TREATMENT OF INDUSTRIAL WASTEWATER DERIVED ORGANIC POLLUTANTS

USING ELECTROCHEMICAL METHODS AND OPTIMIZATION OF OPERATION

PARAMETERS

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota

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ABSTRACT

Industrial operations produce a notable amount of wastewaters with high concentration of chemical oxygen demand (COD), mostly consisting of organic carbon compounds. The treatment performance of electrochemical methods for organic removal and the effects of process parameters are the subject of this research.

Three research tasks were performed. The first task was the removal of organic pollutants from three different industrial wastewaters using two different electrochemical methods; combined electrocoagulation + electrooxidation (EC+EO) and b) electrochemical peroxidation (ECP). Using only EC process was found to be significantly successful in removing suspended and colloidal pollutants and could remove more than 90% COD and 80% of TOC. The study showed that combined EC+EO process had better removal capability compared to ECP when operated under similar process conditions.

The second task was to study the effect of the process parameters; pH, H_2O_2 dosage, current density, and operation time; and to optimize and estimate the best treatment conditions for the methods using Box-Behnken Design (BBD). For sugar beet wastewater, the results showed that EO could remove 75% of organics at optimum conditions of pH 5.3; current density of 48.5 mA/cm^2; and operation time of 393 min. The canola oil refinery wastewater achieved more than 90% pollutant removal when the conditions were optimized at pH 5.8 – 6 with applied current density of 9.2 mA cm^{-2} run for nearly 300 min. The rate of degradation of the wastewater derived organic pollutants followed a first order kinetics for all the wastewaters investigated and the models were validated for goodness of fit with high R^2.

The final task was to compare treatment efficiency between the electrochemical processes. Based on the energy consumed and the performance efficiency to remove COD,

sCOD, TOC and DOC in the three different wastewaters studied, EC+EO process was found suitable for the treatment of canola and sunflower oil wastewater. On the other hand, from the model prediction and the experiments conducted, EO resulted in better removal capability compared to ECP. Also, the consumption of energy by ECP was comparatively higher than EO process while taking longer time of operation for significant removal.

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DEDICATION

To my father Ajit Chandra Sarmah, my mother Purnima Sarmah, my loving and caring husband

Sayan Roy, my brother Judith Kaushik and to my son Snigdhaneil

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LIST OF ABBREVIATIONS

AFF ....Aerated Fixed Film

AOP............................Advanced Oxidation Process

ASU............................Anaerobic Sludge Unit

BBD ....Box-Behnken Design

BDD ....Boron Doped Diamond

BOD ....Biological Oxygen Demand

CCD ....Central Composite Design

COD ....Chemical Oxygen Demand

CV ....Coefficient of Variance

DF ....Degree of Freedom

DO.............................Dissolved Oxygen

DOC ....Dissolved Organic Carbon

DSFF ....Downflow Stationary Fixed Film

EC ....Electrocoagulation

ECP ....Electrochemical Peroxidation

EF..............................Electro-Fenton

EO ....Electrooxidation

IAF ....Induced Air Floatation

MS.............................Mean of Squares

PAC............................Poly Aluminum Chloride

RSM ....Response Surface Methodology

sCOD..........................Soluble Chemical Oxygen Demand

SS ....Sum of Squares

TOC............................Total Organic Carbon

TSS.............................Total Suspended Solids

UAFB.........................Upflow Anaerobic Fixed Bed

UASB.........................Upflow Anaerobic Sludge Bed

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CHAPTER 1. GENERAL INTRODUCTION

1.1. Background

The amount of fresh water on earth is constant while the continuous increase in human population and activities has led to increase in fresh and clean water requirement. Although, about 70% of world is covered by water, only 2.5% of it is fresh water and only 1% of that fresh water is accessible to human beings (Al-Mamun et al., 2018). In addition, wastage of clean water is high because of inefficient water usage. It has been estimated that global water shortage is eminent in the next 20 years.

Several attempts have been made to ensure sustainable future water need. Once the fresh waters used by human being for any purposes, reusing that water after necessary treatment is not applied successfully in any part of the world since public acceptance of reusing the treated wastewaters is very low (Al-Mamun et al., 2018; Chaussard et al., 2013). Therefore, using the treated wastewaters are not increasing the amount of current freshwater sources.

Water usage in many industries, including agricultural and food industries, is inevitable and is increasing due to increase in production and demands of products from these industrial activities. The discharged of generated wastewater into surrounding water bodies are of great ecological concern (Tak et al., 2015). Usually, wastewater from food processing plant contains high concentration of organic materials that supports proliferation of pathogenic microorganisms and often result into production of volatile odorous and toxic metabolites. This has led to the advent of sustainable agricultural practices and food processing. The concept of environmentally friendly consciousness is a necessary step towards discontinuing the future ecological problems caused by wastewater discharged.

Biological methods are the most acceptable current methods of treatment of industrial wastewaters. However, these processes demand a significant land area and facility combined with long treatment duration (Nguyen et al., 2016; Tak et al., 2015). An appropriate system should provide efficient pollutant reduction, use less treatment time, require simple installation, maintenance, and operation with the addition of little or no chemical compounds (Tak et al., 2015). Although membrane separation techniques such as ultrafiltration(Sharifi et al., 2014), microfiltration (Hua et al., 2007), nanofiltration (Sadeghian et al., 2010) and reserve osmosis (Yu et al., 2010) guarantee good quality effluent, their applications are limited due to initial investment and operating costs.

Electrocoagulation (EC) is a frequently preferred method in the treatment of oily wastewaters, since it is effective for the destabilization of oil-in-water emulsions (Calvo et al., 2003; Fouad, 2014; Fouad et al., 2009; Un et al., 2009a). During the electrocoagulation, the breaking of emulsions is explained by as follows: (i) compression of the diffuse double layer, (ii) charge neutralization and (iii) floc formation (An et al., 2017). In this process, dissolution of sacrificial anode (iron or aluminum) leads to the formation of hydroxo-metal species and electrochemical reduction of water at the cathode generates hydrogen bubbles cause upwards momentum flux resulting pollutant removal by flotation (Holt et al., 2002). As mentioned in many studies published before, the electrocoagulation process is an easy, economically feasible and environmentally friendly (high treatment efficiency, less sludge production etc.) method (Mollah et al., 2001). Due to its advantages, many researchers reported that electrocoagulation process was applied successfully for industrial wastewater such as textile (Alinsafi et al., 2005), paper (Uğurlu et al., 2008), olive oil (Inan et al., 2004), dairy (Un et al., 2014), tannery (Apaydin et al., 2009) and slaughterhouse (Bayramoglu et al., 2006). Many researchers have

focused on to determine optimum operating conditions such as initial pH, current density, electrolysis time which effects EC performance.

The electrooxidation process (EO) using boron-doped diamond (BDD) anodes can be used to (i) complete oxidation of organics to carbon dioxide, (ii) lower molecular weight compounds, (iii) the conversion of toxic organic matters into biodegradable compounds (Alfaro et al., 2006). Direct oxidation occurs by electron transfer on the anode surface, while indirect oxidation occurs in bulk solution via electro-chemical generated strong oxidants (Souza and Ruotolo, 2013). At the same time, when the EO process is applied in the presence of chloride, no further negativities (such as scavenging effect) that may be encountered in other advanced oxidation processes. EO can be used both as pre-treatment (Gonzalez-Olmos et al., 2018) and alone (Canizares et al., 2006) by considering the wastewater composition and need.

Electrochemical peroxidation (ECP) process is a hybrid method which is formed by combining oxidation and electrocoagulation processes. In this process, ferrous ions generated based on the anodic dissolution of sacrificial iron electrodes reacts with externally added H_2O_2 creating Fenton's reagent. In conventional Fenton the ferrous ions are added as salts which leads to secondary contamination.

1.2. Research Problem Statement

Wastewater originated pollution is a crucial environmental problem that causes detrimental effect on surface waters. Almost all the potential sources of industrial, agricultural, and domestic wastewaters contribute to organic pollutant discharge to the aquatic systems. These organic compounds accumulate in receiving waters such as rivers, estuaries, and lakes over the period of time thereby acting as significant nutrient source for the algae, phytoplankton and various other aquatic species. Consumption of these compounds enhances the growth of the

aquatic plants in receiving waters and decreases dissolved oxygen (DO) level. Reduction in DO level in water bodies affects aquatic life critically by causing hypoxia and resulting in eutrophication. As reported by the Pew Oceans Commission in 2003, two thirds of estuaries and bays in the United States (US) are extremely deteriorated due to eutrophication caused from uncontrollable growth of aquatic plants. Then, eutrophication poses serious environmental problem causing reduction in light penetration, increase in algal blooms and creating more hypoxic and anoxic conditions from production of biomass (Bronk et al., 2010). Over the years, the environmentalists have been trying to find a solution to treat these pollutants at its source of origin. Several countries has recently stipulated additional stringent conditions that require the presence of pollutant in treated wastewater at a lesser level (Nguyen et al., 2016). For instance, Korea, USA, and France have recently implemented effluent phosphorous standards as <0.2, 0.5 – 1.0, and 1 – 2 mg/L, respectively (Nguyen et al., 2016). Conventional biological processes efficiently remove biodegradable organics, yet these treatments fail to prevent the accumulation of nonbiodegradable organic compounds (Ahmad et al., 2007; Habets and Knelissen, 1997; Hermosilla et al., 2015), such as high molecular weight organic compounds (Yeber and Cid, 2013; Yeber et al., 2007), lignin and lignin-derived compounds (Chang et al., 2004; Dahlman et al., 1995; Eriksson and Kolar, 1985; Thompson et al., 2001) and toxic chlorinated organics (Balcioglu et al., 2007). The storage ponds in associated with biological process not only require large spaces but also pose as a breeding habitat for various pathogens and other microbes utilizing the organics from wastewater for proliferation. During peak production periods, the organic loading into the anaerobic system increases drastically thereby causing a performance decline in separating solids from the anaerobic reactor overflow. The treatment system leaves unacceptable concentration of organic pollutants and chemical oxygen demand (COD) in the

effluent. One of the most important disadvantages of these anaerobic systems is the sensitivity of microbes towards environmental factors. Most important microbes involved in anaerobic digestion are methanogens and acetogens. These microbes are extremely sensitive to acids, pH, salts, substrate composition, metal cations and temperature (Storry, 1998). Another disadvantage is the requirement to heat the system thereby requiring larger tank volumes and increased cost. The failure of anaerobic systems can be attributed to the high organic loading, presence of toxins, temperature, inadequate concentration of microbial population, and early washout of microbes before proliferation.

With the increase in the demand to improvise the standards in drinking as well as processed water, electrochemical methods have found its application in the recent decades. Technologies involving electrochemical methods are proving to more efficient than any other existing methods in terms of cost, ease of operation as well as time efficiency (Chen, 2004). The most common electrochemical methods studied for the treatment of various industrial wastewaters are EC, EO and traditional electro-Fenton (EF) processes. These methods have been proven successful in treating pollutants resulting from industries such as dairy (Chakchouk et al., 2017), textile dye (GilPavas et al., 2017), tannery (Azarian et al., 2018), petroleum (Bhagawan et al., 2016), and other such processed wastewater sources. Very few studies have been reported regarding the use of ECP in wastewater treatment. The studies using EC, EO and ECP mostly investigated the reduction of total COD in the wastewater. Studies on combination of EC and EO on industrial wastewaters is limited. Treatment efficiency of combined EC and EO process on canola, sunflower and sugar beet wastewater has not been investigated. The EC, EO and ECP processes have found its exclusive application on various industrial wastewaters. There is a knowledge gap on the efficiency of these treatment processes on soluble COD (sCOD) and

dissolved organic carbon (DOC) present in these industrial wastewaters. Although, successful treatment studies have been reported regarding the application of these methods when applied individually, yet there is no comparative study between the three processes or as combined processes. It is unclear which process takes precedence with respect to treatment performance. Most of all, there is limited or no knowledge on treatment comparison between combined EC+EO and ECP process on industrial wastewater. Understanding if various operation parameters could affect the treatment performance between these processes is important. In order to focus on commercial application, it would be beneficial to understand which process would be a preferred choice with respect to pollutant removal, energy consumption and kinetics.

1.3. Statement of Objectives

The major objectives and corresponding hypotheses of this study are:

1. Removal of organic pollutants from canola, sunflower oil and sugar beet wastewater using EC, EO and ECP

Hypothesis: Concentration of both suspended as well as dissolved organic pollutants decrease with the application of EC, EO and ECP

2. Optimization of process parameters using response surface methodology Box-Behnken Design (BBD) and the reaction rate of optimized process using kinetic approach.

Hypothesis: Effect of interaction between various operation parameters determines the process efficiency and the removal rate follows a first order kinetics.

3. Evaluate and compare the treatment performance of EC+EO and ECP on industrial wastewater based on organic removal efficiency and energy consumption.

Hypothesis: EC and EO or combined EC+EO has better removal rate along with low energy consumption.

1.4. Dissertation Organization

The dissertation is divided into 6 chapters. Chapter 1 contains general introduction, research problem statement, objectives and this section. Chapter 2 provides a critical literature review of the available studies on treatment of industrial wastewaters, impact of EC, EO and ECP on wastewater treatment and optimization of process parameters using response surface methodology. Chapter 3 is a study on the treatment of canola oil wastewater and is based on a manuscript and a proceeding entitled Paper 1-"Treatment of canola-oil refinery effluent using electrochemical methods: A comparison between combined electrocoagulation+electrooxidation and electrochemical peroxidation methods" and "Organic pollutant removal from edible oil process wastewater using electrocoagulation" respectively. The manuscript has been published in *Chemosphere* (Sharma and Simsek, 2019) and the proceeding was published in IOP Conference Series: Earth and Environmental Science 142 (1), 012079. Chapter 3 also entails a study of optimization of treatment parameters of Canola oil refinery wastewater for removal of organic pollutants using BBD. Chapter 4 describes the treatment performance of EC+EO and ECP on sunflower oil wastewater and is based on manuscript (Paper 2) "Estimation of best treatment conditions of sunflower oil wastewater for organic removal using response surface methodology." This manuscript will be submitted for journal publication. Chapter 5 describe the work (Paper 3) entitled "Sugar beet industry process wastewater treatment using electrochemical methods and optimization of parameters using response surface methodology." This manuscript has been published in *Chemosphere* (Sharma and Simsek, 2020). Chapter 6 presents a general conclusion summarizing the results derived from the three papers (1-3) and recommendations for future work. Finally, supplementary figures and tables supporting the study are presented as two appendices (Appendices A and B).

CHAPTER 2. LITERATURE REVIEW

2.1. Vegetable Oil Industry Wastewater

The amount of wastewaters discharged from edible oil industries is high because of a large volume of water required during the processing steps. The compositions and characteristics of wastewaters from vegetable oil refinery facilities vary depending on the type of crop used to produce oil (Un et al., 2009a). Vegetable oil industry wastewaters contain high amount of organic compounds along with high concentration of oil composites. The biological oxygen demand (BOD)/chemical oxygen demand (COD) ratio of 0.2 – typical of vegetable oil effluent – is enough to destroy microbes required for biodegradation. Most of the times, the vegetable oil wastewater discharge, although supposedly treated, does not meet the environmentally acceptable level because of high concentration of influent organic loading. A number of methods such as absorption, coagulation, anaerobic treatment, reverse osmosis, and ultrafiltration have been applied for treatment of vegetable oil wastewaters (Un et al., 2009a).

Yu et al., (2010) investigated the feasibility of treating vegetable oil wastewater using an integrated microfiltration (MF)-reverse osmosis (RO) system to remove oil and DOC. The MF was run for 150 minutes through optimization of operating conditions followed by RO at room temperature and transmembrane pressure of 1.3 MPa. The entire operation was conducted for 420 minutes resulting in nearly zero concentration of DOC and free of oil. Treatment of vegetable oil wastewater using ultrafiltration achieved 90% removal in COD, 87% in DOC and 100% in TSS. However, these methods are not suitable for waters with higher concentration of organic loads. The membranes used are highly prone to fouling and requires maintenance and replacement from time to time. In addition to that, proper pre-treatment methods needs to be implemented to prevent fouling of membranes. These methods are also not economically

profitable for scale up operations considering its cost and high maintenance involved (Cheryan and Rajagopalan, 1998). Thus, these methods are not very cost effective. On the other hand, a study on the limitations of physico-chemical treatment methods on vegetable oil refinery wastewater was conducted by Chipasa (2001). The study found that physico-chemical treatment methods like coagulation, flocculation and dissolved air floatation were critically used in the treatment process (Chipasa, 2001).

The wastewater originated from an oil refinery plant and it was primarily segregated as acidic. It was observed that the treatment efficiency depended on the targeted pollutant load and characteristics. Although the physico-chemical treatment was able to remove sulfates, phosphates, and insoluble organic matter due to use of chemical coagulants (calcium chloride and alum) in the treatment process, this treatment method increased the amounts of chlorine in the final treated wastewater. Due to the residue formation issues, the industries had to introduce biological treatment to remove heavy metals and other organic compounds thereby resulting in time consuming process (Chipasa, 2001). Thus, over the years, electro chemical methods have found attention due to its environmental compatibility, versatility of operation, cost effectiveness and time saving attributes (Martinez-Huitle and Ferro, 2006).

Sunflower oil refinery facilities generate a large amount of wastewaters during the production. The process of sunflower oil production yields free fatty acids that results in acidic and oily wastewater (Decloux et al., 2007). The common treatment methods applied to treat sunflower oil wastewaters are crossflow microfiltration (Decloux et al., 2007), chemical coagulation, and anaerobic digestion. Nevertheless, all these methods are time consuming, not economic and results in fouling of processes over the period of time.

Un et al., (2009) studied the treatability of sunflower oil refinery wastewaters using aluminum (Al) electrodes with addition of sodium sulphate and poly aluminum chloride (PAC) for the removal of COD. However, the study was conducted only using EC and the method applied in the above study combines chemical dosage of PAC along with Al electrodes.

The wastewater collected from the local oilseed facility has an in-house treatment plant. The wastewater passes through a chemical coagulation unit using ferric chloride ($FeCl_3$) into Induced Air Floatation (IAF). The effluent from the IAF is feed into an anaerobic sludge unit (ASU). The effluent from the biological process is then discharged to a storage pond from where the effluent is directed to the city wastewater treatment plant.

2.2. Sugar Beet Processing Wastewater

Sugar beet factory wastewater contains high concentration of organics from the washing and processing of sugar production. These high organic loads pose a serious threat to the surrounding environment if discharged to water bodies without treatment.

The recent acceptable method in the treatment of sugar industry wastewater involves filtration, sedimentation of solids, and load equalization followed by combined anaerobic and aerobic biological treatment (Farhadian et al., 2007; Guven et al., 2009). Typically, this chain of treatment process is effective in reduction of COD from sugar beet industrial wastewater. However, the process requires equalization ponds or lagoons that cause algal proliferation, oxygen depletion, unpleasant odor emissions, and ultimately cause groundwater contamination (Farhadian et al., 2007; Perendeci and Sural, 2004; Perendeci et al., 2013). Over the recent decades, advanced technologies involving anaerobic digestion such as upflow anaerobic fixed bed (UAFB) (Farhadian et al., 2007), upflow anaerobic sludge blanket (UASB) (Lettinga and Pol, 1991), anaerobic downflow stationary fixed film (DSFF)(Pradeep et al., 2014), aerated fixed

film (AFF) (Hamoda and Al-Sharekh, 1999), and anaerobic batch reactors were considered to be preferred methods of sugar beet wastewater treatment. Yet, economic commercialization of these processes is yet to be feasible due to large land requirements, by-product formation, and high operational costs.

2.3. Electrochemical Methods

Electrochemical processes are gaining attention in the treatment of various wastewaters. EC is found to be effective in the removal of small colloidal and suspended particles. However, it is proved to be less effective in the removal of organic pollutants. On the other hand, advanced oxidation processes (AOPs) have been likely effective in the removal of small organic compounds via oxidation. EC when coupled with EO has proved to achieve better treatment process in carwash, petroleum, tobacco as well as olive oil processed wastewater. The application of EC and EO has achieved more than 80% removal of suspended solids (SS) and decreasing concentration of organic carbon pollutants (Esfandyari et al., 2015; Hu and Li, 2011b; Ma et al., 2015a; Rubi-Juarez et al., 2015). The effectiveness of EC and EO is influenced mainly by current density, Ph, electrolyte, contact time and electrode type (Avsar et al., 2012).

2.3.1. Electrocoagulation (EC)

The process of coagulation is used to remove dissolved substances and colloids from water in order to enhance efficient sedimentation. Colloidal particles are aggregates which could not be settled by gravity due to its smaller diameter. The density of such particles are nearly equal to water. These particles are stable enough in the disperse motion due to its repulsion between colloids. The process of coagulation minimizes this repulsion and encourage to form inter-colloidal bonds. Colloids contribute towards turbidity and color to water. A colloidal suspension is grouped into two phases: 1) the dispersed phase and 2) dispersion medium. In

terms of wastewater, solids (the dispersed phase) dissociates in the water (dispersion medium). The process involved in EC has been described to be segregated into three phases: a) coagulant formation due to oxidation of the sacrificial anode, b) contaminant destabilization, suspension of particulates and break down of emulsions, and c) formation of flocs (Mollah et al., 2001).

EC processes have proved to be promising methods for wastewater treatment and thus attracted the attention of researchers around the world. EC techniques involve metallic dissolution through anodic reaction for creation of metallic hydroxide (El-Taweel et al., 2015). The positive metallic ion react with negative charged particles in the wastewater forming complex molecules – flocs – that coagulate without the addition of chemical (Un et al., 2009a). Many reports have shown that EC can reduce heavy metals (El-Taweel et al., 2015), nutrients (Nguyen et al., 2016), natural organic matters (Feride et al., 2014), dissolved organic carbons (Feride et al., 2014), COD (Al-Shannag et al., 2014; Tak et al., 2015), dyes (Alinsafi et al., 2005; Hanafi et al., 2010; Kim et al., 2002) and microorganisms (Cotillas et al., 2013; Massoudinejad et al., 2014) from different wastewaters. Among the agriculture and food processing wastewaters that reportedly treated using EC are from vegetable oil refinery (Un et al., 2009a), olive mill (Hanafi et al., 2010), slaughterhouse (Asselin et al., 2008; Bayar et al., 2011; Ün et al., 2009), baker's yeast (Al-Shannag et al., 2014; Gengec et al., 2012; Kobya and Delipinar, 2008), dairy and tannery (Feng et al., 2007; Tchamango et al., 2010; Şengil, 2006), and restaurant (Chen et al., 2000). Apart from heavy metals and chemical pollutants reduction, EC has been applied to removal of biological constituents such algae (Azarian et al., 2007; Gao et al., 2010a; Gao et al., 2010b; Souza et al., 2016), microbes and nutrients (Symonds et al., 2015) and sludge (Yazdanbakhsh et al., 2015). For their abundant availability and cheaper in cost, aluminum (Al) and iron (Fe) have found extensive applications as electrodes for the EC treatment process. The

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use of Al in the EC process has found immense application in the removal of COD, color, turbidity and hardness in water and wastewater (Yazdanbakhsh et al., 2015). Gao et al. (2010) studied the effect of electrode material, current density, Ph, algal cell density and water temperature on algae removal using EC process. The study concluded that Al achieved better algal removal compared to iron electrodes. Better removal was obtained at an acidic pH range between 4-7 and a current density of 1 mA cm^{-2} (Gao et al., 2010b). Al electrodes has its wide application when EC process is coupled with various biological processes in the treatment of oily wastewater using fixed film (Perez et al., 2016), with submerged membrane bioreactor to treat grey water (Bani-Melhem and Smith, 2012), activated sludge bioreactor to treat industrial effluents (Moises et al., 2010) and rotating hybrid membrane bioreactor in municipal wastewater (Nguyen et al., 2014) for the removal of COD, color, turbidity, nutrients and suspended solids.

The significant advantages of EC application are (Mollah et al., 2001):

1. Requires simple equipment and easy operation

2. Provides colorless, odorless, and palatable water

3. Produces low and easily settable sludge

4. Large, stable and acid resistant flocs are formed making it easy for filtration

5. Produces low total dissolved solids contributing to lower water recovery cost.

6. Unlike chemical coagulation, no secondary pollutants or by products formed.

7. The pollutant accumulated at the top is concentrated and easily removable.

8. Convenient for rural areas with scarce or electricity due to its compatibility with solar panels.

EC process also possess certain disadvantages; however, mitigation of those disadvantages is easy and readily applicable. The disadvantages are:

1. The sacrificial electrodes need to be replaced regularly.

Mitigation: Electrodes with low economic value and locally available. Iron and aluminum could be tested for performance.

2. Use of electricity may be expensive in certain places.

Mitigation: Solar energy or other form of renewable energy can be tested as alternative.

3. An impermeable oxide layer is formed at the cathode leading to loss of efficiency

Mitigation: Alternate switching of polarity between anode and cathode can prevent the formation of oxide layers.

4. High conductivity of wastewater is required.

Mitigation: Addition of common salt (NaCl) is an easily applicable as well as economically viable option to increase the conductivity of electrolyte.

2.3.2. Electrooxidation (EO)

EO has received immense attention due to its efficiency in the removal of organic pollutants in wastewater. As well known, oil processing wastewater has an intensely high concentration of organic pollutants due to its raw materials involved. Although EC has proved efficient enough in the removal of inorganic compounds, EO, on the other hand, has found its application in the breakdown of the organic macro pollutants to its inorganic forms (Sarkka et al., 2015a; Sarkka et al., 2015b; Sillanpaa et al., 2015). The mechanism of EO may follow two different oxidation process based on the anode material; a) direct oxidation and b) indirect oxidation. Direct oxidation occurs at the surface of the anode whereas, indirect oxidation occurs away from the anode (Feng et al., 2003). In direct oxidation, pollutants interact directly with anode in electron transfer without the support or involvement of other substances. In indirect oxidation, the pollutants mediate through electro-generated reactive species for the electron

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transfer which shuttles between the electrode and the pollutants. Indirect EO can be reversible or irreversible reaction (Panizza and Cerisola, 2003). However, direct oxidation has advantages over indirect oxidation as it requires low chemical addition and no production of secondary contaminants (Sarkka et al., 2015a). EO has several advantages over other AOPs. EO easily oxidizes toxic pollutants, require smaller operation areas compared to biological processes, easy control through automation and absence of additional chemicals (Shestakova and Sillanpaa, 2017). Electrical energy is the primary driving force of the EO process. However, the main drawbacks of this process are the passivation, polarization and corrosion of electrodes. A study conducted by Lee et al in 2016 explained that polarization of electrodes is caused by poor mass transfer and gas accumulation on the electrode surface leading to declination of electroactive species (Lee et al., 2016). During electrode reactions, oligomeric and polymeric compounds are formed that leads to passivation of electrodes. Pletcher and Walsh in 1990 suggested that passivation and polarization of electrodes could be mitigated by powerful agitation. The corrosion of electrodes is caused by the oxidation reaction on the anode and the production of corrosive substances on the electrode surface (Couper et al., 1990). Proper selection of electrode type can solve the problem of corrosion of electrodes in the EO process (Shestakova and Sillanpaa, 2017). In EO, various electrode materials were tested for wastewater treatment such as mixed metal oxides, noble metal, carbon, graphite, BDD and mixed type of electrodes (platinized expanded titanium electrodes, stainless steel, copper, titanium alloy metals) (Barbosa et al., 2016; Hu and Li, 2011b). Among the various electrodes used, BDD electrodes are most common due to its longer life, high corrosion resistance, good current efficiency, good conductivity, high over potential towards oxygen evolution and low operation costs (Gengec, 2017; Haider et al., 2003; Ozcan et al., 2008; Panizza et al., 2001; Sarkka et al., 2015a);(Labiadh et al., 2016). BDD

electrodes has found its application in the removal of chemical compounds like ketoprofen (Murugananthan et al., 2010), triclosan (Wang and Farrell, 2004)et al., 2004), progesterone (de Vidales et al., 2012b), sulfamethoxazole (de Vidales et al., 2012a), chlorpyrifos (Robles-Molina et al., 2012), chloroxylenol (Skoumal et al., 2008), diclofenac (Brillas et al., 2010) from synthetic wastewater, COD and TOC removal from coking wastewater (Zhu et al., 2009), paper mill effluent (Guinea et al., 2010), municipal wastewater (Feng et al., 2003). According to a study conducted by Patel et al. (2013), the performance of BDD electrodes is more efficient in concentrated solutions and low current densities (Patel et al., 2013). The EO process was applied on edible olive process wastewaters using BDD electrodes. The effect of initial organic loading (from 1340 to 10,000 mg L^{-1} COD), reaction time (from 30 to 120 min), current intensity (from 5 to 14 A), initial pH (from 3 to 7) and H_2O_2 (500 mg L^{-1}) on the treatment performance were investigated. The result on the COD removal performance showed that. first three parameters were found to be effective on the removal while pH and H_2O_2 found statistically not affecting. In the optimum condition, about 73% of initial COD (10,000 mg L^{-1}) was removed using BDD electrode EO process (Deligiorgis et al., 2008).

2.3.3. Combination of EC and EO in Wastewater Treatment

Although EC and EO processes are applied individually in the treatment of various wastewaters, combination of EC and EO have proven to be successful in the removal of bio refractory organic pollutants (Linares (Azarian et al., 2018; Gengec, 2017; Linares-Hernandez et al., 2010). Combined EC/EO process has been used for the treatment of dairy (Chakchouk et al., 2017), tannery (Azarian et al., 2018), petroleum (Bhagawan et al., 2016), textile (GilPavas et al., 2017), carwash reclamation (Rubi-Juarez et al., 2015) and container washing wastewater (Nayir and Kara, 2018). Combination of EC using Al electrodes and EO process using BDD electrodes

has been successfully applied to the removal of COD and TOC in toxic cardboard plant wastewater (Gengec, 2017), container washing wastewater (Nayir and Kara, 2018), carwash wastewater (Rubi-Juarez et al., 2015), and canola oil refinery wastewater (Sharma and Simsek, 2019).

2.3.4. Electrochemical Peroxidation (ECP)

Fenton's chemistry was pioneered by Fenton in 1876 while using a mixture of hydrogen peroxide (H_2O_2) and Fe^{2+} to breakdown tartaric acid. The effectiveness of Fenton's regent depends on Ph, temperature, H_2O_2 and the amount of Fe^{2+} added into the reaction. Fenton's process has found its application in the organic wastewater treatment (Ren et al., 2016). Its eco-friendly properties also make it more acceptable among the treatment technologies. The electro-Fenton (EF) process is most effective at pH 2.8-3.0 since the concentration of Fe^{2+} is maximum in that pH range thereby increasing the rate of EF reaction. H_2O_2 plays an important role along with pH. Brillas et al., (2009) illustrated the reaction kinetics involved in EF process. Controlling the pH at optimum 2.8 is very significant to have an effective EF reaction as the Fenton's reagent is prone to production of other compounds and reactive species that could inhibit or limit the main reaction required for the EF process. The reaction can have different products based on the presence and absence of H_2O_2. It has been observed that, in the presence of H_2O_2, Fe^{3+} is the only species at pH whereas beyond pH 4.0, it completely disappears and this replaced by hydroxyl complexes such as $[Fe(OH)^+]$, $[Fe(OH)^{2+}]$, and $[Fe(OH)^{4+}]$. Similarly, in the absence of H_2O_2, the same species gets replaced by hydroperoxy complexes (Nidheesh and Gandhimathi, 2012; Ren et al., 2016).

EF process has been used in a number of wastewater sources such as olive oil mill wastewater (Flores et al., 2016), dairy (Davarnejad and Nikseresht, 2016), textile (Dermentzis et

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al., 2011; Xu et al., 2017), and petrochemical wastewaters (Dermentzis et al., 2014) , wastewater from flame retardant industry , alcohol distillery (Davarnejad and Azizi, 2016), slaughterhouse wastewater (Davarnejad and Nasiri, 2017), and landfill leachates wastewaters (Poblete et al., 2017; Sabour and Amiri, 2017). The process has found its application mainly in the removal of COD and DOC. The EF process is an ambient temperature and atmospheric pressure dependent process and it is found highly effective in wastewater treatment technologies. It generates a highly oxidizing hydroxyl radical (OH·) that is unstable and plays a predominant part in the degradation processes. OH· is generally produced during the reaction chemistry attacking organic molecules following: 1) dehydrogenation of hydrogen atom to water 2) hydroxylation to a non-saturated bond, and 3) redox reactions. OH can be formed using hydrogen peroxide that produce oxygen gas and water as byproducts (Brillas et al., 2009).

Among the different variants of EF, ECP is a variant of EF process where Fe electrode is used as the sacrificial anode for the electro generation of Fe^{2+} ions and H_2O_2 is added externally to the treated sample. When added externally, H_2O_2 oxidizes the organic matter with OH· formed from Fenton's reaction. This process was first proposed by Lemley's group as an electrochemical peroxide method in the treatment of aqueous herbicide solutions. The study showed that ECP led to better removal of COD compared to direct EC (Brillas et al., 2009; Pratap and Lemley, 1994). The removal of organic molecules depends highly on the precipitate formed with Fe hydroxide and the current density that applied (Brillas et al., 2009). ECP has been widely used in the treatment of various wastewaters such as olive oil mill (Khoufi et al., 2006; Ün et al., 2006), tannery (Kurt et al., 2007), textile (Martins et al., 2006), organic fertilizer (Akyol et al., 2013) and industrial (Barrera-Dıaz et al., 2003) wastewaters.

ECP process has been applied to remove copper and arsenic from copper smelter wastewaters. The concentric iron electrodes were used and H_2O_2 is added dropwise to the reactor. Synthetic and real wastewater samples were used. The initial concentration of arsenic and copper were 1,000 and 300 mg L^{-1} in both types of wastewaters, respectively. Copper was removed more efficiently from both types of wastewater (99% removal) while arsenic was removed more efficiently from real wastewater (99% removal). The results showed that pH in ECP process was an important parameter for copper and arsenic removal that affected the speed and efficiency of the treatment (Gutierrez et al., 2010).

Landfill leachate wastewater originated from domestic waste treated using ECP process. Electrode voltage; polarity switching rate; leachate pH; and H_2O_2 concentration were optimized as 1.9 V; 5 cycle min^{-1}; 4; and 200 mg L^{-1}, respectively. In this optimum condition, the initial COD concentration (3,825 mg L^{-1}) in the wastewater was reduced about 52% using ECP process (Paton et al., 2009).

2.4. Reaction Mechanism Involved in Electrochemical Processes

The mechanism involving the electrodes for the removal of ions using EC are described below (Al-Shannag et al., 2014; dos Santos et al., 2014; Khandegar and Saroha, 2013):

$$M \rightarrow M^{n+} + ne^- \text{ (anode)} \tag{1}$$

$$H_2O + 2e^- \rightarrow 2OH^- + H_2 \text{ (cathode)} \tag{2}$$
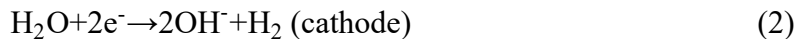
where M is the anode material and R is organic pollutants.

Thus, Al upon electrolytic dissolution produces cationic species such as Al^{3+}, $Al(OH)_2^+$, $Al(OH)_3$ and polymeric forms $Al_n(OH)_{3n}$.

$$Al \rightarrow Al^{3+}(aq) + 3e^- \tag{3}$$

$$Al_{(aq)}^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H_{(aq)}^+ \tag{4}$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \tag{5}$$
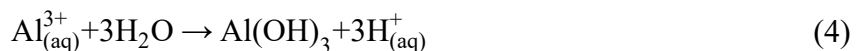
During EO using boron doped diamond electrodes, the $OH^{\cdot}$ formed completely mineralize the organic pollutants in the wastewater by the following reactions, R: organic pollutants in wastewater (Gengec, 2017; Scialdone et al., 2008; Sires et al., 2014).

$$M + H_2O \rightarrow M(HO^{\cdot}) + H^+ + e^- \tag{6}$$

$$M(HO^{\cdot}) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \tag{7}$$
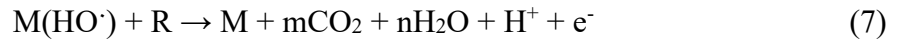
The reaction mechanism involved in ECP process are

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\cdot}OH + OH^- \quad \text{(in bulk solution)} \tag{8}$$

$$Fe^{2+} + {\cdot}OH \rightarrow Fe^{3+} + OH^- \text{ (in bulk solution)} \tag{9}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\cdot}\text{(in bulk solution)} \tag{10}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{11}$$
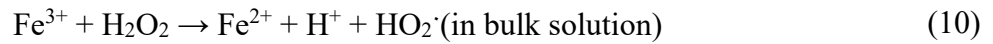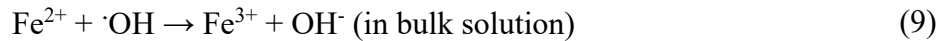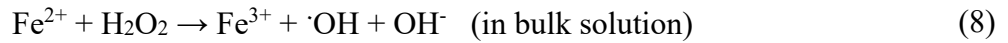
2.5. Optimization of Process Parameters Using Response Surface Methodology

While it is important to investigate the feasibility of a treatment method on wastewater, optimization of the process parameters and design criteria play a vital role in predicting the economic sustainability and process performance upon commercialization. As an effective method to optimize process conditions, response surface methodology (RSM) is a widely accepted statistical-based method for empirical model building (Li et al., 2010; Myers, 1999). The primary objective of RSM is to optimize the response surface and identify the relationship between the input parameters and the response variable (Tak et al., 2015). The two major types of RSM are Central Composite Design (CCD) and Box Behnken Design (BBD). BBD is little more efficient than CCD and significantly better than three-level factorial designs in addressing the experimental boundaries. Moreover, BBD does not contain highest or lowest combinations of factors simultaneously that avoids the occurrence of unsatisfactory results under extreme

conditions where the efficiency of one experimental design is defined as the number of coefficients in the estimated model divided by the number of experiments. The number of experiments required in BBD is $N = 2k(k-1) + C_0$ compared to that of CCD where $N = 2^k + 2k + C_0$, where k is number of factors and C_0 is the number of central points (Ferreira et al., 2007). BBD has been successfully applied to different processes for optimization of experimental design in the treatment of livestock (Tak et al., 2015), biodiesel (Chavalparit and Ongwandee, 2009), petrochemical (Kumar et al., 2008), textile (GilPavas et al., 2018; Kaur et al., 2019), olive mill (Ersanli and Ozsen, 2019), dairy (Khosroyar and Arastehnodeh, 2018), and mineral oil (Tetteh and Rathilal, 2018) wastewaters.

CHAPTER 3. TREATMENT OF CANOLA-OIL REFINERY EFFLUENT USING ELECTROCHEMICAL METHODS: A COMPARISON BETWEEN COMBINED ELECTROCOAGULATION + ELECTROOXIDATION AND ELECTROCHEMICAL PEROXIDATION METHODS

3.1. Abstract

A comparative study of combined EC+EO and ECP treatment processes were carried out to treat canola oil refinery (COR) wastewaters. The effect of applied current density and operation time in the removal of organic pollutants were investigated and discussed. TCOD, sCOD, TOC, DOC and total suspended solids (TSS) were measured. Using only EC process was found to be significantly successful in removing suspended and colloidal pollutants and could remove more than 90% TCOD and 80% of TOC at current densities between 0.91 and 13.66 mA cm^{-2}. From the statistical model, the optimized conditions for TCOD at a current density of 7.61 mA cm^{-2} and TOC at 7.99 mA cm^{-2} under 40 min operation, validated to remove 93.45% and 94.5% respectively. However, the maximum removal of dissolved organic pollutants was relatively low in EC process and reported to be 75% for sCOD and 74% for DOC. Therefore, EC+EO process were run to increase the removal of sCOD and DOC to 99 and 95%, respectively. On the other hand, treatment using ECP process achieved a removal of sCOD and DOC between 77 and 86%. TSS were removed completely in both EC+EO and ECP processes. A statistical model was applied to compare the performance of two methods and found that the combined EC+EO process provided lightly better treatment compared to ECP method.

3.2. Introduction

Vegetable oil industry wastewaters contain high amount of organic compounds along with high concentration of oil composites. Vegetable oil refinery wastewater usually has a COD/BOD ratio of 0.2. Depending on the production processes, the concnetration of COD ranges from 2000 ppm to 30,000 ppm (Azbar and Yonar, 2004; Pandey et al., 2003; Sridhar et al., 2002). It generates highly acidic and oily wastewaters from various steps during the production processes include degumming, de-acidification, deodorization and neutralization processes. The generated wastewater contains sulphates and phosphates from sodium salts of fatty acid soap stocks produced in the neutralization step. The amount and characteristics of organic loading in the wastewaters varies depending on the type of oil processed and the operating conditions in the facility (Sharma et al., 2014). The treatment technologies of edible oil wastewater generally comprises of pretreatment through screening and air floatation. It is more commonly followed by biological treatment using activated sludge or lagoon/storage pond treatment. In some facilities, a pretreatment method using chemical coagulation are installed between air floatation and biological treatment (Pathe et al., 2000; Saha et al., 1998). The physicochemical process mainly involves addition of chemicals which can successfully eliminate color and turbidity along with successful reduction of dissolved, colloidal and suspended compounds. However, chemical treatment involves difficult sludge management and high chemical cost for the industries (Ma et al., 2015b). On the other hand, although biological processes are the most practical and low cost, yet the processes require large facility space combined with long treatment duration (Nguyen et al., 2016; Tak et al., 2015). An appropriate treatment system provides efficient pollutant reduction; uses less treatment time; and requires

simple installation, maintenance, and operation with the addition of little or no chemical compounds (Kliaugaite et al., 2013; Kobya et al., 2003).

Electrochemical methods have found its application in the recent decades with the increase in the demand to improvise the standards in drinking waters as well as processed wastewaters. Technologies involving electrochemical methods are proving to be more efficient than any other existing methods in terms of cost, operation as well as time efficiency (Chen, 2004). The process of electrocoagulation (EC) is used to remove dissolved substances and colloids from wastewater in order to enhance efficient sedimentation. The process involved in EC has been described to be segregated into three phases: a) coagulant formation due to oxidation of the sacrificial anode, b) contaminant destabilization, suspension of particulates and break down of emulsions, and c) formation of flocs (Mollah et al., 2001). The total COD (COD) removal efficiency of tannery liming drum wastewater with COD influent concentration of 25,300 mg L^{-1} was about 82% without a destructive effect on the organic compounds (Sengil et al., 2009). El-Nas et al. (2009) studied sulfate and COD removal from petroleum refinery wastewater using stainless steel, aluminum, and iron electrodes. They concluded that aluminum performed better in the removal process compared to the other two electrode materials (El-Naas et al., 2009). Kobya et al. (2003) compared the removal efficiency of COD applying EC using Fe and Al electrodes in textile industry wastewater. It was observed that the applied current density and operating time exhibited similar effects on the removal performance. It was concluded that using a pair of Al electrodes removed between 61 and 65% color in textile industry wastewaters at operating time between 10 and 30 min (Kobya et al., 2003).

Although EC is a relatively fast process and effective in removing suspended and colloidal particles, it was able to remove only half of the sCOD in dairy wastewater (Chakchouk et al., 2017).

On the other hand, advanced oxidation processes such as electrooxidation (EO) has received immense attention due to its efficiency in the removal of organic pollutants from wastewaters. In EO, platinized expanded titanium electrodes, copper, titanium alloy metals or BDD materials are found to be used as anodes and stainless steel (St) as cathodes (Barbosa et al., 2016; Hu and Li, 2011b).

However, despite of many efforts to use chemical supporting electrolyte, EO process alone is insufficient for complete removal of organic pollutants (Azarian et al., 2018; Isarain-Chavez et al., 2014; Sundarapandiyan et al., 2010). Therefore, combined EC/EO processes in the treatment of various industrial wastewaters have proven to be successful in the removal of bio-refractory organic pollutants to a concentration that suitable for reuse in agricultural and industrial purposes (Azarian et al., 2018; Linares-Hernandez et al., 2010). Combined EC/EO process has been used for the treatment of dairy (Chakchouk et al., 2017), tannery (Azarian et al., 2018), petroleum (Bhagawan et al., 2016), textile (GilPavas et al., 2017), carwash reclamation (Rubi-Juarez et al., 2015) and container washing wastewater (Nayir and Kara, 2018). However, this process has not been used in edible oil-refinery wastewaters.

In addition to EC and EO processes, electro-Fenton (EF) process has found its application in the organic wastewater treatment (Ren et al., 2016). Its eco-friendly properties also make it more acceptable among the treatment technologies. EF process has been used in a number of wastewaters such as olive oil mill (Flores et al., 2016; Inan et al., 2004), dairy (Davarnejad and Nikseresht, 2016; Davarnejad and Sahraei, 2016), textile (Dermentzis et al., 2011; Xu et al.,

2017), petrochemical (Dermentzis et al., 2014), flame retardant industry, alcohol distillery (Davarnejad and Azizi, 2016), slaughterhouse (Davarnejad and Nasiri, 2017), and landfill leachates wastewaters (Poblete et al., 2017; Sabour and Amiri, 2017). The process have found its application mainly in the removal of total COD and TOC. Among the different variants of EF, ECP is a variant of EF process where Fe electrode is used as the sacrificial anode for the electro-generation of Fe^{2+} ions and H_2O_2 is added externally to the treated sample. When added externally, H_2O_2 oxidizes the organic matter with $OH^{\cdot}$ formed from Fenton's reaction as shown in Eqs. (8) through (11) as described in chapter 2, section 2.4.

There are studies available using EC, EO and ECP methods separately for the removal of organic pollutants, TSS, and oil content in oily wastewaters. According to a study by Isarain-Chavez et al. (2014), the TOC removed using EO, EC and ECP processes were 73.6, 64.9 and 71.8% respectively. Nayir and Kara studied the effect of EC only and combined EC+EO process in the treatment of Scod in container washing wastewater treatment using Al and Fe electrodes for EC and BDD electrodes for EO process. They found that EC alone was ineffective in removing sCOD compared to high removal efficiency of combined EC and EO process. The post treatment with EO process could remove as high as 89% of sCOD from the treated wastewater sample (Nayir and Kara, 2018). To our knowledge, there is no study available using EC, EO, and ECP or EC+EO methods to treat canola-oil refinery (COR) wastewaters. Therefore, for the first time, EC + EO and ECP processes were used to treat COR wastewaters in this study. The removal of COD, sCOD, TOC, DOC and TSS were evaluated.

3.3. Materials and Methods

3.3.1. Sample Collection and Preparation

About 5-gallon raw grab sample of COR wastewater was collected once or twice a week from a local canola-oil refinery facility (Cargill Corp.) in West Fargo, North Dakota, USA. The raw wastewater samples contained high concentration of organic carbon (OC) and TSS (Table 3.1) and thus tested for TOC, COD and TSS. The samples were filtered using glass microfiber filter of grade GF/C, 1.2 µm pore size, 47 mm diameter (Whatman, USA) and then further filtered using cellulose membrane filters of 0.45 µm pore size and 47 mm diameter (Merck Millipore Ltd., USA). The filtrate sample was tested for sCOD and DOC. The remaining samples were preserved at 4 °C in the refrigerator for later usage. Every 2 days, any remaining refrigerated wastewater samples were discarded, and the fresh samples were collected from the facility.

Table 3.1. Influent characteristics of the COR wastewater.

Sample location	COD (mg L^{-1})	sCOD (mg L^{-1})	TOC (mg L^{-1})	DOC (mg L^{-1})	TSS (mg L^{-1})
Primary effluent	24140±1580	6,403±805	9110±650	1,778±359	540±45

3.3.2. Experimental Devices

The methods included three different types of electrochemical methods; EC, EO and ECP. Aluminum (Al) electrodes were used as both anode and cathode for the EC process, while BDD and stainless steel (St) (grade 304) electrodes were used on the anode and cathode for the EO process, respectively. The ECP process used iron electrodes as anode and cathode and H_2O_2 was added externally to the sample.

The effective area for all the electrodes submerged in the wastewater for EC, EO and ECP experiments were kept equal during the entire experiments. The dimensions of each electrode were 12 cm (length) × 6.5 cm (width) × 2 mm (thick) and were flat rectangular in shape. The effective surface area of the electrodes was constant throughout the experiments and was measured as 109.8 cm^2. Once the electrode started to worn-out, it was replaced with the new electrode to retain the original effective area. The anode and the cathode were connected externally to a DC power supply (EXTECH, Grainger). In each experimental set up, the inter-electrode distance was kept constant at 1 cm apart. The wastewater sample was the acting electrolyte. The conductivity of the wastewater sample was around 143 μS cm^{-1}, which was insufficient to initiate treatment process. Thus, 2.0 g L^{-1} sodium chloride was added to the sample to increase the conductivity to about 4.93 mS cm^{-1}. The variables in these experiments were time and current density.

3.3.3. Methodology

The study was conducted in two different methical approaches and each method was divided into batch experiments as shown in Fig.3.1a and b. Two different electrochemical treatment methods (3.3.3.1 and 3.3.3.2) were applied in this study and the methods were compared to determine the best removal performance based on the parameters studied in COR wastewaters. The first method (3.3.3.1) was using a combined EC and EO process wherein the raw wastewater sample was introduced into EC process and the electrocoagulated effluent was subjected to EO process. In the second method (3.3.3.2), only ECP process was applied to the same raw wastewater sample for the same amount of time and working volume as method 1. In both EC+EO and ECP experiments, 1.5 L of glass reactors with a working volume of 1 L were used.
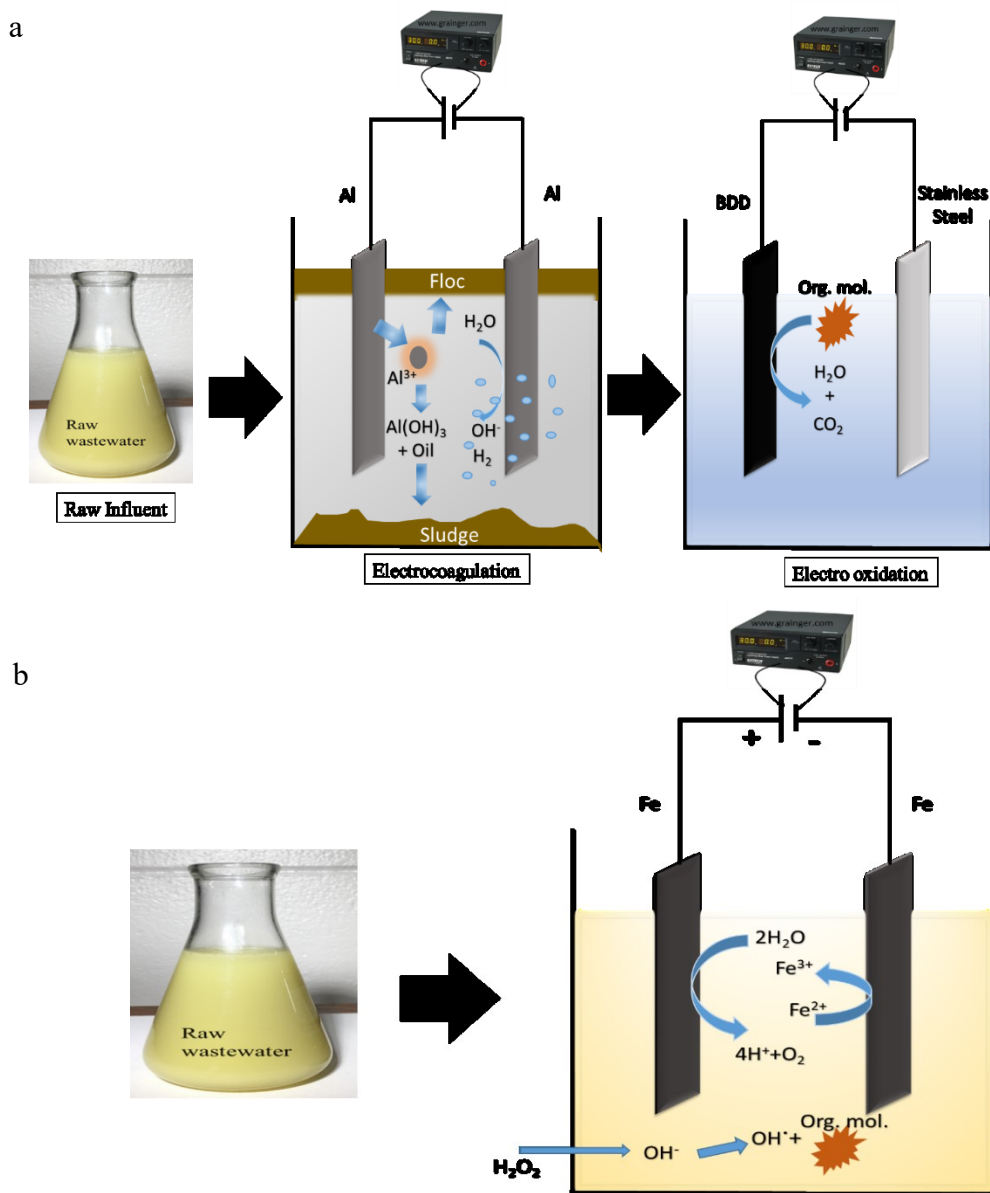
Figure 3.1. Schematic of the experimental design for a) combined electrocoagulation and electro-oxidation b) electrochemical peroxidation for canola oil refinery wastewater.

3.3.3.1. Method 1: EC+EO Application

3.3.3.1.1. Phase 1: EC Application

Raw-process wastewater samples were added to the glass reactor and a pair of anode and cathode metal electrodes were submerged. In this study, Al electrodes were used for the EC process. The Al electrodes were immersed into the electrolyte and connected to the power

supply. The system was run at varying current densities and time to obtain the best combination for the EC process. The system was tested at 7 different current densities of 0.9, 1.8, 2.7, 3.6, 4.5, 9.1 and 13.7 mA cm^{-2}. At each current density during the experiments, five ml of samples were collected every minute for first 10 min and every 5 min from 10 to 70 min. The data was analyzed for the removal of COD, sCOD, TOC, DOC and TSS. The process was optimized using a polynomial regression model. Once the optimized data was achieved from the model, the wastewater samples were treated using the given optimized parameters and the effluent from the treatment were further introduced to EO process.

3.3.3.1.2. Phase 2: EO Application

After EC application (3.3.3.1.1), the electrocoagulated effluent samples (EC effluent) were introduced to EO process without changing the reactor from phase 1. The only changes were made was the electrodes. Al electrodes were replaced with BDD as the anode and St as the cathode (Fig. 3.1a). One liter of the wastewater sample after EC processes was transferred into EO reactor and the electrodes were submerged into the wastewater sample in the reactor. The experiments in EO process were operated at four different current densities of 0.91, 4.5, 9.1 and 13.66 mA cm^{-2}. The system was run for 7 h and about 5 ml of the supernatant sample was collected every hour consecutively to measure DOC, TSS, and sCOD.

3.3.3.2. Method 2: ECP Application

ECP experiments were conducted separately from the experiments that explained at method 1. However, exactly the same wastewater source was used simultaneously in both methods. Fe electrodes were used in the oxidation process. Three ml 30% H_2O_2 per 250 ml of wastewater sample were added into the reactor. The reactor was set up as and was connected to the DC power supply (Fig. 3.1b). The system was run similarly as for EO process at four current

densities of 0.91, 4.5, 9.1 and 13.66 mA cm^{-2}. The operation was carried for 7 h and the samples were collected once in every hour during the experiments. Five ml of the supernatant sample was used to determine DOC, TSS, and sCOD.

3.3.4. Analysis

The concentration of COD and sCOD were measured using test kits TNT 821 (0-150 mg L^{-1}) and TNT 822 (20-1500 mg L^{-1}) manufactured by Hach company (Loveland, CO) using USEPA approved (5220D) closed reflux, colorimetric method. TOC and DOC were analyzed in Shimadzu TOC-L analyzer using high-temperature catalytic oxidation technique (EPA 415.3). TSS was measured following the procedure described in Standard Methods (2005), 2540D and EPA (1983) Method 160.2. The removal efficiency (Re) of COD, sCOD, TOC, DOC, and TSS were calculated using Eq. (12):

$$R_e(\%) = \frac{Z_i\text{-}Z_f}{Z_I} \times 100 \tag{12}$$

where; R_e is the removal effciency, Z_i and Z_f are initial and final concentration of COD, sCOD, TOC, DOC, or TSS.

3.3.5. Modeling Approach Using Stepwise Regression

The modelling was conducted to compare between the two methods, EC+EO and ECP. In EC+EO process, the model was first designed for the EC method to obtain the optimal conditions in this process. Once the model run and predicted the optimal conditions for EC, further experiments were performed to validate the model. The effluent from the model-obtained conditions were further taken for EO process. Once the EO process was completed, the overall removal of organic pollutants was calculated using Eq. (12). The data for ECP was also obtained from a separate set of experiments as explained in 3.3.3.2above.

A stepwise regression model was then used to compare between the two methods, EC+EO and ECP processes. Experimental data were fitted to a second order polynomial regression model and the coefficients were determined. The model was applied using the statistical software Minitab 18. Stepwise regression picks terms with highest association with the response variable in subsequent steps. The terms are added and removed according to the rules of hierarchy. The main effects of the models are (i) continuous factors; current density (X_1), time (X_2), and (ii) categorical factor; method (X_3). The generalized second order polynomial model used in the response variable (Y) was as represented by Eq. (13):

$$Y = \beta_0 + \sum \beta_i X_I + \sum \beta_{ii} X_{ii}^2 + \sum \beta_{ij} X_{ij} + \varepsilon \tag{13}$$

Where; $\beta_0, \beta_I, \beta_{ii}$ and β_{ij} are the regression coefficients for linear, quadratic and interaction terms respectively, whereas X_i and X_j are the independent variables; current density and time respectively. The performance of the model is explained by the coefficient of determination (R^2).

The response variables selected for the model are removal efficiency of sCOD and DOC. The model was developed in two stages. In the first phase, the optimization and prediction for EC process was obtained. The model fit was analyzed and the optimum conditions for EC process was achieved. Next, the model was developed to compare between the two methods namely EC+EO and ECP and provided the optimized conditions for the chosen model. The model considers all the related variables and their interactions.

3.3.6. Optimization of Treatment Parameters Using Box-Behnken Design

The statistical analysis and modelling were performed using Design-Expert® software based on Myers and Montgomery desirability function methodology, which is a method to optimize a series of quadratic models simultaneously using measurements on a set of outcomes all at once instead of optimizing each outcome separately (Kuhn, 2016). The experimental range

and levels of the independent variables used in EC, EO and ECP experiments are presented in Table 3.2.

Table 3.2. Coded levels and independent variables for the experimental design.

Factor	Electrocoagulation (EC)			Electrooxidation (EO)			Electrochemical peroxidation (ECP)			
	Variable	Level					Variable	Level		
		-1	0	1	-1	0	1		-1	0	1
X_1	pH	5	6	7	5	6	7	H_2O_2 dosage (ml L^{-1})	10	20	30
X_2	Current density (mA cm^{-2})	4.5	9.1	13.6	4.5	9.1	13.6	Current density (mA cm^{-2})	4.5	9.1	13.6
X_3	Time (Min)	10	20	30	180	300	420	Time (Min)	180	300	420

The generalized second order polynomial model used for predicting the relationship between the independent variables and the response variable (Y) was as shown in Eq. (13). The analysis of variance (ANOVA) was conducted to analyze the results and to validate the statistical significance of the fitted quadratic models. The model compares the two methods based on relationship between the variables. In EC+EO process, the model was first designed to obtain the optimal conditions for EC and extra experiments were conducted to validate the model. The effluent from the optimized EC process were investigated for EO process. The model for EO process was further designed as presented in Table 3.2. The variables considered for EC+EO were current density, pH and time of operation. Similarly, the BBD was performed for ECP systems with independent variables current density, H_2O_2 dosage and operation time. The optimized parameters were obtained using fitted models and validated by conducting separate experiments. In addition, the economic analyses of EC+EO and ECP systems were studied by calculating the energy consumption of the processes under optimum conditions. The energy consumption along with removal efficiency were analyzed for the method selection.

3.3.7. Kinetic Modelling

The chosen method was further investigated using a kinetic approach to understand the extent to which pollutant reduction occurred in the process. In this study, the removal rate of COD, sCOD, TOC, and DOC were tested with respect to time using zero, first, and second order kinetics [Eqs. (14) through (16)].

Zero order reaction:

$$\frac{-d[A]}{dt} = k \tag{14}$$

First order reaction:

$$\frac{-d[A]}{dt} = k[A] \tag{15}$$

Second order reaction:

$$\frac{-d[A]}{dt} = k[A]^2 \tag{16}$$

where, A is the residual reactant concentration in the wastewater (g L^{-1}).

In order to check the validity of the kinetic model, the plots of each rate order of ΔC, ln (C/C_0), and $[(1/C_0) - (1/C)]$ were plotted against operation time obtained at optimized parameter combination. C_0 and C are initial and final pollutant concentrations, respectively.

3.4. Results and Discussion

3.4.1. Preliminary Experiments

3.4.1.1. Method 1 – Phase 1. COD, sCOD, TOC, and DOC Removal in EC Process

Literature reviews showed that EC was efficient enough in the removal of suspended and colloidal compounds (Feride et al., 2014; Sarkka et al., 2015b). In this study, Al|Al electrode combination achieved more than 90% of COD and 85% of TOC at all seven current densities studied from 0.91 to 13.6 mA cm^{-2}. The current density is an important parameter as it affects the

response time and it influences the dominant pollutant separation mode (Holt et al., 2005). The

inter-electrode distance was retained fixed and the current density was supplied continuously.

The reactor was stirred continuously during the operation.
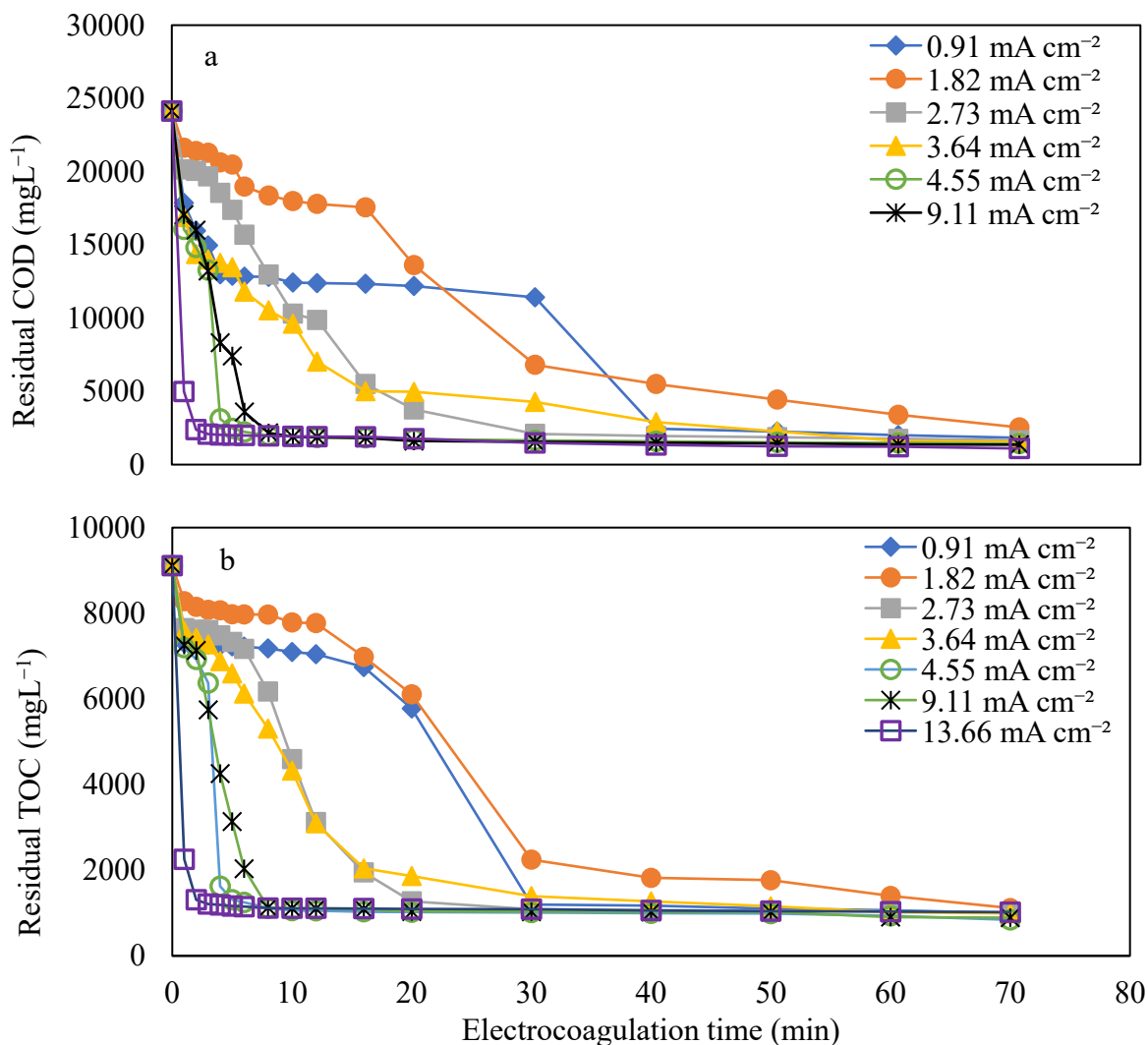
Figure 3.2. (a) COD and b) TOC removal using electrocoagulation on canola oil refinery
wastewater using Al-Al electrodes.

Fig. 3.2a and b shows an analogous fashion to the COD and TOC removal respectively

with respect to current density and time. It was observed that the time required for complete

coagulation depends on the applied current density. The increases in the current density

significantly decreases the coagulation time. When a higher current density of 13.66 mA cm^{-2}

was applied to the sample in the reactor, the coagulation was achieved within 10 min of

operation. However, once a lower current density of .91 mA cm $^{-2}$ as applied, the coagulation was achieved after 40 min of operation. Thus, a direct relation between the current density and the time could be observed.
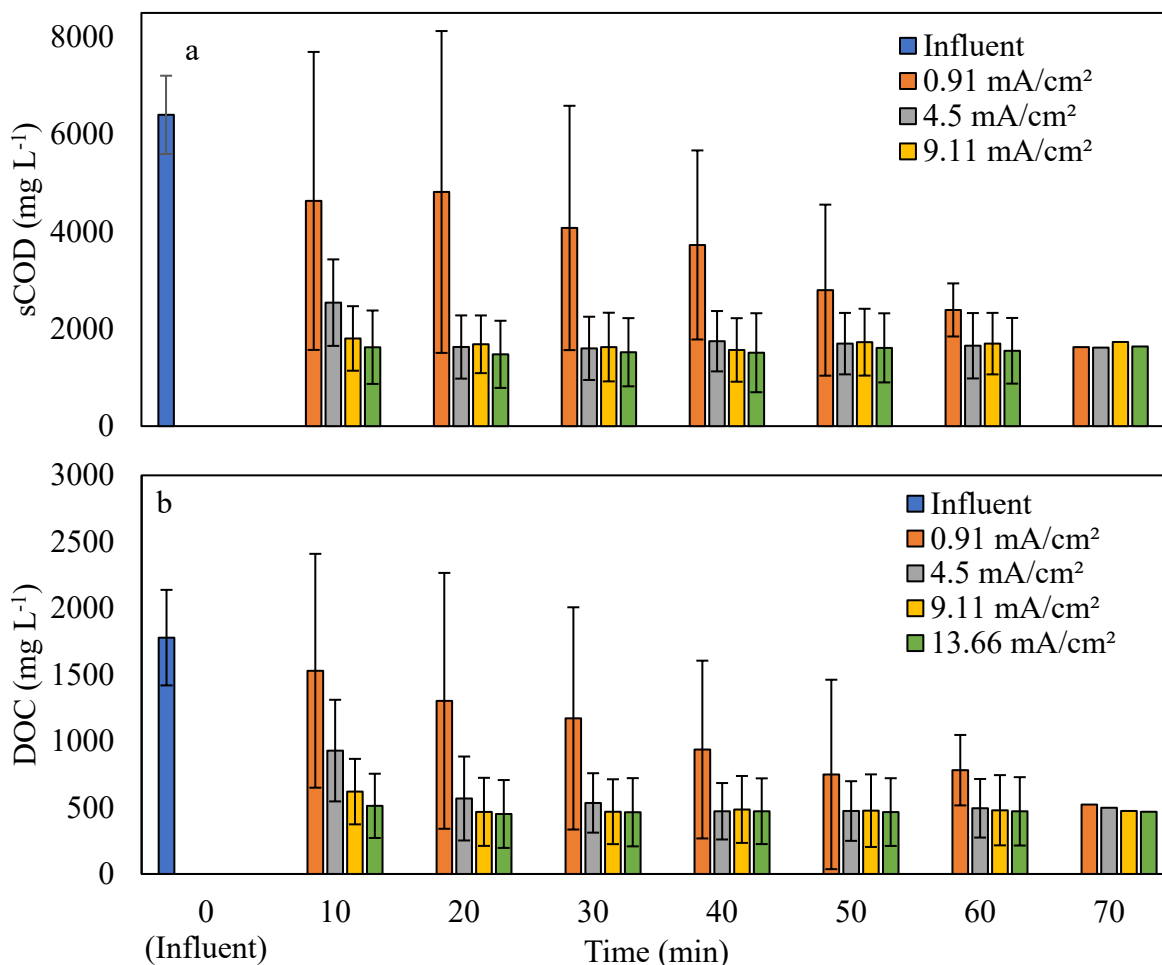
Figure 3.3. (a) sCOD and b) DOC removal using electrocoagulation on canola oil refinery wastewater using Al-Al electrodes.

EC process was found to be significantly successful in removing suspended and colloidal pollutants. However, the removal of dissolved organic pollutants was relatively low in EC process. At the end of 70 min of operation, sCOD removal ranged between 73% and 75% and DOC ranged between 72% and 74% at the applied current densities 0.91, 4.5, 9.1 and 13.66 mA cm^{-2} (Fig. 3.3a and b).

3.4.1.2. Method 1 – Phase 2. sCOD and DOC Removal in EO Process

The electrocoagulated effluent was used as the influent of next phase (phase 2) of the experiment to perform EO treatment. Compared to EC process, EO process takes longer time to attain significant removal rate. This is because EC is efficient in the removal of suspended and colloidal organic substances whereas EO is mostly for the breakdown of dissolved organic substances. The process was run for 7 h to achieve the steady state conditions. It was observed that performing EO after EC could remove more than 80% of remaining EC effluent organic concentration. However, as current density and contact time increased, the concentration of pollutants in the sample decreased. This is different from that observed in EC process where after a certain time and a certain current density, the concentration of pollutants tends to stay constant in the sample. Ye and Li (2016) concluded in their comparison study between various electrochemical methods that, diamond-stainless electrode provides superior removal rate in EO process compared to other electrode combinations when introduced to petroleum refinery effluents (Ye and Li, 2016).

The concentration of sCOD tend to decrease in EO process with the increase in time and current density (Fig. 3.4a). At both current densities of 9.11 and 13.66 mA cm^{-2}, the sCOD removal increased from 29% in the first hour to as high as 96% at the end of 6-7 h of operation in the remaining EC effluent organic concentration. However, it was observed that the removal rate was not more than 23% at current density of 0.91 mA cm^{-2} after 7 h of operation. At all four current densities studied, the system achieved steady state conditions after 4 h from the time of start of each run. The EO treatment of Kraft bagasse bleaching effluent reported a 53% removal of COD when applied a current density of 0.0087 A cm^{-2} for 1.75 h of operation (Antony and

Natesan, 2012). Buzzini et al. (2006) achieved 63% COD removal in a cellulose pulp mill effluent applying 0.225 A cm^{-2} current for 2 h of time period (Buzzini et al., 2006).

The DOC removal in the COR wastewater was achieved mainly through EO process (Fig. 3.4b). The electrocoagulated effluent (influent to EO process) DOC content in the COR wastewater was at an average of 557 mg L^{-1}. The breakdown of organic carbon content using EO process could yield more than 78% of the total DOC. At higher current densities, the removal of DOC showed an increase as time increased.
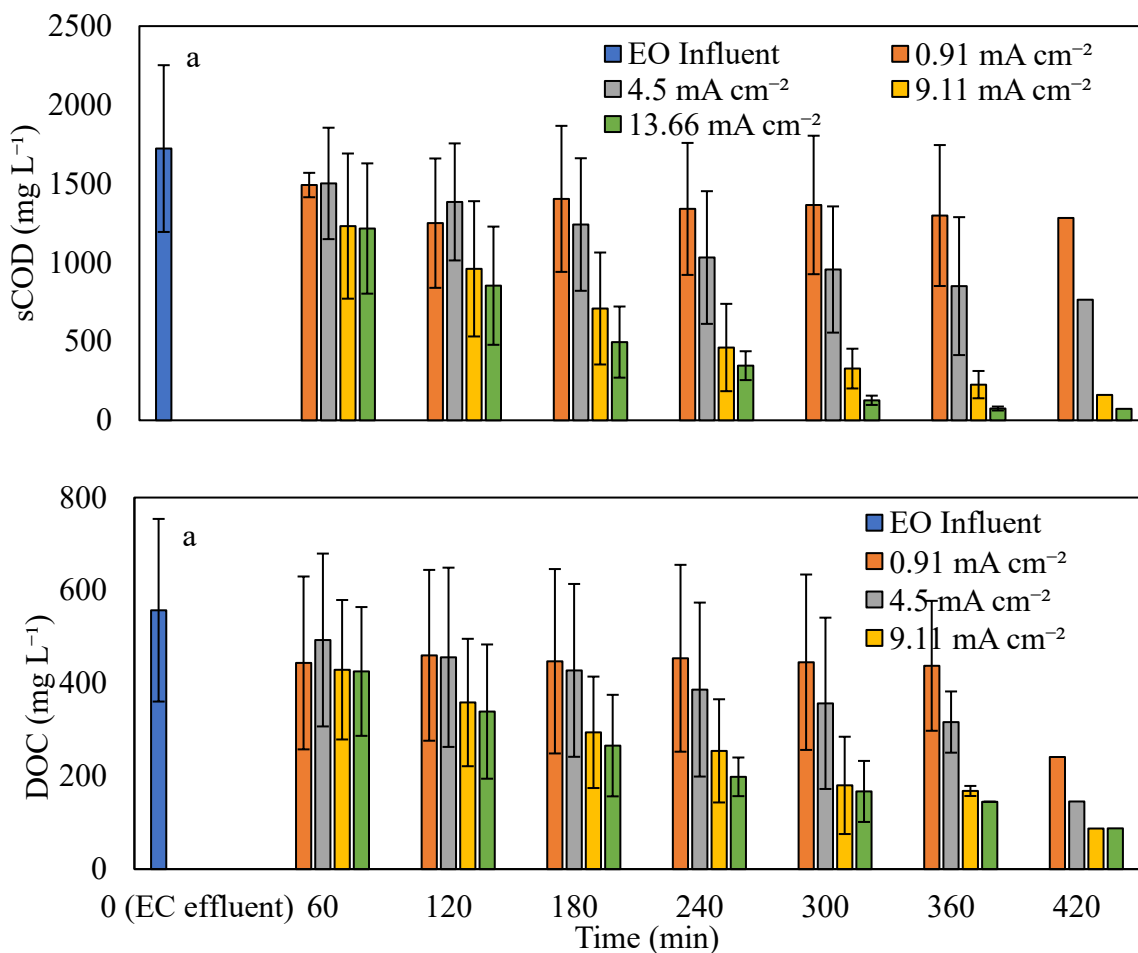
Figure 3.4. (a) sCOD and b) DOC removal using electrooxidation on canola oil refinery wastewater.

The overall removal of sCOD using combined EC+EO in the treatment of COR wastewater is presented in Fig. 3.5a. Results showed that when the system was run for 7 h, 80%

of sCOD was removed at current density of 0.91 mA cm^{-2}. As the current density increased, the removal efficiency also increased. Nearly 100% removal was achieved at the current densities of both 9.11 and 13.66 mA cm^{-2}. It should be noted that although the system was run for 7 h, steady state conditions were achieved by the end of 4 h. The initial concentration of SCOD was measured as about 6,403 mg L^{-1}, which was gradually degraded to a final concentration of about 72.40 mg L^{-1} at 13.66 mA cm^{-2} current density.

The removal of DOC (Fig. 3.5b) ranged between 85 and 95% at the end of 7 h of operation in between the current densities of 0.91 and 13.66 mA cm^{-2}. As of our knowledge, there is not a study available in the literature for COR wastewater treatment using combined EC and EO methods. Therefore, our current results were compared with the other wastewater sources that applied EC and EO methods.

A study was conducted to treat industrial wastewaters using combined EC+EO powered by solar cells. The goal of the research was to remove COD, TOC, color and turbidity using copper and diamond electrodes. The maximum removal of COD and TOC at a current density of 0.24 A cm^{-2} were 99.70 and 70.26% operated for 3 h, respectively (Garcia-Garcia et al., 2015). A study conducted by Azarian et al. (2018) concluded a similar observation in the treatment of tannery industry wastewater. The study investigated the removal efficiency of COD using EC, EO and EC+EO in the wastewater from tannery industry. The results showed that EC process at optimum conditions were able to remove 82.2% COD producing a concentration of 1620 mg L^{-1} and EO produced about 92 (removal efficiency 98.9%) after treating an influent concentration of 8800 mg L^{-1}. However, when the EC and EO were combined, the process could bring down the COD concentration to less than 5 mg L^{-1} (nearly 100% removal efficiency) that was suitable for agricultural and industrial reuse (Azarian et al., 2018).
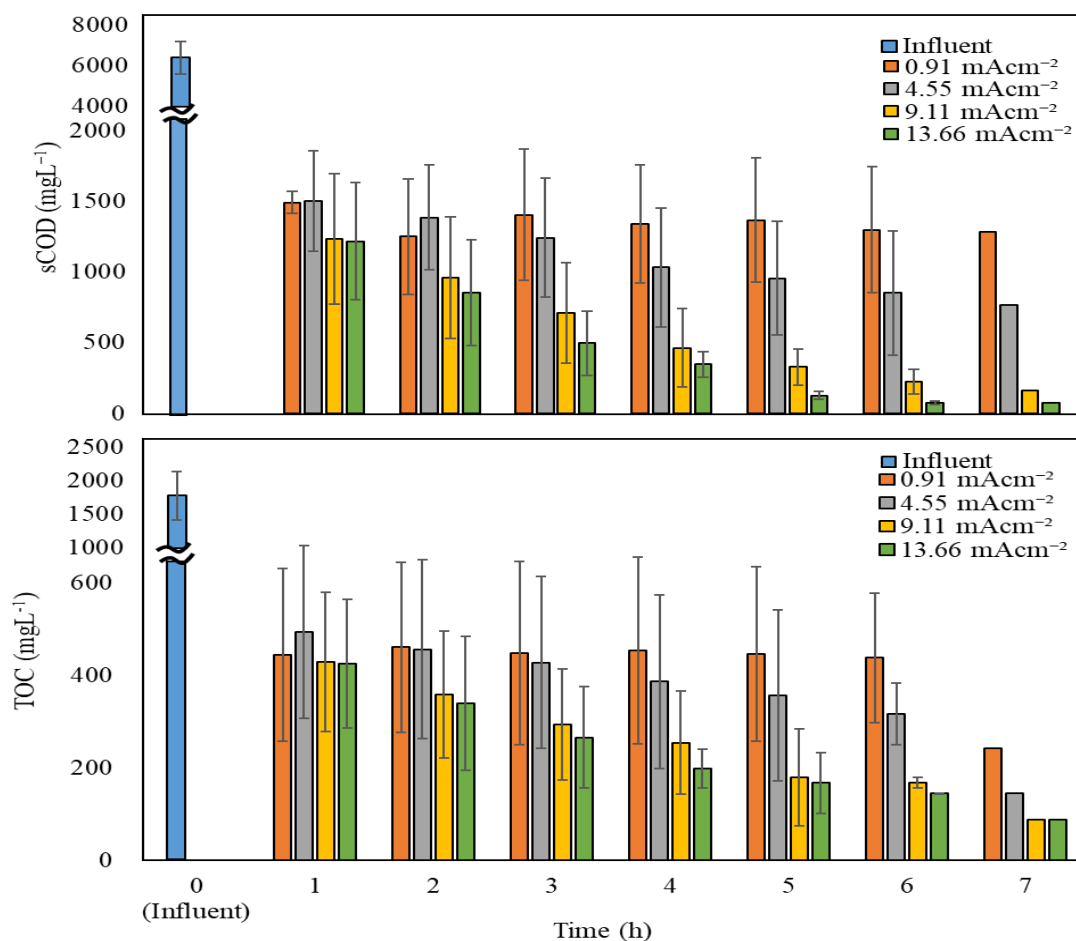
Figure 3.5. a) sCOD and b) DOC removal from canola oil refinery wastewaters using electrocoagulation + electrooxidation method.

3.4.1.3. Method 2. sCOD and DOC Removal in ECP Process

Similar to the other electrochemical methods, pH is very important in ECP processes. ECP process was run for 7 h and the samples were collected every hour to measure the degradation of pollutants. It was observed in Figs. 3.6a and b that, ECP process could remove 77-86% of both sCOD and DOC, respectively at varying current densities. The increase in current density in the ECP process increased removal of SCOD and DOC from the COR wastewaters. Unlike EC+EO process, the removal efficiency remains consistent in ECP process after the first hour of operation at 4.55, 9.11 and 13.66 mA cm^{-2} current densities. Fluctuation in the concentration of sCOD and DOC was observed throughout the time of operation in the

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wastewater sample at the current density of 0.91 mA cm^{-2}. The maximum reduction in the concentration of organic pollutants using ECP method was 88 and 86% for sCOD and DOC concentrations, respectively. Selvabharathi et al. (2010) reported 95% removal of COD from a biologically treated newsprint paper-industry wastewater using EF method as a tertiary treatment method. It was also concluded in the study that treatment efficiency at higher pH decreased due to precipitation of iron hydroxides (Selvabharathi and Kanmani, 2010). Un et al. (2006) removed 70% of COD from olive oil mill wastewater using ECP in an undivided iron tank equipped with iron stirrer while adding H_2O_2 externally to the treated solution. The process removed 100% turbidity in 3 h of operation.
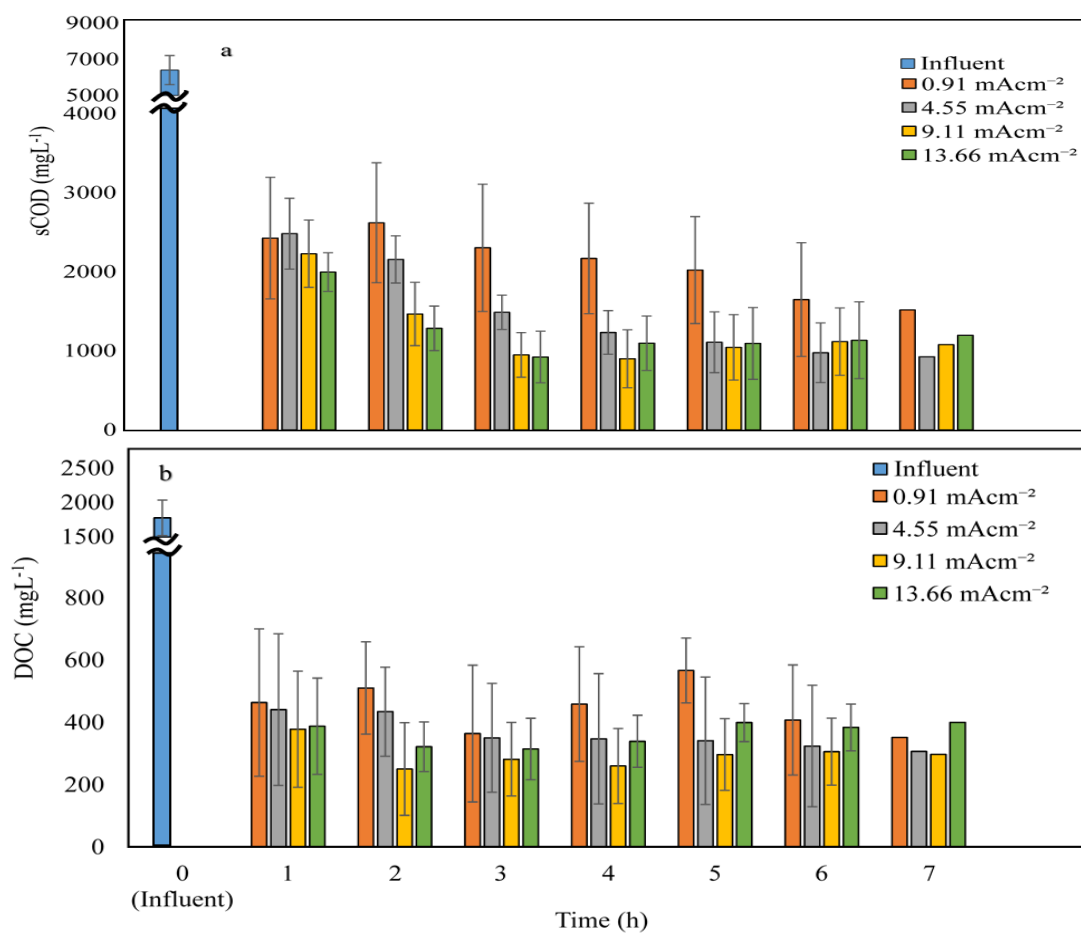
Figure 3.6. (a) sCOD and **b)** DOC removal using electrochemical peroxidation process on canola oil refinery wastewater.

3.4.2. Model Development and Validation Using Stepwise Regression

3.4.2.1. *Optimization of COD and TOC in EC Process*

The COD concentration is an important parameter indicating the turbidity and organic pollutant loading in a wastewater sample (Tir and Moulai-Mostefa, 2008). Degradation of TOC indicates the removal of COD in the tested sample. In this study, the COD and TOC removal efficiency were correlated by using stepwise regression analysis model.
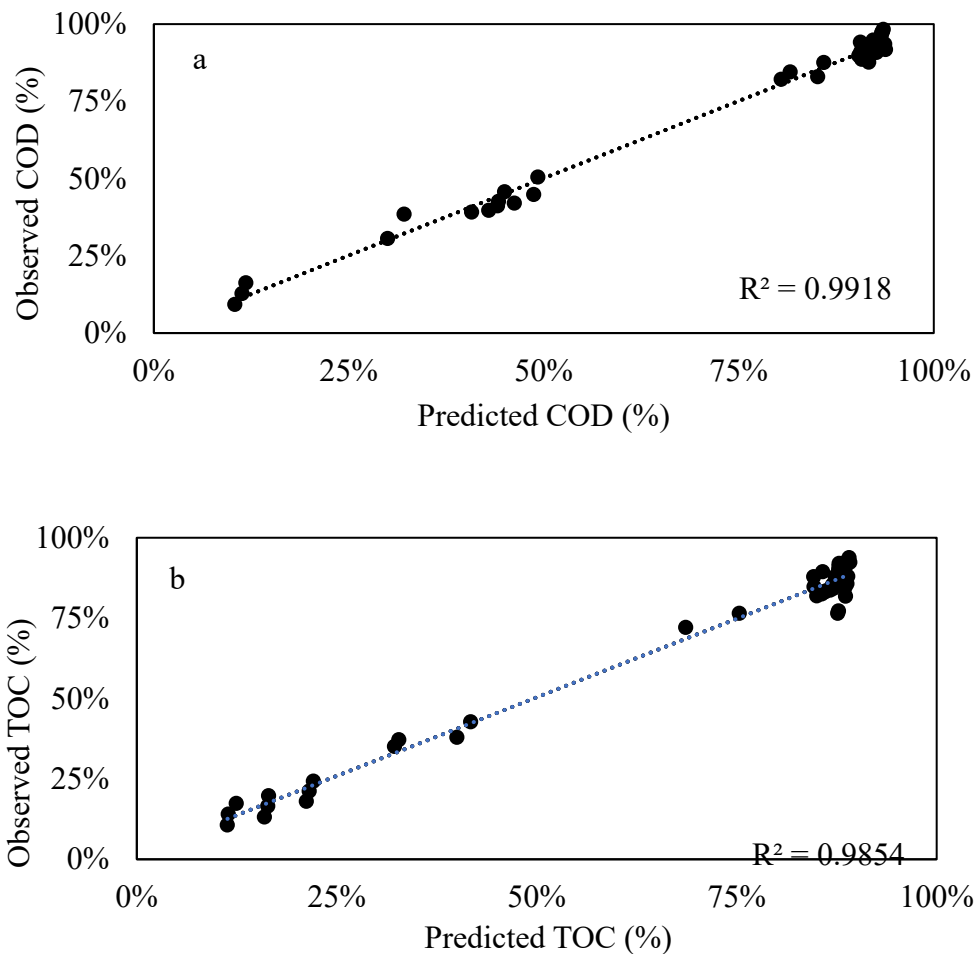
Figure 3.7. a) Predicted vs observed value for COD removal (%) in EC process, b) Predicted vs observed value for TOC removal (%) in electrocoagulation process.

Two design factors were used in the model as current density (X_1) and time (X_2). A second-order (quadratic) polynomial equations for the two variables (X_1 and X_2) are presented in Eqs. (17) and (18) for COD and TOC, respectively.

$$COD = -0.1945 + 1.3405X_1 + 0.04054X_2 - 0.4234X_1^2 - 0.000380X_2^2 - 0.02046X_1X_2 \qquad (17)$$

$$TOC = -0.2092 + 1.1092X_1 + 0.03977X_2 - 0.2913X_1^2 - 0.000361X_2^2 - 0.01740X_1X_2 \qquad (18)$$

The second order regression model developed for EC process satisfies for the operating variables of COD and TOC as the predicted versus observed values approximate along a straight line as shown in Figs. 3.7a and b, respectively.

Table 3.3. ANOVA for COD and TOC removal in EC process.

Source	DF	Adj SS	Adj MS	F-value	P-value
Regression for COD	5	8.32	1.66	374.59	0
Current (A)	1	1.1	1.1	247.12	0
Time (min)	1	2.36	2.36	530.54	0
Current (A)*current (A)	1	0.41	0.4	91.2	0
Time (min)*time (min)	1	1.13	1.13	253.72	0
Current (A)*time (min)	1	0.5	0.5	112.96	0
Error	117	0.52	0		
Total	122	8.84			
Regression for TOC	5	12.5	2.5	273.75	0
Current (A)	1	1.18	1.18	128.97	0
Time (min)	1	3.23	3.23	353.57	0
Current (A)*current (A)	1	0.27	0.27	29.75	0
Time (min)*time (min)	1	1.41	1.41	154.68	0
Current (A)*time (min)	1	0.57	0.57	62.59	0
Error	134	1.22	0.01		
Total	139	13.72			

The testing of the model that was performed using analysis of variance (ANOVA) for both COD and TOC are presented in Table 3.3. ANOVA for COD and TOC removal in EC process. The regression analysis showed that the model was significant and the p-values ($p < 0.05$) suggested that the terms added to the model and its interaction between the terms were significant. The R^2 for both COD and TOC at 0.94 and 0.91 indicates that the total variation

could not be explained by the model for only 5.8% and 8.9%, respectively. From Eq. (14), the optimal conditions for COD removal in EC process were estimated as 7.61 mA cm^{-2} and 31.12 min for current density and time, respectively. Under these conditions, the maximum COD removal efficiency was predicted as 99.15%. Similarly, from Eq. (15), the optimal conditions for TOC removal was estimated as 7.99 mA cm^{-2} and 34.19 min for current density and time, respectively. The maximum removal of TOC was predicted as 95.5%. To confirm the validity of the statistical model, experiments were carried out in the given optimal conditions and the removal efficiency of COD was 96.81% and that of TOC was 93.45%. The optimal conditions were considered for EC process prior to EO. The effluent from the EC reactor was further taken to perform EO under varying current density and time of operation.

3.4.2.2. Model Comparison Between EC+EO and ECP Process

The main objective of this study was to compare the treatment efficiencies between EC+EO and ECP methods and determine which method was more efficient. Therefore, the optimum conditions for the efficient method was determined. A quadratic polynomial regression model was chosen for determining the removal efficiency of sCOD and DOC and the model was validated through performed experiments on the given conditions. Here, it is important to observe that unlike in EC process, the removal efficiency of sCOD and DOC are considered in lieu of COD and TOC. This is due to the need to remove dissolved organic loading along with suspended and colloidal organic pollutants. Studies have shown that oxidation processes such as EO and ECP are successful in degradation of dissolved organic compounds (Ren et al., 2016; Sarkka et al., 2015a; Sarkka et al., 2015b; Sillanpaa et al., 2015). The model predicted the equations for sCOD and DOC removal for each of EC+EO and ECP process. The design factors for the model were: two continuous variables namely current density (X_1), time (X_2) and one

categorical variable method (X_3) in coded units. Eqs. (19) and (20) were obtained for removal efficiency of sCOD and DOC from EC+EO process, respectively.

$$COD = 0.5600 + 0.2832X_1 + 0.001090X_2 - 0.0973X_1^2 - 0.000001X_2^2 \qquad (19)$$

$$TOC = 0.5409 + 0.3113X_1 + 0.000629X_2 - 0.1041X_1^2 - 0.000151X_1X_2 \qquad (20)$$

The removal efficiency of sCOD and DOC for ECP process were obtained using the second order polynomial regression model presented at Eqs. (21) and (22).

$$COD = 0.4973 + 0.2369X_1 + 0.001090X_2 - 0.0973X_1^2 - 0.000001X_2^2 \qquad (21)$$

$$TOC = 0.6873 + 0.2308X_1 + 0.000209X_2 - 0.1041X_1^2 - 0.000151X_1X_2 \qquad (22)$$

The model satisfies for both EC+EO and ECP methods as the predicted versus observed values were distributed along a straight line. Figs. 3.8a and b shows the predicted versus observed values distributed for sCOD and DOC in EC+EO process. The model yielded combined EC+EO process as the preferred method over ECP process for both sCOD and DOC removal efficiencies. The optimal conditions yielded by the model for EC+EO process for sCOD were; current density of 13.27 mA cm^{-2} for time of 403 min, and for DOC were; current density of 10.83 mA cm^{-2} for time of 420 min. The removal efficiency under these conditions using EC+EO method was estimated as 98.6% for sCOD removal and 95.28% for DOC removal. The model variation was explained by R^2 which was achieved to be 92.33% for sCOD and 93.27% for DOC indicating that only 7.67 and 6.73% of the variation could not be explained by the empirical model for sCOD and DOC, respectively. The model was validated by performing extra experiments at the given optimal condition for combined EC+EO process and the measured value for sCOD and DOC achie ved 98.6% and 95.28% removal respectively.
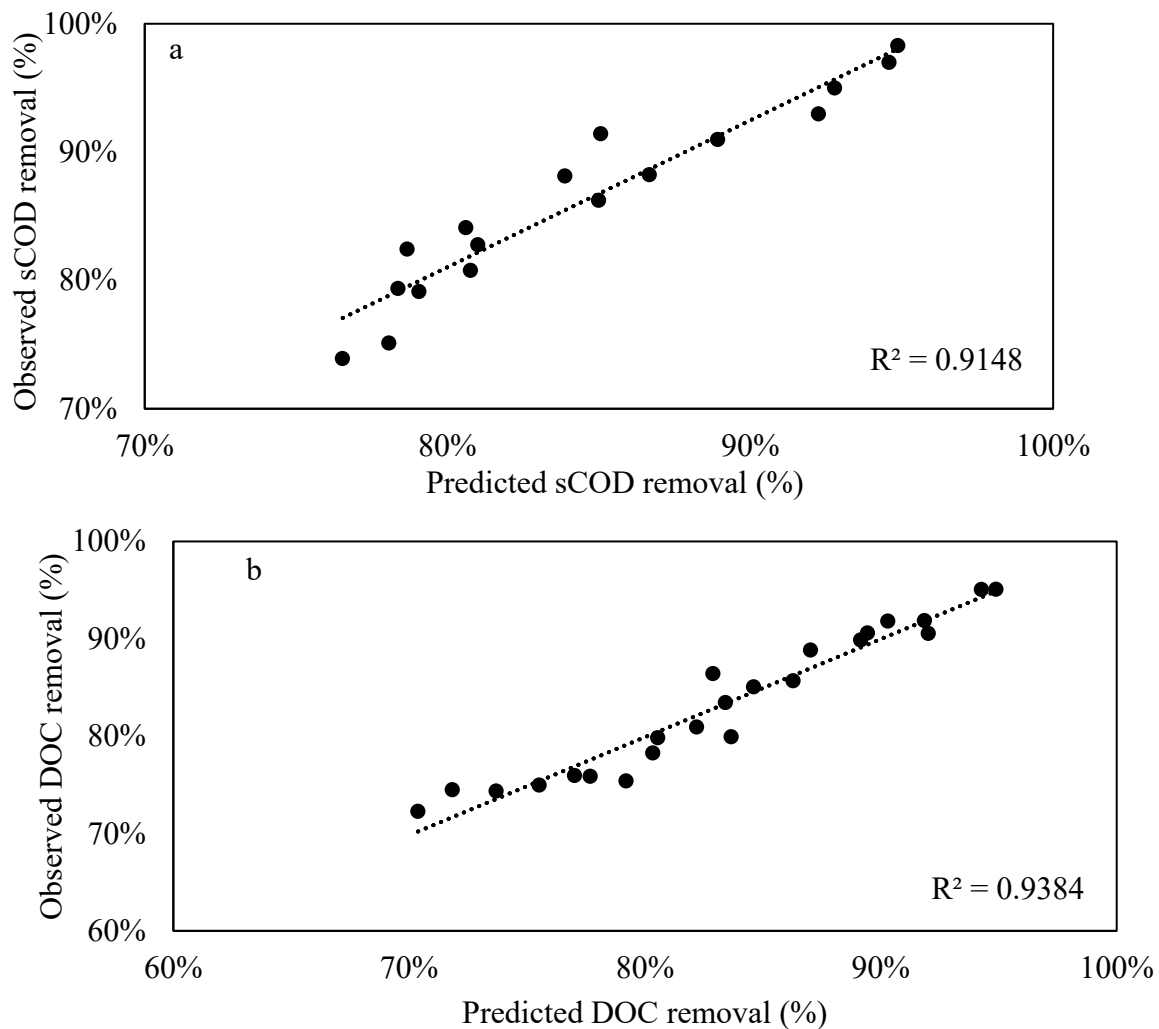
Figure 3.8. a) Predicted vs observed sCOD removal (%) b) Predicted vs observed DOC removal (%) in electrocoagulation+electrooxidation process.

3.4.3. Model Analysis and Parameter Optimization Using BBD

3.4.3.1. Statistical Analysis and Interpretation by BBD

In this study, EC+EO and ECP processes were conducted statistical interpretation using BBD. The statistical model for EC+EO process was designed in two phases: a) BBD designed for EC process to study the effect of current density (4.5-13.6 mA cm^{-2}), pH (5-7) and time of operation (10-30 min) as described in Table 3.2. The input variables of the EC model were optimized for the removal of COD, sCOD, TOC and DOC. Furthermore, the EO model was

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designed for the optimized EC effluent to investigate the effects of current density

(4.5 - 13.6 mA cm^{-2}), pH (5-7) and time of operation (180-420 min). Similarly, the model for

ECP process was designed and the effects and interaction of H_2O_2 dosage (10-20 ml L^{-1}), current

density (4.5-13.6 mA cm^{-2}), and time of operation (180-420 min) in the removal of COD, sCOD,

TOC and DOC in the canola oil wastewater.

The data for EC, EC+EO and ECP were fitted to quadratic models and the adequacy of

the model and statistical significance were tested using ANOVA as presented in Table 3.4. the p-

values less than 0.05 and the F-test values indicated good significance of the models in the

removal of the response variables COD, sCOD, TOC and DOC. Low coefficient of variation and

high R^2 and adjusted R^2 explained that the models are well explained with high precision and

reliability.

The removal efficiency of COD, sCOD, DOC and TOC expressed by EC, EC+EO and

ECP process are presented in Eqs. (23) through (34):

a) Removal efficiency by EC reaction

$$COD = 93.98 - 4.66\ X_1 - 1.12\ X_2 - 3.18\ X_3 - 2.67\ X_1X_2 - 2.48$$
$$X_1X_3 - 2.56\ X_2X_3 - 12.97\ X_1{}^2 - 4.01\ X_2{}^2 - 11.04\ X_3{}^2 \tag{23}$$

$$sCOD = 78.11 - 3.37\ X_1 - 2.24X_2 - 2.32\ X_3 - 4.28\ X_1X_2 -$$
$$3.96X_1X_3 - 3.32\ X_2X_3 - 9.02\ X_1{}^2 + 0.69\ X_2{}^2 - 5.54\ X_3{}^2 \tag{24}$$

$$TOC = 88.84 - 4.78\ X_1 - 1.12\ X_2 - 3.31X_3 - 2.67X_1X_2 -$$
$$2.23X_1X_3 - 2.56\ X_2X_3 - 10.27\ X_1{}^2 - 1.56\ X_2{}^2 - 8.35\ X_3{}^2 \tag{25}$$

$$DOC = 75.84 - 3.88\ X_1 - 2.89X_2 - 1.98\ X_3 - 4.25\ X_1X_2 - 4.00$$
$$X_1X_3 - 4.54\ X_2X_3 - 9.81\ X_1{}^2 + 0.73\ X_2{}^2 - 5.53\ X_3{}^2 \tag{26}$$

Table 3.4. ANOVA for COD, sCOD, TOC and DOC removal in canola oil refinery wastewater.

Response (Y %)	Source	Electrocoagulation					Electrocoagulation+Electrooxidation					Electrochemical Peroxidation				
		SS	DF	MS	F-value	p-value	SS	DF	MS	F-value	p-value	SS	DF	MS	F-value	p-value
COD	Model	1358.99	9	151.0	38.6	0.00	1355.31	9	150.59	39.14	0.00	935.96	9	104.00	49.09	0.00
	Residual	15.75	5	3.15			19.24	5	3.85			10.59	5	2.12		
	Lack of Fit	14.89	3	4.96	11.54	0.08	18.51	3	6.17	16.98	0.05	10.12	3	3.37	14.13	0.06
	Pure Error	0.86	2	0.43			0.73	2	0.36			0.4773	2	0.2386		
	Total	1374.74	14				1374.54	14				946.56	14			
		R² =0.98 Adj R²=0.96 C.V. %=2.25					*R² =0.98 Adj R²=0.96 C.V. %=2.3*					*R² = 0.988 Adj R²= 0.968 C.V.%= 1.89*				
sCOD	Model	752.85	9	83.65	16.23	0.0034	720.12	9	80.01	18.20	0.00	1091.96	9	121.33	24.28	0.00
	Residual	25.77	5	5.15			21.98	5	4.40			24.98	5	5.00		
	Lack of Fit	24.01	3	8.00	9.10	0.1006	20.28	3	6.76	7.92	0.11	24.55	3	8.18	38.06	0.03
	Pure Error	1.76	2	0.88			1.71	2	0.85			0.43	2	0.22		
	Total	778.62	14				742.10	14				1116.94	14			
		R² = 0.96 Adj R²=0 .901 C.V.%=3.21					*R² = 0.97 Adj R²= 0.92 C.V.%=2.31*					*R² = 0.97 Adj R²= 0.94 C.V.%=3.04*				

Table 3.4. ANOVA for COD, sCOD, TOC and DOC removal in canola oil refinery wastewater (continued).

Response (Y %)	Source	Electrocoagulation					Electrocoagulation+Electrooxidation					Electrochemical Peroxidation				
		SS	DF	MS	F-value	p-value	SS	DF	MS	F-value	p-value	SS	DF	MS	F-value	p-value
TOC	Model	956.72	9	106.3	35.10	0.0005	1052.48	9	116.94	30.44	0.00	744.67	9	82.74	23.74	0.00
	Residual	15.14	5	3.03			19.21	5	3.84			17.43	5	3.49		
	Lack of Fit	14.47	3	4.82	14.30	0.0661	18.22	3	6.07	12.24	0.07	16.57	3	5.52	12.84	0.07
	Pure Error	0.67	2	0.34			0.99	2	0.49			0.86	2	0.43		
	Total	971.86	14				1071.69	14				762.10	14			
		$R^2 = 0.98$ Adj R^2= 0.95 C.V.%=2.23					$R^2 = 0.98$ Adj R^2= 0.94 C.V.%=2.35					$R^2 = 0.97$ Adj R^2= 0.94 C.V.%=2.42				
DOC	Model	889.48	9	98.83	25.83	0.0011	675.95	9	75.11	11.27	0.00	762.26	9	84.70	52.71	0.00
	Residual	19.13	5	3.83			33.33	5	6.67			8.03	5	1.61		
	Lack of Fit	18.43	3	6.14	17.59	0.0543	31.25	3	10.42	10.01	0.0922	7.53	3	2.51	10.04	0.09
	Pure Error	0.69	2	0.34			2.08	2	1.04			0.50	2	0.25		
	Total	908.61	14				709.28	14				770.29	14			
		$R^2 = 0.97$ Adj R^2= 0.94 C.V.%=2.7					$R^2 = 0.95$ Adj R^2= 0.86 C.V.%=2.94					$R^2 = 0.98$ Adj R^2= 0.97 C.V.%=1.66				

b) Removal efficiency by EC+EO reaction:

$$COD = 97.67 - 4.22\ X_1 - 1.23\ X_2 - 2.99\ X_3 - 3.28\ X_1X_2 - 1.87X_1X_3 - 2.68\ X_2X_3 - 13.09\ X_1^2 - 4.70\ X_2^2 - 11.09X_3^2 \tag{27}$$

$$sCOD = 98.03 - 2.57X_1 - 2.93\ X_2 - 2.47\ X_3 - 3.71\ X_1X_2 - 4.00X_1X_3 - 3.50\ X_2X_3 - 8.79\ X_1^2 + 0.62X_2^2 - 5.50\ X_3^2 \tag{28}$$

$$TOC = 94.62 - 4.63\ X_1 - 1.23\ X_2 - 3.40\ X_3 - 3.26\ X_1X_2 - 2.66\ X_1X_3 - 2.44\ X_2X_3 - 10.77\ X_1^2 - 1.38\ X_2^2 - 9.08\ X_3^2 \tag{29}$$

$$DOC = 94.33 - 2.92X_1 - 2.62\ X_2 - 1.63\ X_3 - 4.75\ X_1X_2 - 3.52X_1X_3 - 3.54\ X_2X_3 - 8.89\ X_1^2 + 0.52\ X_2^2 - 4.06\ X_3^2 \tag{30}$$

c) Removal efficiency by ECP reaction:

$$COD = 88.01 - 4.86\ X_1 - 1.84\ X_2 - 2.82\ X_3 - 2.63\ X_1X_2 - 3.29\ X_1X_3 + 1.13\ X_2X_3 - 9.98\ X_1^2 - 2.72\ X_2^2 - 8.20\ X_3^2 \tag{31}$$

$$sCOD = 83.68 - 5.87\ X_1 - 2.68\ X_2 - 4.10\ X_3 - 3.67\ X_1X_2 - 4.96\ X_1X_3 + 0.73\ X_2X_3 - 9.46\ X_1^2 - 2.80\ X_2^2 - 6.63\ X_3^2 \tag{32}$$

$$TOC = 85.27 - 4.94\ X_1 - 3.00\ X_2 - 2.98\ X_3 - 2.45\ X_1X_2 - 2.89X_1X_3 + 1.58X_2X_3 - 7.04\ X_1^2 - 1.44\ X_2^2 - 7.01\ X_3^2 \tag{33}$$

$$DOC = 84.99 - 5.35X_1 - 1.66\ X_2 - 1.84\ X_3 - 1.79\ X_1X_2 - 3.70X_1X_3 + 1.40\ X_2X_3 - 7.73\ X_1^2 - 0.97\ X_2^2 - 7.71\ X_3^2 \tag{34}$$

The models are satisfied for the processes as the experimental versus the predicted values shows to be in good agreement as it distributes along a straight line as shown in fig. 3.9.

3.4.3.2. Effects of Variables on COD, sCOD, TOC, and DOC Removal Efficiency Through Response Surface Plotting

The 3-D plots are presented in Fig. 3.11 and 3.12 explaining the interaction and main effects of the independent variables on the individual responses. The plots with significant terms (p<0.05) (as shown in **APPENDIX A. TABLES**, Table A.1) are presented in these figures. The plots with statistical insignificance are included in APPENDIX B, Fig. B.1.

3.4.3.3. Effect of Initial pH/H_2O_2 Dosage (X_1) and Current Density (X_2)

The interaction effect of pH and current density in EC+EO process has a significant positive impact in the removal of COD, sCOD, TOC and DOC from canola oil refinery wastewater. From fig. 3.10 a, d, g and i, it is observed that in the EC process, the removal efficiency is maximum in the pH range between 5.5 and 6.5. Increase in current density within this pH range resulted in removal of nearly 90% of COD from the wastewater sample. However, in the removal of sCOD and DOC, the range of pH further narrows to 6 at current densities above 9 mA cm^{-2}. In the combined EC+EO process, the interaction between current density and pH shows a similar trend. The removal of sCOD and DOC has excellent removal of 95-100% between pH of 5.5 and 6.5 and current densities between 4.06 and 10 mA cm^{-2} when ran for 300 min. The removal efficiency decreases after 10 mA cm^{-2} irrespective of the initial pH concentration (Fig. 3.11 a, c, f and h).

Similarly, in the ECP process, the dosage of H_2O_2 between 13 and 18 ml L^{-1} at applied current densities between 7 and 11 mA cm^{-2} shows the maximum removal of COD, sCOD and DOC with a percentage degradation between 80 and 85% at the end of 300 min. 3-D surface plots indicating the effect of current density and H_2O_2 dosage is presented in Fig. 3.12 a, c, and f.

However, the interaction between current density and H_2O_2 dosage did not show a considerable impact in the removal of TOC.

3.4.3.4. Effects of Current Density (X_2) and Time (X_3)

The removal of COD and TOC in EC process showed more than 85% when current density applied was increased from 7 to 11 mA cm^{-2} between 15 and 25 min. Whereas, sCOD and DOC was removed efficiently between 5 and 7 mA cm^{-2} at a pH 6 and operation time within 15 and 25 min (Fig. 3.10 c, f, h and k). When the interaction of current density and time was observed for the combined EC+EO process, it was observed that the removal of pollutants was highest at current density between 7.1 and 9.7 mA cm^{-2} and operation time within 240 and 360 min. The change in current density and time significantly impact the removal of COD, sCOD, and DOC (Fig. 3.11b, e and j). The data also coincides with the results obtained in a previous study in canola oil refinery wastewater (Sharma and Simsek, 2019). However, it was observed from the BBD model that interaction between current density and time was not statistically significant in the ECP treatment process.

3.4.3.5. Effects of Initial pH/H_2O_2 Dosage and Time

In EC+EO process, pH and time impacts the removal of COD, sCOD and DOC. Maximum removal was obtained when the initial pH concentration was maintained between 5.5 and 6.5 and the time operation was kept between 240 and 300 min. In this range, the removal of COD, sCOD, TOC and DOC was excellent with more than 90% removal. However, pH outside this range tend to decrease the removal efficiency and the time of operation played a significant role in determining its treatment efficiency. When the H_2O_2 dosage was applied in the ECP process between 13 and 18 ml L^{-1}, 85% of TOC and 80% of COD, sCOD and DOC was removed between 240 and 300 min.
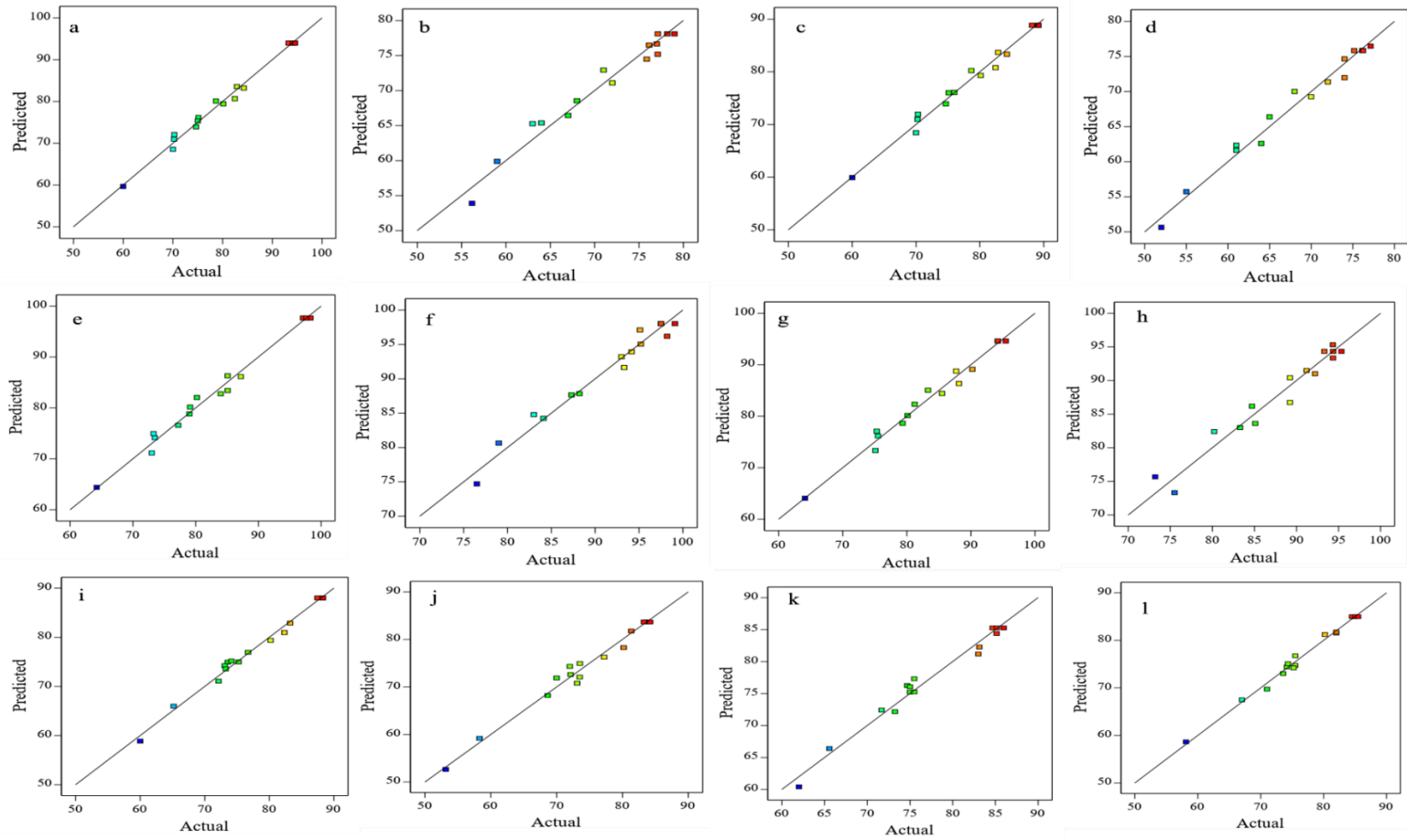
Figure 3.9. Experimental vs predicted values from RSM describing removal of a) COD, b) sCOD, c) TOC, and d) DOC using electrocoagulation; e) COD, f) sCOD, g) TOC, and h) DOC using electrocoagulation + electrooxidation ; and i) COD, j) sCOD, k) TOC, and l) DOC using electrochemical peroxidation.

3.4.3.6. Optimization of Process Parameters and Method Selection Through Economic Comparison

From the BBD results, the process parameters were optimized for both EC+EO and ECP methods. The optimized conditions for each of EC were found to be at pH 5.5 with applied current density of 9.76 mA cm^{-2} for 23.4 min. The experiments were carried out under these conditions and the effluent from the EC reactor were fed into the EO reactor. The model further optimized the conditions of EC+EO based on its total removal, which was at pH 5.4, applied current density of 9.12 mA cm^{-2} for 294 min. The close values of pH of both the processes made it easier to adjust the pH without significantly changing the characteristics of the treated effluent. Extra experiments were conducted to validate the predicted removal efficiency under the optimized conditions. The experimental data was observed to be in good agreement with the prediction model as presented in table 3.5. Similarly, for ECP the optimized conditions were calculated at a H$_2$O$_2$ dosage of 13.4 ml L^{-1}, 8.28 mA cm^{-2} current density applied for 203 min. Based on the discussion above and the available data, the economic analyses were summarized from the current efficiency and electrical consumption. The removal efficiency and electrical consumption could be applied in the comparison between EO and ECP in the treatment of sugar beet wastewater. The electrical energy consumption can be calculated using Eq. (35) (Ferreira et al., 2007).

$$E = VIt \tag{35}$$

where, E is the electrical energy (Wh), V is the cell voltage (V), I is the current intensity (A) and t is the time of operation (h).
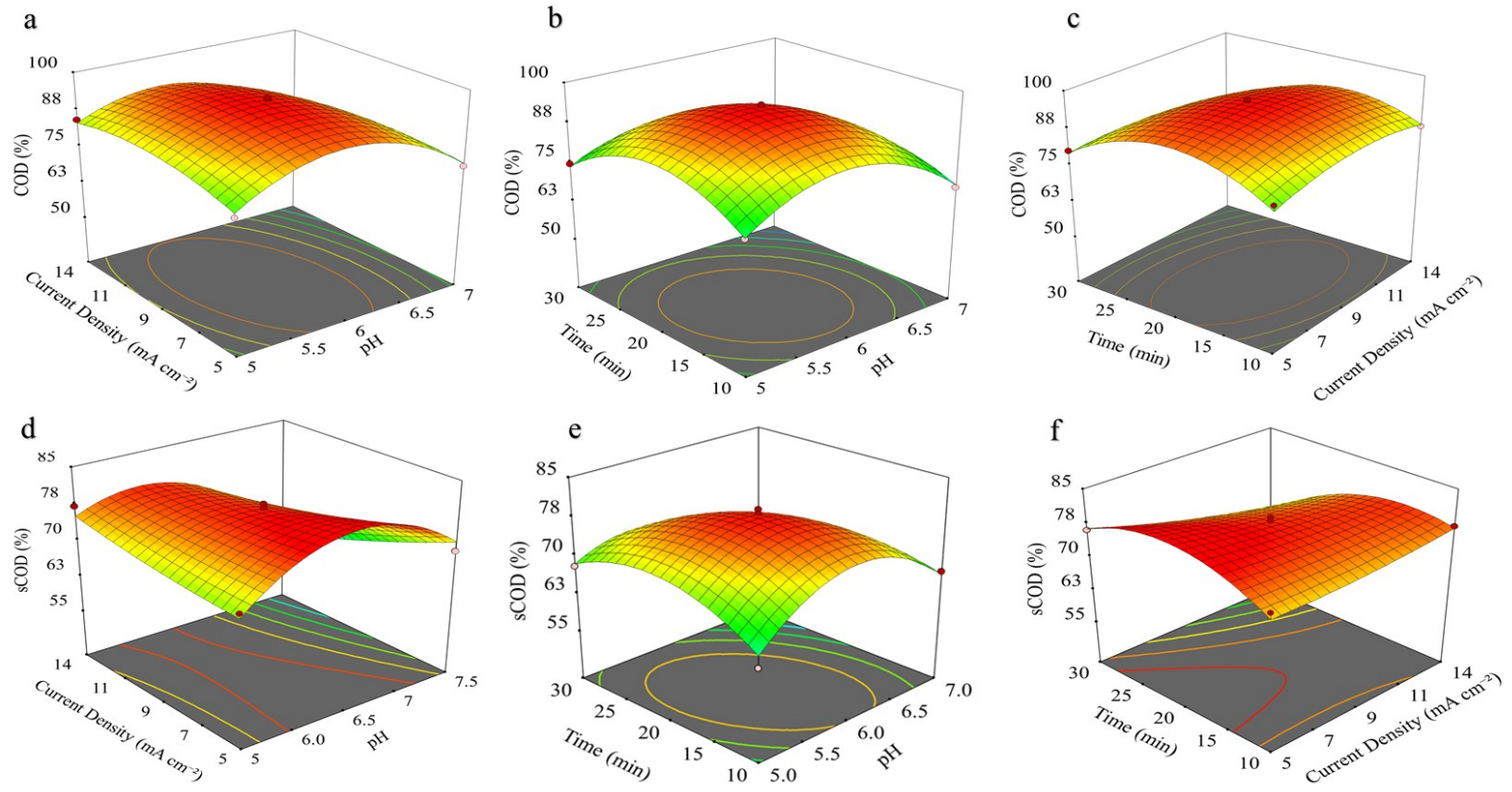
Figure 3.10. Interaction effects of current density, pH and time in the electrocoagulation process.
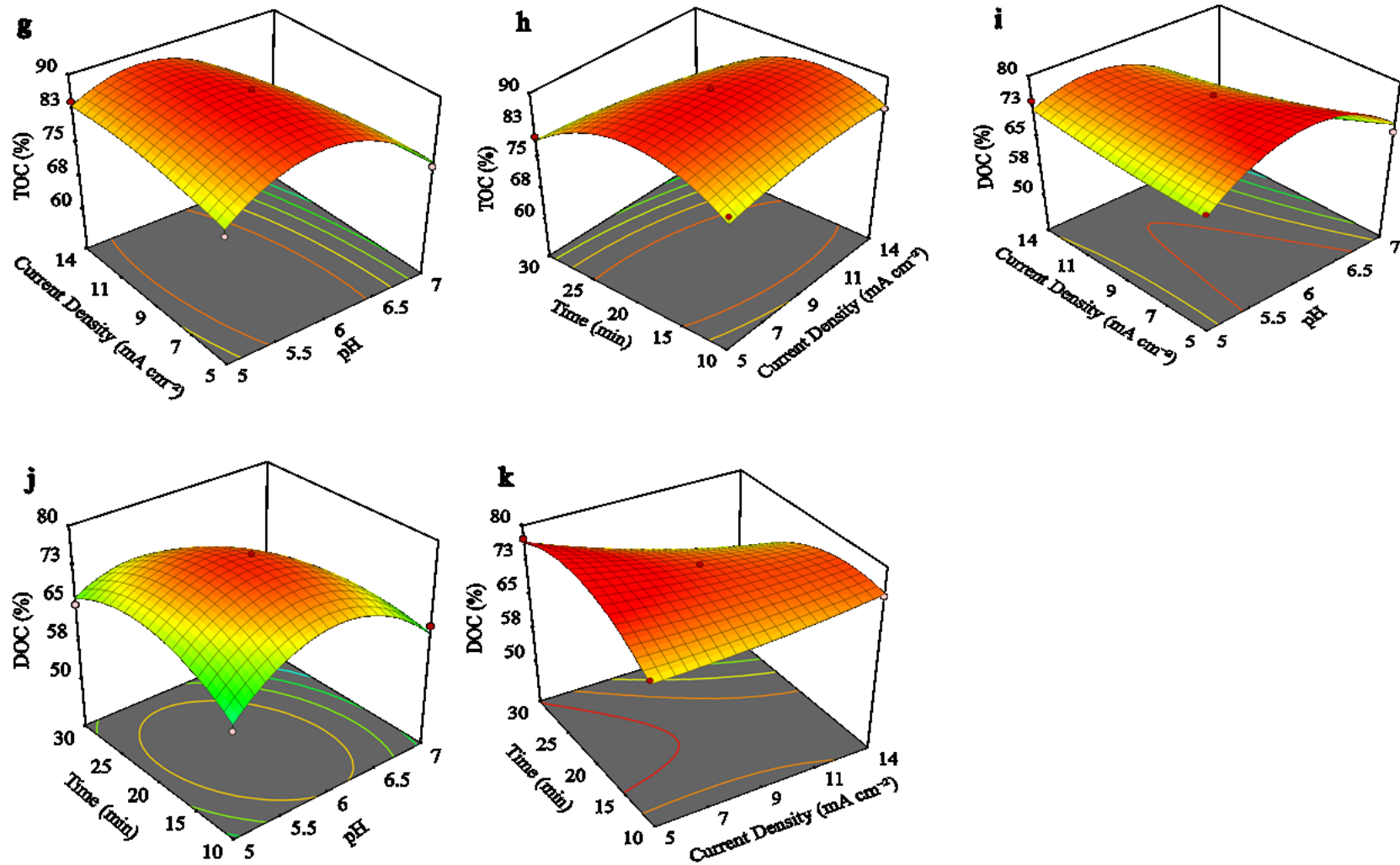
Figure 3.10. Interaction effects of current density, pH and time in the electrocoagulation process (continued)
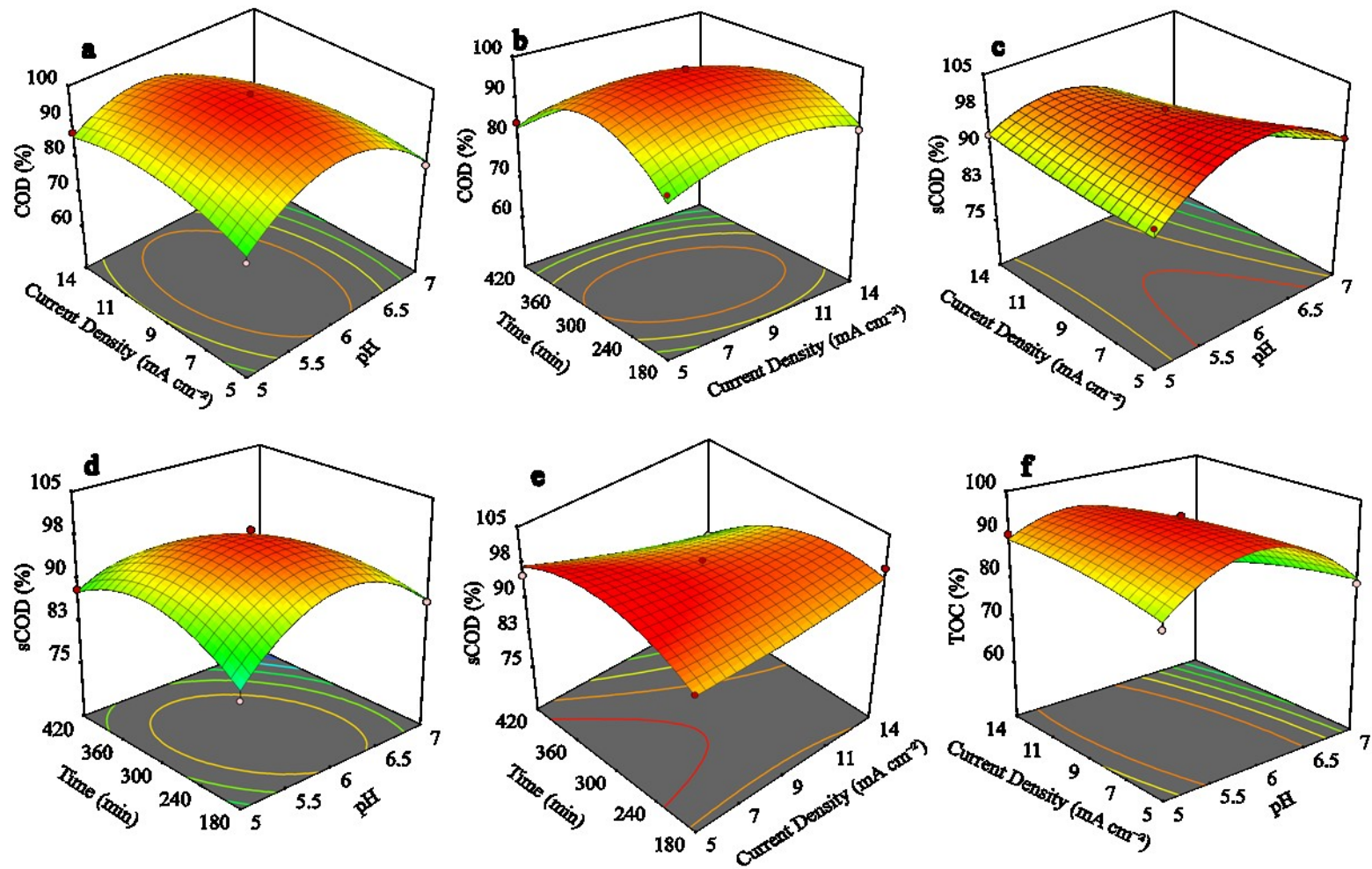
Figure 3.11. Interaction effects of current density, pH and time in the electrocoagulation + electrooxidation process.
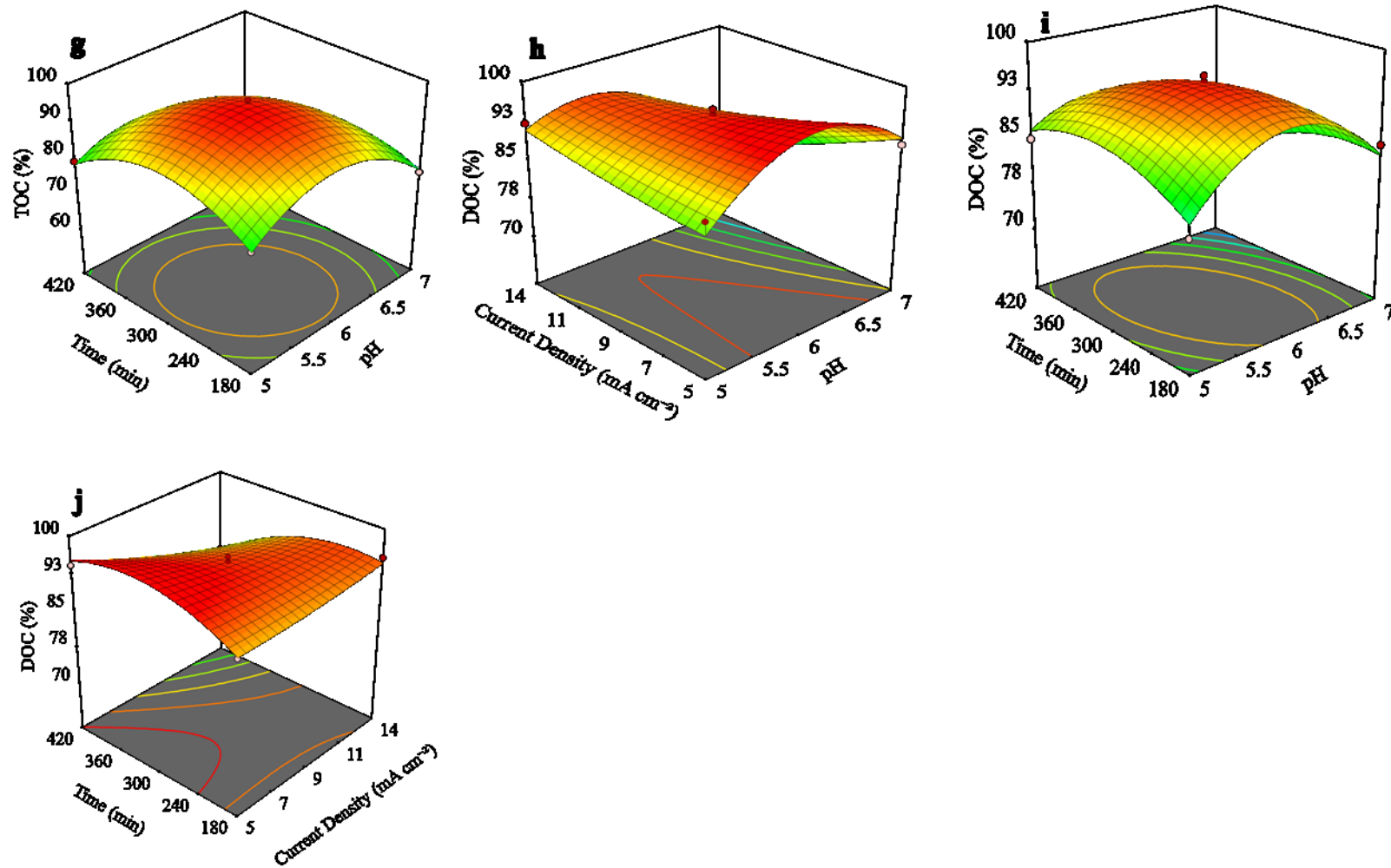
Figure 3.11. Interaction effects of current density, pH and time in the electrocoagulation + electrooxidation process (continued).
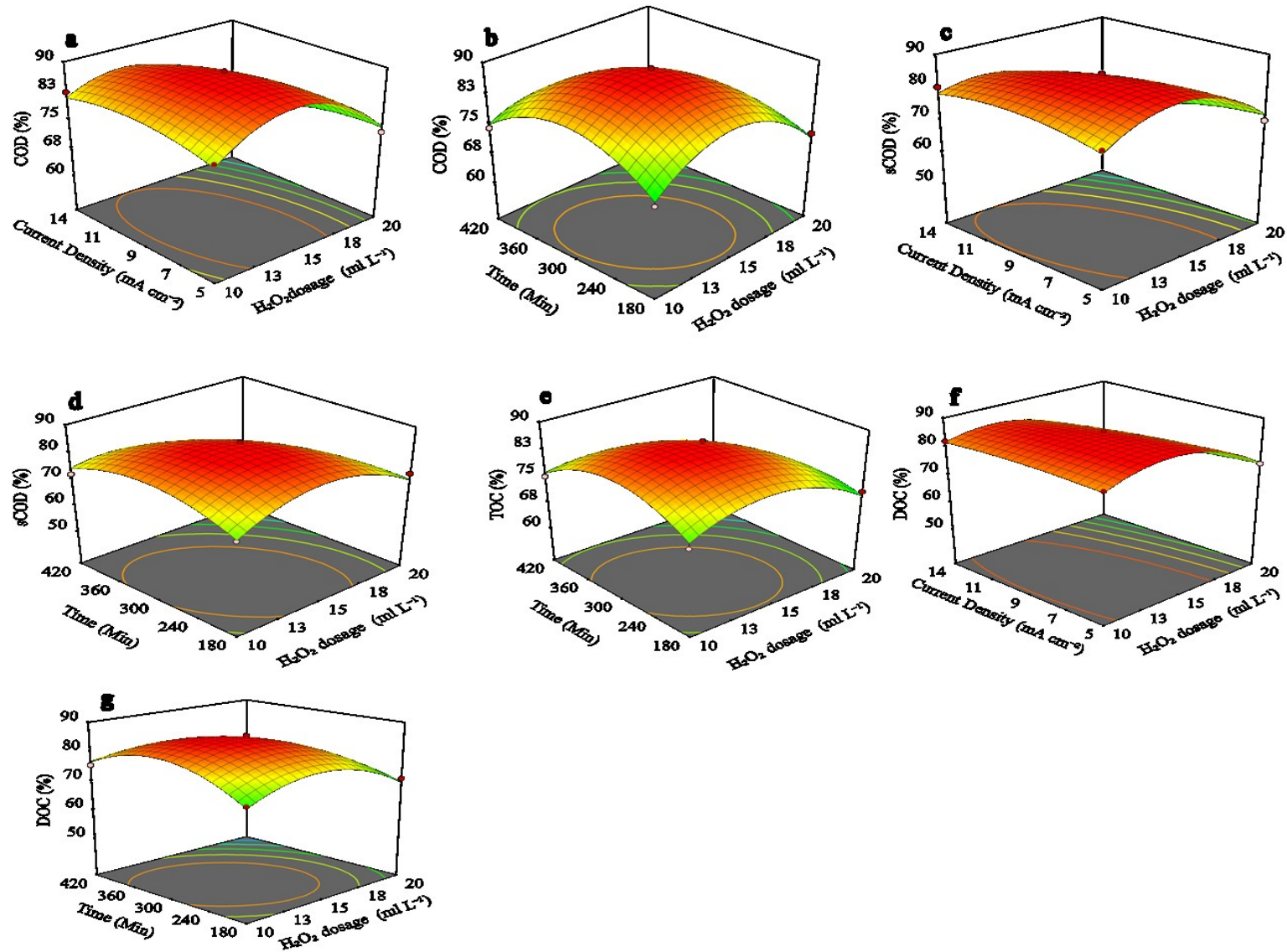
Figure 3.12. Interaction effects of current density, H₂O₂ dosage and time in the electrochemical peroxidation process.

Table 3.5. Predicted versus actual values at optimal conditions and energy consumed for EC+EO and ECP.

Response	Electrocoagulation			Electrooxidation + Electrocoagulation			Electrochemical Peroxidation		
	Predicted (%)	Actual (%)	Energy consumption (kWh m^{-3})	Predicted (%)	Actual (%)	Energy consumption (kWh m^{-3})	Predicted (%)	Actual (%)	Energy consumption (kWh m^{-3})
COD	91.05	92.13	0.15	95.87	95.52	1.67	84.89	82.12	1.19
sCOD	76.67	74.23	0.69	96.61	95.07	6.31	82.59	80.03	4.59
TOC	86.88	87.98	0.41	93.81	91.02	4.63	83.78	83.11	3.11
DOC	74.42	74.46	2.47	93.07	90.35	23.92	81.77	78.89	16.76

The electric energy consumed to remove 1.0 g of organic pollutants (COD, sCOD, TOC, and DOC) was calculated using Eq. (36).

$$E_c \,(\text{Wh/g}) = \frac{E}{(C_0 - C)} \qquad (36)$$

The energy consumed by each of the processes under optimum conditions are presented in Table 3.5. The energy consumed in the removal of COD using EC process with Al as electrodes consumed 0.15 kWh m^{-3} to remove 92% of the initial concentration under 25 min. The consumption is comparatively less than a study conducted by Un et al. (2009) on edible oil wastewater to remove COD at 35 mA cm^{-2} when operated with Al electrodes for 90 min. The energy consumed in the process was 131 kWh per kg COD. The study also reported to reduce the energy consumption to 96 kWh per kg COD when added poly aluminum chloride (Un et al., 2009a). Whereas, in the current study, no addition of additives or chemical coagulants were used, and the current density applied is less compared to the above study. Tir and Moulai-Mostefa (2008) reported the power consumption for treating the oily wastewater with the EC process, ranging from 0.115 to 11.38 kWh m^{-3} (Tir and Moulai-Mostefa, 2008). The EC+EO process consumed 23 kWh m^{-3} to remove 95% of COD and 93% of TOC in approximately 300 mins

compared to 16.76 kWh m^{-3} consumed by ECP to remove less than 85% of organic pollutants in 203 min. Comparing the removal efficiency under the time of operation stated and the energy consumed, EC+EO process was chosen over ECP.
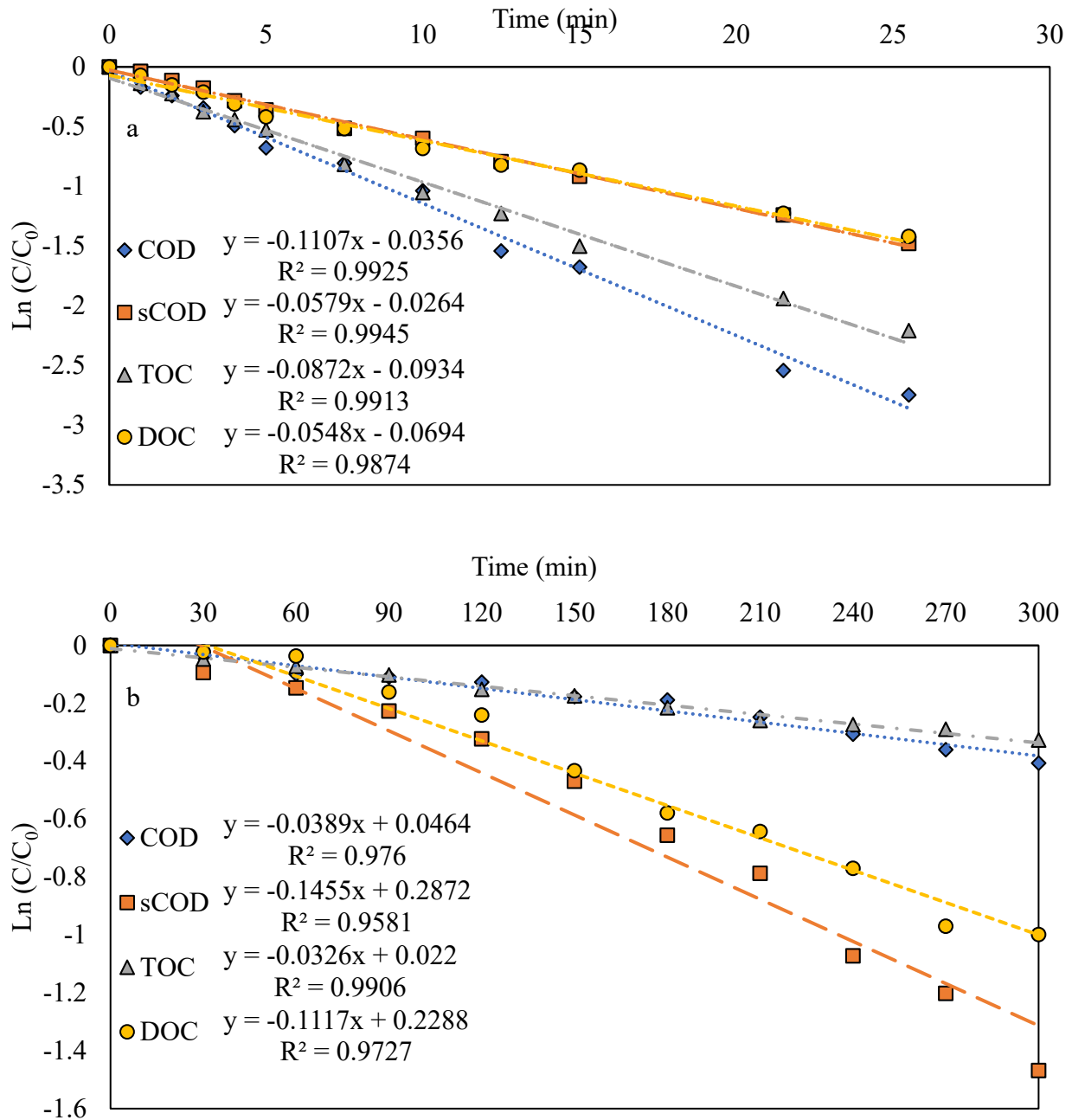
Figure 3.13. Linearized first-order kinetic model for a) electrocoagulation process and b) electrooxidation process on the treatment of COD, sCOD, TOC, and DOC.

3.4.4. Reaction Kinetics

The kinetic models were tested on the reduction rate of COD, sCOD, TOC and DOC under optimized conditions using EC+EO process. The reactions were observed to follow a first order kinetic model for both EC and EO process. The plots $Ln(C/C_0)$ for COD, sCOD, TOC and DOC are presented in Fig. 3.13.

The R^2 is high and the residual concentration of COD, sCOD, TOC and DOC fit a straight line indicating a good fit of the first order kinetic model to demonstrate the rate of reaction constant in the degradation organic pollutants in the treatment of canola oil wastewater. The reaction rate constant, k, obtained from the slope of each plot along with R^2 values are presented in Table 3.6.

Table 3.6. Values of first-order kinetic constant, k and coefficient of determination R^2 for the responses of EC and EO processes under optimum conditions.

Response	EC		EO	
	k (min^{-1})	R^2	k (min^{-1})	R^2
COD	0.111	0.993	0.039	0.098
sCOD	0.058	0.995	0.145	0.958
TOC	0.087	0.991	0.033	0.991
DOC	0.055	0.987	0.112	0.973

3.4.5. TSS Removal in EC, EC+EO, and ECP Processes

The primary objective of EC is to remove TSS by forming flocs. The results (Fig. 3.14) showed that Al electrodes achieved almost 100% removal of TSS at the end of each operation time. However, it is important to mention that maintaining the pH of the electrolyte solution determines the time required for coagulation. Asselin et al. (2008) conducted a study on the effectiveness of EC in the removal of organic pollutants from slaughterhouse wastewater and achieved around $89 \pm 4\%$ removal in TSS using bipolar aluminum electrodes. Other studies that was conducted in textile, dairy and tannery wastewaters found similar results in the removal of

TSS using EC method (Asselin et al., 2008; Khandegar and Saroha, 2013; Mollah et al., 2001; Un et al., 2009b). ECP process also achieved removal of TSS between 94 and 96% at current densities of 4.55, 9.11 and 13.66 mA cm^{-2} at the end of 7 h of operation. However, only 36% of TSS could be removed at 0.91 mA cm^{-2} current density. Inan et al. (2004) applied EC method to olive oil wastewaters and achieved 68% removal in TSS using Al electrodes at a current density of 20 mA cm^{-2} for 15 min operation at a pH of 6.1. The study concluded that with increase in EC time, the removal yield of TSS increased monotonically (Inan et al., 2004).
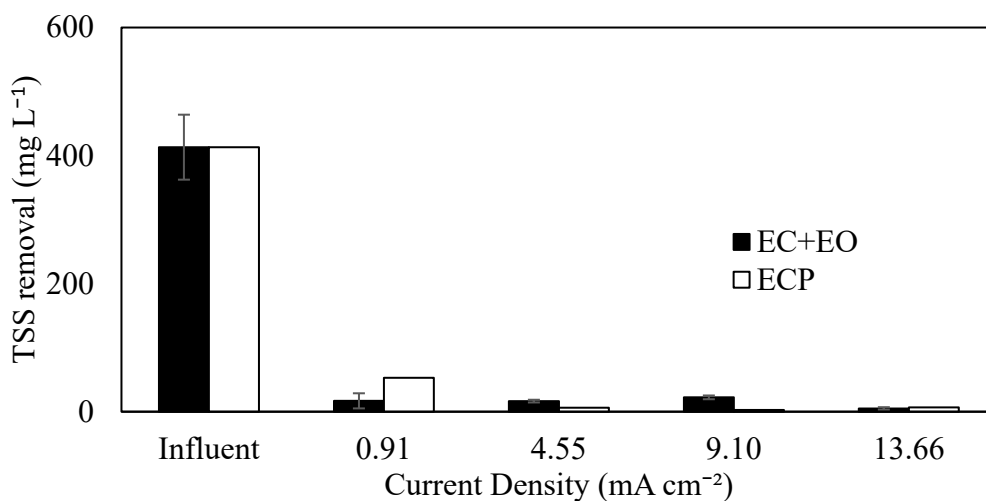
Figure 3.14. TSS removal by EC+EO and EF process on canola oil refinery wastewater

3.5. Conclusion

In this study, a comparison between two different electrochemical treatment methods namely EC+EO and ECP has been presented. Considering the treatment efficiency, both EC + EO and ECP techniques could be suggested as effective alternative treatment techniques for COR wastewaters. However, a stepwise regression modelling results suggested that combined EC+EO process was superior to ECP process for the removal of sCOD and DOC in COR wastewaters.

The study discussed about the impact of current density and operation time in the degradation of organic pollutants using advanced electrochemical oxidation processes. For EC+EO process, the optimal conditions were achieved for sCOD removal at 13.27 mA cm^{-2} current density and 403 min operation time; and DOC removal was achieved at 10.83 mA cm^{-2} current density and 420 min operation time. The removal efficiency under these conditions using EC+EO method was estimated as 98.6% for sCOD removal and 95.28% for DOC removal. The time required to remove organic pollutants is correlated to the amount of current density applied to the wastewater sample.

Application of combined EC+EO has a significant potential in the treatment of canola oil refinery wastewater overcoming the issues related to biological processes. BBD was applied to understand the interaction effects between the process parameters and to optimize the treatment processes. EC+EO process was chosen as a suitable method for the removal of COD, sCOD, TOC and DOC compared to ECP process based on the removal efficiency and energy consumed in the removal of each pollutant. The study showed that EC+EO process could remove 95% of COD, sCOD and 90% of TOC and DOC under optimum conditions with energy consumed between 1.67 and 23 kWh m^{-3}. The removal rate followed a first order reaction kinetics indicating the reaction rate to be proportional to removal of the reactants under consideration.

As a future study, laboratory and full scale continuous studies of EC+EO process could be conducted to understand the economic feasibility and power consumption of the method. Additionally, fractionation of COD and its characterization in the COR wastewater could be applied to evaluate the performance efficiency of the combined process.

CHAPTER 4. ESTIMATION OF BEST TREATMENT CONDITIONS OF SUNFLOWER OIL WASTEWATER FOR ORGANIC REMOVAL USING RESPONSE SURFACE METHODOLOGY

4.1. Abstract

Combined EC+EO process was compared with ECP treatment process to treat sunflower oil refinery wastewater. The effect of applied current density, pH/H_2O_2 dosage and operation time in the removal of COD, sCOD, TOC and DOC were studied using BBD. In EC process, decrease in organic concentration was observed as the time and current density increased. The optimized conditions for EC process were achieved at pH 6.07 when a current density of 5.69 mA cm^{-2} was applied to the EC process for 18 min. The EO removed about 90% of DOC at an optimized pH of 5.27 at 11.56 mA cm^{-2} when operated for 400 min. The combined EC+ EO process was successful in removing between 90-95% of organic pollutant from the sunflower oil wastewater. The energy consumption was calculated to compare between the process efficiency of EC+EO and ECP. The reaction rate followed a first order kinetics validated with a high R^2.

4.2. Introduction

Based on United States Department of Agricultural (USDA), all over the world major oilseed (soybeans, rapeseed, sunflower seed, peanuts and cottonseed) production reached 551.31 million metric tons in 2017/2018 to meet demand (USDA, 2019). The share of sunflower seed in total production is approximately 8.65%. Sunflower oil refinery is characterized by intensive water consumption and large amounts of wastewater production (Aslan et al., 2009; Decloux et al., 2007). Wastewater generation is observed at degumming, deacidification, deodorization and

neutralization process in sunflower oil production (Sridhar et al., 2002). Acidic sunflower oil wastewater (SOW) has high organic content, oil and grease, fatty acids, sulphate, phosphate and phenolic chemicals (Aslan et al., 2009). Oily waste water causes serious problems such as toxic effect on aquatic organisms, reduced oxygen penetration and deterioration of natural photosynthetic activity when discharged into the receiving water bodies without treatment or inadequately treated (Azbar and Yonar, 2004; Seres et al., 2016).

Generally, physico-chemical (flocculation, coagulation, air flotation, skimming of oil) followed by biological processes (anaerobic and aerobic) are adopted for treatment of sunflower oil wastewater (Mkhize et al., 2000; Rajkumar et al., 2010). Although it is possible to effectively remove dissolve, suspended and colloidal pollutants using conventional physicochemical methods, the major disadvantages of these processes are the difficulties encountered in sludge management and high chemical cost (Ma et al., 2015b).

The BOD/COD ratio is one of the indicator parameters in determining whether biological processes can be used as an effective treatment alternative. The BOD/COD ratio is recommended to be > 0.6 for aerobic or anaerobic processes, while this ratio is approximately 0.2 in the edible vegetable oil industry (Un et al., 2009a). And also, inhibition of microorganisms in biological treatment is an important problem because sunflower oil wastewaters contain high amounts of lipids (Cisterna, 2017).

The wastewater collected from the local oilseed facility has an in-house treatment plant. The wastewater passes through a chemical coagulation unit using ferric chloride ($FeCl_3$) into Induced Air Floatation (IAF). The effluent from the IAF is feed into an anaerobic sludge unit (ASU). The effluent from the biological process is then discharged to a storage pond from where the effluent is directed to the city wastewater treatment plant.

To overcome the frequently encountered problems in the treatment of sunflower oil wastewaters, it requires the introduction of new approaches such as electrochemical treatment methods. Despite an extensive literature survey, to the best of our knowledge no study available to have been conducted on the application of electrochemical peroxidation and combination of electrocoagulation and electrooxidation for sunflower oil wastewater. The aim of this study is to compare between two electrochemical methods: combined EC+EO and ECP based on removal efficiency and energy consumption and optimized the operation parameters using RSM. The optimized method is further investigated for determination of reaction rate through kinetic approach.

4.3. Materials and Methods

4.3.1. Sample Sources

The sunflower refinery oil wastewater was collected from a local oil refinery located at Fargo, North Dakota. The samples were transported in high density polyethylene pails and analyzed within an hour of collection for the initial constituent concentration of the wastewater. The samples were stored at 4°C and the fresh samples were collected every three days. The initial concentration of the analyzed parameters: $17,030 \pm 950$ mg L^{-1} COD; 4923 ± 175 mg L^{-1} sCOD; 6375 ± 163 mg L^{-1} TOC; and 1324 ± 90.3 mg L^{-1} DOC.

4.3.2. Methodology

4.3.2.1. Preliminary Experiments

The treatment of sunflower refinery oil wastewater was conducted using two different operational approach: a) combined EC and EO and b) ECP. In combined EC+EO process, the raw influent wastewater was initially introduced to the EC process using Al electrodes as anode and cathode. The treated effluent from EC was then subjected to EO where BDD electrode was

used as anode and stainless steel as cathode. On the other hand, ECP process, as described above, is a hybrid process integrating coagulation and advanced oxidation process. Thus, the raw wastewater was applied ECP process using iron electrodes and H_2O_2 was gradually poured externally into the reactor. The detailed method description of the two processes were followed as described in section 3.3.3 (Sharma and Simsek, 2019). The inter-electrode distance for all the three processes were kept at 1 cm apart with an effective surface area of 109.8 cm^2. The electrodes were connected externally to a DC power supply. Due to insufficient electrical conductivity (less than 150 μS cm^{-1}), 2.0 g L^{-1} of NaCl was added to the wastewater to increase the conductivity to 4.50 mS cm^{-1}.

4.3.3. Statistical Analysis and Modelling Using RSM

The statistical analysis and modelling were performed using Design-Expert® software and the experimental range and levels of the independent variables used in EC, EO and ECP experiments are presented in Table 3.1. The generalized equation and the independent and response variables were kept the same as described in chapter 3 eq. (13).

4.3.4. Kinetic Approach

The samples were collected from the EC, EC+EO and ECP at specified time intervals to follow changes in COD, sCOD, TOC, and DOC. The removal rate was tested with respect to time using zero, first, and second order kinetics [Eqs. (14) through (16)].

4.4. Results and Discussion

4.4.1. Preliminary Experiments

4.4.1.1. Method 1- Phase 1. COD, sCOD, TOC and DOC Removal in EC Process

In EC, the time of coagulation decreased with increase in current density. Al|Al electrode combination achieved a high removal of COD concentration ranging between 90 – 93% at all

current densities (0.09, 1.8, 2.7, 3.6, 4.5, 9.1, 13.6 mAcm^{-2}) (Fig. 4.1a). In the samples tested, aluminum electrodes achieved 78 – 80% of sCOD removal at all the current densities that applied (0.91, 4.5, 9.1 and 13.66 mA cm^{-2}) (Fig. 4.1b). The Al electrodes removed between 75 and 77% of DOC (Fig. 4.1c) at all current densities in this study.

4.4.1.2. Method 1 - Phase 2. sCOD and DOC Removal in EO Process

The effluent from EC process was used as the influent of next phase of the experiment to perform EO treatment. Compared to EC process, EO process takes longer time to attain significant removal rate. The process was run for 7 h. It was observed that performing EO after EC could remove more than 80% of remaining EC effluent organic concentration (Fig 4.2a and 4.2b). However, as current density and contact time increased, the concentration of pollutants in the sample decreased. This is different from that observed in EC process where after a certain time and a certain current density, the concentration of pollutants tends to stay constant in the sample. The concentration of sCOD tend to decrease in EO process with the increase in time and current density (Fig 4.2a). At both current densities of 9.11 and 13.66 mA cm^{-2}, the sCOD removal increased from 29% in the first hour to as high as 90% at the end of 6-7 h of operation in the remaining EC effluent organic concentration. However, it was observed that the removal rate was not more than 52% at current density of 0.91 mA cm^{-2} after 7 h of operation. The DOC removal in the sunflower wastewater was achieved mainly through EO process (Fig 4.2b).

The influent DOC content in the sunflower wastewater was at an average of 557 mg L^{-1}. The breakdown of organic carbon content using EO process could yield more than 78% of the total DOC. At higher current densities, the removal of DOC showed an increase as time increased.
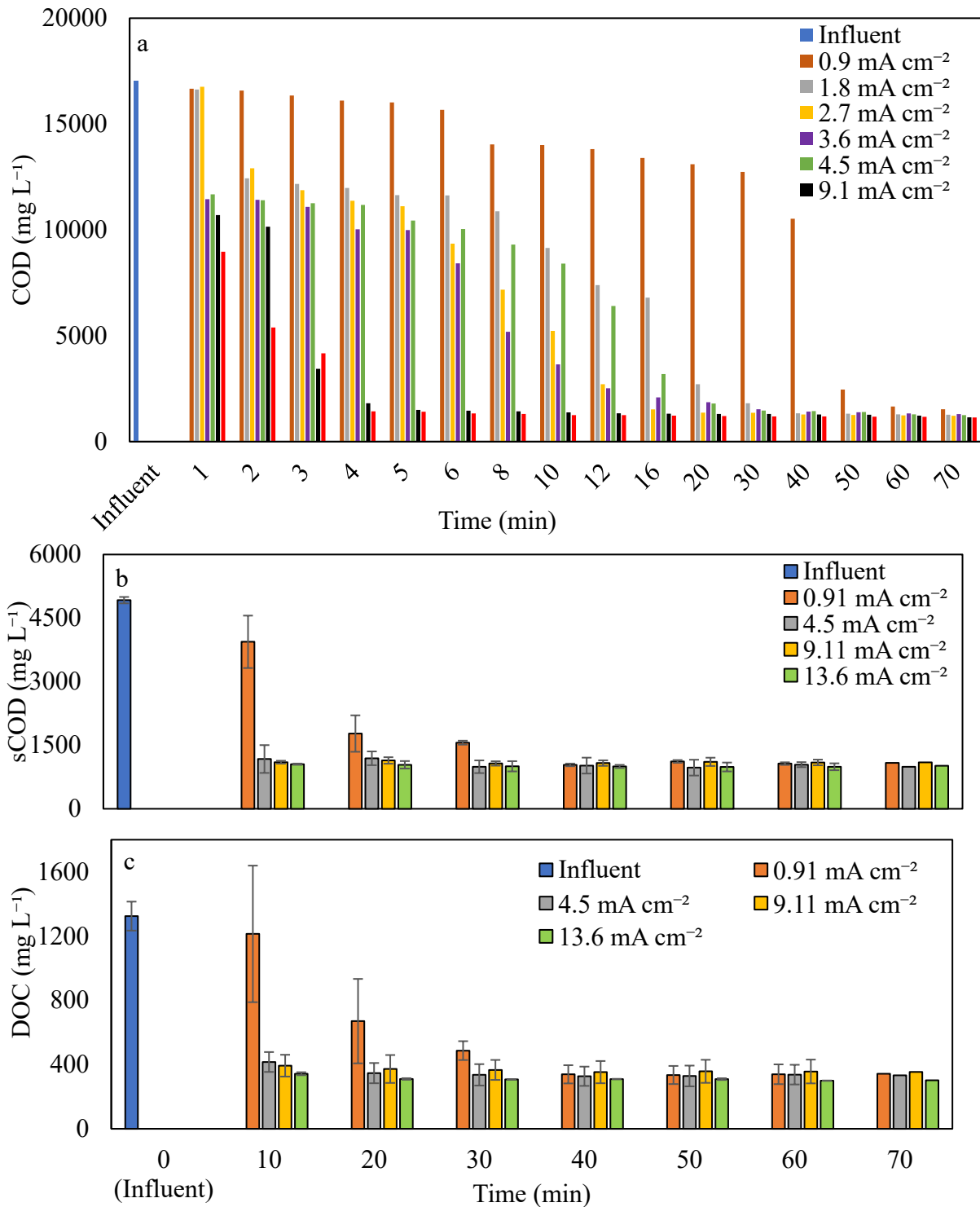
Figure 4.1. a) COD b) sCOD and c) DOC removal from sunflower oil refinery wastewater using electrocoagulation.
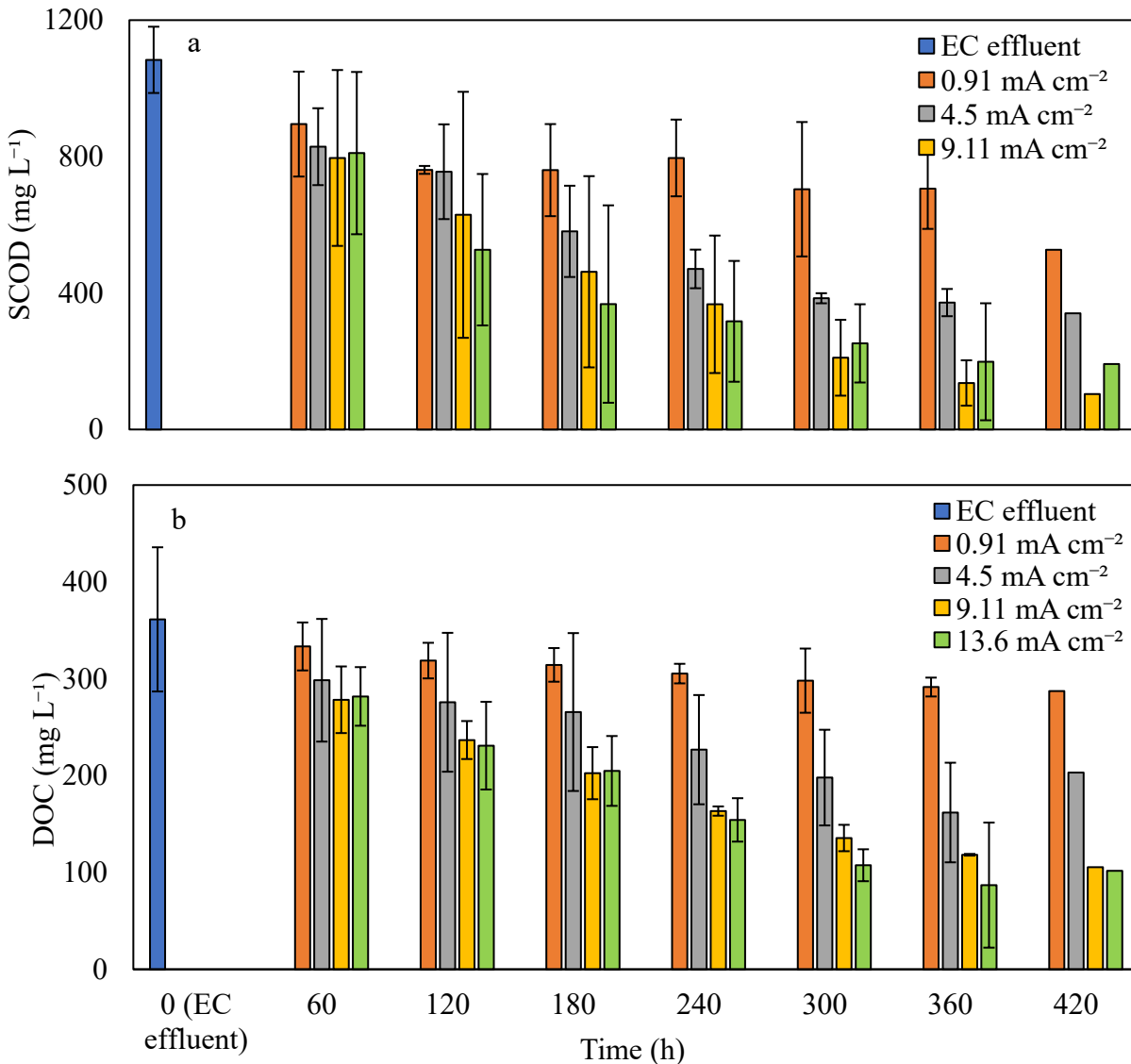
Figure 4.2. a) sCOD and b) DOC removal from sunflower wastewaters using EO process to the EC effluent.

The overall removal of sCOD using combined EC + EO in the treatment of sunflower oil refinery wastewater is presented in Fig. 4.3a. Results showed that when the system was run for 7 h, 89% of sCOD was removed at current density of 0.91 mA cm^{-2}. As the current density increased, the removal efficiency also increased. sCOD concentration reduced up to 98% and 96% of the initial concentration at current densities 9.11 and 13.66 mA cm^{-2} respectively. The initial concentration of sCOD was measured as about 4923 mg L^{-1} which was gradually degraded

to a final concentration of about 104 mg L^{-1} at 9.11 mA m^{-2} current density. The removal of DOC (Fig. 4.3b) ranged between 85 and 95% at the end of 7 h of operation in between the current densities of 0.91 and 13.66 mA cm^{-2}.
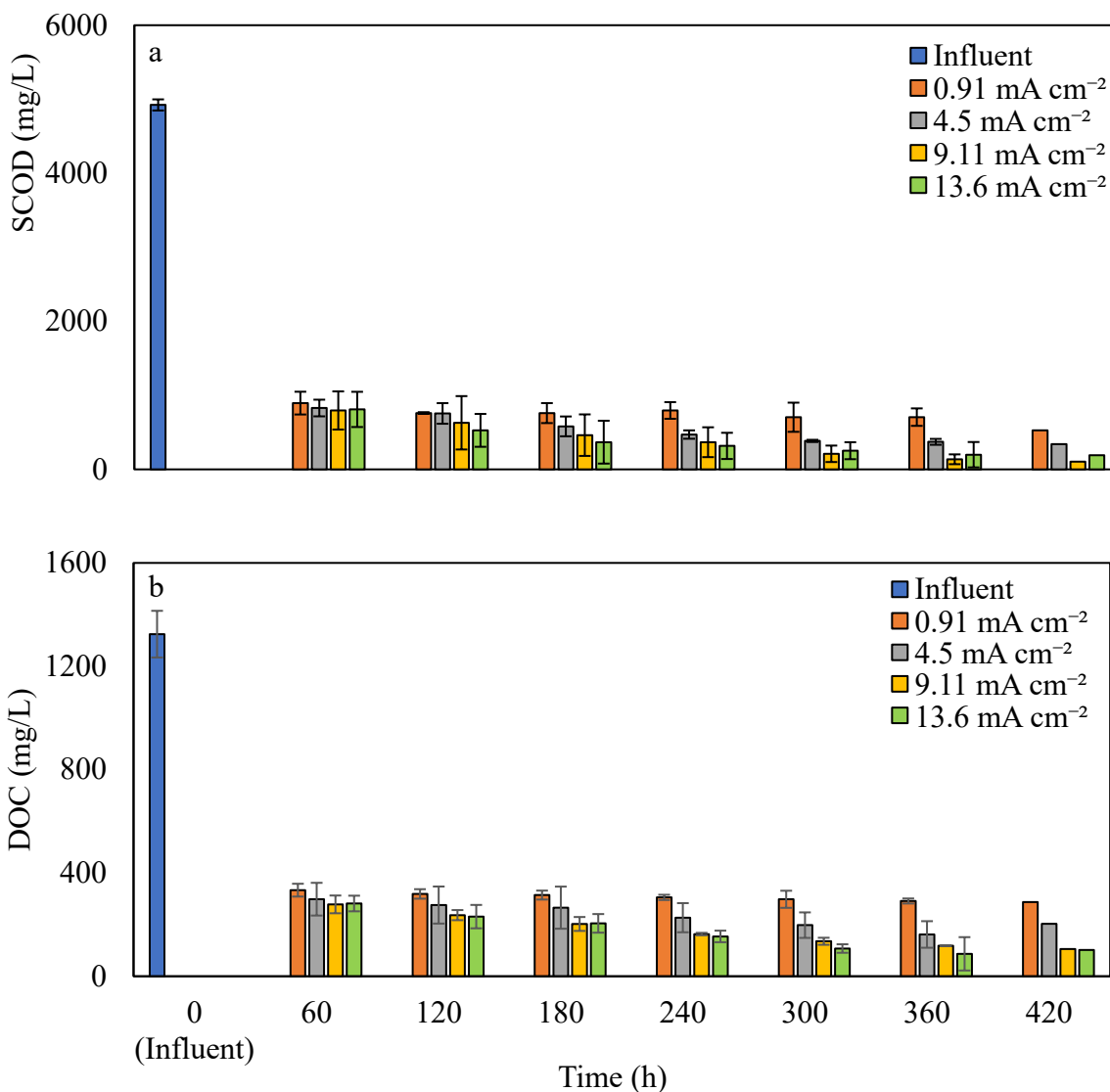
Figure 4.3. Overall removal of a) sCOD and b) DOC from sunflower wastewaters using EC+EO process.

4.4.1.3. Method 2. sCOD and DOC Removal in ECP Process

ECP process was run for 7 h and the samples were collected every hour to analyze the presence of sCOD and DOC in the effluent wastewater sample. The operation estimated a sCOD

removal of 77% at current density 0.91 mA cm^{-2} and 84% at 13.6 mA cm^{-2} at the end of 420 min.

It was observed that the removal of DOC yielded identical percentage removal ranging between

77% and 83% when the applied current density was increased from 0.91 to 13.6 mA cm^{-2}.
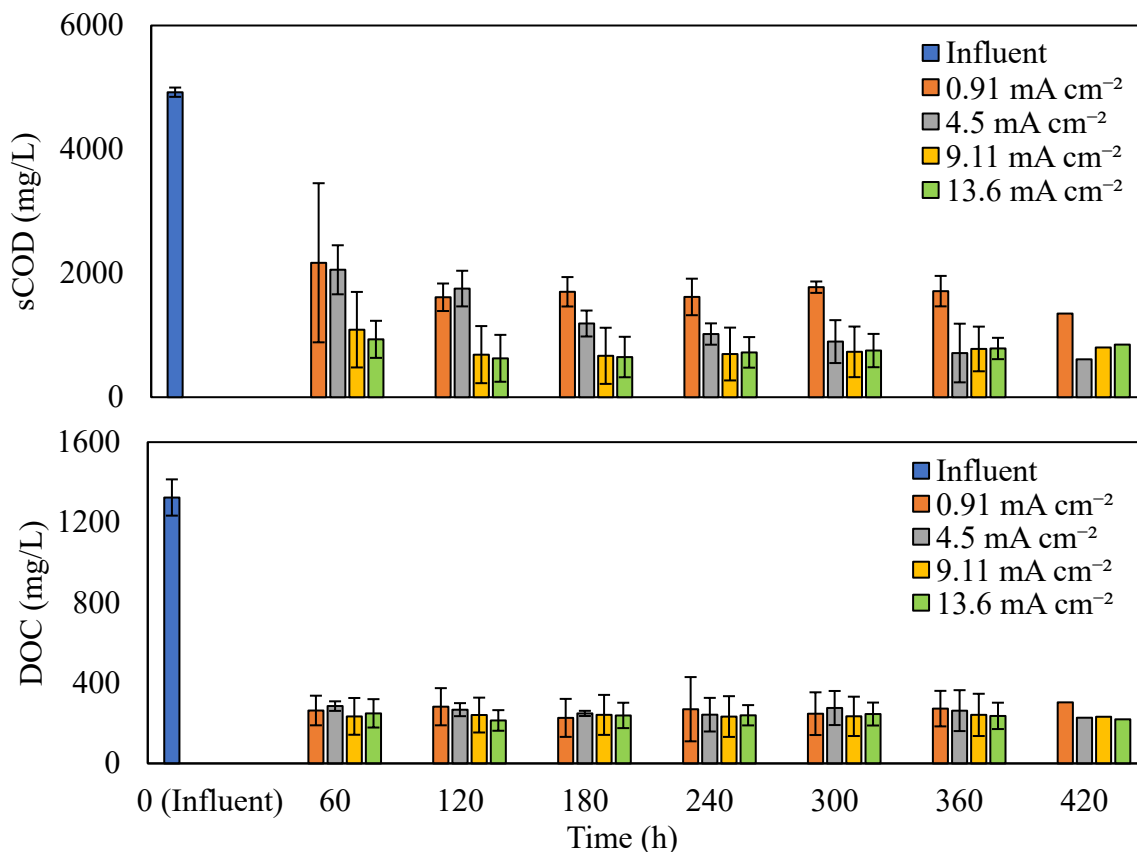
Figure 4.4. a) sCOD and b) DOC removal from sunflower refinery oil wastewater using electrochemical peroxidation.

4.4.2. Statistical Analysis and Interpretation by BBD

The data for EC, EC+EO and ECP were fitted to quadratic models and the model adequacy and the significance were tested by ANOVA as presented in Table 4.1. The low p-values (<0.05) along with F-test indicated high significance of the models in the removal of COD, sCOD, TOC and DOC. The high R^2 and adjusted R^2 indicated that the total variation could be explained by the model as well as vouched for high significance. High precision and reliability of the experiments were explained by the low coefficient of variation.

The high R^2 and adjusted R^2 explained the significance of the operation parameters current density, pH/H_2O_2 dosage and time operation in the treatment of sunflower oil wastewater. The response functions with the determined coefficients explained by independent variables are presented in Eqs. (37) through (48).

a) Removal efficiency by EC reaction:

$$COD = 91.23 - 4.25\ X_1 - 1.62\ X_2 - 3.13\ X_3 - 3.00\ X_1X_2 - 5.00 \quad (37)$$
$$X_1X_3 - 2.75\ X_2X_3 - 11.40\ X_1{}^2 - 8.15\ X_3{}^2$$

$$sCOD = 80.69 - 3.50\ X_1 - 2.13X_2 - 2.63\ X_3 - 3.75\ X_1X_2 - \quad (38)$$
$$4.25X_1X_3 - 3.00\ X_2X_3 - 10.71 - 6.96\ X_3{}^2$$

$$TOC = 85.33 - 2.88\ X_1 - 3.00\ X_2 - 2.13X_3 - 5.75X_1X_2 - 3.50 \quad (39)$$
$$X_1X_3 - 11.67\ X_1{}^2 - 3.42\ X_2{}^2 - 4.67X_3{}^2$$

$$DOC = 76.92 - 3.50\ X_1 - 2.25X_2 - 2.50\ X_3 - 3.75X_1X_2 - \quad (40)$$
$$4.25X_1X_3 - 2.75\ X_2X_3 - 10.12\ X_1{}^2 - 6.62\ X_3{}^2$$

b) Removal efficiency by EC+EO reaction:

$$COD = 95.15 - 3.63\ X_1 + 3.00\ X_2 + 1.88\ X_3 - 2.00\ X_1X_2 - \quad (41)$$
$$1.75X_1X_3 + 1.50\ X_2X_3 - 4.27\ X_1{}^2 - 4.52\ X_2{}^2$$

$$sCOD = 93.54 - 3.75X_1 + 3.12\ X_2 + 1.88\ X_3 - 2.75\ X_1X_2 - \quad (42)$$
$$2.75X_1X_3 - 3.94\ X_1{}^2 - 5.19X_2{}^2$$

$$TOC = 92.85 - 4.25\ X_1 + 3.00\ X_2 + 1.50\ X_3 - 1.75X_1X_2 - \quad (43)$$
$$2.75X_1X_3 - 3.23\ X_1{}^2 - 4.23X_2{}^2$$

$$DOC = 91.00 - 3.25X_1 + 2.50\ X_2 + 1.50\ X_3 - 2.25X_1X_2 - \quad (44)$$
$$2.75X_1X_3 - 3.00\ X_1{}^2 - 4.00\ X_2{}^2$$

c) Removal efficiency by ECP reaction:

$$\text{COD} = 89.67 - 5.50\ X_1 - 2.38\ X_2 - 4.13X_3 - 3.50\ X_1X_2 - 5.00$$

$$X_1X_3 - 10.96\ X_1{}^2 - 3.21\ X_2{}^2 - 8.21\ X_3{}^2 \tag{45}$$

$$\text{sCOD} = 88.67 - 5.50\ X_1 - 2.00\ X_2 - 4.25\ X_3 - 5.00\ X_1X_2 -$$

$$6.00\ X_1X_3 - 11.08\ X_1{}^2 - 4.08\ X_2{}^2 - 9.58\ X_3{}^2 \tag{46}$$

$$\text{TOC} = 82.15 - 5.50\ X_1 - 1.75\ X_2 - 3.75\ X_3 - 2.25\ X_1X_2 -$$

$$5.25X_1X_3 - 9.27\ X_1{}^2 - 8.77\ X_3{}^2 \tag{47}$$

$$\text{DOC} = 80.62 - 5.50X_1 - 1.63\ X_2 - 3.38\ X_3 - 2.25\ X_1X_2 -$$

$$5.25X_1X_3 + 2.00\ X_2X_3 - 8.83\ X_1{}^2 - 8.08\ X_3{}^2 \tag{48}$$

The models satisfy for EC, EC+EO and ECP processes as the predicted versus the experimental values approximates along a straight line with high correlation as presented in fig. 4.5(a) through (l).

4.4.3. Effects of Variables on COD, sCOD, TOC, and DOC Removal Efficiency Through Response Surface Plotting

The response surface contour plots of the second-order quadratic models with one variable kept at the central level and the other two variables within the experimental ranges can be used to demonstrate the effects of independent parameters (process variables) on response.

4.4.3.1. Effect of Initial pH/H₂O₂ Dosage (X₁) and Current Density (X₂)

The effect of pH/H_2O_2 dosage (X_1) and current density (X_2) on COD, sCOD, TOC, and DOC removal efficiency illustrated in Fig 4.6. pH controls aluminum floc species (monomeric or polymeric) during the EC process. It is observed from Fig. 4.6 a, d, f and h that in EC process the most effective pH range is between 5.5 and 6.5 at all current densities tested.

Based on our experiments, increasing the pH up to 6, the removal efficiency for all monitored parameters was increased. The predominant anodic dissolution hydrolysis products

are $Al(OH)_2^+$ and $Al(OH)^{2+}$ for in range pH 5-6. After that point, EC performance adversely affected by increasing pH. When the process was run for 20 min at an initial pH concentration of 5.5 to 6.5, almost all the current densities tested achieved nearly 80% COD and TOC removal and 75% of DOC and sCOD degradation. The overall EC+EO process achieved a removal of 95% of each of COD, sCOD, TOC and DOC in the range of 9.7 to 13.6 mA cm^{-2}. However, from the fig. 4.7. a, d, f and h, the most effective pH achieving maximum removal is between 5 and 5.5. From the findings of the study, it was perceived that both EC using Al electrodes and EO using BDD could be operated successfully at pH between 5 and 6. Previous studies have concluded that Al electrodes achieved better removal efficiency at pH between 5.5 and 6 when used in EC process (El-Naas et al., 2009; Kobya et al., 2003).

The anodic dissolution in the EC and the Fe^{2+} formation in the ECP are realized as a function of the current density. Choosing the most appropriate value for current density which has an undeniable effect on operating costs in electrochemical processes is of great importance for sustainability.

Table 4.1. ANOVA results for the quadratic models for sunflower oil wastewater.

Response (Y, %)	Source	EC					EC+EO					ECP				
		SS	DF	MS	F-value	p-value	SS	DF	MS	F-value	p-value	SS	DF	MS	F-value	p-value
COD	Model	1094.13	8	136.77	50.44	<0.0001	376.50	8	47.06	53.98	<0.0001	1229.77	8	153.72	29.59	0.0003
	Residual	16.27	6	2.71			5.23	6	0.8718			31.17	6	5.19		
	Lack of Fit	14.27	4	3.57	3.57	0.2308	4.56	4	1.14	3.42	0.2387	28.50	4	7.13	5.34	0.1638
	Pure Error	2.00	2	1.0000			0.6667	2	0.3333			2.67	2	1.33		
	Total	1110.40	14				381.73	14				1260.93	14			
		R^2 =0.9853 Adj R^2=0.958 C.V.%=2.04					R^2 =0.9863 Adj R^2=0.9680 C.V%=1.03					R^2 = 0.9753 Adj R^2=0.9423 C.V.%=2.93				
sCOD	Model	923.26	8	115.41	25.02	0.0005	427.01	7	61.00	34.64	<0.0001	1424.57	8	178.07	39.33	0.0001
	Residual	27.67	6	4.61			12.33	7	1.76			27.17	6	4.53		
	Lack of Fit	25.67	4	6.42	6.42	0.1393	10.33	5	2.07	2.07	0.3576	24.50	4	6.13	4.59	0.1867
	Pure Error	2.00	2	1.0000			2.00	2	1.0000			2.67	2	1.33		
	Total	950.93	14				439.33	14				1451.73	14			
		R^2 = 0.9709 Adj R^2=0.9321 C.V.%=3.01					R^2 = 0.9719 Adj R^2=0.9439 C.V.%=1.50					R^2 = 0.9813 Adj R^2=0.9563 C.V.%=2.82				
TOC	Model	929.73	8	116.22	55.05	<0.0001	375.50	7	53.64	36.70	<0.0001	1074.00	7	153.43	31.84	<0.0001
	Residual	12.67	6	2.11			10.23	7	1.46			33.73	7	4.82		
	Lack of Fit	12.00	4	3.00	9.00	0.1025	9.56	5	1.91	5.74	0.1550	31.73	5	6.35	6.35	0.1417
	Pure Error	0.6667	2	0.3333			0.6667	2	0.3333			2.00	2	1.0000		
	Total	942.40	14				385.73	14				1107.73	14			
		R^2 = 0.9866 Adj R^2=0.9686 C.V.%=1.94					R^2 = 0.9735 Adj R^2= 0.947 C.V.%=1.36					R^2 = 0.9695 Adj R^2=0.9391 C.V.%=3.03				
DOC	Model	856.94	8	107.12	23.75	0.0005	289.93	7	41.42	41.42	<0.0001	997.16	8	124.64	40.55	0.0001
	Residual	27.06	6	4.51			7.00	7	1.000			18.44	6	3.07		
	Lack of Fit	25.06	4	6.26	6.26	0.1424	6.33	5	1.27	3.80	0.2214	15.78	4	3.94	2.96	0.2683
	Pure Error	2.00	2	1.0000			0.6667	2	0.3333			2.67	2	1.33		
	Total	884.00	14				296.93	14				1015.60	14			
		R^2 = 0.9694 Adj R^2=0.9286 C.V.%=3.12					R^2 = 0.9764 Adj R^2=0.9529 C.V.%=1.15					R^2 = 0.9818 Adj R^2=0.9576 C.V.%=2.45				
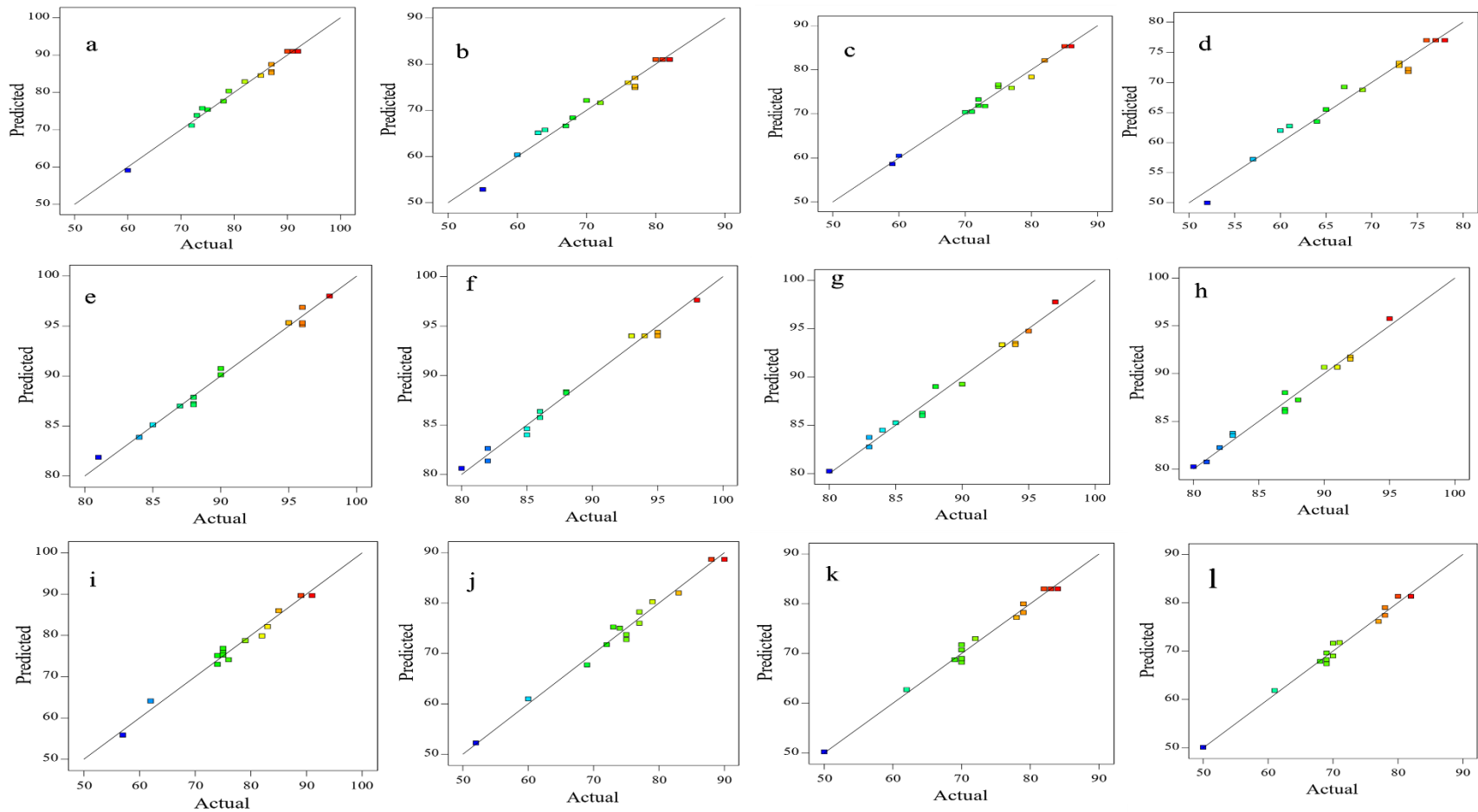
Figure 4.5. Experimental vs predicted values from RSM describing removal of a) COD, b) sCOD, c) TOC, and d) DOC using electrocoagulation; e) COD, f) sCOD, g) TOC, and h) DOC using electrocoagulation + electrooxidation ; and i) COD, j) sCOD, k) TOC, and l) DOC using electrochemical peroxidation

The change in current density has limited effect on the treatment of sunflower wastewater in EC and ECP processes, whereas it is the most influential process variable on treatment performance in EC + EO processes.

In the ECP process, the removal of COD, sCOD and DOC was impacted by the change in current density and H_2O_2 dosage applied to the process. The determination of the optimal H_2O_2 dose in the ECP is of great importance due to H_2O_2 is the main responsible reagent that generates OH radicals. Considering the study range of the independent variables determined as a result of the preliminary experimental studies, it was determined that the addition of the reagent after the 15 ml L^{-1} H_2O_2 dose did not have a positive effect on the COD, sCOD, TOC, and DOC removal efficiency. The removal is effective between 13 and 15 ml L^{-1} when the current density is applied between 5.8 and 9.7 mA cm^{-2}. More than 85% removal was achieved for COD, sCOD and DOC when the process was run for 300 min (Fig. 4.8 a, c, and f).

4.4.3.2. Effects of Current Density (X₂) and Time (X₃)

The effect of interaction between current density and time did not have a significant role in the removal of sCOD, TOC and DOC. Although COD removal in the EC+EO process shows a dependence in the interaction, yet, the range of applied current density and time of operation is significantly wide. The effect of current density (X_2) and time (X_3) on COD, sCOD, TOC, and DOC removal efficiency are given in Fig B.2. As seen Fig B.2, for the maximum efficiency of all parameters, independent of the treatment technique, the electrolysis time of about 20 min is sufficient. Compared to alternative treatment methods, the relatively short duration of electrolysis should be considered as a significant advantage. These applications can significantly reduce footprint and cost of treatment.

The results showed that increase in current density decreases the time required to remove the organics. However, the percentage removal remains consistent at all current densities applied. The ECP process also yielded similar results and the removal was comparatively lower than that of EC+EO process.

Previous study conducted by Sharma and Simsek (2019) investigating the effect of current density and time in the canola oil refinery wastewater using EC+EO and ECP process achieved similar conclusions. It was observed that increase in applied current density significantly decreases the time of operation maintaining a consistent removal.

4.4.3.3. Effects of Initial pH/H$_2$O$_2$ Dosage and Time

As both X$_1$ (initial pH for EC and EC+EO and H$_2$O$_2$ dosage for ECP) and X$_3$ (electrolysis time) approach the center point (coded value is "0"), an increase in treatment efficiency is observed. Both EC+EO and ECP processes, the removal of COD, sCOD, TOC and DOC was the most effective when the time operated was between 240 and 360 min and current density applied at 9.05 mA cm^{-2}. It is observed from Fig 4.6 b, e, g and i, EC process is sufficient when applied between 15 and 22 min. pH range of 5-6 could sufficiently remove between 90 and 95% of COD, sCOD, TOC and DOC from the sunflower oil wastewater (Fig. 4.7 b, e, g and i). H$_2$O$_2$ dosage and time had a positive effect on the removal process. It was observed that application beyond 15 ml L^{-1} of H$_2$O$_2$ did not have influential impact on the removal.

4.4.4. Optimization of Process Parameters and Method Selection Through Economic Comparison

The model calculated the optimized parameters for each of EC, EC+EO and ECP processes based on the effect of current density, pH/H$_2$O$_2$ dosage and time of operation in the removal of COD, sCOD, TOC and DOC in the removal of sunflower oil wastewater. The

optimized conditions for EC process was yielded to be at pH 6.07 and current density of 5.69 mA cm^{-2} operated for 18 min. The effluent from the EC reactor were then fed into the EO reactor. Based on its removal characteristics, the optimized conditions attained were at pH 5.27 at 11.56 mA cm^{-2} for 400 min. The operation parameters of ECP process was simultaneously optimized to compare the treatment efficiency of both EC+EO and ECP processes. The BBD yielded an optimized H$_2$O$_2$ dosage of 14.2 ml L^{-1} at an applied current density of 7.56 mA cm^{-2} to be run for 278 min. Separate experiments were conducted to validate the prediction capability of the models (Table 4.2).

Table 4.2. Predicted versus actual values at optimal conditions and energy consumed for EC+EO and ECP.

Response	Electrocoagulation			Electrooxidation + Electrocoagulation			Electrochemical Peroxidation		
	Predicted (%)	Actual (%)	Energy consumption (kWh m^{-3})	Predicted (%)	Actual (%)	Energy consumption (kWh m^{-3})	Predicted (%)	Actual (%)	Energy consumption (kWh m^{-3})
COD	91.1	90.0	0.16	94.3	95.6	2.47	89.8	86.2	1.85
sCOD	81.1	78.8	0.64	92.8	93.1	8.76	89.0	85.2	6.42
TOC	85.4	73.7	0.53	92.4	93.2	6.76	83.4	81.3	5.18
DOC	77.1	72.1	2.60	89.9	90.1	33.68	81.8	80.0	25.12

The energy consumed in the removal of COD, sCOD, TOC and DOC using EC+EO and ECP processes are presented in Table 4.2. The EC process consumed between 0.16 and 3 kWh m^{-3} in the removal of organic pollutants at a current density of 5.69 mA cm^{-2} when operated for 18 min. The combined process of EC and EO together consumed between 2.47 and 33.68 kWh m^{-3}. The maximum energy was consumed when the process removed DOC from the wastewater sample. From the degradation rate reported for DOC, it could be observed that the initial concentration of DOC is significantly less compared to the total COD and TOC.
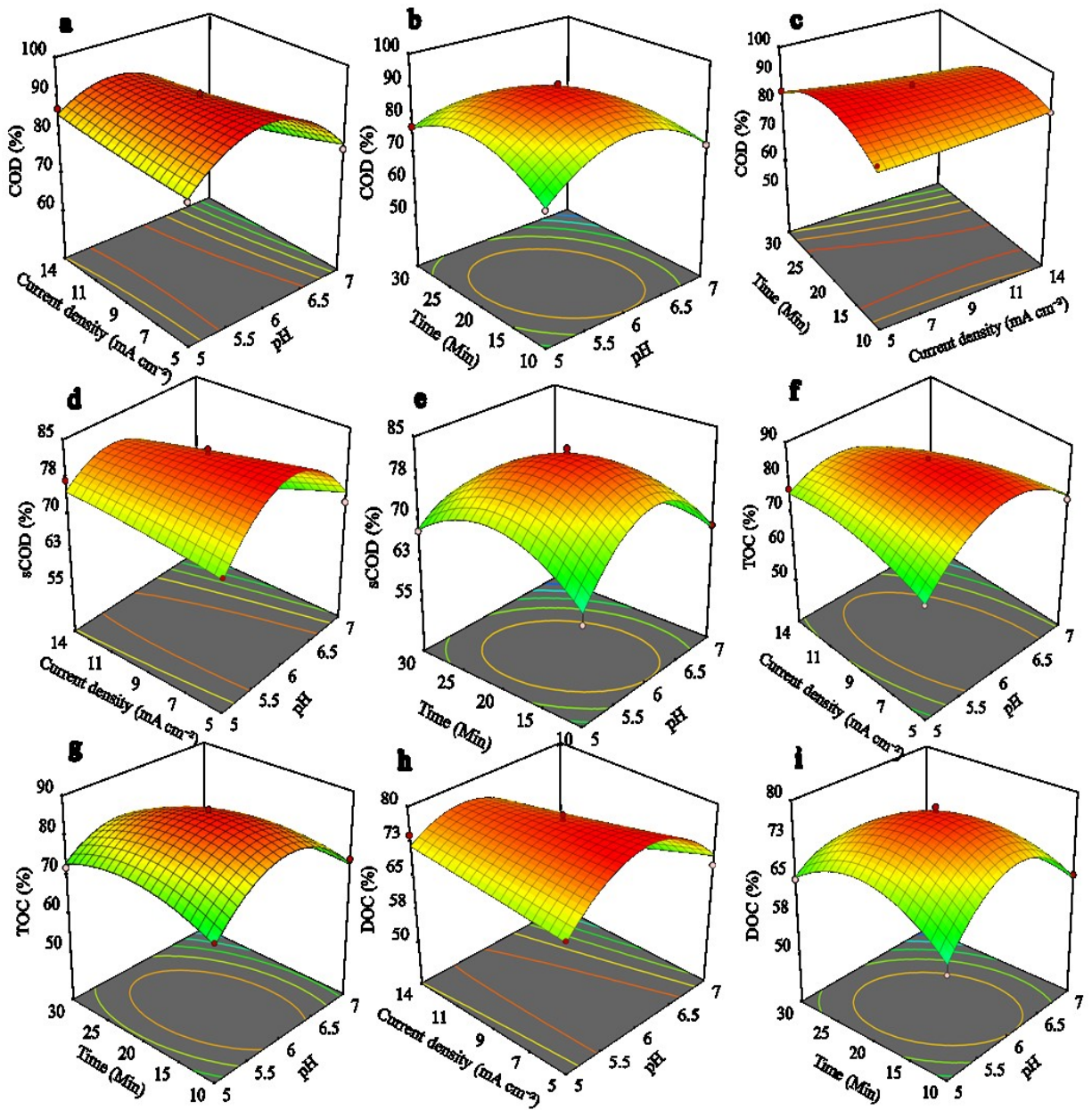
Figure 4.6. Interaction effects of current density, pH and time in the electrocoagulation process.
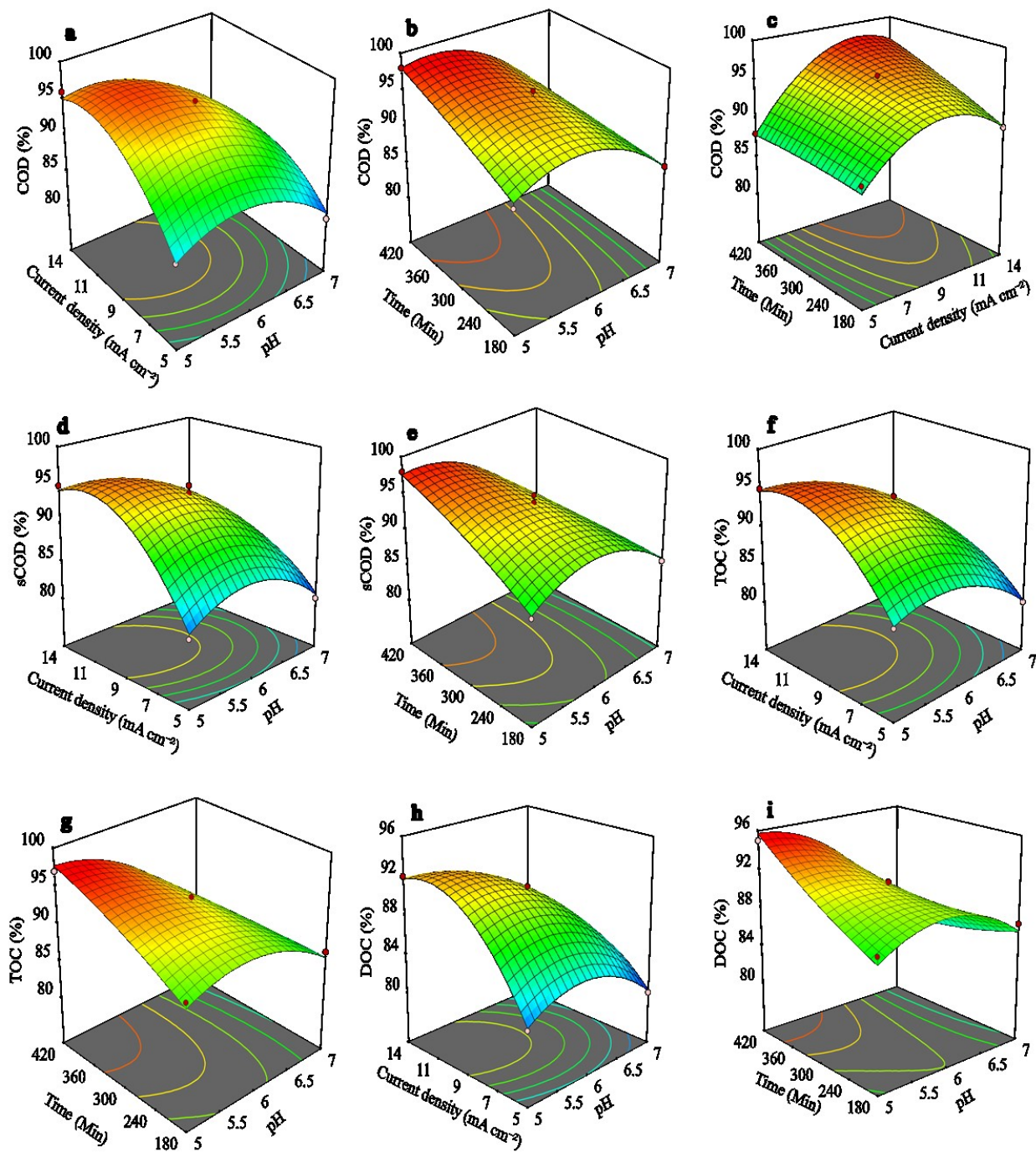
Figure 4.7. Interaction effects of current density, pH and time in the electrocoagulation + electrooxidation process.
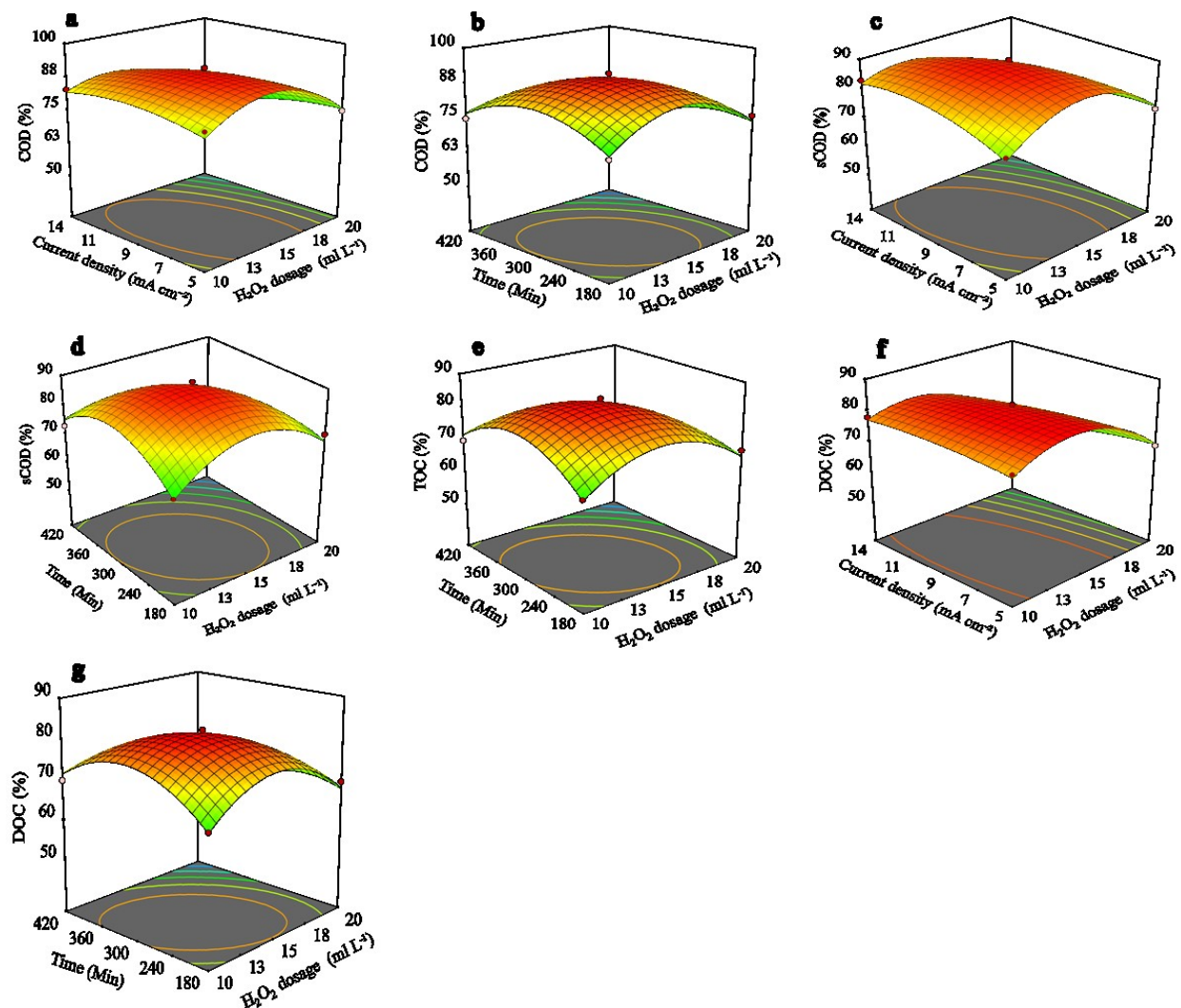
Figure 4.8. Interaction effects of current density, H$_2$O$_2$ dosage and time in the electrochemical peroxidation process.

Moreover, the removal of remaining DOC concentration using EO was slow compared to that of EC. The low removal of DOC could be accorded to the presence of refractory organic compounds in the wastewater sample. ECP process yielded an energy consumption between 1.85 and 25.12 kWh m^{-3} when operated for 278 min. The ECP process was less efficient in the treatment compared to EC+EO considering the percentage degradation and time of operation. Also, the iron electrodes in the ECP process was required to replace every 2-3 days after turning on the process for 7 h a day. Whereas, BDD electrodes in the EO process could be used over and

over without any loss in its effectivity and shape for the entire period of research. A sample of electrode passivation and deformation is shown in Fig. 4.9. Thus, EC+EO was considered as the preferred process compared to that of ECP.

4.4.5. Reaction Kinetics

The degradation rate of COD, sCOD, TOC and DOC were calculated using the kinetic models described in 3.3.7. It was evident from the plots that the removal rate follows a first order kinetic model presented in Fig. 4.10a and b. The reaction rate constant, k, was obtained from the slope of each response variable COD, sCOD, TOC and DOC and the R^2 was noted in Table 4.3.
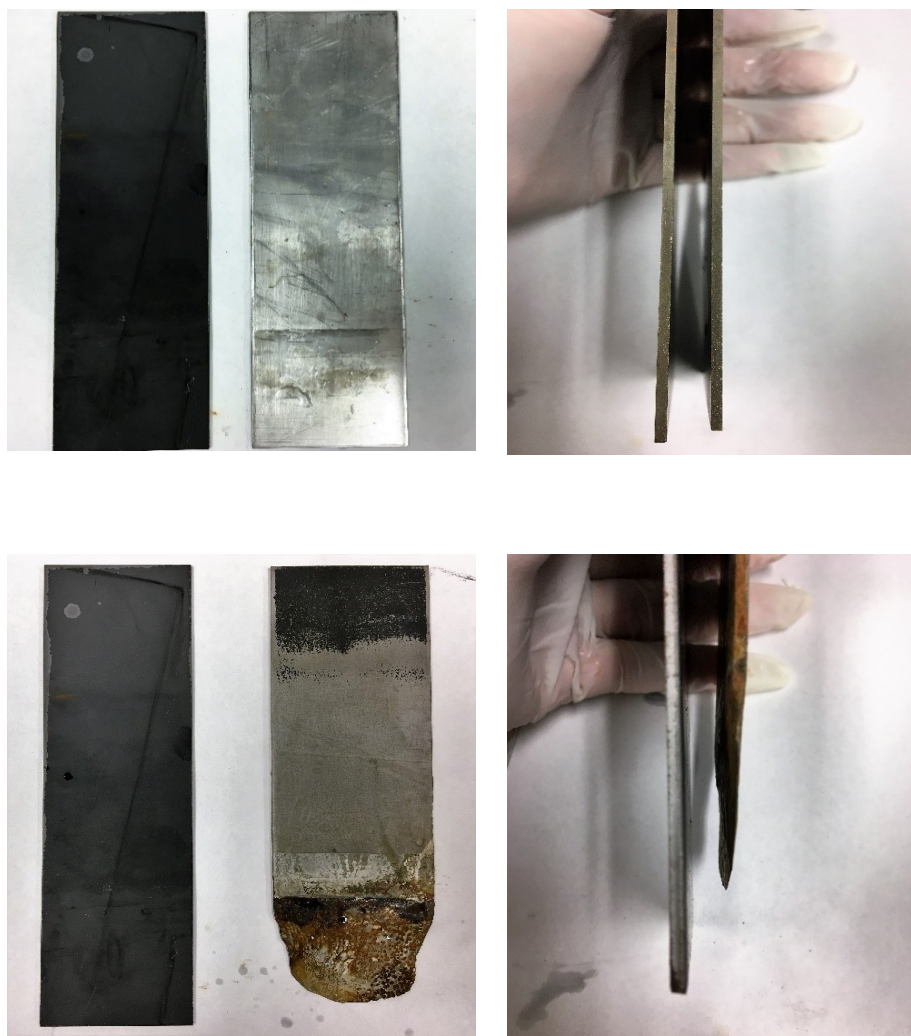
Figure 4.9. Impact of the stress on iron and boron doped diamond electrodes during electrochemical peroxidation and electrooxidation process.

The goodness of fit of the models could be accounted from the high R^2 values and the residual concentration fits approximately a straight line. Thus, the proportionality of the concentration degradation to the reaction rate could be conferred from the model.
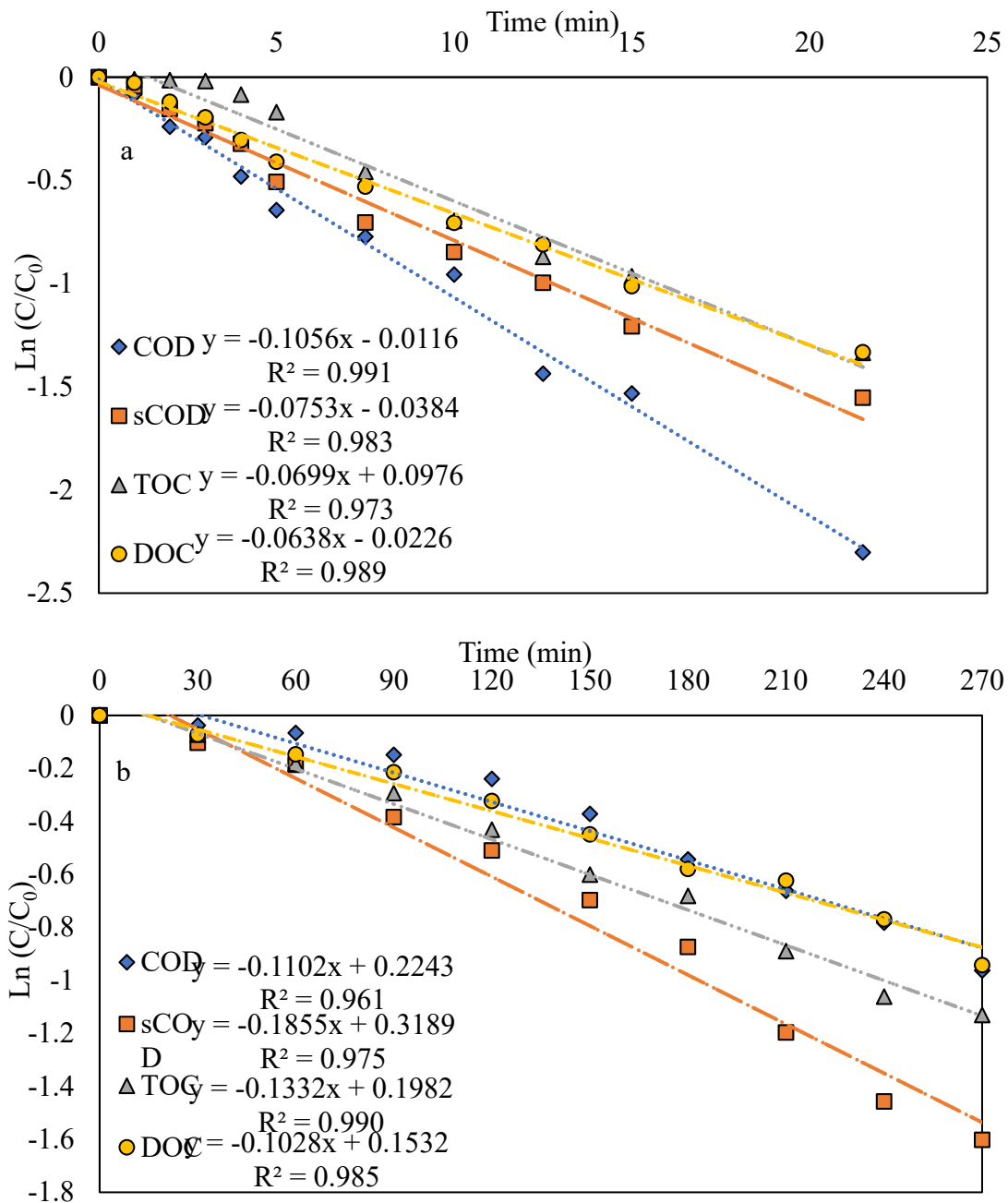
Figure 4.10. Linearized first-order kinetic model for a) electrocoagulation process and b) electrooxidation process on the treatment of COD, sCOD, TOC, and DOC.

Table 4.3. Values of first-order kinetic constant, k and coefficient of determination R2 for the responses of EC and EO processes under optimum conditions.

Response	EC		EO	
	$k\ (min^{-1})$	R^2	$k\ (min^{-1})$	R^2
COD	0.106	0.991	0.11	0.961
sCOD	0.075	0.983	0.186	0.975
TOC	0.069	0.973	0.133	0.990
DOC	0.064	0.989	0.103	0.985

4.5. Conclusion

The sunflower oil refinery wastewater was treated using combined EC+EO and ECP processes to remove wastewater derived organic pollutants. The effect of various parameters current density, pH/H_2O_2 dosage and time of operation were studied using BBD and the process parameters were optimized. It was observed that EC+EO process is a suitable treatment method compared to ECP when the optimized parameters are maintained. The optimized conditions for EC process was found to be at pH 6.07, applied current density of 5.69 mA cm^{-2} and operation time of 18 min. Operating the EC process under these conditions achieved more than 75% of organics degradation. The treated effluent from EC were fed into the EO process and removed 90 – 95% under optimized condition of pH 5.27 at 11.56 mA cm^{-2} for 400 min. The energy consumption of both EC+EO and ECP processes were calculated. The removal rate of EC+EO process follows a first order kinetics and the model was validated with high R^2.

CHAPTER 5. SUGAR BEET INDUSTRY PROCESS WASTEWATER TREATMENT USING ELECTROCHEMICAL METHODS AND OPTIMIZATION OF PARAMETERS USING RESPONSE SURFACE METHODOLOGY

5.1. Abstract

Sugar production is a water intensive process that produces a large amount of wastewaters with high concentration of COD, mostly consists of organic carbon compounds. Conventional treatment methods are limited to provide the necessary treatment of effluent COD to meet the regulatory limits prior to discharge. The treatment performance of EO and ECP for organic removal were investigated in a laboratory scale study. The experimental conditions were optimized for both EO and ECP using BBD and the models provided highly significant quadratic models for both treatment methods. The effects of pH, H_2O_2 dosage, current density, and operation time were investigated using BBD. The results showed that EO could remove 75% of organics at optimum conditions of pH 5.3; current density of 48.5 mA cm^{-2}; and operation time of 393 min. The predicted values were in reasonable agreement with measured values. ECP could remove total and soluble COD and total and dissolved organic carbon by 65, 64, 66, and 63%, respectively at optimum conditions of H_2O_2 dosage of 21 ml L^{-1}; current density of 48 mA cm^{-2}; and operation time of 361 min. The methods were compared based on removal efficiency and energy consumption during operation.

5.2. Introduction

Wastewaters generated from sugar beet processing industry contain high concentration of organic compounds, especially soluble and insoluble polysaccharides, which produced by

microbes presence in the system (Guven et al., 2009; Lettinga and Pol, 1991; Matsuyama et al., 1999). Similarly, the composition of sugar beet wastewater contains pathogens, crop pests, and pesticides residue (Guven et al., 2009). Since the compositions of sugar beet wastewater meet the nutritional needs of microbes, the microbes proliferate and cause environmental problems.

The recent acceptable method in the treatment of sugar industry wastewater involves filtration, sedimentation of solids, and load equalization followed by combined anaerobic and aerobic biological treatment (Farhadian et al., 2007; Guven et al., 2009). Typically, this chain of treatment process is effective in reduction of COD from sugar beet industrial wastewater. However, the process requires equalization ponds or lagoons that cause algal proliferation, oxygen depletion, unpleasant odor emissions, and ultimately cause groundwater contamination (Farhadian et al., 2007; Perendeci and Sural, 2004; Perendeci et al., 2013). Over the recent decades, advanced technologies involving anaerobic digestion such as upflow anaerobic fixed bed (UAFB) (Farhadian et al., 2007), upflow anaerobic sludge blanket (UASB) (Lettinga and Pol, 1991), anaerobic downflow stationary fixed film (DSFF) (Pradeep et al., 2014), aerated fixed film (AFF) (Hamoda and Al-Sharekh, 1999), and anaerobic batch reactors were considered to be preferred methods of sugar beet wastewater treatment. Yet, economic commercialization of these processes is yet to be feasible due to large land requirements, by-product formation, and high operational costs.

The local sugar industry American Crystal Sugar Company (ACSC) in Moorhead, Minnesota, USA produces about 3 billion pounds of sugar every processing season that begins on August and ends in May the following year. The total wastewater production during a season accounts to 1.5 – 2 million gallons per day (MGD). The industry currently has an in-house treatment facility that runs on biological process and stores excess wastewater on storage and

equalization ponds until fit to discharge to the local water bodies. The factory wastewater passes through a primary clarifier and flows to large covered storage ponds. The ponds serve as an influent controller into the treatment system and storage for wastewater. It also allows time for chemical degradation to takes place which in turn reduces the organic load being pumped into the treatment system. The wastewater from the pond flows through a heat exchanger into the anaerobic reactor for biological treatment. The treated wastewater then flows through a lamella clarifier and separating the solids from the wastewater. The solids are recycled back to the anaerobic reactor for sustaining the microbial population. The clarifier overflow flows into an aerobic reactor for further treatment and then flows into a final clarifier. The effluent from the final clarifier is transported to a holding pond from which the treated wastewater is discharged to the local river from time to time. This treatment system is referred to as the Anamet system (Perendeci et al., 2013). Typically, this chain of treatment process is effective in reduction of COD from sugar beet industrial wastewater. However, the process requires equalization ponds or lagoons that cause algal proliferation, oxygen depletion, unpleasant odor emissions, and ultimately cause groundwater contamination (Farhadian et al., 2007; Perendeci and Sural, 2004; Perendeci et al., 2013).

To overcome the limitations posed by the biological processes, researchers investigated the feasibility of electrochemical treatment in the reduction of COD in sugar beet industrial wastewater (Guven et al., 2009; Hajiagha et al., 2019; Leentvaar et al., 1979). Although ample studies have been conducted using electrochemical treatment in cane sugar industry wastewaters, only a handful of studies available in sugar beet wastewaters. In 1979, Leentvaar et al. conducted jar tests using chemical coagulants on aerated lagoon effluent of sugar beet wastewater to investigate the pH range, coagulant doses, and its effect on the reduction of COD. The study

reported that varying pH of the coagulant can significantly impact the removal of COD. It was concluded that coagulation/flocculation combined with anaerobic digestion could be a successful pre-treatment process for beet sugar wastewater.

Recently, advanced oxidation processes (AOPs) have shown evidence in its ability to degrade and mineralize organics when applied to different types of industrial wastewaters (Ghatak, 2014). AOPs generate hydroxyl radical (OH·) which is one of the highly reactive radical species known. OH· in the sample reacts rapidly with organic pollutants in the wastewater and transforms the organics into harmless products (Ghatak, 2014; Martinez-Huitle and Ferro, 2006). AOPs involving chemical oxidation processes include electrooxidation (EO) (Martinez-Huitle and Ferro, 2006) and electro-chemical peroxidation (ECP) (Brillas et al., 2009) and are broken down and transformed organic contaminants into carbon dioxide, water, and inorganics through mineralization. These processes are encouraged for its versatility, energy efficiency, amenability to automation, environmental compatibility, and cost effectiveness analysis (Martinez-Huitle and Ferro, 2006; Rajeshwar et al., 1994). EO and ECP processes have been widely applied in the removal of COD and total organic carbon (TOC) from the wastewaters (Barbosa et al., 2016; Hu and Li, 2011a; Ren et al., 2016). The reaction mechanism involved in EO and ECP process is described in Chapter 2, section 2.4.

AOPs such as EO and photo-Fenton oxidation processes were studied by Guven et al. and Hajiagha et al., respectively in the treatment of sugar beet industrial wastewater. EO was applied on simulated sugar beet factory wastewater to study the effect of waste concentration, applied voltage, and electrolyte concentration in the removal of COD (Guven et al., 2009). Fe, carbon, and stainless-steel electrodes were tested as electrode materials and the performance of COD removal was reported as 59.42%, 15.15%, and 42.86%, respectively after 8 h of operation. The

study yielded 79.7% of COD removal under optimum conditions of 12 V and 8 h of reaction time. Similarly, Hajiagha et al. (2019) worked on the removal of COD and color by combining photo-Fenton oxidation with coagulation process from sugar beet industrial wastewater. The group (Hajiagha et al., 2019) studied the effect of pH, time of operation, and Fenton's reagent dosage to determine the treatment efficiency. The wastewater sample was exposed to UV radiation followed by chemical coagulation. The coagulated effluent was allowed to settle for 2 h and the supernatant was measured for COD and color. The process achieved 59 and 83.9% COD and color reduction, respectively in a reaction time of 30 min.

Guven et al. (2009) and Hajiagha et al. (2019) applied CCD for the optimization of process parameters in the treatment of sugar beet wastewater using AOPs. Although studies using AOPs were conducted for sugar beet wastewater, to the best of our knowledge, no study is available to investigate process performance of EO using BDD electrode and ECP. This study presents a competitive comparison between EO and ECP in the treatment of sugar beet wastewater through process optimization using BBD and determining the reaction rate through kinetic approach.

5.3. Materials and Methods

5.3.1. Sample Sources

Sugar beet wastewater samples were collected from the primary effluent location in American Crystal Sugar Company at Moorhead, MN, USA. Samples were transported in high density polyethylene pails and analyzed within an hour of collection to determine the initial concentrations of wastewater constituents. The remaining samples were stored at 4 °C to use in next three days and fresh samples were collected in every three days. During the course of study, the effluent has been analyzed at different times over a period of two campaign seasons. The

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effluent contains high concentration of soluble organics. The experiments were completed in 24 months and, hence the effluent concentrations of the parameters during these times were fluctuated. The initial concentrations of the parameters were; 15673 ± 1790 mg L^{-1} COD, 13027 ± 363 mg L^{-1} sCOD, 7072 ± 128 mg L^{-1} TOC, 6460 ± 50 mg L^{-1} DOC.

5.3.2. Experimental Set-up

The treatment of sugar beet wastewater was carried out using two different AOPs; a) EO and b) ECP process. These two methods were compared based on the removal efficiency of organics presented in the wastewater and the effect of the operational parameters in the removal process. In this study, the experiments were carried out in 1.5 L plexiglass reactors with a working volume of 1 L. Different types of metal plate electrodes were used in EO and ECP processes, however the dimension and effective area for all the electrodes used in the entire study remained the same. The reactor was equipped with two parallel rectangular electrodes: one anode and one cathode with dimension of 12 cm length ×6.5 width cm ×2 mm thickness with an effective surface area of 109 cm^2. The electrodes were cleaned with acetone after each run and were replaced with a new electrode from time to time to maintain the same surface area throughout the study. The electrodes were connected externally to a DC power supply (EXTECH, Grainger) to provide regulated current to the reactor. The inter electrode distance was maintained at 1 cm apart for all the experiments. The wastewater sample was the acting electrolyte. The electrical conductivity was adjusted by adding NaCl to the electrolyte. All the runs were performed at constant temperature (25 °C) and agitation speed (200 rpm).

5.3.2.1. Method 1. EO Process

The primary wastewater was introduced to the EO reactor (Fig. 5.1a). BDD and stainless steel (St) (grade 304) electrodes were used as anode and cathode, respectively. The electrodes

were immersed into the reactor and connected to the external power supply as described earlier. The effect of current density, pH, and operation time were studied.

5.3.2.2. Method 2. ECP Process

The primary wastewater was introduced to the ECP reactor. Fe electrodes were used as both anode and cathode for the oxidation process (Fig. 5.1b). Hydrogen peroxide was added into the reactor externally for the oxidization of organic matters. For Fenton reaction to occur, the pH was adjusted to 2.8 (Brillas et al., 2009). The effect of H_2O_2 dosage, current density, and time of operation were studied.
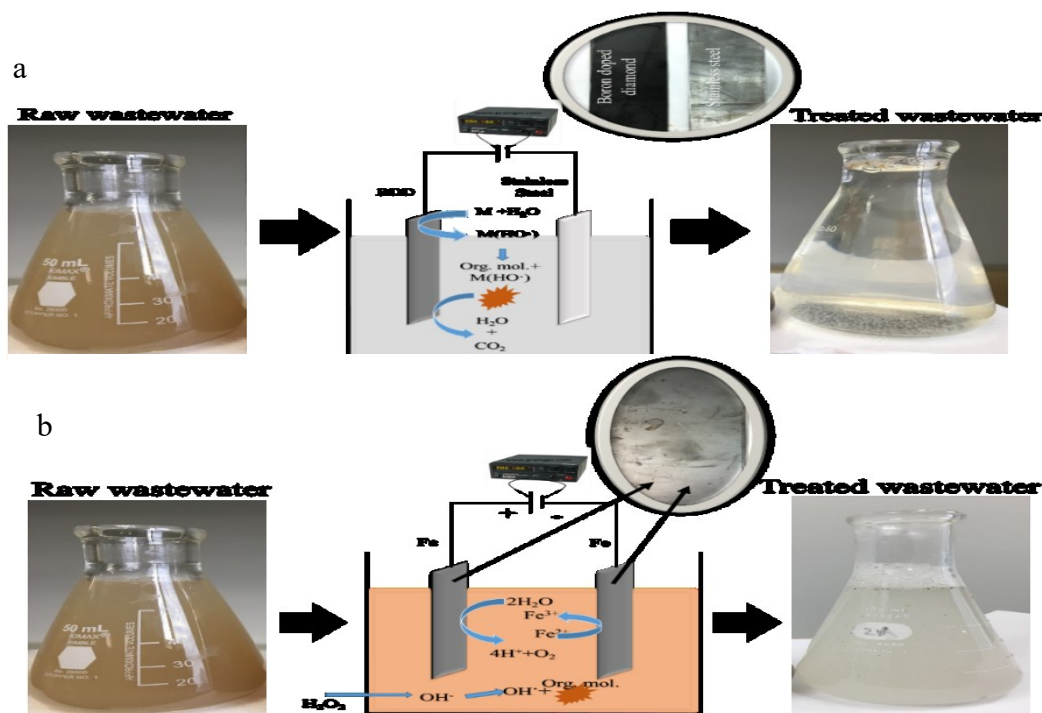
Figure 5.1. a) Electrooxidation process and b) Electrochemical peroxidation process in sugar beet wastewater.

5.3.3. Analytical Techniques

During the experiments, the samples were taken after each process and analyzed for the presence of COD, sCOD, TOC, and DOC. For COD and TOC analysis, the wastewater samples were measured without any filtration, while for sCOD and DOC analysis, the wastewater

samples were subjected to a series of filtration using (i) glass microfiber filter of grade GF/C, 1.2 µm pore size, 47 mm diameter (Whatman, USA) and (ii) cellulose membrane filter, 0.45 µm pore size and 47 mm diameter (Merck Millipore Ltd., USA). The organic pollutants passing through 0.45 µm pore size was considered to be in soluble or dissolved form. All the analyses for COD, sCOD, TOC, and DOC were performed as described in section 3.3.4.

5.3.4. Statistical Analysis and Modelling Using BBD

The statistical analysis and modelling were performed using Design-Expert® software based on Myers and Montgomery desirability function methodology. The experimental range and levels of the independent variables used in EO and ECP experiments are presented in Table 5.1. The ANOVA was conducted to analyze the results and to validate the statistical significance of the fitted quadratic models. The model compares the two methods based on relationship between the variables. The optimized parameters were obtained using fitted models and validated by conducting separate experiments. In addition, the economic analyses of EO and ECP systems were studied by calculating the energy consumption of the processes under optimum conditions. The energy consumption along with removal efficiency were analyzed for the method selection.

Table 5.1. Coded levels and independent variables for the experimental design.

Factor	Electrooxidation (EO)				Electrochemical peroxidation (ECP)			
	Variable	Level			Variable	Level		
		-1	0	1		-1	0	1
X_1	pH	3	5	7	H_2O_2 dosage (ml L^{-1})	10	20	30
X_2	Current density (mA cm^{-2})	23	46	69	Current density (mA cm^{-2})	23	46	69
X_3	Time (Min)	180	300	420	Time (Min)	180	300	420

5.4. Results and Discussion

5.4.1. Preliminary Experiments

Preliminary EO and ECP experiments were conducted on the sugar beet wastewater to determine the best treatment range of current densities (13.7, 23, 46, and 69 mA cm^{-2}); pH (3, 5, 7, and 8); H_2O_2 dosage (5, 10, 20, and 30 ml L^{-1}); and operation times (0 to 420 min) for successful removal of COD, sCOD, TOC, DOC. The data presented in Fig. B.2a shows the removal of COD, sCOD, TOC and DOC using a) EO at pH 8 and b) ECP at H_2O_2 dosage of 5 ml L^{1} respectively at current density of 13.7 mA cm^{-2}. It was observed that the removal of both COD and sCOD at pH 8 could not remove more than 52% at the end of 360 min when EO process was applied using BDD and stainless-steel electrodes. Similarly, TOC and DOC removal was considerably low ranging between 35 and 44%. Enache et al. (2009) reported that the electro generation of hydroxyl radicals was not observed at pH > 9, resulting in weaker electrooxidation of organics when BDD electrodes are used as anodes (Enache et al., 2009). Fig. B 2b represents the removal at 5 ml H_2O_2 dosage using ECP yielding COD and sCOD degradation of 52 and 36%, respectively. TOC and DOC also showed poor removal of maximum 38 and 27 % respectively.

The preliminary experiment results showed that the removal of organics using EO tend to decrease at alkaline condition and current density less than 23 mA cm^{-2}. Similarly, ECP showed an increased removal with the amount of H_2O_2 ranged from 10 to 20 ml L^{-1}. Thus, based on the results achieved, the statistical model was designed for range of parameters producing desired removal efficiency of organics.

5.4.2. Statistical Analysis and Interpretation by BBD

In this study, EO and ECP was investigated to treat sugar beet wastewater under the effect of operation parameters include; current density (23-69 mA cm^{-2}), initial pH (3-7), H_2O_2 dosage (10-30 ml L^{-1}), and operation time (180-420 min) in batch mode. BBD was employed using three factors with three levels in each method as shown in Table 5.1 to investigate and optimize the effects of the input variables on COD, sCOD, TOC, and DOC removal. The data of EO and ECP were fitted to two quadratic models respectively tested by ANOVA for model significance and adequacy as shown in Table 5.2. The F-test for all the regression models with low p-values (<0.0001) indicated that the models are highly significant in the removal of COD, sCOD, TOC, and DOC. The high R^2 for all the models in both EO and ECP indicated that the total variation could be explained by the models. The adjusted R^2 reported also vouched for the high significance of the models and low coefficient of variation (< 2%) in all the models suggested high precision and reliability of the experiments.

High R^2 and R^2_{adj} values indicated that the operation parameters; current density, time, pH, and H_2O_2 dosage have significant impact on the removal of COD, sCOD, TOC, and DOC in the sugar beet wastewater treatment. The predicted values made by the model in the removal of organic pollutants are in good agreement with the experimental data. As shown in supplementary table (Table A.3), it is evident that linear effect and square term of coefficients X_1, X_2, and X_3 i.e. pH/H_2O_2 dosage, current density, and time are significant in the treatment processes. Interactive effect of current density and time has stronger influence than the rest of the interactive terms in EO and ECP process. The interactive effect of pH and current density is significant in COD removal in EO process. Likewise, H_2O_2 dosage and current density influence TOC and DOC removal in ECP process.

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Table 5.2. ANOVA results for the quadratic models.

Response (Y, %)	Source	Electrooxidation					Electrochemical Peroxidation				
		SS	DF	MS	F-value	p-value	SS	DF	MS	F-value	p-value
COD	Model	1189.08	9	132.12	226.49	< 0.0001	1239.68	9	137.74	359.33	< 0.0001
	Residual	2.92	5	0.5833			1.92	5	0.3833		
	Lack of Fit	2.25	3	0.7500	2.25	0.3224	1.25	3	0.4167	1.25	0.4733
	Pure Error	0.6667	2	0.3333			0.6667	2	0.3333		
	Total	1192.00	14				1241.60	14			
		R^2 =0.9976		*Adj R^2=0.993*		*C.V%=1.18*	R^2 = 0.998		*Adj R^2= 0.995*		*C.V.%= 1.2*
sCOD	Model	1197.82	9	133.09	347.19	< 0.0001	1239.68	9	137.74	359.33	< 0.0001
	Residual	1.92	5	0.3833			1.92	5	0.3833		
	Lack of Fit	1.25	3	0.4167	1.25	0.4733	1.25	3	0.4167	1.25	0.4733
	Pure Error	0.6667	2	0.3333			0.6667	2	0.3333		
	Total	1199.73	14				1241.60	14			
		R^2 = 0.9984		*Adj R^2= 0.9955*		*C.V.%=1.01*	R^2 = 0.998		*Adj R^2= 0.9957*		*C.V.%=1.16*
TOC	Model	966.98	9	107.44	716.28	< 0.0001	1207.48	9	134.16	157.84	< 0.0001
	Residual	0.7500	5	0.1500			4.25	5	0.8500		
	Lack of Fit	0.7500	3	0.2500			2.25	3	0.7500	0.7500	0.6148
	Pure Error	0.0000	2	0.0000			2.00	2	1.0000		
	Total	967.73	14				1211.73	14			
		R^2 = 0.9992		*Adj R^2= 0.9978*		*C.V.%=0.59*	R^2 = 0.996		*Adj R^2= 0.9902*		*C.V.%=1.78*
DOC	Model	1354.07	9	150.45	205.16	< 0.0001	1214.73	9	134.97	224.95	< 0.0001
	Residual	3.67	5	0.7333			3.00	5	0.6000		
	Lack of Fit	3.00	3	1.0000	3.00	0.2599	1.0000	3	0.3333	0.3333	0.8075
	Pure Error	0.6667	2	0.3333			2.00	2	1.0000		
	Total	1357.73	14				1217.73	14			
		R^2 = 0.9973		*Adj R^2= 0.9924*		*C.V.%=1.34*	R^2 = 0.998		*Adj R^2= 0.996*		*C.V.%=1.16*

The response functions with the determined coefficients explained by independent variables are presented in Eqs. (49) through (56).

a) Removal efficiency by EO reaction:

$$COD = 75.33 + 4.12\ X_1 + 8.37\ X_2 + 3.00\ X_3 - 1.25\ X_1X_2 -$$
$$0.5000\ X_1X_3 - 1.50\ X_2X_3 - 6.54\ X_1^2 - 7.04\ X_2^2 - 5.79\ X_3^2 \tag{49}$$

$$sCOD = 71.67 + 4.62\ X_1 + 8.12\ X_2 + 3.50\ X_3 - 0.7500\ X_1X_2 -$$
$$0.5000\ X_1X_3 - 1.00\ X_2X_3 - 6.46\ X_1^2 - 6.96\ X_2^2 - 5.71\ X_3^2 \tag{50}$$

$$TOC = 74.00 + 4.62\ X_1 + 6.25\ X_2 + 3.63\ X_3 + 0.0000\ X_1X_2 -$$
$$0.2500\ X_1X_3 - 2.50\ X_2X_3 - 7.12\ X_1^2 - 6.87\ X_2^2 - 3.13\ X_3^2 \tag{51}$$

$$DOC = 74.33 + 4.75\ X_1 + 7.50\ X_2 + 5.50\ X_3 - 0.7500\ X_1X_2 -$$
$$0.2500\ X_1X_3 - 1.25\ X_2X_3 - 9.04\ X_1^2 - 7.04\ X_2^2 - 3.54\ X_3^2 \tag{52}$$

b) Removal efficiency by ECP reaction:

$$COD = 62.33 + 4.62\ X_1 + 8.12\ X_2 + 3.50\ X_3 - 0.7500\ X_1X_2 -$$
$$0.5000\ X_1X_3 - 1.00\ X_2X_3 - 6.79\ X_1^2 - 7.29\ X_2^2 - 6.04\ X_3^2 \tag{53}$$

$$sCOD = 64.33 + 4.62\ X_1 + 8.12\ X_2 + 3.50\ X_3 - 0.7500\ X_1X_2 -$$
$$0.5000\ X_1X_3 - 1.00\ X_2X_3 - 6.79\ X_1^2 - 7.29\ X_2^2 - 6.04\ X_3^2 \tag{54}$$

$$TOC = 61.00 + 4.37\ X_1 + 7.50\ X_2 + 5.38\ X_3 - 1.50\ X_1X_2 -$$
$$0.2500\ X_1X_3 - 0.5000\ X_2X_3 - 8.12\ X_1^2 - 5.87\ X_2^2 - 3.13\ X_3^2 \tag{55}$$

$$DOC = 63.00 + 4.5\ X_1 + 7.5\ X_2 + 5.25\ X_3 - 1.25\ X_1X_2 - 0.2500$$
$$X_1X_3 - 0.7500\ X_2X_3 - 8.38\ X_1^2 - 5.87\ X_2^2 - 2.88\ X_3^2 \tag{56}$$

The models satisfy for both EO and ECP methods as the predicted versus actual values distributes along a straight line as (high correlation) shown in Fig. 5.2(a) through 5.2(h).

5.4.3. Effects of Variables on COD, sCOD, TOC, and DOC Removal Efficiency Through Response Surface Plotting

The 3-D response surfaces regarding the interaction between the independent variables are presented in Fig. 5.3 and 5.4 for EO and ECP, respectively. 3-D response surfaces plots in these figures provide understanding of main and interaction effects of independent variables on the response (Adinarayana and Ellaiah, 2002; Wu et al., 2009; Yetilmezsoy et al., 2009). The independent variables, of which interaction coefficients were significant (p-value < 0.05) (Table A.3), were chosen to plot in Fig. 5.3 and 5.4. Current density played a significant role in the removal efficiency in both the EO and ECP processes compared to initial pH/H_2O_2 dosage and time.

5.4.3.1. Effect of Initial pH/H_2O_2 Dosage (X_1) and Current Density (X_2)

The initial pH and current density showed a significant interaction in the removal of COD in EO process (Fig. 5.3a). Fig. 5.3a shows a positive effect on the COD removal as the current density was increased from 40 to 69 mA cm^{-2} and pH increased from acidic 4 to neutral 7. It was also observed that increase in pH without increase in current density did not contribute much to the removal of COD. The percentage removal of COD was increased from 65 to 75% with the increase in both current density and pH. However, the interaction between pH and current density in the removal of sCOD, TOC, and DOC did not show a significant effect in the EO process as shown in supplementary figures, Fig. 5.5a, b, and c, respectively.
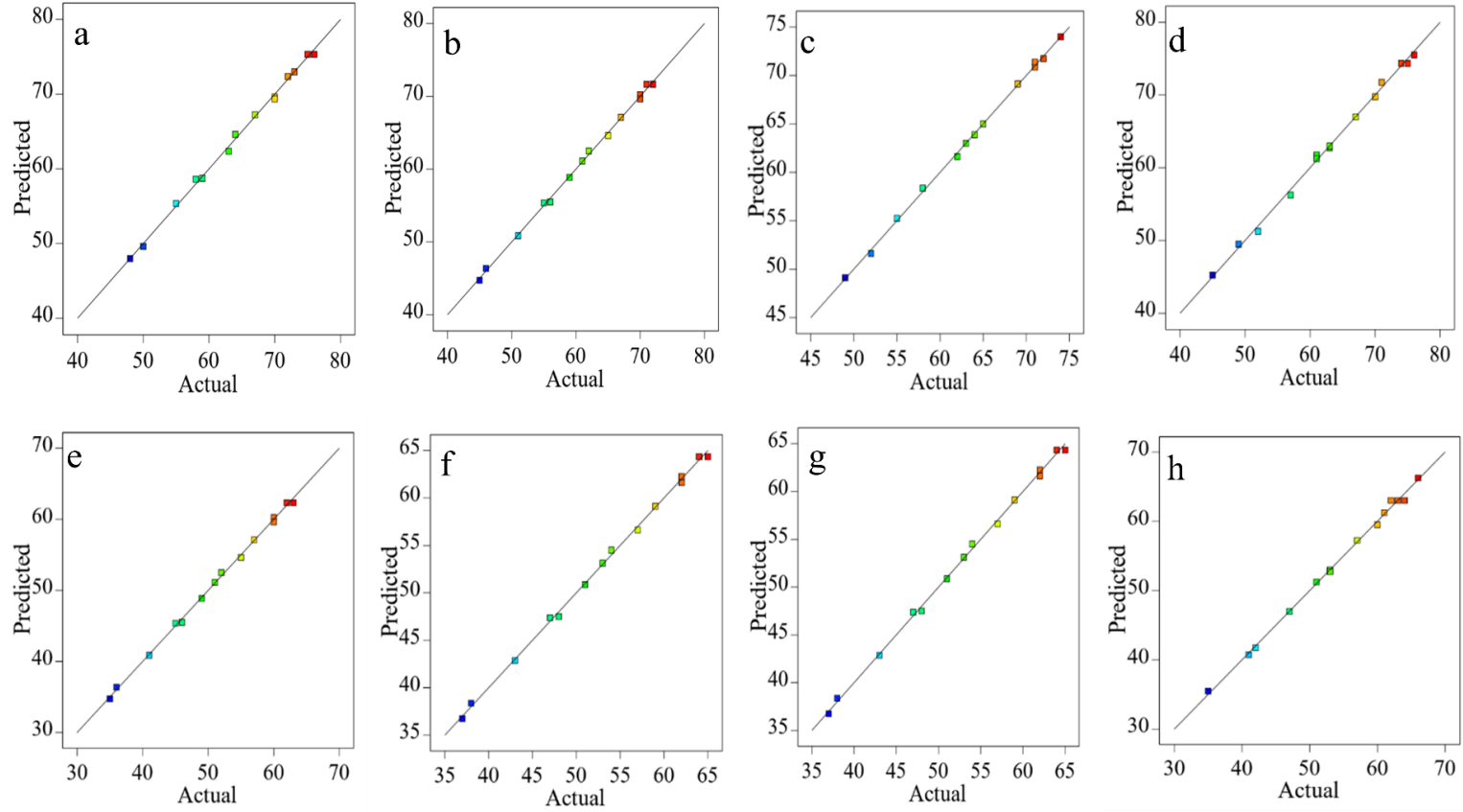
Figure 5.2. Actual vs predicted values from RSM describing removal of a) COD, b) sCOD, c) TOC, and d) DOC using electrooxidation and e) COD, f) sCOD, g) TOC, and h) DOC using electrochemical peroxidation.
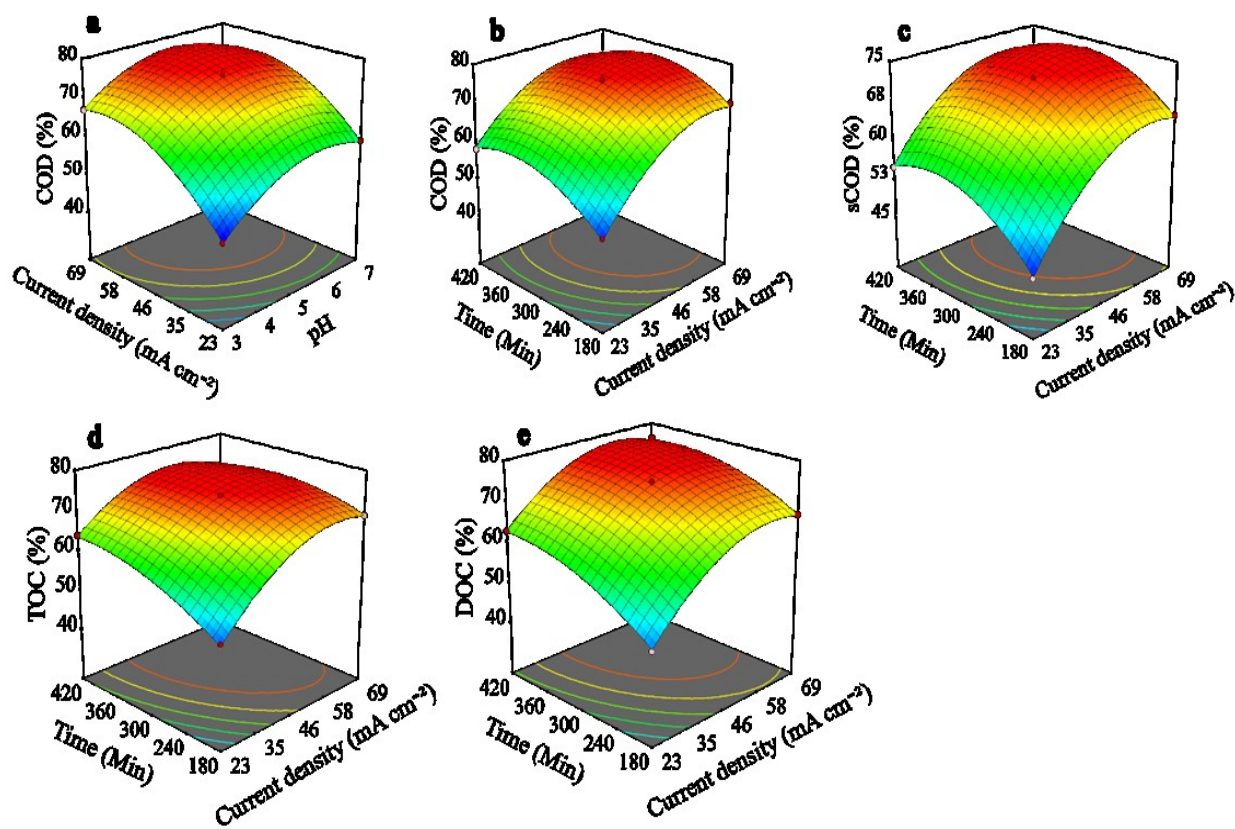
Figure 5.3. Three-dimensional contour plots illustrating the effect of pH and current density in a) COD using EO, time and current density in b) COD, c) sCOD, d) TOC and e) DOC using electrooxidation.

On the other hand, mutual interaction effect of current density and initial H_2O_2 dosage played an important role in the removal of TOC and DOC in the ECP process. Fig. 5.4a presented an estimate of TOC removal between 55 and 65% when the current density was operated in the range 42 – 69 mA cm^{-2} and initial H_2O_2 dosage tested between 17 and 28 ml L^{-1}. Similarly, removal of DOC was achieved to be more than 60% when the current density was applied between 40 and 69 mA cm^{-2} and H_2O_2 was applied between 15 and 30 ml L^{-1} (Figs. 5.4b). Moreover, increasing current density and H_2O_2 dosage at fixed time of 20 min enhanced the removal of TOC (Fig. 5.4a) and DOC (Fig. 5.4b) in the ECP process.

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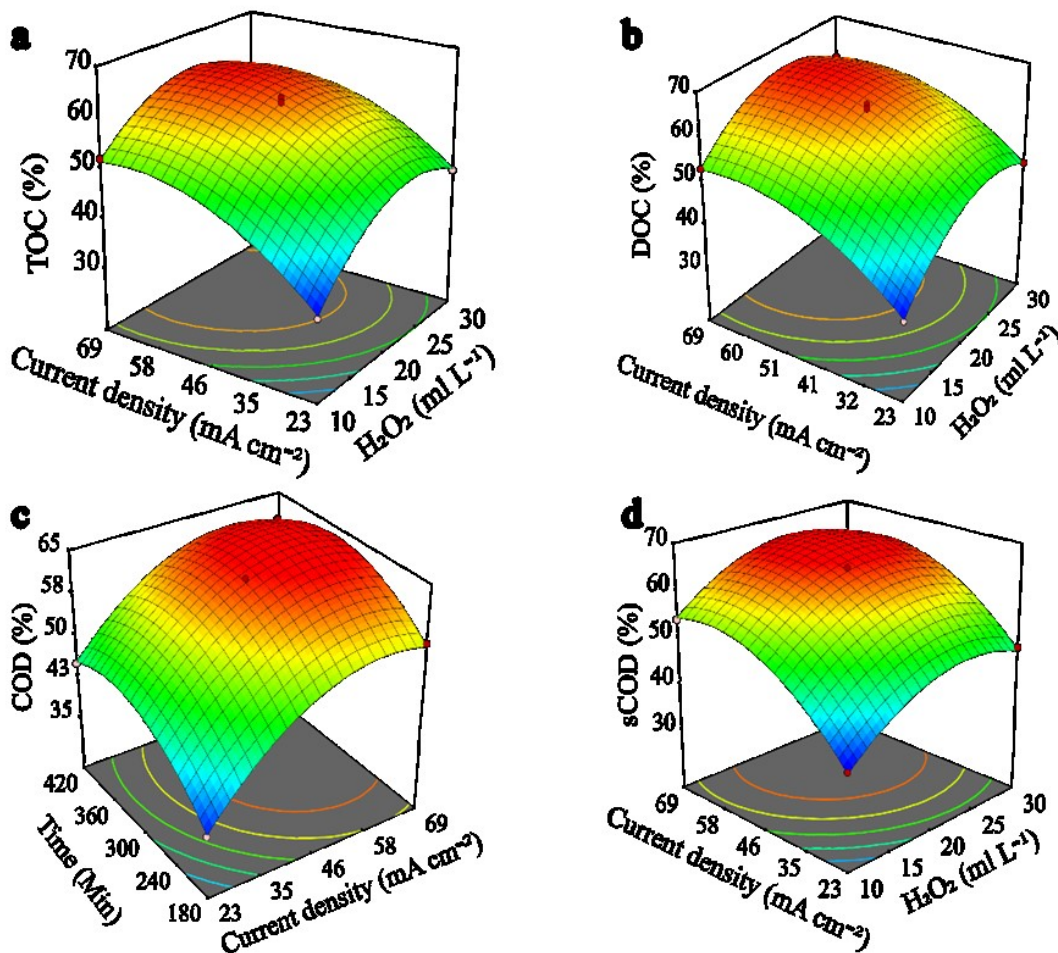
Figure 5.4. Current density and H_2O_2 dosage in a) TOC, b) DOC using electrochemical peroxidation, Current density and time in c) COD, d) sCOD using electrochemical peroxidation.

5.4.3.2. Effects of Current Density (X_2) and Time (X_3)

The mutual effects of current density and time as an estimate of response removal efficiency are shown for EO (Fig. 5.3) and ECP (Fig. 5.4) processes through contour plots and 3-D response surfaces plots. In EO process, current density and time interacted to achieve significant removal of COD (Fig. 5.3b), sCOD (Fig. 5.3c), TOC (Fig. 5.3d), and DOC (Fig. 5.3e). Increase in applied current density from 41 to 69 mA cm^{-2} achieved 70-75% of COD removal at all time of operation at a fixed pH of 5 (Fig. 5.3b). Fig. 5.3c showed that efficient sCOD removal was achieved between 50 and 69 mA cm^{-2} and time of operation in the range of

240 – 420 min. It was observed from Fig. 5.3c, further increased in current density and time tend to decrease the removal efficiency of sCOD. The maximum removal of TOC of 75% was achieved when the current density was applied in the range between 46 and 62 mA cm^{-2} and operation time of 280 and 420 min (Fig. 5.3d). In Fig. 5.3e, DOC showed maximum removal at maximum applied current density and operation time.

In ECP process, current density and time had a potential impact on the removal of COD (Fig. 5. 4c) and sCOD (Fig. 5.4d). The removal efficiency of COD and sCOD ranged between 60-63% when current density was increased between 45 and 65 mA cm^{-2} and time increased from 180 to 420 min at constant H_2O_2 dosage of 20 ml L^{-1}. However, the effect of current density and time that applied in this study had an insignificant effect on the TOC and DOC removal (Fig. B.4a and b).

5.4.3.3. Effects of Initial pH/H_2O_2 Dosage and Time

The interaction effects of pH and time in EO process and interaction between H_2O_2 dosage and time (Fig. B.4c, d, e and f) in the ECP process did not yield statistically significant results in the removal of organic pollutants from sugar beet wastewater. The change in the removal at initial pH range 3-7 and at operation time from 200-420 min is very less in the EO process (Fig. B.3 d, e, f and g). Similar trend could be observed in the ECP process, when current density was fixed, interaction effect of initial H_2O_2 dosage and time did not influence significant removal of pollutants. This may be due to the decrease in the availability of H_2O_2 to form OH˙ radical with the increase in time. Also, studies have shown that electro generation of H_2O_2 is low in EF processes due to low solubility of oxygen in water, which in turn may contribute towards low removal efficiency (Chou et al., 1999; Zhu et al., 2011).Studies have shown that EO and ECP processes are successful in the removal of organic pollutants from various wastewaters

(Sarkka et al., 2015a; Sarkka et al., 2015b; Ren et al., 2016). Antony and Natesan, (2012) treated Kraft bagasse bleaching effluent using EO process at an applied current density of 0.0087 A cm^{-2} for 1.75 h achieving 53% removal of COD (Antony and Natesan, 2012). Buzzini et al. (2006) achieved 63% COD removal in a cellulose pulp mill effluent applying 0.225 A cm^{-2} current for 2 h of time period (Buzzini et al., 2006). Iniesta et al. (2001) oxidized phenol to CO_2 using BDD electrodes in EO process for wastewater treatment (Iniesta et al., 2001).

Sharma and Simsek (2019) treated canola oil refinery wastewater using ECP process and achieved a sCOD and DOC removal of 86% when current density of 13.66 mA cm^{-2} was applied for 7 h. Selvabharathi et al. (2010) used EF as a tertiary treatment method to remove 95% COD from biologically treated newsprint paper-industry wastewater. The study concluded that increase in pH decreased treatment efficiency due to precipitation of iron hydroxides (Selvabharathi et al., 2010)

5.4.4. Optimization of Process Parameters and Method Selection Through Economic Comparison

The process parameters based on the experimental outcomes were optimized for the maximum removal efficiency of COD, sCOD, TOC, and DOC. To sum up the results of the quadratic models and the response surface contour plots, the optimum value of the reaction conditions for EO was obtained at pH of 5, current density of 49.1 mA cm^{-2}, and operation time of 294 min. Whereas, for ECP, the optimal conditions were found to be at a H_2O_2 dosage of 21.86 ml L^{-1}, current density of 51 mA cm^{-2}, and operation time of 295 min. The predicted values were further validated by conducting extra experiments performed under the optimized conditions and the data is presented in Table 5.3. The experimental values agreed well with the model predictions for all COD, sCOD, TOC, and DOC removal efficiencies.

Table 5.3. Predicted versus actual values at optimal conditions for EO and ECP.

Response	Electrooxidation			Electrochemical Peroxidation		
	Predicted (%)	Actual (%)	Energy consumption (kWh m^{-3})	Predicted (%)	Actual (%)	Energy consumption (kWh m^{-3})
COD	76.17	74.81	28.43	66.25	65.75	39.54
sCOD	72.44	71.15	35.97	64.28	63.04	49.62
TOC	74.53	75.32	62.59	64.65	62.87	91.65
DOC	74.89	74.65	69.14	62.64	61.51	102.55

It was observed that the energy consumed in ECP in the removal of COD, sCOD, TOC, and DOC were higher compared to that of in EO. Moreover, the removal efficiency of EO using BDD electrodes achieved more than 70% removal with lower energy consumption compared to ECP that achieved not more than 65% at 1.5 times higher energy consumption. The energy that required to remove 75% of COD at a current density of 49 mA cm^{-2} in 294 min was 28 kWh m^{-3} using EO as the treatment process. Whereas, when ECP was applied, only 65% of COD was removed at a higher current density of 51 mA cm^{-2} and energy consumption of 39 kWh m^{-3}. Although there is no study available to compare energy consumption on sugar beet wastewater using AOPs, the energy consumption values reported in this study agree with that COD removal from textile effluent using BDD electrodes (Aquino et al., 2011; Solano et al., 2013). Aquino et al. (2011) reported complete removal of COD from textile effluent using BDD electrodes required 30 kWh m^{-3} with addition of 1.5 g L^{-1} of NaCl at a current density of 5 mA cm^{-2}. Energy consumed in the study conducted by Solano et al. (2013) in textile effluent COD removal for 10 h of operation time at current density of 40 mA cm^{-2} was reported to be 36.96 kWh m^{-3}.

Very few studies were conducted in the treatment of sugar beet wastewater using AOPs (Guven et al., 2009). Guven et al. (2009) investigated the performance of electrochemical oxidation using Fe electrodes on simulated sugar beet wastewater in the removal of COD through RSM (CCD). Simulated wastewater achieved 79.66% of COD removal under optimum

conditions. Hajiagha et al. (2018) evaluated the treatability of sugar beet wastewater by combining photo-Fenton oxidation with coagulation/flocculation and achieved 59% reduction of COD at a reaction time of 30 min. The findings of the above studies agree with the current study where EO achieved better treatment performance compared to ECP. Thus, from the analysis of removal efficiency and energy consumption calculation, it can be concluded that EO was the preferred method over ECP.

5.4.5. Reaction Kinetics

Reaction kinetics during the operation of EO process in sugar beet wastewater using BDD electrodes under optimum conditions have been investigated. It should be noted that reaction mechanism and rate may differ from one pollutant to another. In a batch reaction, rate term is expressed in terms of initial pollutant removal rate if the reaction medium is of complex nature (Guven et al., 2009). For this reason, this study used a simplified integral approach in which a kinetic model is assumed to be described in terms of pollutant concentration. The models were tested to describe the reduction rate of COD, sCOD, TOC, and DOC using EO process. It was observed that reactions in COD, sCOD, TOC, and DOC removal follows a first order model. The plots of Ln (C/C_0) versus time for each of COD, sCOD, TOC, and DOC at optimum conditions of current density 49.1 mA cm^{-2}, pH 5 and time of operation 294 min are presented in Fig. 5.5.

Table 5.4. Values of first-order kinetic constant, k and coefficient of determination R^2 for the responses at pH 5, current density 49.1 mA cm^{-2} and time 294 min.

Response	k (min^{-1})	R^2
COD	0.131	0.9902
sCOD	0.125	0.9940
TOC	0.153	0.9909
DOC	0.147	0.98867

It is clear from Fig. 5.5 that residual concentration of COD, sCOD, TOC, and DOC fit a straight line for the conditions considered. The corresponding values of kinetic parameter, k, obtained from the slope of each plot along with the R^2 are presented in Table 5.4. It is evident that all the values of R^2 are close to one. This indicates the goodness of fit of the first-order kinetics to demonstrate the removal of pollutants adequately.
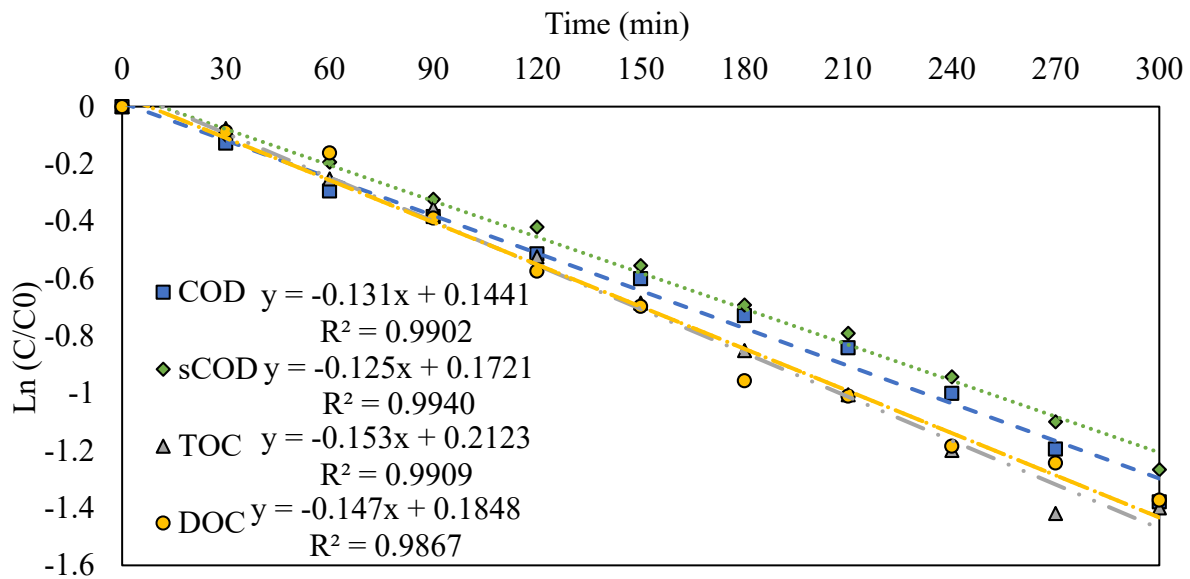
Figure 5.5. Linearized first-order kinetic model for EO treatment at pH 5, current density 49.1 mA cm^{-2} and operation time of 294 min.

5.5. Conclusion

The RSM data demonstrated significant effects of the variables include pH, H_2O_2 dosage, current density, and time of operation as well as their interactive effects in the reduction of pollutants. High R^2 values for all the models through ANOVA indicated that the accuracy of the polynomial model was acceptable. The optimum conditions were obtained for both EO and ECP and energy consumption was calculated for each process at its optimal conditions. EO process was selected as the preferred method based on removal efficiency as well as energy consumption.

The optimum conditions for EO was found as follows; pH was 5, current density was 49.1 mA cm^{-2}, and operation time was 294 min. The experiments showed a removal of 75% of COD, TOC and DOC, and 71% of sCOD using EO process. Moreover, the reaction rate constant was calculated using first-order kinetic model for each of COD, sCOD, TOC, and DOC and the goodness of fit of the model was validated with high values of R^2. This study implies that EO process could be a successful alternative treatment processes compare to traditional treatment methods for sugar beet industrial wastewater treatment.

CHAPTER 6. GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

6.1. Conclusions

A comprehensive study was conducted to investigate the treatment performance of electrochemical methods in industrial wastewater derived organic pollutants. The wastewater collected were from a canola oil, sunflower oil refinery and a sugar beet processing factory. The oil wastewaters consist of high concentration of suspended and colloidal organic compounds, whereas, the sugar beet wastewater has consequential concentration of soluble organic pollutants which contribute to proliferation of microbes. Although biological processes are currently employed as the most acceptable treatment method for these industrial wastewaters, these processes come with its own disadvantages of considerable demand for large space requirements involving high cost of operation, time consuming and inefficient removal of refractory organic compounds. The literature related to application of electrochemical methods and the effect of the process parameters in the treatment of these three wastewaters is strictly limited.

This study incorporates the performance of EC, EO and ECP in degradation of organic pollutants from the wastewaters collected. The effect of various process parameters such as current density, pH, H_2O_2 dosage and time of operation were investigated and the interaction effects between the parameters were studied to understand its impact on the removal of COD, sCOD, TOC and DOC. Using the BBD, the process conditions were optimized, and the quadratic models were obtained with high significance. The interaction effect of current density and pH/H_2O_2 dosage had a significant positive effect on the removal process. In sunflower and canola oil refinery wastewater, the interaction effect of current density and time was statistically insignificant. From the results obtained, it was accorded that increase in current density

remarkably decreases the time of operation. However, the removal efficiency remains consistent at all current densities. From the optimization models, it was perceived that Al electrodes in the EC process yields better removal at a pH range of 5.5 – 6 in the treatment of oil wastewaters. The less time required by EC process in the removal of COD and TOC could contribute significantly towards cost and energy saving strategies. Comparing the three wastewaters studied, it was observed that dissolved organic removal requires high current densities copared to colloidal or suspended organic pollutant removal. The time required is also higher for dissolved organic compounds.

The kinetic model tested to determine the reduction rate of COD, sCOD, TOC and DOC followed a first order kinetics and the goodness of fit of the model was validated with high values of R^2. From the energy consumption calculated for both the processes, ECP consumed comparatively higher energy for low removal over longer time of operation. Also, from the experimental standpoint, the replacement of electrodes in the ECP was notably frequent compared to the EO process. Unlike Fe electrodes, BDD electrodes used in the EO process is not a sacrificial electrode and has high resistance to corrosion thus retaining its longevity throughout the entire experimental process.

From the results obtained based on removal efficiency of COD, sCOD, TOC and DOC, energy consumption data and the optimization models using BBD, the study concludes that EC+EO process was found suitable for the treatment of canola and sunflower oil refinery wastewater. On the other hand, EO process was a successful alternative to the biological process in the sugar beet processing wastewater treatment.

6.2. Recommendations for Future Work

In addition to issues addressed in this research, the study should be extended to:

1. Study the effect of size and shape of electrodes used in the electrochemical processes.

2. Characterization of organic compounds for better understanding of the removal mechanism involved. It would also help in formulating treatment mechanism for targeted pollutants.

3. Study mass transfer processes between the electrode surface and the bulk liquid in the reactor.

4. Study the effect of continuous operation of the processes to understand the impact of retention time of metal ions discharged into the bulk liquid.

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APPENDIX A. TABLES

Table A.1. Estimated regression coefficients and corresponding significance level for process parameters canola oil refinery wastewater.

	Electrocoagulation											
Factor	COD			sCOD			TOC			DOC		
	C	SE	SL	C	SE	SL	C	SE	SL	C	SE	SL
β_0	93.98	1.02	0	78.11	1.31	0	88.84	1	0	75.84	1.13	0
β_1	-4.66	0.63	0	-3.37	0.8	0.01	-4.78	0.62	0	-3.88	0.69	0
β_2	-1.12	0.63	0.13	-2.24	0.8	0.04	-1.12	0.62	0.13	-2.89	0.69	0.01
β_3	-3.18	0.63	0	-2.32	0.8	0.03	-3.31	0.62	0	-1.98	0.69	0.04
β_{12}	-2.68	0.89	0.03	-4.28	1.14	0.01	-2.68	0.87	0.03	-4.25	0.98	0.01
β_{13}	-2.48	0.89	0.04	-3.96	1.14	0.02	-2.23	0.87	0.05	-4	0.98	0.01
β_{23}	-2.57	0.89	0.03	-3.32	1.14	0.03	-2.57	0.87	0.03	-4.54	0.98	0.01
β_{11}	-12.97	0.92	0	-9.02	1.18	0	-10.27	0.91	0	-9.81	1.02	0
β_{22}	-4.01	0.92	0.01	0.69	1.18	0.58	-1.56	0.91	0.15	0.72	1.02	0.51
β_{33}	-11.04	0.92	0	-5.54	1.18	0.01	-8.35	0.91	0	-5.53	1.02	0

	Electrocoagulation + electrooxidation											
Factor	COD			sCOD			TOC			DOC		
	C	SE	SL	C	SE	SL	C	SE	SL	C	SE	SL
β_0	97.67	1.13	0	98.03	1.21	0	94.62	1.13	0	94.33	1.49	0.01
β_1	-4.22	0.69	0	-2.57	0.74	0.02	-4.63	0.69	0	-2.92	0.91	0.02
β_2	-1.23	0.69	0.14	-2.93	0.74	0.01	-1.23	0.69	0.14	-2.62	0.91	0.04
β_3	-3	0.69	0.01	-2.47	0.74	0.02	-3.4	0.69	0	-1.63	0.91	0.13
β_{12}	-3.28	0.98	0.02	-3.71	1.05	0.02	-3.27	0.98	0.02	-4.75	1.29	0.01
β_{13}	-1.87	0.98	0.11	-4	1.05	0.01	-2.66	0.98	0.04	-3.52	1.29	0.04
β_{23}	-2.68	0.98	0.04	-3.5	1.05	0.02	-2.44	0.98	0.06	-3.54	1.29	0.04
β_{11}	-13.09	1.02	0	-8.79	1.09	0	-10.77	1.02	0	-8.89	1.34	0
β_{22}	-4.7	1.02	0.01	0.62	1.09	0.6	-1.38	1.02	0.23	0.52	1.34	0.72
β_{33}	-11.09	1.02	0	-5.5	1.09	0	-9.08	1.02	0	-4.06	1.34	0.03

	Electrochemical peroxidation											
Factor	COD			sCOD			TOC			DOC		
	C	SE	SL	C	SE	SL	C	SE	SL	C	SE	SL
β_0	88.01	0.84	0	83.68	1.29	0	85.27	1.08	0	84.99	0.73	0
β_1	-4.86	0.51	0	-5.87	0.79	0	-4.94	0.66	0	-5.35	0.45	0
β_2	-1.84	0.51	0.02	-2.68	0.79	0.02	-3	0.66	0.01	-1.66	0.45	0.01
β_3	-2.82	0.51	0	-4.1	0.79	0	-2.99	0.66	0.01	-1.84	0.45	0.01
β_{12}	-2.63	0.73	0.02	-3.67	1.12	0.02	-2.46	0.93	0.05	-1.79	0.63	0.04
β_{13}	-3.29	0.73	0.01	-4.96	1.12	0.01	-2.89	0.93	0.03	-3.7	0.63	0
β_{23}	1.13	0.73	0.18	0.74	1.12	0.54	1.58	0.93	0.15	1.4	0.63	0.08
β_{11}	-9.98	0.76	0	-9.46	1.16	0	-7.04	0.97	0	-7.73	0.66	0
β_{22}	-2.72	0.76	0.02	-2.8	1.16	0.06	-1.44	0.97	0.2	-0.97	0.66	0.2
β_{33}	-8.2	0.76	0	-6.63	1.16	0	-7.01	0.97	0	-7.71	0.66	0

Table A.2. Estimated regression coefficients and corresponding significance level for process parameters sunflower oil refinery wastewater.

| | Electrocoagulation | | | | | | | | | | | |
| Factor | COD | | | sCOD | | | TOC | | | DOC | | |
	C	SE	SL	C	SE	SL	C	SE	SL	C	SE	SL
β_0	93.98	1.02	0	78.11	1.31	0	88.84	1	0	75.84	1.13	0
β_1	-4.66	0.63	0	-3.37	0.8	0.01	-4.78	0.62	0	-3.88	0.69	0
β_2	-1.12	0.63	0.13	-2.24	0.8	0.04	-1.12	0.62	0.13	-2.89	0.69	0.01
β_3	-3.18	0.63	0	-2.32	0.8	0.03	-3.31	0.62	0	-1.98	0.69	0.04
β_{12}	-2.68	0.89	0.03	-4.28	1.14	0.01	-2.68	0.87	0.03	-4.25	0.98	0.01
β_{13}	-2.48	0.89	0.04	-3.96	1.14	0.02	-2.23	0.87	0.05	-4	0.98	0.01
β_{23}	-2.57	0.89	0.03	-3.32	1.14	0.03	-2.57	0.87	0.03	-4.54	0.98	0.01
β_{11}	-12.97	0.92	0	-9.02	1.18	0	-10.27	0.91	0	-9.81	1.02	0
β_{22}	-4.01	0.92	0.01	0.69	1.18	0.58	-1.56	0.91	0.15	0.72	1.02	0.51
β_{33}	-11.04	0.92	0	-5.54	1.18	0.01	-8.35	0.91	0	-5.53	1.02	0

| | Electrocoagulation + electrooxidation | | | | | | | | | | | |
| Factor | COD | | | sCOD | | | TOC | | | DOC | | |
	C	SE	SL	C	SE	SL	C	SE	SL	C	SE	SL
β_0	97.67	1.13	0	98.03	1.21	0	94.62	1.13	0	94.33	1.49	0.01
β_1	-4.22	0.69	0	-2.57	0.74	0.02	-4.63	0.69	0	-2.92	0.91	0.02
β_2	-1.23	0.69	0.14	-2.93	0.74	0.01	-1.23	0.69	0.14	-2.62	0.91	0.04
β_3	-3	0.69	0.01	-2.47	0.74	0.02	-3.4	0.69	0	-1.63	0.91	0.13
β_{12}	-3.28	0.98	0.02	-3.71	1.05	0.02	-3.27	0.98	0.02	-4.75	1.29	0.01
β_{13}	-1.87	0.98	0.11	-4	1.05	0.01	-2.66	0.98	0.04	-3.52	1.29	0.04
β_{23}	-2.68	0.98	0.04	-3.5	1.05	0.02	-2.44	0.98	0.06	-3.54	1.29	0.04
β_{11}	-13.09	1.02	0	-8.79	1.09	0	-10.77	1.02	0	-8.89	1.34	0
β_{22}	-4.7	1.02	0.01	0.62	1.09	0.6	-1.38	1.02	0.23	0.52	1.34	0.72
β_{33}	-11.09	1.02	0	-5.5	1.09	0	-9.08	1.02	0	-4.06	1.34	0.03

| | Electrochemical peroxidation | | | | | | | | | | | |
| Factor | COD | | | sCOD | | | TOC | | | DOC | | |
	C	SE	SL	C	SE	SL	C	SE	SL	C	SE	SL
β_0	88.01	0.84	0	83.68	1.29	0	85.27	1.08	0	84.99	0.73	0
β_1	-4.86	0.51	0	-5.87	0.79	0	-4.94	0.66	0	-5.35	0.45	0
β_2	-1.84	0.51	0.02	-2.68	0.79	0.02	-3	0.66	0.01	-1.66	0.45	0.01
β_3	-2.82	0.51	0	-4.1	0.79	0	-2.99	0.66	0.01	-1.84	0.45	0.01
β_{12}	-2.63	0.73	0.02	-3.67	1.12	0.02	-2.46	0.93	0.05	-1.79	0.63	0.04
β_{13}	-3.29	0.73	0.01	-4.96	1.12	0.01	-2.89	0.93	0.03	-3.7	0.63	0
β_{23}	1.13	0.73	0.18	0.74	1.12	0.54	1.58	0.93	0.15	1.4	0.63	0.08
β_{11}	-9.98	0.76	0	-9.46	1.16	0	-7.04	0.97	0	-7.73	0.66	0
β_{22}	-2.72	0.76	0.02	-2.8	1.16	0.06	-1.44	0.97	0.2	-0.97	0.66	0.2
β_{33}	-8.2	0.76	0	-6.63	1.16	0	-7.01	0.97	0	-7.71	0.66	0

Table A.3. Estimated regression coefficients and corresponding significance level for sugar beet wastewater.

Factor	Electrooxidation

Factor	COD			sCOD			TOC			DOC		
	C	SE	SL	C	SE	SL	C	SE	SL	C	SE	SL
β_0	75.3	0.4	< 0.0001	71.7	0.4	< 0.0001	74	0.2	< 0.0001	74.3	0.5	< 0.0001
β_1	4.1	0.3	< 0.0001	4.6	0.2	< 0.0001	4.6	0.1	< 0.0001	4.8	0.3	< 0.0001
β_2	8.4	0.3	< 0.0001	8.1	0.2	< 0.0001	6.3	0.1	< 0.0001	7.5	0.3	< 0.0001
β_3	3	0.3	0.0001	3.5	0.2	< 0.0001	3.6	0.1	< 0.0001	5.5	0.3	< 0.0001
β_{12}	-1.3	0.4	0.0221	-0.8	0.3	0.0599	0	0.2	1	-0.8	0.4	0.1402
β_{13}	-0.5	0.4	0.2474	-0.5	0.3	0.1672	-0.3	0.2	0.2532	-0.3	0.4	0.5847
β_{23}	-1.5	0.4	0.0111	-1	0.3	0.0232	-2.5	0.2	< 0.0001	-1.3	0.4	0.033
β_{11}	-6.5	0.4	< 0.0001	-6.5	0.3	< 0.0001	-7.1	0.2	< 0.0001	-9	0.4	< 0.0001
β_{22}	-7	0.4	< 0.0001	-7	0.3	< 0.0001	-6.9	0.2	< 0.0001	-7	0.4	< 0.0001
β_{33}	-5.8	0.4	< 0.0001	-5.7	0.3	< 0.0001	-3.1	0.2	< 0.0001	-3.5	0.4	0.0005

Factor	Electrochemical peroxidation

| Factor	COD			sCOD			TOC			DOC		
	C	SE	SL	C	SE	SL	C	SE	SL	C	SE	SL
β_0	62.3	0.4	< 0.0001	64.3	0.4	< 0.0001	61	0.5	< 0.0001	63	0.4	< 0.0001
β_1	4.6	0.2	< 0.0001	4.6	0.2	< 0.0001	4.4	0.3	< 0.0001	4.5	0.3	< 0.0001
β_2	8.1	0.2	< 0.0001	8.1	0.2	< 0.0001	7.5	0.3	< 0.0001	7.5	0.3	< 0.0001
β_3	3.5	0.2	< 0.0001	3.5	0.2	< 0.0001	5.4	0.3	< 0.0001	5.3	0.3	< 0.0001
β_{12}	-0.8	0.3	0.0599	-0.8	0.3	0.0599	-1.5	0.5	0.0226	-1.3	0.4	0.0233
β_{13}	-0.5	0.3	0.1672	-0.5	0.3	0.1672	-0.3	0.5	0.6109	-0.3	0.4	0.5471
β_{23}	-1	0.3	0.0232	-1	0.3	0.0232	-0.5	0.5	0.3276	-0.8	0.4	0.1106
β_{11}	-6.8	0.3	< 0.0001	-6.8	0.3	< 0.0001	-8.1	0.5	< 0.0001	-8.4	0.4	< 0.0001
β_{22}	-7.3	0.3	< 0.0001	-7.3	0.3	< 0.0001	-5.9	0.5	< 0.0001	-5.9	0.4	< 0.0001
β_{33}	-6	0.3	< 0.0001	-6	0.3	< 0.0001	-3.1	0.5	0.0013	-2.9	0.4	0.0008
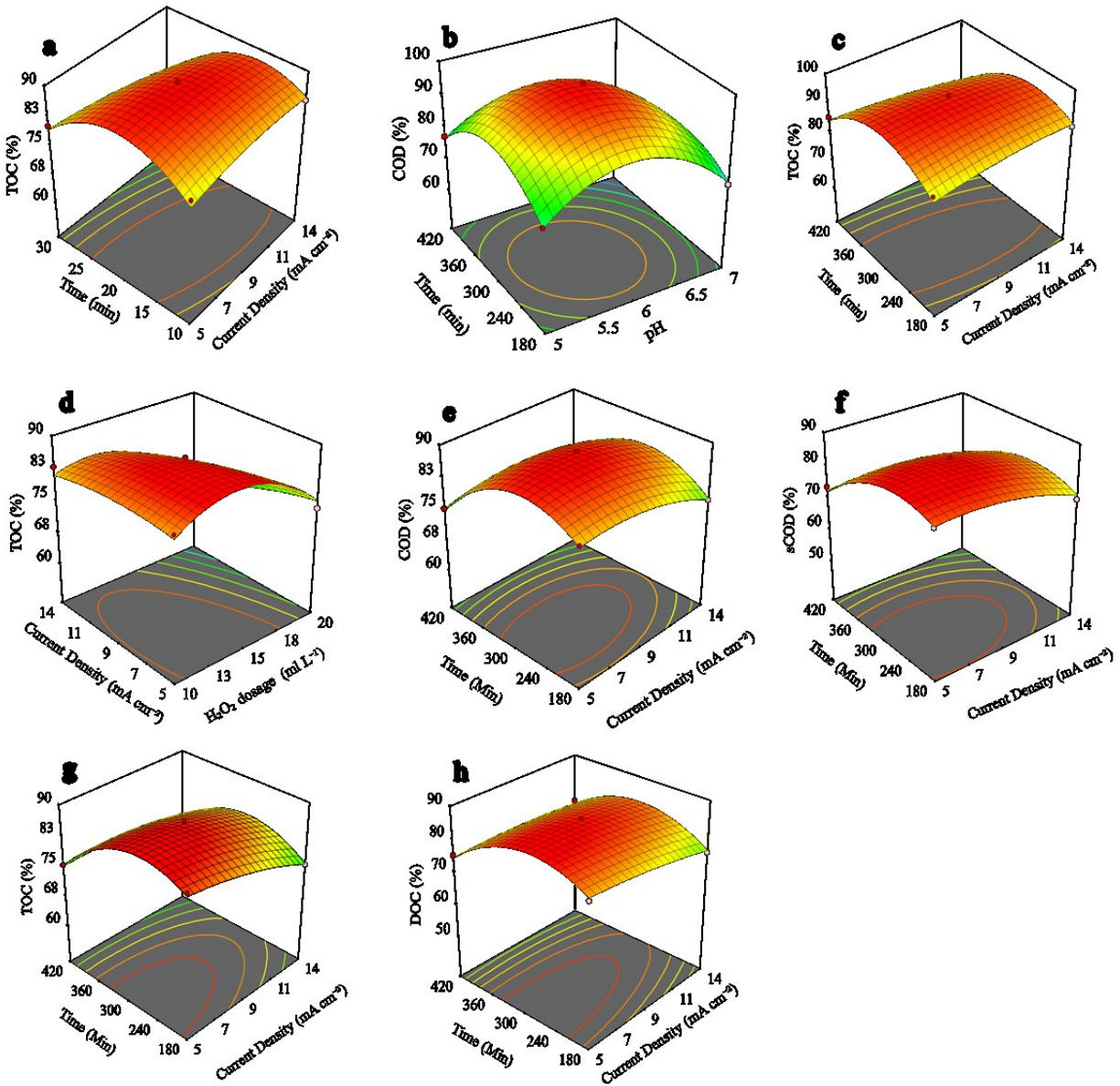
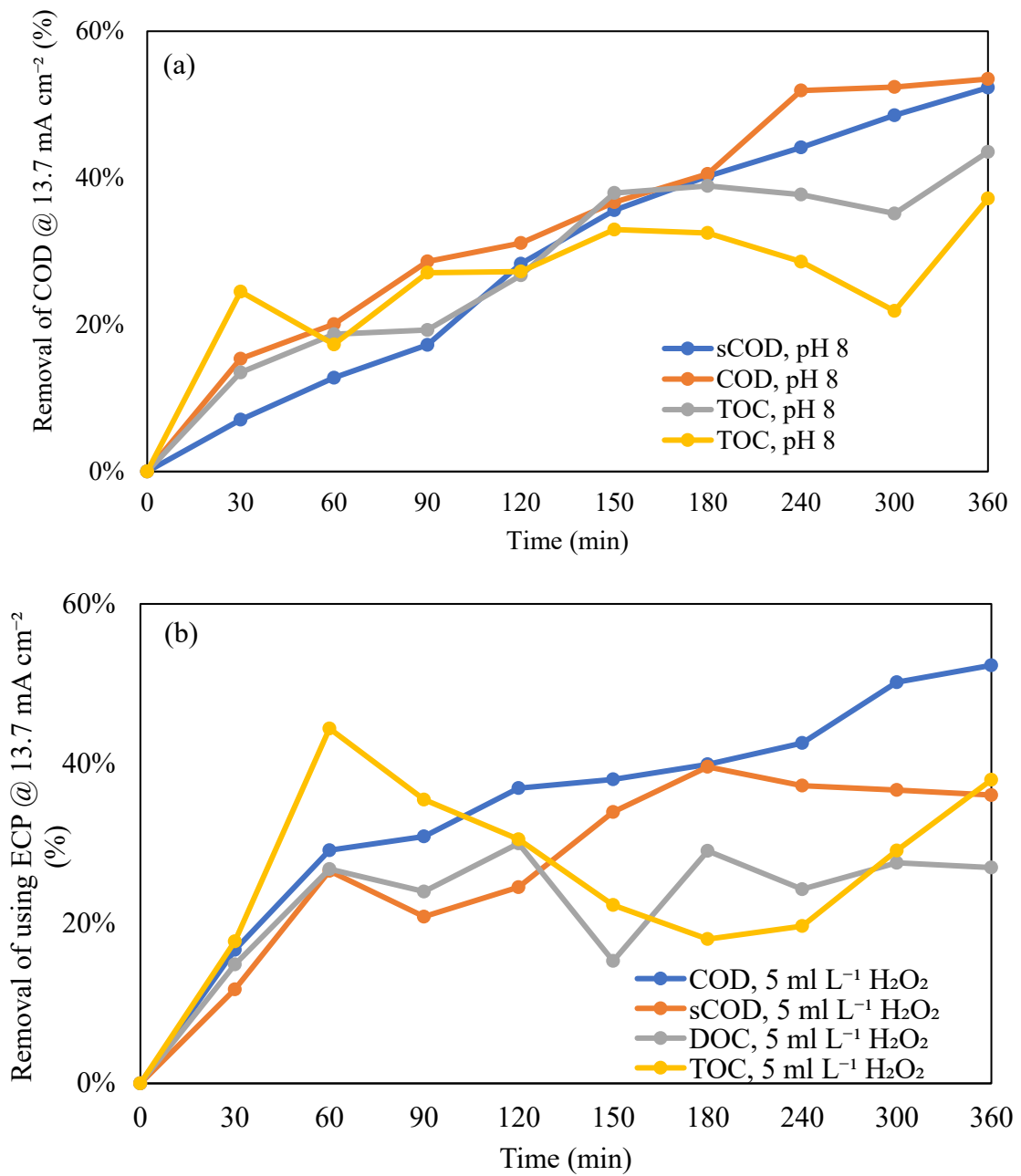**Figure B.1**. Interaction effect between current density, time, pH and H_2O_2 dosage in EC+EO and ECP process.

Figure B.2. a) Removal using electrooxidation at pH 8 and 13.7 mA cm^{-2} b) Removal electrochemical peroxidation at H$_2$O$_2$ dosage of 5 ml L^{-1} and 13.7 mA cm^{-2}.
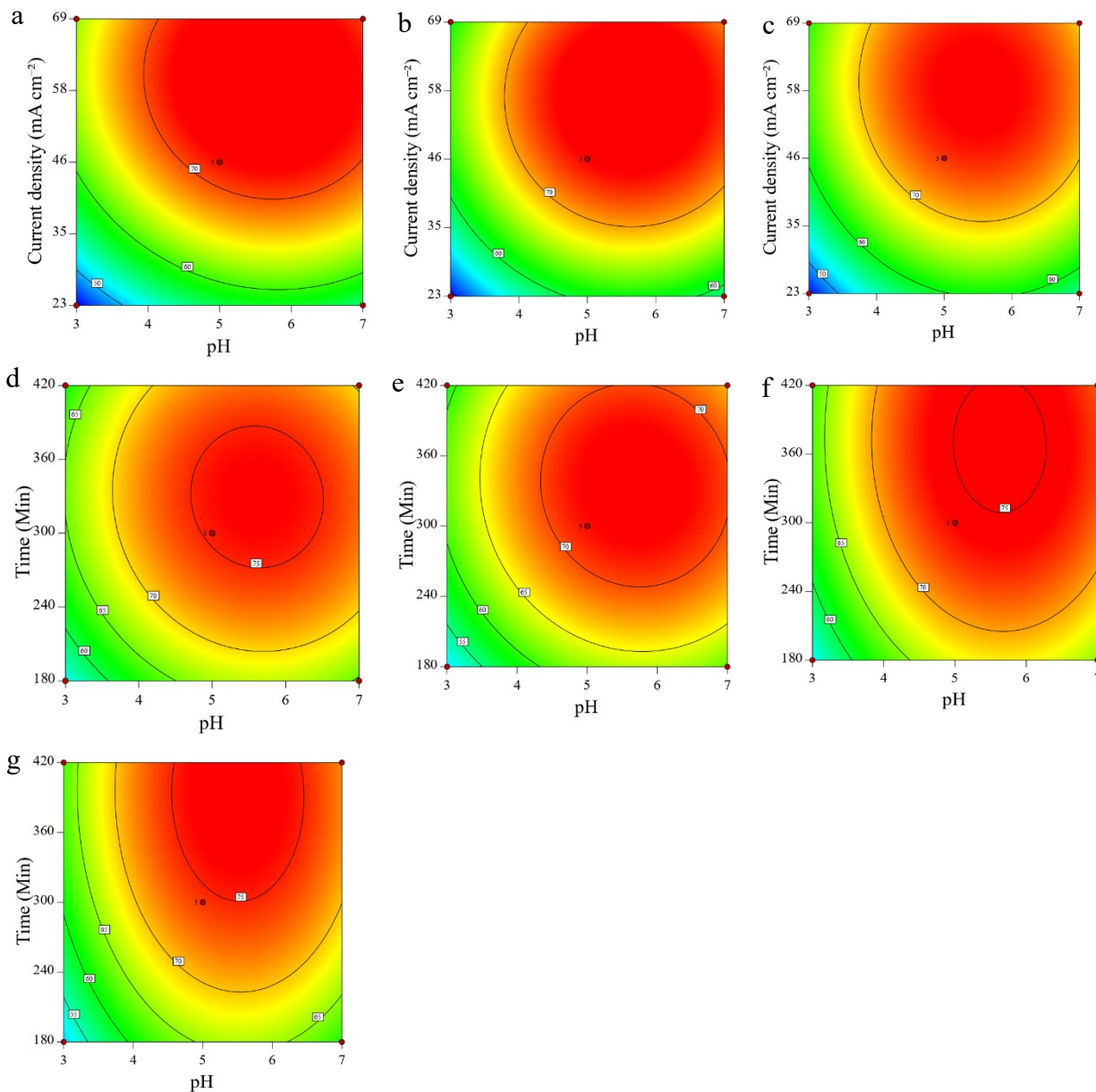
Figure B.3. Two-dimensional contour plots illustrating the interaction effect of two independent variables in electrooxidation process, a) current density and pH for sCOD, b) current density and pH for TOC c) current density and pH for DOC, d) time and pH for COD, e) time and pH sCOD, f) time and pH for TOC g) time and pH for DOC.
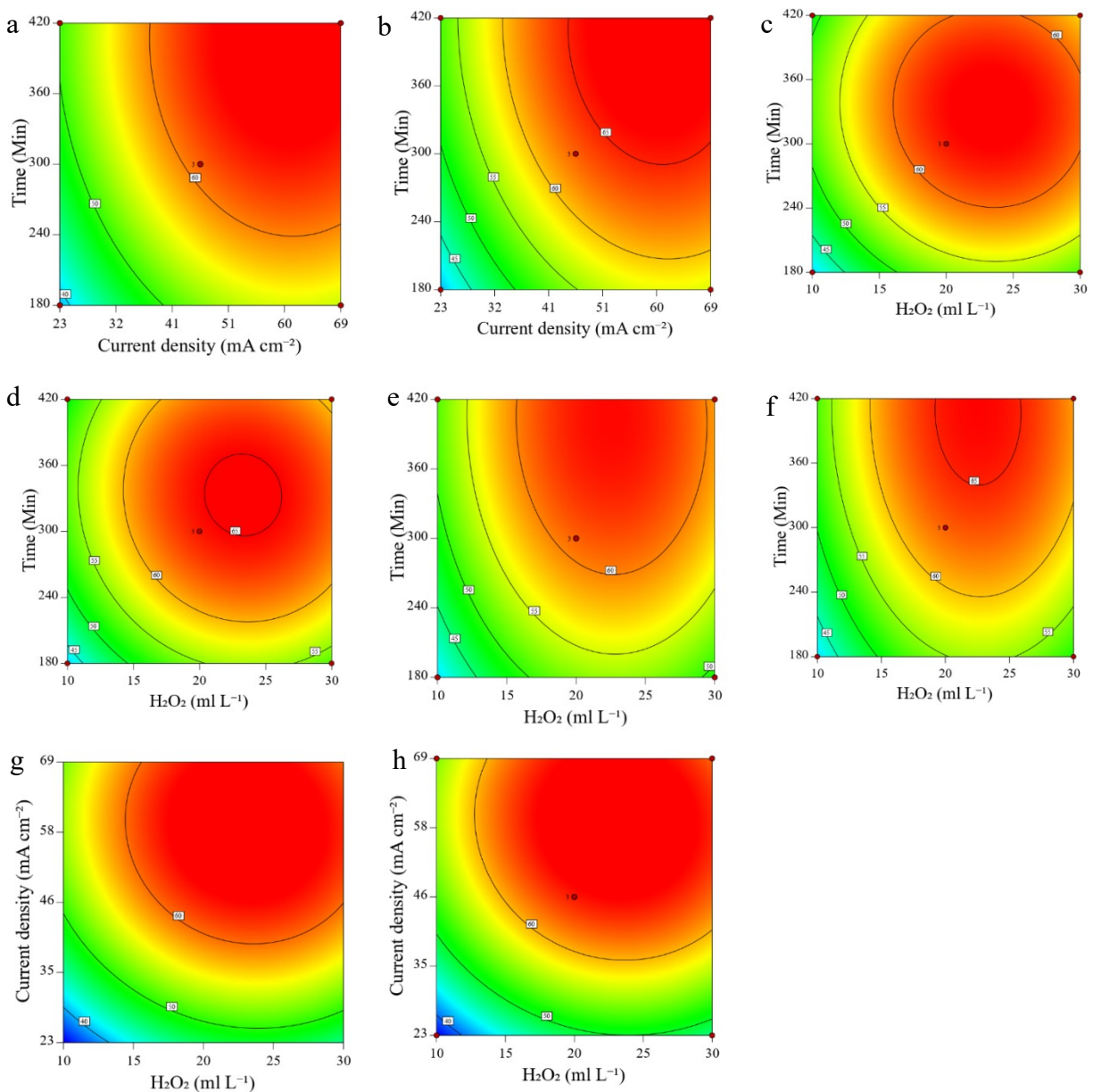
Figure B.4. Two-dimensional contour plots illustrating the interaction effect of two independent variables in electrochemical peroxidation process, a) current density and time for TOC, b) current density and time for DOC, c) time and H2O2 dosage for COD, d) time and H_2O_2 dosage sCOD, **e**) time and H_2O_2 dosage for TOC, f) time and H_2O_2 dosage for DOC, g) current density and H_2O_2 dosage for COD, h) current density and H_2O_2 dosage for sCOD.