapsed time × flow rate	6.85	1	6.85	1.11	0.3261	
Elapse time × current	590.76	1	590.76	96.17	<0.0001	
Flow rate× current	49.67	1	49.67	8.09	0.0249	
Residual	43	7	6.14			
Lack of fit	25.34	3	8.45	1.91	0.2688	
Pure error	17.65	4	4.41			
Cur total	2851.74	16				

Table 4.27 Analysis of the variance for mass transfer coefficient in continuous mode

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	0.38	9	0.042	57.26	<0.0001	
Elapsed time	0.044	1	0.044	59.83	0.0001	Highly significant
Flow rate	0.19	1	0.19	264.84	<0.0001	
Current	2.290E-004	1	2.290E-004	0.31	0.5944	Highly significant
Elapsed time^2	0.011	1	0.011	14.46	0.0067	
Flow rate^2	0.097	1	0.097	131.27	<0.0001	
Current^2	4.420E-0.003	1	4.420E-003	6.01	0.0441	
Elapsed time × flow rate	1.980E-003	1	1.980E-003	2.69	0.1449	
Elapse time × current	9.458E-003	1	9.458E-003	12.85	0.0089	
Flow rate× current	0.016	1	0.016	21.52	0.0024	
Residual	5.152E-003	7	7.359E-004			
Lack of fit	5.152E-004	3	1.717-003			
Pure error	0.000	4	0.000			
Cur total	0.38	16				

Significant terms in continuous mode for the oil removal efficiency (%) and COD removal efficiency (%) was elapsed time highly significant parameters as shown in Table 4.23 and 4.25 respectively. For turbidity removal efficiency (%), elapsed time and flow rate were highly significant parameters as illustrated in Table 4.24. Elapsed time and current were highly significant terms for energy consumption and mass transfer coefficient as shown in Table 4.26 and 4.27 respectively.

The actual and the predicted results for the responses T_{C1}, T_{C2}, T_{C3}, T_{C4} and T_{C5} by EO process are shown in Figures 4.7 and 4.8.

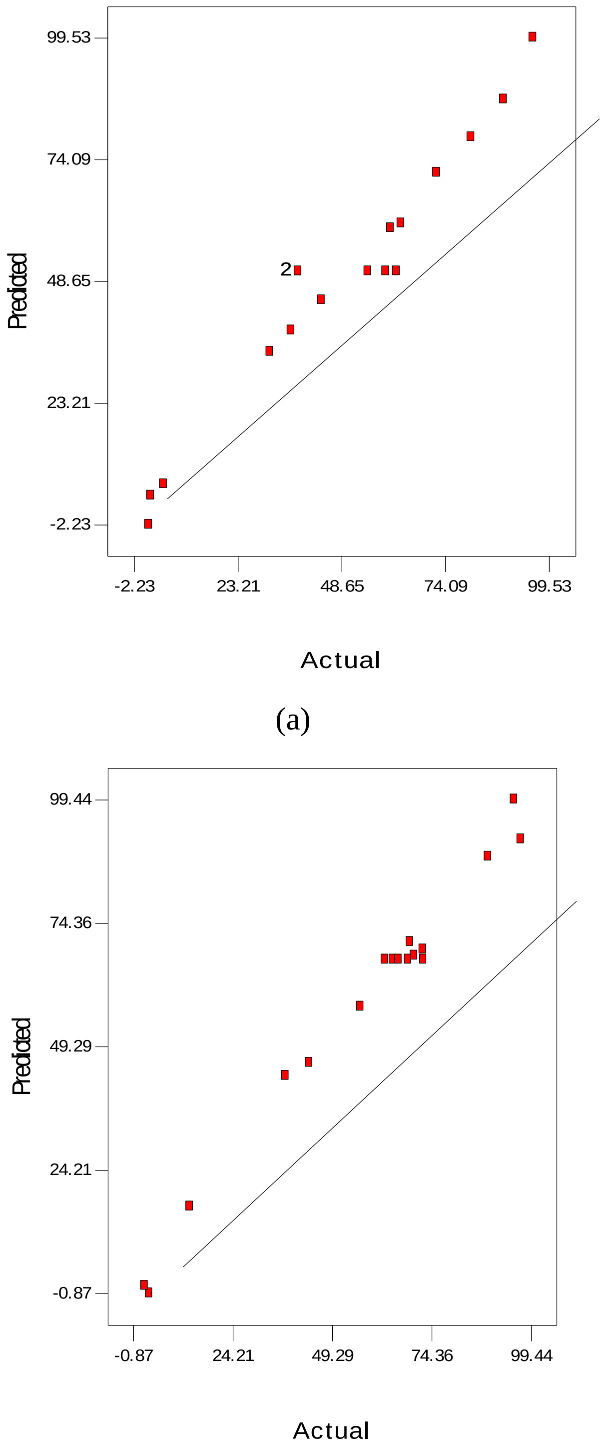
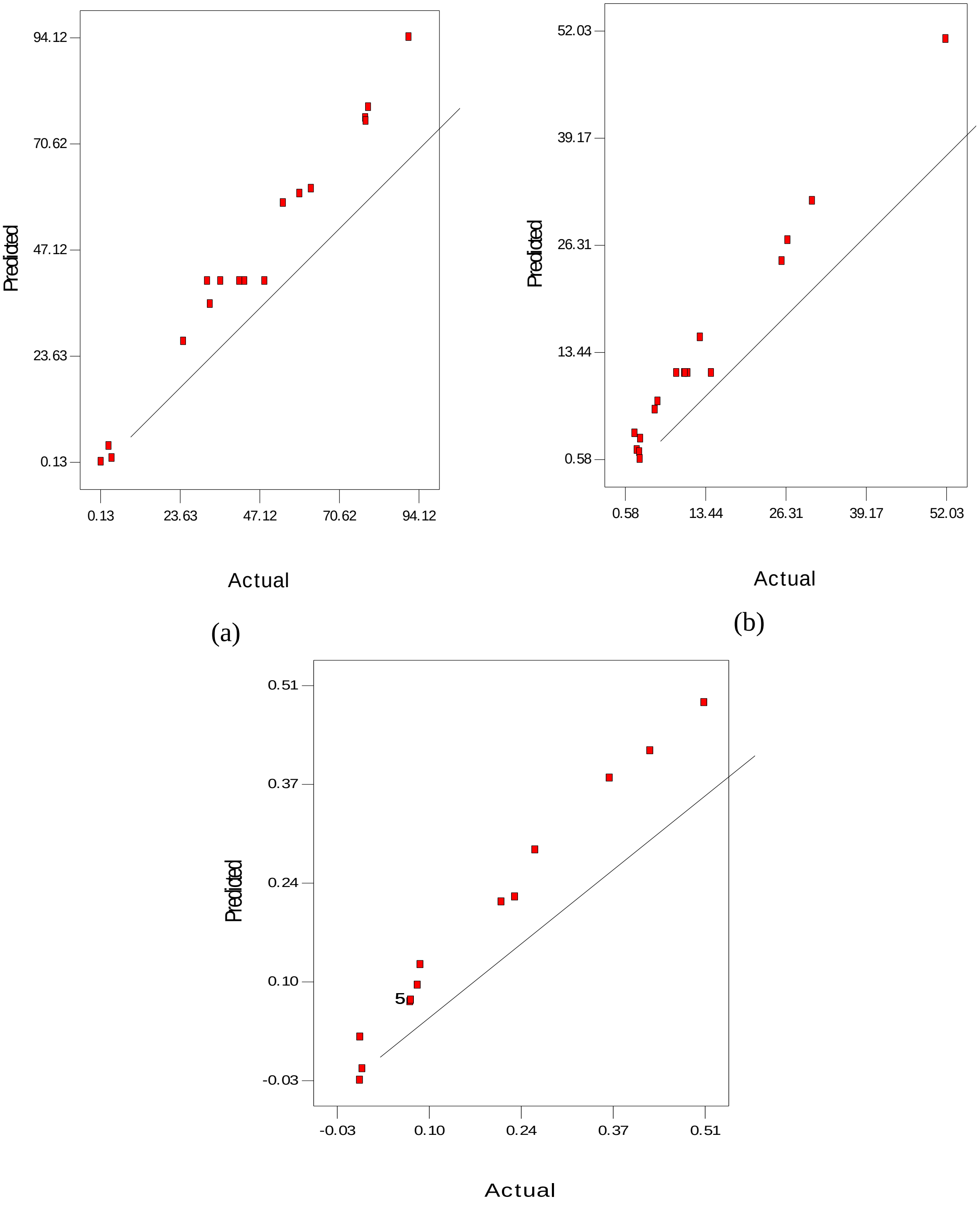


Figure 4.7 Comparison between predicted results with actual results (a) oil removal efficiency (%) and (b) turbidity removal efficiency (%) in continuous mode



(a)

(b)

(c)

Figure 4.8 Comparison between predicted results and actual results (a) COD removal efficiency (%), (b) energy consumption and (c) mass transfer coefficient in continuous mode

4.1.3 Effects of variables on removal efficiency

To investigate the impact of various operational parameters i.e *t*, *Q* and *i* on responses $T_{C1,}$ T_{C2}, T_{C3}, T_{C4} and T_{C5} for the treatment of soluble cutting oil by continuous process, three dimensional response surface graph obtained from RSM were studied. Figure 4.14 shows the effect of *Q* and *t* on the T_{C1}. It is observed that $Q \approx 2$ to 2.5, the steady state in achieved at $t = 170$ min but at higher *Q* values. Higher *t* value is required to form steady state degradation. Figure 4.15c shows the effect of *Q* with increase in *i* value on T_{C2}. At the lower range of $Q \approx 2$ to 2.5 with time in *i* value T_{C2} is increased.

Figure 4.16a shows that T_{C3} is decreases with increases in the *Q* at all the *t* values. But it shows maximum removal at higher *t* and lower *Q* value. Figure 4.16b concluded that T_{C3} is maximum at the lower side of *Q* value at all the *i* value. The effect of *Q* on T_{C4} has direct relation with *i*. T_{C4} is increased with increase in *Q* value at the *i* values. It is minimum at lower side of *i* and *Q* values shown in Figure 4.17.

Figure 4.18 show the T_{C5} with respect to *Q* and *t* values. T_{C5} is ≈0 at higher *Q* values at lower t values. But it is highest at lower *Q* value and increases with increase in *t*.

T_{C5} is increased with the decreases in *Q* because of extended reaction time. T_{C5} is directly related to flow-rate, electrode area, current and physical properties of oil emulsion (Alvarez et al., 2002), also dependent upon *t* and COD concentration (Equation. 3.2). The mass transfer is high at lower *Q* values, showing negligible film resistance because of turbulent flow.

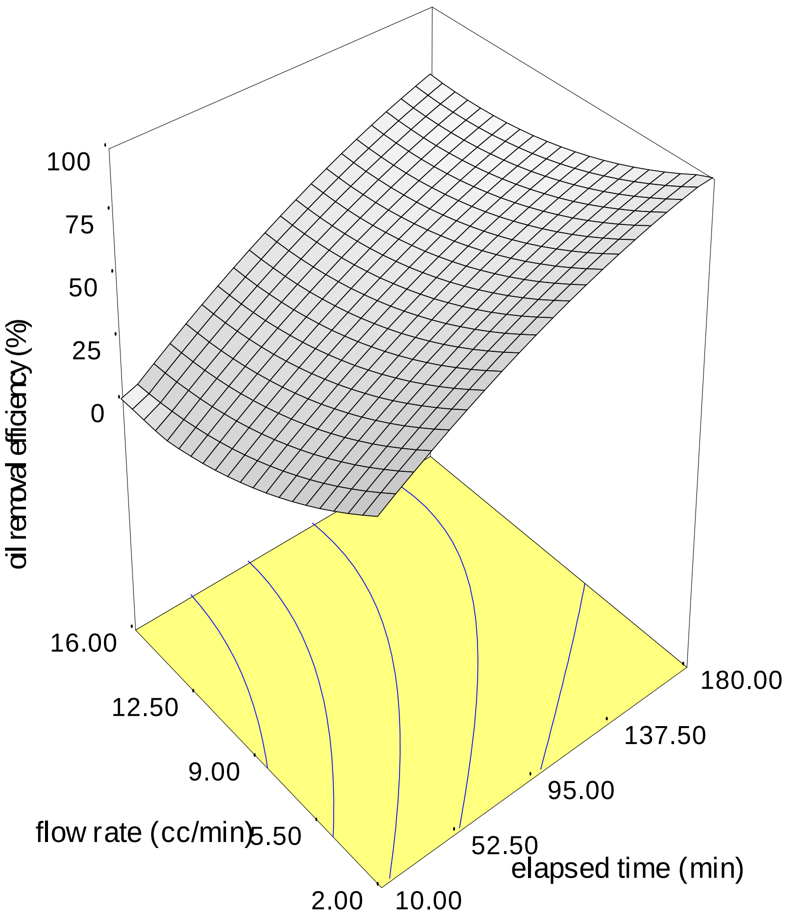


Figure 4.9 3D response surface graph for the treatment of cutting oil emulsion by electro-oxidation process with combined effect of flow rate Q (cc/min)- elapsed time (min) for continuous on percentage of oil removal efficiency

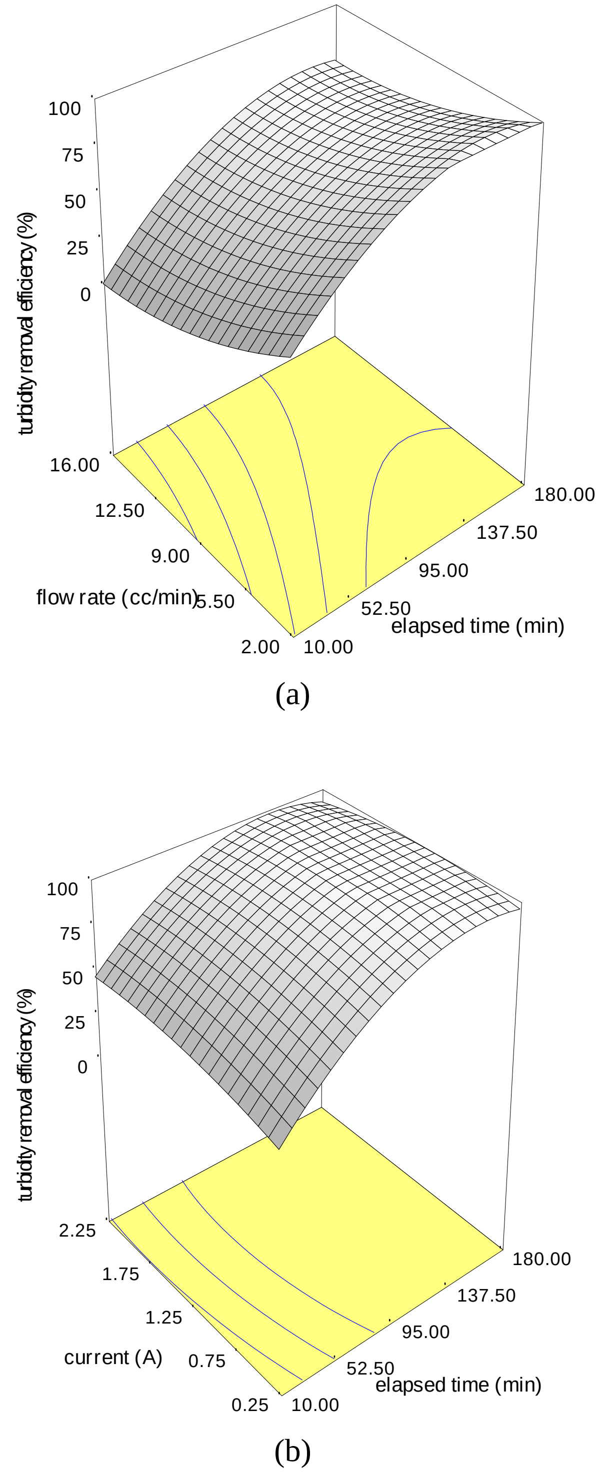
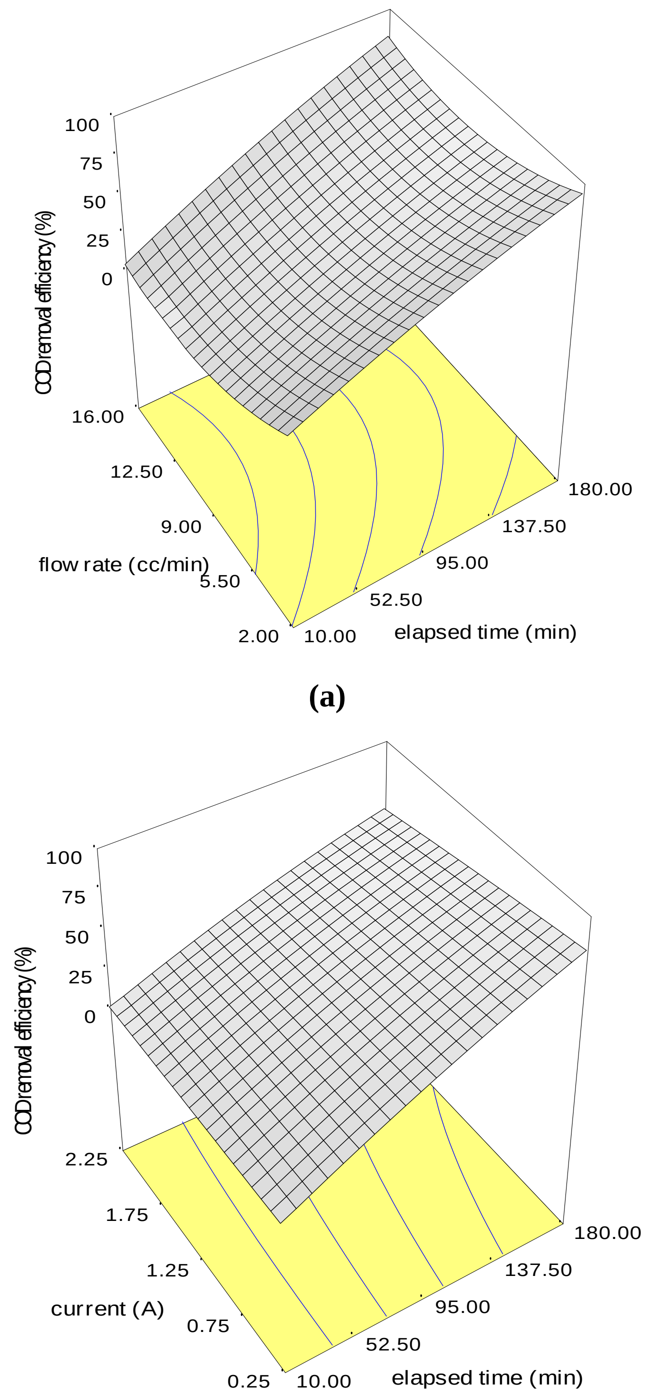


Figure 4.10 3D response surface graphs for the treatment of cutting oil emulsion by electro-oxidation process with combined effect of (a) flow rate- elapsed time and (b) current – elapsed time for continuous process on percentage of turbidity removal



(a)

(b)

Figure 4.11 3D response surface graphs for the treatment of cutting oil emulsion by electro-oxidation process with combined effect of (a) flow rate- elapsed time and (b) current – elapsed time for continuous process on percentage of COD removal

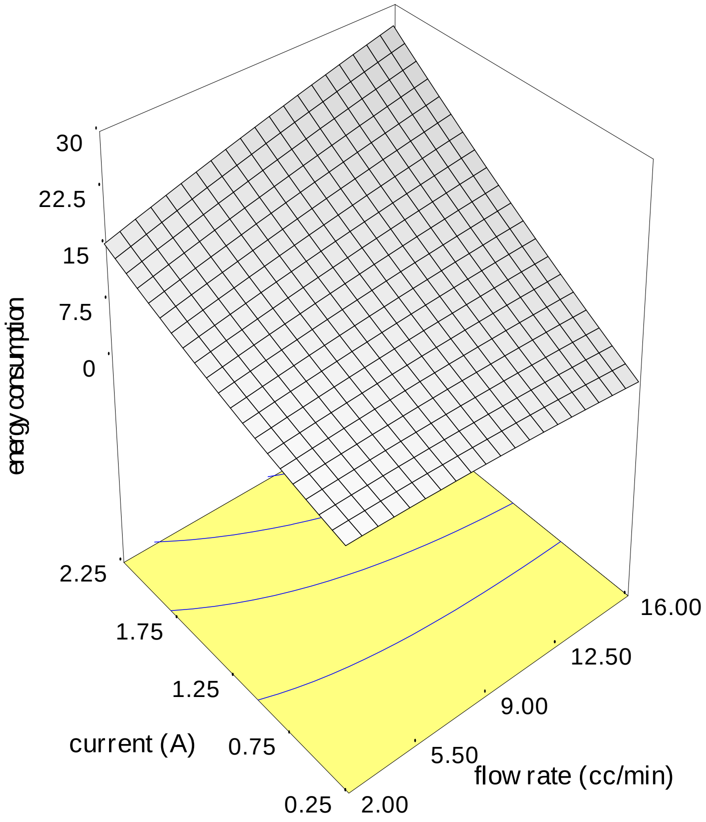


Figure 4.12 3D response surface graphs for treatment of cutting oil emulsion by electro-oxidation process with combined effect of current – flow rate for continuous process on energy consumption

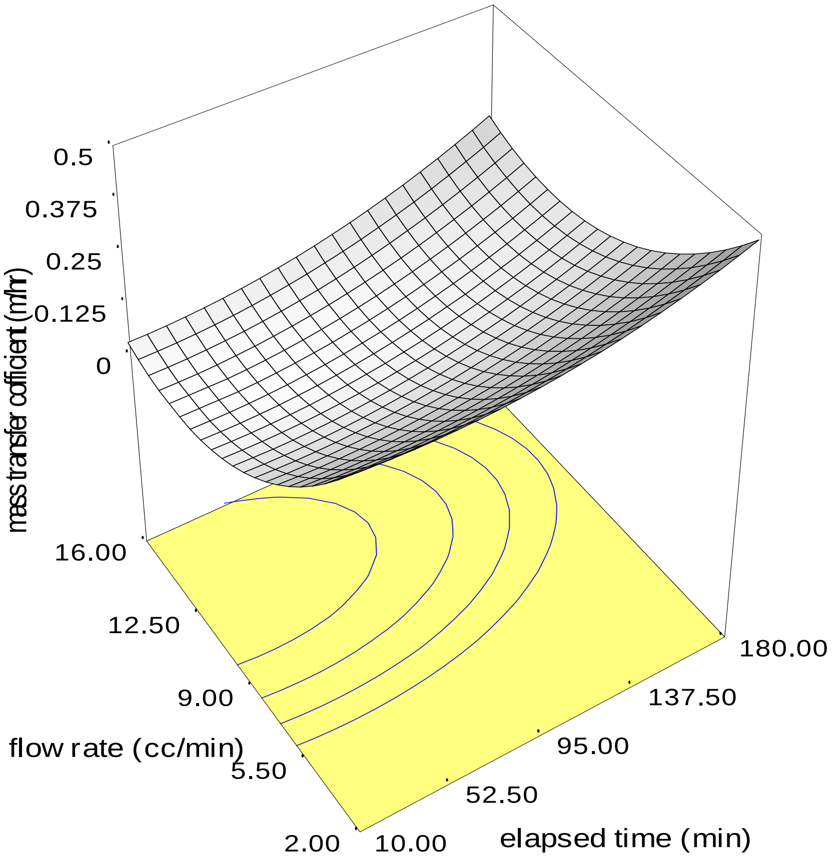


Figure 4.13 3D Response graph for treatment of cutting soluble oil emulsion by electro-oxidation process with combined effect of flow rate-elapsed time for continuous process on mass transfer coefficient

4.1.4 Optimization analysis

In present study, electro-oxidation of cutting oil emulsion was optimized by RSM in terms of maximization of response T_{C1}, T_{C2}, $T_{C3,}$ T_{C5} and minimization of response T_{C4} simultaneously with the help of desirability (D) function approach.

Optimum condition for EO process of treatment soluble cutting oil emulsion was to be flow rate 2.2 cc/min, current 1.11 (A), and elapsed time 170 (min) which produced overall desirability 0.9708 as shown in Table 4.28

Table 4.28 Optimum Conditions for electro-oxidation process for treatment of cutting oil emulsion

Variables	Optimum Values
t	170 min
Q	2.2 cc/min
i	1.11 A

Constraints applied for optimization of electro-oxidation process for cutting oil emulsion in continuous mode shown in Table 4.29

Table 4.29 Constraints applied for optimization of electro-oxidation process for cutting oil emulsion

Parameter	Goal	Lower Limit	Upper Limit
t (min)	Is in range	10	180
Q (cc/min)	Is in range	2	16
i (A)	Is in range	0.25	2.25
Oil Removal Efficiency (%)	Maximize	1.51	95.79
Turbidity Removal Efficiency (%)	Maximize	2.14	97
COD Removal Efficiency (%)	Maximize	0.5	91.36
Energy Consumption (KWh/m^3)	Minimize	2.213	52.03
Mass Transfer Coefficient (m/hr)	Maximize	0.0005	0.51

Optimum condition for electro-oxidation of cutting oil emulsion was experimentally verified. The response T_{C1}, T_{C2}, $T_{C3,}$ T_{C4} and T_{C5} were 92.90%, 98.99%, 91.36%, 19.57 KWh/m^3 and 0.658 m/hr respectively. In order to confirm the result found by optimization, four confirmation experiments were conducted with the optimized set of operational parameters. The predicted value of response T_{C1}, T_{C2}, $T_{C3,}$ T_{C4} and T_{C5} were found to be 95.78%, 100%, 93.70%, 20.64 KWh/m^3 and 0.970 m/hr respectively, which are very close to predicted value. The experiments were performed in duplicate by the RSM, it shows that predicted results were very close to the experimental results.

Differentiation between the predicted and experimental values of response at optimum condition as shown in Table 4.30

Table 4.30 Differentiation between the predicted and experimental values of response at optimum condition

Response	Predicted	Experimental
Oil removal efficiency (%)	95.78	92.90
Turbidity removal efficiency (%)	100	98.99
COD removal efficiency (%)	93.70	91.36
Energy consumption (KWh/m^3)	20.64	19.57
Mass transfer coefficient (m/hr)	0.970	0.658

Chapter-5

CONCLUSIONS

The treatment of cutting oil emulsion was studied in an electro-oxidation process in batch and continuous modes. Important operational parameters were determined for their impacts on process responses efficiency. The following conclusion are drawn from the present study:

- The treatment of cutting oil emulsion by electro-oxidation method with Ti/RuO_2 anode was done successfully.
- Operational parameters for the treatment cutting oil of emulsion were optimized by RSM in batch and continuous mode.
- The proposed model fits very well with the experimental data. The R^2 value removal efficiencies for oil, turbidity, COD and energy consumption were 0.983, 0.989, 0.997, 0.991 in batch process, 0.953, 0.985, 0.981, 0.984 and 0.978 for oil, turbidity, COD, energy consumption and mass transfer coefficient in continuous process.
- The experimental results for oil, turbidity and COD removal at optimized conditions were found to be 98.83 %, 99.90% and 94.93% for batch process and 92.90%, 98.99% and 91.36% for continuous process, respectively. Mass transfer coefficient for continuous process found to be 0.658 (m/hr). Minimum energy consumption for batch and continuous process are 2.833 (KWh/m^3) and 19.57 (KWh/m^3).
- % removal efficiencies of oil, turbidity and COD was observed in the acidic as well as in basic conditions so, it is claimed that direct and indirect oxidation were responsible for the treatment of soluble cutting oil. The optimum pH was 7.23, which shows that ·OH mediated oxidation was prominent for the maximum removal. Direct oxidation is eminent and the oxidation potential of ·OH is very high. So, the chances of the formation of chloro-compounds is limited during the treatment process.

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