

**Treatment of High Strength Brewery Wastewater Using Combined Electro-Oxidation and  
Electro-Fenton Process**

Sharmin Sultana

A Thesis  
In The Department of  
Building, Civil and Environmental Engineering

Presented in Partial Fulfillment of the Requirements  
For the Degree of Master of Applied Science (Civil Engineering) at  
Concordia University,  
Montreal, Quebec, Canada  
January 2017

© Sharmin Sultana, 2017

**CONCORDIA UNIVERSITY**

School of Graduate Studies

This is to certify that the thesis prepared

By: Sharmin Sultana

Entitled: Treatment of High Strength Brewery Wastewater Using Combined Electro-Oxidation and Electro-Fenton Process

and submitted in partial fulfillment of the requirements for the degree of **Master of Applied Science (Civil Engineering)** complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the final Examining Committee:

_____	Chair
Dr. Catherine Mulligan	
_____	Examiner
Dr. Fuzhan Nasiri	
_____	Examiner
Dr. Muthu Packirisamy	
_____	Supervisor
Dr. Saifur Rahaman	

Approved by,

_____	Graduate Program Director
Dr. Fariborz Haghighat	
_____	Dean of Faculty
Dr. Amir Asif	

Date: \_\_\_\_\_ 2017

## Abstract

### Treatment of High Strength Brewery Wastewater Using Combined Electro-Oxidation and Electro-Fenton Process

Sharmin Sultana

In this study, the performance of the anodic oxidation (AO) process was first evaluated for treating brewery wastewater using BDD/Graphite as electrodes, then  $\text{Fe}^{2+}$  was introduced into the system externally to investigate the combined effect of electro-Fenton (EF) and AO. The AO system showed up to 96% of COD removal with increasing current density yet a current density of  $16 \text{ mA/cm}^2$  was used for the rest of the analysis as increasing this parameter past this point improved the performance by only 5% yet consumed 51% more electrical energy. The EF-AO system showed a minor improvement in performance which prompted a hypothesis: the threshold catalytic amount of  $\text{Fe}^{2+}$  is already present in the brewery sample to initiate the Fenton reaction. Further analysis was performed to support this hypothesis: reactive oxygen species (ROS) and total Fe along with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  speciation. The ROS (i.e.  $\text{H}_2\text{O}_2$  and  $\bullet\text{OH}$ ) generation showed slight variations in AO and combined EF-AO process and iron speciation study showed significant reduction of  $\text{Fe}^{2+}$  over the electrolysis period and the available form of iron is  $\text{Fe}^{3+}$  which passivates easily at the experimental condition used, therefore, external addition of  $\text{Fe}^{2+}$  showed no improvement in performance. However, the pre-existing concentration of iron ( $66 \mu\text{g/L}$ ) in brewery wastewater makes the treatment of this type of wastewater using anodic oxidation a dual performing system and therefore, shows satisfactory results. For this dual system, a set of experiments was performed to investigate removal of COD, TN, and TP at different pH conditions with electrolytes. From these analyses, the removal efficiencies were found to be 94, 86, and 100% for COD, TN, and TP respectively at a pH of 7.

## **Acknowledgement**

I would like to seize the opportunity to acknowledge the contributions of and offer my sincere gratitude to my supervisor, Dr. Saifur Rahaman, for granting me a chance of a lifetime to work with such an amazing research group at Concordia University. His inspiring words and continuous guidance during my graduate studies have motivated me to complete this research project successfully. I would also like to appreciate the contribution of many people from Labatt Brewery specifically: Jean Daoust, Claude Danis, and Alexander Baltodano.

Honorable mentions: All the members in Rahaman research group and Hong Guan (lab technician, Concordia University)

# Table of Contents

<b>LIST OF FIGURES .....</b>	<b>VIII</b>
<b>LIST OF TABLES .....</b>	<b>XI</b>
<b>LIST OF TERMS.....</b>	<b>XII</b>
<b>CHAPTER 1 .....</b>	<b>1</b>
<b>INTRODUCTION AND RESEARCH OBJECTIVE .....</b>	<b>1</b>
1.1 BACKGROUND .....	1
1.2 MOTIVATION .....	3
1.2.1 Threats to Aquatic Life .....	3
1.2.2 High Discharge Cost .....	4
1.3 OBJECTIVES OF THE DISSERTATION .....	5
1.4 ORGANIZATION OF THE DISSERTATION .....	6
<b>CHAPTER 2 .....</b>	<b>7</b>
<b>LITERATURE REVIEW .....</b>	<b>7</b>
2.1 BREWERY WASTEWATER .....	7
2.2 BREWING BEER AND SOURCE OF BREWERY WASTEWATER GENERATION.....	8
2.2.1 Brewing Process .....	8
2.2.2 Characteristics of Brewery Wastewater .....	10
2.3 TRADITIONAL PRACTICE TO TREAT BREWERY WASTEWATER .....	10
2.3.1 Conventional methods of pre-treating brewery wastewater.....	11
2.3.1.1 Physical methods .....	11
2.3.1.2 Chemical methods.....	11
2.3.1.3 Biological methods .....	14
2.4 TREATMENT OF BREWERY WASTEWATER FOR REUSE – STATE OF ART TECHNOLOGIES.....	15
2.4.1 Membrane filtration.....	15
2.4.2 Membrane bioreactor (MBR) .....	16
2.4.3 Non-thermal quenched plasma.....	16
2.4.4 The use of Nanomaterials .....	17

2.4.5 <i>Electrochemical methods</i> .....	17
2.4.6 <i>Microbial fuel cells</i> .....	17
2.5 LIMITATIONS OF CONVENTIONAL/EXISTING METHODS .....	18
2.6 INTRODUCTION OF EAOPs - APPLICATION OF EAOPs FOR INDUSTRIAL WASTEWATER TREATMENT.....	19
2.6.1 <i>Types of EAOPs based treatment methods</i> .....	20
2.6.1.1 <i>Electro-Fenton</i> .....	20
2.6.1.2 <i>Anodic Oxidation</i> .....	21
2.6.1.3 <i>Sono-electrochemical and Photo-electrochemical</i> .....	22
2.7 APPLICATION OF EAOPs IN FOOD AND BEVERAGE INDUSTRY WASTEWATER.....	23
2.8 EVOLUTION OF EAOP .....	23
2.9 OPPORTUNITIES AND CHALLENGES OF ELECTROCHEMICAL PROCESSES IN TREATING INDUSTRIAL WASTEWATER.....	24
<b>CHAPTER 3 .....</b>	<b>24</b>
<b>MATERIALS AND METHODS .....</b>	<b>24</b>
3.1 MATERIALS .....	24
3.1.1 <i>Sample Preparation</i> .....	25
3.1.2 <i>Physical-chemical Characteristics of Brewery Wastewater</i> .....	25
3.2 EXPERIMENTAL SETUP .....	27
3.3 ANALYSIS.....	28
3.3.1 <i>Electrochemical Measurements</i> .....	28
3.3.2 <i>Analytical Measurements</i> .....	29
3.3.3 <i>H<sub>2</sub>O<sub>2</sub> Measurement</i> .....	30
3.3.4 <i>•OH Measurement</i> .....	31
3.3.5 <i>Measurement of Fe (II), Fe (III) and Total Fe</i> .....	32
<b>CHAPTER 4.....</b>	<b>33</b>
<b>RESULTS AND DISCUSSION .....</b>	<b>33</b>
4.1 ELECTROCHEMICAL CHARACTERISTICS OF BREWERY WASTEWATER – CYCLIC VOLTAMMETRY .....	33

4.2 ELECTRO-OXIDATION AND ELECTRO-FENTON DEGRADATION PROFILES FOR COD AND TOC	35
.....	35
4.2.1 <i>Effect of Current density on COD reduction</i> .....	35
4.2.2 <i>Effect of Initial Fe<sup>2+</sup> dose on COD and TOC reduction</i> .....	35
4.2.3 <i>Kinetic Study</i> .....	39
4.3 CONCENTRATION OF REACTIVE OXYGEN SPECIES .....	42
4.3.1 <i>In-situ generated hydrogen peroxide</i> .....	42
4.3.2 <i>Hydroxyl Radical</i> .....	44
4.3.2.1 <i>Effect of Initial SA Concentration on •OH production</i> .....	45
4.3.2.2 <i>Effect of Reaction time for Effective trapping of •OH</i> .....	46
4.3.2.3 <i>Effect of reaction time on production of hydroxylated products of SA and COD reduction</i> .....	47
4.4 TOTAL IRON AND IRON (II) CONCENTRATION .....	49
4.5 ENHANCEMENT OF AO PERFORMANCE AT DIFFERENT pH VALUE WITH THE ADDITION OF ELECTROLYTIC SOLUTION.....	51
4.6 ENERGY CONSUMPTION AND CURRENT EFFICIENCY – AN ANALYSIS OF RELATIVE COST.....	53
4.7 CONTINUOUS EXPERIMENT – ELECTRODE FOULING.....	55
<b>CHAPTER 5</b> .....	<b>56</b>
<b>CONCLUSIONS AND FUTURE PERSPECTIVES</b> .....	<b>56</b>
<b>CHAPTER 6</b> .....	<b>58</b>
<b>REFERENCES</b> .....	<b>58</b>
<b>APPENDIX</b> .....	<b>65</b>

## List of Figures

Figure 1 Illustration of effect of highly concentrated industrial/brewery wastewater discharge on aquatic lives. ....	4
Figure 2 Schematic diagram of the brewing process and areas of potential wastewater generation. Legends reading guideline: “Name of the process” – “Ingredients/Composition”. ....	9
Figure 3 Schematic of the electrolysis cell with five electrode plates configuration (two anodes and three cathodes) .....	28
Figure 4 Formation of hydroxylated products from the reaction between salicylic acid and hydroxyl radical <sup>59</sup> . ....	31
Figure 5 Cyclic voltammetry analysis of brewery wastewater as a function of applied potential. [Experimental condition: room temperature, scan rate = 50, 100 mV/s, pH = 3, working electrode = BDD, counter electrode = stainless Steel, reference electrode = Ag/AgCl, inset shows the magnified view of selected CV curve]. ....	34
Figure 6 Degradation profile of COD over time (a) at different current densities (anodic oxidation system), (b) at different initial Fe (II) concentration (combined electro-Fenton and anodic oxidation). [Experimental condition: room temperature, pH 3, sample volume = 450 ml]. .	36
Figure 7 TOC degradation profile over time for the combined electro-Fenton and anodic oxidation system. [Experimental condition: room temperature, current density = 16 mA/cm <sup>2</sup> , sample volume = 450 ml]. ....	37
Figure 8 Kinetic study of a) COD degradation (anodic oxidation), b) COD degradation (combined electro-Fenton and anodic oxidation), and c) TOC degradation (combined electro-Fenton and anodic oxidation) [Experimental condition: room temperature, initial pH 3, current density = 16 mA/cm <sup>2</sup> , electrolysis time = 6h, sample volume = 450 ml]. ....	40
Figure 9 Absorption spectra of DPD <sup>+</sup> (Product of DPD/HRP and H <sub>2</sub> O <sub>2</sub> ) with different H <sub>2</sub> O <sub>2</sub> concentrations. ....	42
Figure 10 Cathodic H <sub>2</sub> O <sub>2</sub> production v/s electrolysis time in anodic oxidation and combined electro-Fenton and anodic oxidation system. [Experimental condition: room temperature, initial pH 3, current density = 16 mA/cm <sup>2</sup> , initial [Fe (II)] = 0.2 mM, sample volume = 450 ml]. ....	43
Figure 11 Absorption spectra of SA, 2,3-DHBA and 2,5-DHBA shows three different maxima at 303, 309 and 323 nm respectively. ....	45



Figure 12 Effect of (a) initial [SA], (b) reaction time on effective OH radical trapping by “trap and trigger” method. [Experimental condition: reaction time = 35 min for (a), initial SA concentration = 5 mM for (b)]..... 46

Figure 13 (a) Production of hydroxylated products, (b) Consumption of hydroxyl radical for COD reduction over time, in different electrochemical system..... 48

Figure 14 Trend of total iron concentration over time in an integrated electro-Fenton and anodic oxidation system. .... 50

Figure 15 Variation of Fe species concentration over time in the integrated electro-Fenton and anodic oxidation system. .... 51

Figure 16 Effect of pH and electrolyte addition on the performance of anodic oxidation system in terms of COD removal over time. [Experimental condition: room temperature, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 6h, [Na<sub>2</sub>SO<sub>4</sub>] = 30 mM, sample volume = 450 ml]..... 52

Figure 17 Total nitrogen (TN) removal at different initial pH values using the anodic oxidation system. [Experimental condition: room temperature, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 6h, [Na<sub>2</sub>SO<sub>4</sub>] = 30 mM, sample volume = 450 ml]. .... 53

Figure 18 Effect of pH and electrolyte addition on the performance of anodic oxidation system (a) electrical energy consumption; (b) instantaneous current efficiency. [Experimental condition: room temperature, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 6h, sample volume = 450 ml]..... 54

Figure 19 COD degradation profile for the continuous set of experiments. [Experimental condition: room temperature, initial pH 7, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 12 h, flow rate = 0.078 L/h]. .... 55

Figure 20 Change of conductivity (average) over time in different electrochemical treatment systems. [Experimental condition: room temperature, initial pH 3, sample volume = 450 ml]. .... 65

Figure 21 Change of voltage requirement (average) over time in different electrochemical treatment methods used in this study. [Experimental condition: room temperature, initial pH 3, sample volume = 450 ml]. .... 66

Figure 22 Change of initial pH (average) over time in different electrochemical treatment methods used in this study. [Experimental condition: room temperature, sample volume = 450 ml]. 66

Figure 23 Effect of initial pH and electrolyte addition on the requirement of voltage over time in anodic oxidation system. [Experimental condition: room temperature, sample volume = 450 ml]..... 67

Figure 24 Electrical energy consumption as a function of current density (CD), mA/cm<sup>2</sup> for anodic oxidation system. As CD increases the energy consumption also increases where increment of CD from 8 to 16 consumes 34% more energy than the lower one and an increment from 16 to 24 consumes 51% more energy than 16 mA/cm<sup>2</sup>..... 67

Figure 25 Changes of instantaneous current efficiency (ICE) over time at different current density. Significant difference in ICE can be observed at 0.5 and 6 hr respectively at various current density..... 68

Figure 26 Electrical energy consumption as a function of current density (CD), mA/cm<sup>2</sup> for combined electro-Fenton and anodic oxidation system. The addition of Fe (II) showed no significant effect on electrical energy consumption. [Experimental condition: room temperature, initial pH 3, current density = 16mA/cm<sup>2</sup>, electrolysis time = 6 h, sample volume = 450 ml]. ..... 68

Figure 27 Changes of instantaneous current efficiency (ICE) over time at different initial iron (II) concentration. The range of concentration used in this study showed slight variation in ICE at every time interval tested. [Experimental condition: room temperature, Initial pH 3, current density = 16mA/cm<sup>2</sup>, electrolysis time = 6h, sample volume = 450 ml]. ..... 69

## List of Tables

Table 1 Typical characteristics of brewery wastewater .....	12
Table 2 Summary of existing treatment methods of brewery wastewater .....	18
Table 3 Classification of anodic materials .....	22
Table 4 Labatt brewery wastewater characteristics .....	25
Table 5 Kinetic study parameters .....	41
Table 6 Calibration curves equation, $R^2$ value and range of linear relations (both hydrogen peroxide and OH radicals) .....	44

## List of Terms

EF	Electro-Fenton
AO	Anodic oxidation
EO	Electro-oxidation
EAOPs	Electrochemical advanced oxidation processes
BDD	Boron doped diamond
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
TOC	Total organic carbon
DO	Dissolved oxygen
DO <sub>sat</sub>	Saturated dissolved oxygen
TN	Total nitrogen
TP	Total phosphate
MBR	Membrane bioreactor
AnMBR	Anaerobic membrane bioreactor
UASB	Up-flow anaerobic sludge blanket
RO	Reverse Osmosis
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration

NPs	Nanoparticles
UV-Vis	Ultraviolet-visible
ICP-MS	Inductively coupled plasma mass spectroscopy
ICE	Instantaneous current efficiency
EEC	Electrical current consumption
DI water	De-ionized water
SHE	Standard hydrogen electrode
Mash Tun	In brewing, mashing is the process of combining a mix of milled grain, and water, and heating this mixture. Mashing allows the enzymes in the grain to break down the starch in the grain into sugars, to create a malty liquid called wort
Lauter Tun	Lautering is the process of separating the mash into the clear liquid (wort) and residual grain to brew beer
Trub	Trub is the layer of sediment that appears at the bottom of the fermenter after yeast has completed the bulk of the fermentation. It is composed mainly of heavy fats, proteins and inactive yeast

## Chapter 1

### Introduction and Research Objective

#### 1.1 Background

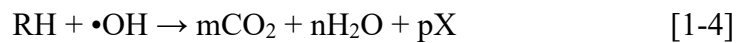
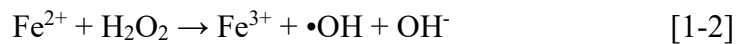
The brewing industry typically produces a significant amount of wastewater from production (by-products with effluents) and non-production (washing and cooling) units. The process of brewing beer takes in large quantities of water and it has been reported that up to 70% of it is discharged as wastewater<sup>1</sup>. The main constituents of this type of wastewater include sugars, soluble starch, ethanol, VFAs and total suspended solids which mainly comes from the production unit<sup>2</sup>. The combination of production and non-production unit produces an enormous amount of polluted water, which contain both chemical and microbial contaminants<sup>3</sup>. It is estimated that in the production of 1 L of beer, 3–10 L of waste effluent is generated, depending on the production technique and specific water usage.

Ideally, the mainstream method of brewery wastewater treatment is based on biological methods which have been reported to be effective in efficiently reducing COD concentration. Common biological methods used for treating this type of wastewater include aerobic sequencing batch reactor<sup>4</sup>, cross-flow ultrafiltration membrane aerobic reactors<sup>5</sup>, up-flow anaerobic sludge blanket reactors (UASB)<sup>6</sup>, and anaerobic membrane bioreactor (AnMBR)<sup>7</sup>. Biological treatment processes are especially effective for wastewater treatment, but require a high-energy input (aerobic) and high maintenance (anaerobic) with higher retention time. Moreover, the biodegradation of microorganisms present in wastewater requires specific bacterial forms to achieve higher removal efficiencies<sup>3, 8</sup>. Therefore, to treat this type of wastewater, a method which consumes lower energy at a higher removal efficiency is needed.

Advanced oxidation processes (AOPs) combined with electrochemical processes, together known as Electrochemical Advanced Oxidation Processes (EAOPs) have been reported as an emerging technology to remove organic pollutants from wastewater. In-situ electro-

generated hydroxyl radicals ( $E^\circ(\bullet\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$ ) are the fundamental aspect of these technologies<sup>9</sup>. For water and wastewater reclamation, EAOPs based Fenton's reaction has substantially evolved over the past decade, showing effectiveness in the treatment of pharmaceutical caffeine<sup>10</sup>, antibiotics<sup>11</sup>, photographic processing wastewater<sup>12</sup>, textile industry wastewater<sup>13</sup>, winery wastewater<sup>14</sup> and a broad swath of other categories of wastewater.

The basis of electro-Fenton (EF) technology is the continuous electrical generation of  $\text{H}_2\text{O}_2$  at a suitable cathode surface saturated with  $\text{O}_2$  or air Eq.(1-1), alongside the addition of iron as a catalyst, producing hydroxyl radicals in the bulk solution via Fenton's reaction Eq.(1-2). In this process,  $\text{Fe}^{3+}$  from Fenton's reaction can be cathodically reduced to  $\text{Fe}^{2+}$  with  $E^\circ = 0.77 \text{ V/SHE}$ <sup>15</sup>, Eq.(1-3). The incorporation of anodic oxidation (AO)/Electro-oxidation (EO) process with EF enhances the production of  $\bullet\text{OH}$  radical and hence increase the removal efficiency significantly. Through the AO/EO process all the organics present in an electrolytic cell are degraded by hydroxyl radical formed as an intermediate from the oxidation of water to  $\text{O}_2$  at the surface of a high oxidation potential anode like  $\text{SnO}_2$ ,  $\text{PbO}_2$ , or boron doped diamond (BDD)<sup>16</sup>. These  $\bullet\text{OH}$  radicals react with organics up to their full/partial mineralization without any selectivity, Eq.(1-4) (i.e., convert them into  $\text{CO}_2$ , water, and inorganic ions<sup>11a, 17</sup>).



Where, R refers to organic matter and X refers to inorganic ions.

The rate of electro-reduction of  $O_2$  and subsequent  $H_2O_2$  generation ( $E^\circ = 1.763 \text{ V/SHE}$ ) greatly influence the production of hydroxyl radicals which are the main agent controlling the degradation efficiency of aqueous organic matters in the EO and EF processes<sup>18</sup>. The inevitable role of these two oxidizing agents (i.e.  $H_2O_2$  and  $\bullet OH$ ) in these types of EAOPs makes it customary to study the generation rate of these species for evaluation of effective treatment and removal efficiency.

## **1.2 Motivation**

Today, the management of environmental issues is a primary concern all over the world and industries are subjected to extended governmental rules and regulations. The amount of waste which is generated from the brewing industry must reach a standard water quality level before discharge to comply with environmental protection laws. The usual practice of wastewater discharge from a brewery has included four options: (a) directly into a river or ocean; (b) directly into a municipal sewer system; (c) into a river or municipal system after pre-treatment; and (d) into the brewery's own waste water treatment plant<sup>2, 19</sup>. Each of these approaches has some limitations which have been explained in brief in the following section.

### **1.2.1 Threats to Aquatic Life**

Direct discharge of highly concentrated wastewater into a body of water presents a great threat to aquatic life and, therefore, is subjected to limitations in terms of organic load, suspended solids, pH, temperature, and chlorine concentration. The organic contents of wastewater require oxygen for their degradation which is consumed from the waterbody<sup>2</sup>. For instance, if wastewater of high strength quality is dumped into a river, all the bacteria present in the river will start degrading the organic matter which requires the consumption of oxygen from the waterbody. It is important to mention that the rate of oxygen consumption for bacterial activity is faster than the physical oxygen regeneration rate from the air to the river, creating a situation of dissolved oxygen deficiency for the aquatic life



in the river. Figure 1 depicts an illustration of how industrial/brewery wastewater discharge affects marine life<sup>20</sup>.



Figure 1 Illustration of effect of highly concentrated industrial/brewery wastewater discharge on aquatic lives.

### 1.2.2 High Discharge Cost

The associated cost of discharging untreated or partially treated wastewater into municipal sewer systems or in rivers is quite high. As mentioned earlier, most breweries discharge 70% of incoming water as effluent; a quantitative analysis showed 4.87 m<sup>3</sup> of water was used as intake per each meter cubic of beer produced whereas 3.33 m<sup>3</sup> of waste water effluent was generated per m<sup>3</sup> of beer produced<sup>4</sup>. In most cases, brewery effluent disposal costs are much higher than water supply costs.

The concept of water treatment for reuse has been shown in the literature recently, as the regulations regarding wastewater disposal have become more rigorous alongside a rising cost for intake water. Primary reasons for wastewater reuse being an uncommon practice in this type of industry include public perceptions and the possible product quality deterioration. As the shortage of water is becoming an increasingly serious global problem day by day, the momentum of brewery wastewater reuse is inescapable<sup>2</sup>.

To maintain the quality of natural ecosystems, it is crucial to build eco-efficient strategies into every industry. Through this study, an attempt has been made to provide a model wastewater treatment plant for the brewery industry that maximizes the removal efficiency

within a short period, holds a low possibility of producing any toxic by-products and has the potential to regenerate usable water from waste effluent.

### **1.3 Objectives of the Dissertation**

The principal objective of this study was to investigate the potential of electrochemical methods for brewery wastewater treatment. The performance of anodic oxidation and integrated anodic oxidation with the electro-Fenton process (addition of Fe (II) from external source to initiate Fenton's reaction) was evaluated for the removal of contaminants from brewery wastewater. To the best of our knowledge, the combination of these two EAOPs for the treatment of this particular type of wastewater has not been reported in the literature at this time. The following items were studied in this research work to achieve the primary goal, sequentially:

1. Physical, chemical and electro-chemical characterization of brewery wastewater,
2. Performance evaluation of anodic oxidation process in the degradation of organics from brewery wastewater with regards to chemical oxygen demand (COD),
3. Integration of the electro-Fenton (EF) technique by adding iron from external source with the anodic oxidation (AO) process to evaluate the possible enhancement in contaminant removal by measuring effluent COD and total organic carbon (TOC) concentration,
4. Determination of the generation rate and concentrations of reactive oxygen species (i.e. hydrogen peroxide and hydroxyl radicals) at different time interval for AO and integrated AO-EF respectively to understand the contribution of each technology in reducing organic concentrations and to develop an appropriate strategy for possible enhancement in performance,
5. Measurement of Fe species in the sample solution throughout the electrolysis period to investigate the available concentration of Fe (II) in the system,
6. Analysis of the effect of the initial pH value and electrolytes on the performance of the treatment system,
7. Evaluation of the performance of the electrochemical treatment system in a continuous mode of operation.

## **1.4 Organization of the Dissertation**

This dissertation is comprised of six chapters and an appendix. A brief discussion on the contents of these sections are as follows,

Chapter 1: Introduction describes the background study, motivation and objectives for this research work.

Chapter 2: Literature review describing, in detail, the characteristics of brewery wastewater, existing technologies and their limitations, application of EAOPs to treat this type of wastewater and critical challenges associated with these processes.

Chapter 3: Material and method section describing about the sample collection from the brew house and storage, experimental setup, reagents used in the study and in-detail steps of analytical measurement.

Chapter 4: Result and discussion section reporting the experimental results of the EAOPs study conducted using real brewery wastewater.

Chapter 5: Conclusion section summarizing the study and providing recommendations for future study.

Chapter 6: A list of references.

Appendix.

## **Chapter 2**

### **Literature Review**

#### **2.1 Brewery Wastewater**

Brewing is one of Canada's oldest industries, and at present Canadian brewers hold an 89% share of the domestic beer market. Canada holds two competitive advantages in terms of making world class beers: proximity to high-quality malt barley and an abundant fresh water supply. Beer is the most popular alcoholic beverage in Canada, in terms of both volume and dollar value<sup>21</sup>.

In general, the food and beverage processing industry is the second largest manufacturing sector in Canada in terms of value of production with shipments worth \$105.5 billion in 2014; it accounts for 17% of total manufacturing shipments and 2% of the national gross domestic product (GDP). It's the largest manufacturing employer and provides employment for 246,000 Canadians<sup>22</sup>.

According to Industrial Water Use, a Publication from Statistics Canada 2011<sup>23</sup>, the total water intake by Canadian manufacturing industries in 2011 was 3,677.5 million cubic metres and the food industry accounted for 9.4% of total water withdrawals. Geographically, manufacturers located in Ontario and Quebec accounted for most of the water intake, with Ontario contributing 40.7% and Quebec responsible for an additional 23.1% of the total. Due to the high economic value of beer production, the number of companies engaged in this type of industry is increasing rapidly and the number of licensed breweries in Canada has risen by almost 108% over the past five years, with 644 breweries in operation in 2015<sup>24</sup>.

## 2.2 Brewing Beer and Source of Brewery Wastewater Generation

### 2.2.1 Brewing Process

Globally, beer is considered as the fifth most consumed beverage behind tea, carbonated beverages, milk and coffee and the pace of its popularity continues with an average consumption of 23 litres/person per year<sup>25</sup>. This popular alcoholic beverage is made from a malted grain (usually barley), water, and possibly a herb or spice for flavor (e.g. hops), with the whole mixture being fermented with yeast<sup>26</sup>.

Brewing beer involves two main steps: a) brewing and b) packaging of the finished product. The by-products (e.g., spent grains from mashing, yeast surplus, etc.) generated from these steps are considered pollutants when mixed with effluent water. Also, the cleaning of tanks, bottles, machines, and floors produce high quantities of polluted water, which contain both chemical (with very high organic content) and microbial contaminants<sup>3</sup>. It is estimated that in the production of 1 L of beer, 3–10 L of waste effluent is generated, depending on the production technique and specific water usage. In other words, large quantities of water are consumed and polluted during the beer brewing process<sup>2,27</sup>. Figure 2 shows the schematic of brewing process and main areas of wastewater generation with possible composition. The composition of beer wastewater comes from different production units, namely cleaning of mash tun and lauter tun, boil kettle, whirlpool, fermentation, and filtration units as well as non-production units such as rinsing, washing, dewatering, rinsing spent hops, and hot trub. Spilling of beer during the production is another source of wastewater generation with a simple composition of mainly water and beer<sup>28</sup>.



Figure 2 Schematic diagram of the brewing process and areas of potential wastewater generation. Legends reading guideline: “Name of the process” – “Ingredients/Composition”.

### **2.2.2 Characteristics of Brewery Wastewater**

Traditionally, to describe brewery wastewater quality, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) have been reported. High concentration of these parameters indicates a nutrient-rich wastewater, one which promotes the growth of algae and bacteria if discharged into a river. The presence of these microorganisms creates a situation of oxygen deficiency in water and subsequently the death of marine life. Studies have been performed characterizing dissolved organics present in wastewater and have reported that these contents are highly heterogeneous with compounds of a variety of different molecular weights, ranging from simple structures to very complex polymers. Janhom et al.<sup>29 29 29 30</sup> reported that brewery wastewater has high levels of DOC (Dissolved Organic Content) and an absorbance at UV<sub>254</sub> indicating a high level of organic content with aromatic structures<sup>29</sup>. Typical physical and chemical characteristics of Brewery wastewater are shown in Table 1. Other than the parameters mentioned, beer wastewater has been shown to contain trace elements such as zinc, manganese, and iron which may originate from the ingredients used (e.g. hops) or the process of making beer<sup>30</sup>.

### **2.3 Traditional Practice to Treat Brewery Wastewater**

High levels of organic matter in the effluent makes the disposal of untreated/partially treated brewery wastewater into water bodies a potential threat to the aquatic life as the removal of organic compounds through microbial means requires oxygen for degradation and creates an oxygen depleted environment which presents a major threat to the survival of non-microbial organisms. As the management of environmental issues is of growing concern these days, the brewing industry, like any other industry, is subject to extensive government regulations and must comply with numerous environmental protection laws.

### **2.3.1 Conventional methods of pre-treating brewery wastewater**

Pre-treatment of brewery wastewater means the alteration of physical, chemical, or biological properties of the effluent before discharge into a municipal sewer or public water body to meet municipal bylaws and/or to improve the performance of municipal treatment plant.

#### **2.3.1.1 Physical methods**

Physical methods of treatment are used to remove coarse solid particles through physical force, allowing particles to settle out or float to the top naturally. Major physical methods used for solid separation are screening, comminution, sedimentation, and flotation. It has been reported that these methods are not suitable in a decontamination process; for instance, the use of sedimentation was found ineffective even with added chemical coagulants and flocculants<sup>2</sup>.

#### **2.3.1.2 Chemical methods**

Chemical pre-treatment of brewery wastewater involves the alteration of water chemistry by pH adjustment or coagulation and flocculation. Adjustment of wastewater pH to neutral levels before discharge is mandatory to protect aquatic life. Primary chemical methods include chemical precipitation<sup>31</sup>, adsorption, disinfection, and chlorination.



Table 1 Typical characteristics of brewery wastewater

<b>Parameters</b>	<b>Harbin Brewery Co., Ltd. (Harbin, China) 2008</b>	<b>United Breweries (UB), Hyderabad, India</b>	<b>Unicer Brewery</b>	<b>Typical Brewery</b>	<b>Opaque Beer</b>	<b>Carlsberg Brewery Malaysia Berhad</b>	<b>Synthetic Brewery Wastewater</b>	<b>Local Craft Brewery</b>	<b>Brewery Wastewater Treatment Plant Influent</b>
<b>pH</b>	6.5±0.2	3-12	6.5-7.9	4.5-12	3.3-6.3	8.5±0.2		5.7±0.5	5.95
<b>Temperature, °C</b>		18-40	30-35	18-20	25-35				
<b>Alkalinity, mg/L as CaCO<sub>3</sub></b>								270±80	380
<b>TS, mg/L</b>		5100-8750			5100-8700				2850
<b>TSS, mg/L</b>	480±70	2901-3000		200-1000	2901-3000	350		950±450	1530
<b>TDS, mg/L</b>		2020-5940							1320
<b>COD, mg/L</b>	2250±418	2000-6000	800-3500	2000-6000	8240-20000	2470	17000±600	11080±2760	2811
<b>BOD, mg/L</b>	1340±335	1200-3600	520-2300	1200-3600		1457			
<b>TOC, mg/L</b>	970±156					820			

<b>TN, mg/L</b>	54±14 <sup>a</sup>	25-80 <sup>b</sup>	12-31	25-80	0.0196- 0.0336	97 <sup>a</sup> 62 <sup>b</sup>	268±18 101±5 <sup>b</sup>	180±10 0 8±3 <sup>b</sup>
<b>TP, mg/L</b>	50±35 <sup>c</sup>	10-50 <sup>c</sup>	9-15	10-50	16-24	56 <sup>c</sup>	66±2 55±2 <sup>c</sup>	55±35 26±19 <sup>c</sup>
<b>Reference</b>	Feng et al. <sup>6</sup>	Rao et al. <sup>32</sup>		A. G. Brito et al. <sup>28</sup>		Krishnan Vijayaragha van et al. <sup>8</sup>	Chen et al. <sup>7</sup>	Scampini et al. <sup>33</sup>

<sup>a</sup>TKN – Total kheljhal nitrogen, <sup>b</sup>NH<sub>3</sub>-N – Total ammonia nitrogen, <sup>c</sup>PO<sub>4</sub>-P – Phosphate as phosphorus, TS – Total solids, TSS – Total suspended solids, TDS – Total dissolved solids, COD – Chemical oxygen demand, BOD – Biochemical oxygen demand, TOC – Total organic carbon, TN – Total nitrogen, TP – Total phosphorus.

### **2.3.1.3 Biological methods**

Biological methods of treatment are based on the induced activity of wide range of microorganisms to convert biodegradable organic matter in the wastewater into benign inorganic by-products. Breweries produce high quantities of polluted water, which contain both chemical (with very high organic content) and microbial contaminants<sup>3</sup> which makes biological treatment effective for this type of wastewater after it has been undergone physical and chemical pre-treatment. Biological treatment of wastewater is divided into two types, either with oxygen (aerobic) or without oxygen (anaerobic).

#### **Aerobic**

Aerobic microorganisms metabolize organic pollutants from wastewater in the presence of oxygen and therefore reproduce and create inorganic end-products (principally CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O). Typical aerobic treatment methods include activated sludge processes, sequencing batch reactor<sup>34</sup>, bio-filtration towers, the rotating biological contactor (RBC) process, and lagoons<sup>2, 35</sup>.

#### **Anaerobic**

This type of wastewater treatment is characterized by the biological conversion of organic compounds by anaerobic microorganisms into biogas, which can be used as a fuel, mainly methane (55-75% by volume) and carbon dioxide (25-40 % by volume) with traces of hydrogen sulfide in the absence of elemental oxygen. Typical anaerobic treatment methods include up-flow anaerobic sludge blanket (UASB) reactor<sup>33</sup>, and fluidized bed reactor.

A full-scale study of UASB reactor seeded with activated sludge was performed by Parawira et al., an average percent removal of 50, 90 and 57% was reported in terms of total solids, settleable solids and COD. The treatment enables the brewery to meet the requirements of the wastewater discharged into public water works yet significantly

increases the concentration of orthophosphates and nitrogen in the UASB effluent and therefore, tends to accumulate these nutrients in the system<sup>36</sup>.

## **2.4 Treatment of brewery wastewater for reuse – State of art technologies**

The brewing industry consumes a large amount of water as influent for brewing, rinsing, and cooling purposes. Water regeneration, or recycling, is gaining more interest as regulations become more stringent and the cost of fresh water rises<sup>37</sup>. As a result, most breweries are interested in installing the appropriate treatment plant to recycle the water, making the overall process more cost effective. Technologies that meet that purpose which have been introduced in the literature are discussed below.

### **2.4.1 Membrane filtration**

Membrane filtration technology is divided into four classes, based on the effective pore size of the membrane: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) or hyperfiltration membrane. These are considered integral components of drinking water and wastewater treatment processes. In the case of brewery wastewater, it has been reported that two areas where membrane processes play useful roles are: (i) loss reduction in the brewing process, and (ii) as a technological alternative to conventional solid–liquid separations<sup>25</sup>. Typically, there are two ways to operate membrane filtration process: dead end and cross flow. In dead-end filtration, all of the feed water flows through the membrane (as permeate) so that all impurities that are too large to pass through the pores accumulate in the filter module. In crossflow mode, feed water flows parallel to the membrane surface, with only a proportion passing through the membrane. Braeken et al. reported that nanofiltration (NF) was sufficient for regeneration when the wastewater was pre-treated biologically<sup>25</sup>.

### **2.4.2 Membrane bioreactor (MBR)**

The membrane bioreactor (MBR) technique is a combination of two well-established treatment methods: enhanced biological treatment using activated sludge, and membrane filtration. The method is divided into two configurations based on how the membrane is integrated with the bioreactor: side-stream and submerged. In side-stream MBRs, membrane modules are placed outside the reactor in series connection, and the reactor mixed liquor circulates over a recirculation loop that contains the membrane. On the other hand, in submerged MBRs, the membranes are placed inside the reactor, submerged in the mixed liquor. MBR technology has been applied in the treatment of brewery wastewater, with significant amounts of COD removal (~90%) reported in most cases. For reuse purpose, the use of MBR after use of a UASB (Up-flow Anaerobic Sludge Blanket) reactor has been shown to be effective, with the MBR system removing 96% of influent COD<sup>2</sup>.

The use of an anaerobic membrane bioreactor (AnMBR) has recently been reported to abate pollutants from brewery wastewater. AnMBR is an integrated anaerobic digestion and membrane filtration process, where a membrane system separates all solid parts from wastewater, improving the effluent quality. A study by Chen et al. reported a 98% removal was achieved with a 0.53 L biogas/gCOD conversion rate for the brewery wastewater when using the AnMBR technology<sup>7</sup>.

### **2.4.3 Non-thermal quenched plasma**

At high temperatures, the intermolecular forces of a highly-ionized gas created by ionic attractions and repulsions give these compositions distinct properties, termed “Plasma” and described as the fourth state of matter. Uniquely, unlike gas, plasma may form structures such as filaments, beams and double layers<sup>2</sup> in the influence of a magnetic field. As a suitable source of plasma gasses, the use of electric discharges is expanding to treat gasses and liquids to evaluate of contaminant removal processes. In an electric discharge, strong oxidizing species such as OH and NO radicals are created which participate in the contaminant abatement processes<sup>3,35</sup>.

In a study by Doubla et al., where an electric gliding arc was discharged in humid air to create plasma, the BOD removal efficiency for brewery industrial wastewaters with values of 385 and 1018 mg/L were 74 and 98%, respectively<sup>3</sup>.

#### **2.4.4 The use of Nanomaterials**

Carbon nanotubes (CNTs) have been found to be highly efficient in adsorbing various organic and inorganic pollutants and hence have been used in different studies to treat brewery wastewater for water reclamation and reuse purpose. A study by G. Simate<sup>31b</sup> used CNTs adsorption in a granular filter bed integrated with coagulation/flocculation and sedimentation in a semi-continuous laboratory scale water treatment plant for turbidity and COD removal. This treatment scheme removed 96.0% of COD and only 5 NTU of residual turbidity remained in the effluent.

#### **2.4.5 Electrochemical methods**

The application of electrochemical methods in the treatment of industrial wastewater has been widely received as it has been shown to achieve partial or complete decomposition of organic substances. In a study by Vijayaraghavan et al. a novel brewery wastewater treatment method based on in situ hypochlorous acid generation was developed where a COD reduction of 97% was achieved when graphite was used as an anode and stainless steel as a cathode in an undivided electrolytic cell<sup>8</sup>.

#### **2.4.6 Microbial fuel cells**

Microbial fuel cell (MFC) is a combined system with anaerobic and aerobic characteristics that treats wastewater and generates electricity at the same time. MFC has been reported as a very effective method in terms of COD removal by many researchers. Feng et al. analysed the efficiency of MFC to treat brewery wastewater in terms of maximum power densities, coulombic efficiencies, and chemical oxygen demand (COD) removal as a function of

temperature and wastewater strength<sup>6</sup>. In their study, an 87% COD removal efficiency was reported where maximum power density was found to be 205 mW/m<sup>2</sup>.

A study by Wang et al. reported that the ionic strength of brewery wastewater would play a significant role in the performance of MFC system as it is inversely proportional to the power/voltage outputs<sup>38</sup>. Table 2 shows the summary of existing treatment methods in literature to treat brewery wastewater<sup>2</sup>.

Table 2 Summary of existing treatment methods of brewery wastewater

<b>Process</b>	<b>COD Reduction (%)</b>
<b>Quenched plasma</b>	98
<b>UASB</b>	73-91
<b>Aerobic reactor</b>	90-98
<b>Combined bioreactor</b>	98
<b>Membrane bioreactor</b>	96
<b>Electrochemical method</b>	97
<b>Microbial fuel cells</b>	94
<b>Nanofiltration</b>	96
<b>Reverse osmosis</b>	100

## **2.5 Limitations of Conventional/Existing Methods**

Brewers are concerned that they are using the best techniques in terms of product quality and cost effectiveness. During production, beer alternately goes through three chemical and biochemical reactions (mashing, boiling, fermentation and maturation) and three solid-liquid separations (wort separation, wort clarification, and rough beer clarification). Consequently, water consumption, wastewater, and solid-liquid separation constitute real economic opportunities for improvements in brewing<sup>25</sup>.

The alteration of physical, chemical, and biological properties of brewery effluent help the brewing industry meet municipal bylaws. Among all these processes categories, biological treatment methods hold three major advantages over the others: (1) the treatment technology is mature, (2) they are highly efficiency in COD and BOD removal, ranging from 80 to 90%, and (3) require a low investment cost. Despite these advantages, the requirements for high energy input limits the application of this method in a large scale<sup>2</sup>. Additionally, biological methods naturally lead to longer hydraulic retention times and are subject to failure due to shock loading and improper maintenance, and specific bacterial strains are required for the biodegradation of flavonoids present in the brewery to achieve higher removal efficiencies<sup>8</sup>.

The major limitation of using MBR and membrane technology for the treatment of wastewaters is membrane fouling. Severe fouling problems significantly increase the chemical cleaning frequency of the membrane module and also rapidly lower retention which reduces the lifetime of the membrane<sup>39</sup>.

The use of nanomaterials in wastewater treatment processes is challenging as they lack dispersion and solubility. Improvements in nanomaterial dispersity through functionalization is required before use. Synthesis of nanomaterials is a complex process, hence expensive, and they require regeneration after use. Application of nanoparticles in slurry form requires an efficient downstream separation process such as membrane filtration to retain and recycle the materials. The retention of nanomaterials on membranes is a critical phenomenon not only because of the cost associated with loss of nanomaterials but also, and more importantly, because of the potential impacts of nanomaterials on human health and ecosystems<sup>2, 31a, 40</sup>.

## **2.6 Introduction of EAOPs - Application of EAOPs for Industrial Wastewater treatment**

Industrial processes produce a significant amount of wastewater that is quite difficult to remove or degrade using conventional means because of the presence of recalcitrant



pollutants in wastewater. The application of Advanced Oxidation Processes (AOP) in such cases has been reported as a promising alternative to attain satisfactory effluent quality.

The principle of AOP relies on the formation of the hydroxyl radical ( $\cdot\text{OH}$ ) which is a highly reactive radical which can degrade recalcitrant organics such as aromatic, chlorinated, and phenolic compounds instantly. The hydroxyl radical can be produced by chemical oxidation processes such as ozonation, Fenton oxidation, and by light or ultrasonic irradiation<sup>16</sup>, whereas in electrochemical-based treatment systems, in situ  $\cdot\text{OH}$  is produced cleanly and efficiently. These processes are particularly useful in the decontamination of wastewater because it offers<sup>41</sup>:

- Faster degradation of organic pollutants while less prone to form toxic species;
- Complete mineralization of organic pollutants (i.e. transformation into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ );
- A limited requirement of or no (i.e. catalytic) chemical reagents at a low energy cost

## 2.6.1 Types of EAOPs based treatment methods

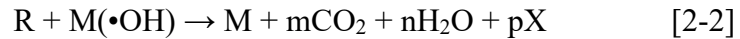
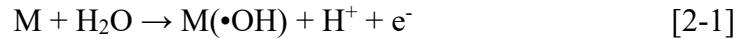
### 2.6.1.1 Electro-Fenton

The Fenton reaction based EAOP, termed Electro-Fenton, is actively considered as the first EAOP due to the generation of hydroxyl radicals which potentially oxidizes organics. A small quantity of Fe (II) is introduced as a catalyst to an acidic solution (at pH 3) in this process to react with electro-generated  $\text{H}_2\text{O}_2$  to produce homogeneous  $\cdot\text{OH}$  and  $\text{Fe}^{3+}$  ions, which is the classical Fenton reaction<sup>11b, 17</sup>. This traditional EAOP technology is based on the<sup>16</sup>:

- Cathodic formation of hydrogen peroxides from the reduction of oxygen, Eq.(1-1),
- Electrochemical regeneration of Fe (II) from Fe (III) species on the cathodic surface, Eq.(1-2), (1-3).

### 2.6.1.2 Anodic Oxidation

Electrodes play a significant role in anodic oxidation processes as the reactions happen on or near of the surface of electrode. In the direct oxidation process, pollutants contained in the bulk of the wastewater must reach the electrode surface, and the oxidation reaction takes places once they are adsorbed onto this surface. Consequently, the nature of the electrode materials influences the selectivity and efficiency of the oxidation process and mass transfer becomes crucial to the process, and is, more often than not, the bottleneck of the oxidation rate<sup>16</sup>. A proposed mechanism of degradation of organics by hydroxyl radicals is as follows<sup>41-42</sup>,



Where,  $M(\bullet OH)$  refers to the  $\bullet OH$  radicals adsorbed on the anode material, M; R refers to organic matter and X refers to inorganic ions.

The effectiveness of AO processes depend on the OEP (oxygen evolution potential) value; electrodes with high OEP show fast and easy mineralization of organics which explains the behavior of different electrode surfaces on oxidizing organics<sup>43</sup>. Table 3 shows a classification of anodic materials based on their oxygen evolution potential<sup>16, 43-44</sup>.

Table 3 Classification of anodic materials

<b>Material</b>	<b>Oxygen Evolution Potential, V (v/s SHE)</b>
<b>RuO<sub>2</sub></b>	1.47
<b>IrO<sub>2</sub></b>	1.52
<b>Pt</b>	1.60
<b>Graphite (Pyrolytic Oriented)</b>	1.7
<b>PbO<sub>2</sub> - PbO<sub>2</sub>/Ti</b>	1.8-1.9
<b>Ti/Ce/Sb/SnO<sub>2</sub></b>	2.16
<b>Ti/Nd/Sb/SnO<sub>2</sub></b>	2.28
<b>Boron Doped Diamond (BDD)</b>	2.40

By combining both AO (e.g. using BDD electrode) and EF process, the effectiveness of the process can be substantially increased.

### 2.6.1.3 Sono-electrochemical and Photo-electrochemical

Recently, the combination of electrochemical treatment with sonochemistry and photocatalytic systems has been explored as a method to decontaminate wastewater. Oxidation processes for these technologies happen both on or near the anode surface and in the bulk solution. The term sonoelectro-Fenton process can be used for the simultaneous action of both EF process and ultrasonic irradiation. In photoelectrochemical systems, an EF reactor would be integrated with a UV lamp and hence, possess the synergic effect of in situ generated H<sub>2</sub>O<sub>2</sub> in the presence of Fe (II) and UV radiation with a possible enhancement in the decontamination process<sup>41, 43</sup>.

## 2.7 Application of EAOPs in Food and Beverage Industry Wastewater

Food industry effluent is typically characterized by high organic content such as sugars, carbohydrates, and fermented products which usually comes from different sectors such as preparation of raw materials, cleaning packing materials, and washing machinery and floors. Most of these organics are not satisfactorily removed by physiochemical or biological processes, failing to meet discharge limit for release into receiving waterbodies<sup>45</sup>. New treatment methods effective in pollution control and removing organics along are essential to abide by environmental rules and regulations. As an alternative to traditional biological methods, interest in the application of EAOP based methods has been increasing to fulfill the requirements of food industry wastewater effectively.

The application of EAOPs based treatment methods in food industry wastewater treatment has not been studied extensively in the literature. Electrochemical oxidation was applied to the treatment of cola-plant wastewater, coffee curing wastewater, olive oil wastewater, olive mill wastewater, green table olive processing wastewater, starchy wastewater, distillery industry wastewater, and beer brewery wastewater<sup>46</sup>. These types of treatment methods have drawn a great deal of attention in the food industry as of late due to their environmental compatibility, versatility, and often zero addition of chemicals<sup>43, 47</sup>.

## 2.8 Evolution of EAOP

In the literature, very few examples have been reported of successful installations of full-scale application of electrochemical processes. Anodic oxidation processes are widely used for disinfection of swimming pool water. BDD anodes have been reported to be used in some cases for on-site rainwater disinfection, as well as disinfection of sewage and industrial process water. High concentrations of persistent organics from tannery, petrochemical plant, dairy, and pulp and paper-mill wastewaters have been treated using anodic oxidation processes. These types of industrial wastewater also contain elevated amounts of chloride (oxidation potential,  $1.36 \text{ V}^{16}$ ) which work as indirect oxidizing agents in the treatment system and ideally contribute to the removal of pollutants from wastewater<sup>48</sup>.

## **2.9 Opportunities and challenges of electrochemical processes in treating industrial wastewater**

There has been extensive research into the removal of a variety of organics and inorganics from wastewater using electrochemical processes. Future opportunities for these kinds of methods include decentralized water treatment plants as the mechanism of these methods are controlled, and electrode potential and cell current are easier to control remotely than conventional chemical and biological processes. Also, variations in influent water quality can be easily adjusted using these treatment methods.

Several studies report significant challenges of electrochemical treatment methods that limit application in large industrial wastewater treatment plants. The formation of toxic by-products and loss of efficiency due to mass transfer limitations and unwanted side reactions top the list of challenges which need to be minimized before designing electrochemical treatment systems. Another major challenge of this technology is the treatment of chloride-containing water as it produces chlorine ( $\text{Cl}_2$ ) and hypochlorous acid which can form halogenated products (e.g. trihalomethanes, THMs) that are often more persistent and toxic than the parent compound<sup>48</sup>.

## **Chapter 3**

### **Materials and Methods**

#### **3.1 Materials**

The following chemicals were purchased from Sigma-Aldrich (unless otherwise stated) and used without further modification: iron (II) sulfate heptahydrate ( $\geq 99\%$ ), hydrogen peroxide (30%, Fisher Scientific), potassium permanganate, oxalic acid ( $\geq 99\%$ ), N, N-diethyl-1,4-phenylene-diamine (97%), peroxidase from horseradish, salicylic acid ( $\geq 99.5\%$ ), 2,3-dihydroxybenzoic acid (99%), 2,5-dihydroxybenzoic acid (99%), nickel-nitriloacetic acid (NTA) resin (50%), and ethanol (95%). All solutions used in this study

were prepared using water from an ultrapure Milli-Q purification system (MQ, Millipore) and for pH adjustment, either 1M H<sub>2</sub>SO<sub>4</sub> or 1M NaOH was used in all experiments.

### 3.1.1 Sample Preparation

Brewery wastewater was collected after fermentation from the Brewhouse, Labatt Brasserie, LaSalle, Quebec every two months and send directly to us. The sample was stored at 2-8°C and before running each experiment the required amount allowed to reach room temperature. A vacuum filtration system with a 0.2 µm ultrafiltration membrane was used to remove all microorganisms and suspended particulates from the brewery wastewater before conducting each experiment and then the sample solution was aerated for 40 minutes to ensure that the sample was air saturated ( $DO_{sat} = 8.38 \pm 0.68$  mg/L) as the concentration of dissolved oxygen is required for the effective production of in-situ hydrogen peroxide at cathode surface, Eq.(1-1).

### 3.1.2 Physical-chemical Characteristics of Brewery Wastewater

Analyses were performed to characterize the Labatt brewery wastewater by measuring some parameters which are listed in the Table 4:

Table 4 Labatt brewery wastewater characteristics

Parameters	Labatt Brewery Sample
<b>pH</b>	6.91±0.38
<b>Conductivity, µS</b>	552 ± 59
<b>TS, mg/L</b>	913 ± 5
<b>TSS, mg/L</b>	148 ± 15
<b>TDS, mg/L</b>	765 ± 20

<b>VTSS, mg/L</b>	135 ± 9
<b>FTSS, mg/L</b>	13 ± 7
<b>COD, mg/L</b>	1860 ± 70
<b>TOC, mg/L</b>	574 ± 32
<b>TN, mg/L</b>	74 ± 10
<b>TP, mg/L</b>	6.71 ± 3.5
<b>TFe, ppb</b>	66 ± 12

The source of high organic content in the brewery wastewater comes from the ingredients used in the process of making beer, and phosphorus and nitrogenous content come from the spent grain. The concentration of iron in brewery wastewater was crucial for this study since its concentration as Fe (II) is the main factor in the commencement of classic Fenton reactions. The concentration of total iron in the brewery wastewater was found to be 66 ppb which may come from raw materials used (water, cereal, hops and yeast) as well as from environmental contamination due to fertilizers, pesticides, industrial processing, and containers. Since iron has a great capacity to form stable compounds, complexed and non-complexed form of iron have been reported to be found in beer<sup>30</sup>.

The total iron content of beer highly depends on the type of beer and the extraction process. For instance, pale beers have been found to have less iron concentration than dark beers. This can be attributed to the production of pale beer, which includes a filtering phase using diatomaceous earth. This type of sedimentary rock has a unique porous structure which traps the iron content and hence makes the beer light<sup>49</sup>. Dark beers, on the contrary, are primarily extracted from hops and malts with different toasting levels; therefore, the difference in iron content could be associated with the raw materials used in the production process<sup>30</sup>. Another source of iron may be the addition of iron sulfate in beer as a foam organoleptic improver, which is a traditional practice in most breweries.

### 3.2 Experimental Setup

An open, cylindrical glass electrolysis cell was used for all experiments in this study with multi-plated (two anodes and three cathodes) electrode configuration in monopolar parallel connection, maintained at room temperature ( $23 \pm 2^\circ\text{C}$ ). BDD (Fraunhofer USA, Inc.) and graphite electrodes of  $25 \text{ cm}^2$  effective surface area were used as anodes and cathodes respectively. Figure 3 is showing the schematic of the experimental setup. A sample volume of 450 ml was added to the cell with pH initially adjusted to 3.0 since ideal pH for Fenton reaction where iron is available as  $\text{Fe}^{2+}$  (unless otherwise mentioned)<sup>16</sup>. The electrodes were placed in vertical alignment and a DC power supply (Agilent Technologies) was used in the galvanostatic mode of operation for all the experiments. Iron (II) sulfate heptahydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Catalyst) was added to the sample solution as the Fe (II) source to initiate the E-Fenton reaction. The BDD electrodes were subjected to an auto cleaning procedure by immersing them in an acid solution (1M  $\text{H}_2\text{SO}_4$ ) for 30-min after each experiment to remove adsorbed molecules at the electrode surface and then rinsed with DI water until the pH of the water was neutral<sup>50</sup>. The graphite cathodes were soaked in alkaline solution (1M NaOH) and acidic solution (1M  $\text{H}_2\text{SO}_4$ ) alternatively for cleaning, and then rinsed with DI water until it reached neutral pH<sup>51</sup>. All samples were mixed vigorously using a vortex mixer before each analysis and all experiments were performed in triplicates.



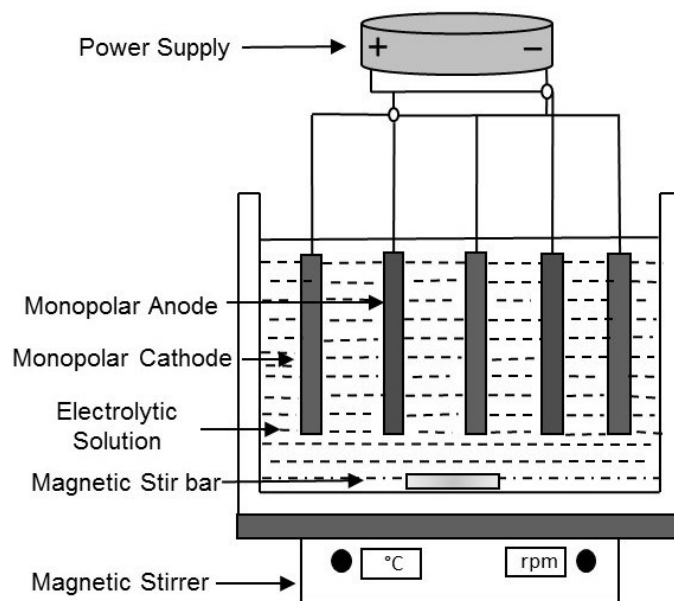


Figure 3 Schematic of the electrolysis cell with five electrode plates configuration (two anodes and three cathodes)

### 3.3 Analysis

#### 3.3.1 Electrochemical Measurements

To characterize the electrochemical behaviour of the electrolysis cell, a cyclic voltammetry (CV) analysis was performed. In CV analysis, a waveform generator is required to produce the excitation signal and hence, a potentiostat is used to apply this signal to the electrochemical cell. The influence of reactions that are taking place in the cell would be restricted by the use of a potentiostat. The final voltammogram would be displayed on the oscilloscope<sup>52</sup>.

In this study, CV analysis of the brewery wastewater sample was carried out at pH 3.0 in a typical three-electrode system using a Potentiostat (Multi-Potentiostats 8 channels + Frequency Analyzer (MPFA)) with a BDD plate as the working electrode, a stainless-steel plate as the counter electrode, and saturated Ag/AgCl electrode as the reference electrode.

The measurements were carried out over a potential range of -1.5 to +2.7 V with a scan rate of 50 mV/s<sup>-1</sup> and 100 mV/s<sup>-1</sup>. The analysis was repeated until the signals were steady.

### 3.3.2 Analytical Measurements

For pH and conductivity measurement, a calibrated pH meter (Oakton Instruments, 310 series, Vernon Hills, IL, USA) and conductivity meter (Oakton Instruments, Vernon Hills, IL, USA) were respectively used. Brewery wastewater is characterized by a high concentration of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). Therefore, it is necessary to study the influence of COD and TOC content on the effectiveness of electro-Fenton treatment on BW. COD, TN, and TP were measured by reactor digestion method using Hach kits. In brief, the measurement of parameters by Hach kits involves the addition of sample solution into a reagent containing vial, which is heated for a specified period of time, then cooled to room temperature. The concentration of the parameter sought is then measured using a spectrophotometer (DR2800, Hach)<sup>53</sup>. The range of the COD vials was 20-1500 mg/L and a proper dilution factor was used to measure concentrations higher than this range. The TOC concentration was measured by catalytic oxidation method using a TOC analyser (Shimadzu Corporation, Japan). The principle underlying this analysis includes the oxidation of samples through heating and combustion at 680°C with a platinum catalyst. The sample gets decomposed in this chamber and generates carbon dioxide. The carbon dioxide produced is cooled and dehumidified, and detected by an infrared gas analyser (NDIR). The concentrations of TC (total carbon) and IC (inorganic carbon) in the sample are obtained through comparison with a pre-prepared calibration curve using a standard solution. The TOC concentration is then calculated by subtracting the IC concentration from the obtained TC concentration<sup>54</sup>.

The instantaneous current efficiency (ICE) based on COD/TOC value was calculated from Eq.(3-1)<sup>55</sup>.

$$ICE = \frac{[(COD)_0 - (COD)_t]}{8It} FV \quad [3-1]$$

Where,  $COD_0$  and  $COD_t$  are the solutions COD values at time 0 and t, respectively (mg/L), V is the solution volume (L), F is Faraday constant (96,485 C/mole), I is the applied current (A) and 8 is the oxygen equivalent mass (g eq<sup>-1</sup>).

The electrical energy consumption (EEC) per unit volume of wastewater treated (kWh/m<sup>3</sup>) was calculated from the following equation<sup>15</sup>:

$$EEC = \frac{UIt}{1000 V} \quad [3-2]$$

Where U is the applied voltage (V).

### 3.3.3 H<sub>2</sub>O<sub>2</sub> Measurement

A modified DPD/HRP assay was used to measure H<sub>2</sub>O<sub>2</sub> concentration. A 1.0 mM H<sub>2</sub>O<sub>2</sub> stock solution was prepared by the dilution of a 30% w/v H<sub>2</sub>O<sub>2</sub> solution and standardized by titration with 0.1N KMnO<sub>4</sub> solution (beforehand, KMnO<sub>4</sub> solution was standardized by titration with oxalic acid). The stock solutions of N, N-diethyl-1,4-phenylene-diamine (DPD) and horseradish peroxidase were prepared and stored in the dark at 5°C. In this measurement technique, DPD (N, N-diethyl-p-phenylenediamine) is oxidized to a colored product DPD<sup>•+</sup> by the chemical reaction with H<sub>2</sub>O<sub>2</sub> and horseradish peroxidase (HRP) as a catalyst. The concentration of H<sub>2</sub>O<sub>2</sub> was measured by periodically collecting a 1 mL subsample, then, by mixing this with 1 mL of phosphate buffer (pH 6), 50 μL DPD (10 mM in 0.1% H<sub>2</sub>SO<sub>4</sub>) and 100 μL of HRP (10 U/mL). The product, DPD<sup>•+</sup>, was then analyzed by UV-VIS spectrophotometry (Agilent Technologies) at 553 nm in quartz cuvettes of 1 cm optical path length. The molar absorption coefficient of DPD<sup>•+</sup> was found to be 14,400 M<sup>-1</sup>cm<sup>-1</sup>. When building standard curves, H<sub>2</sub>O<sub>2</sub> concentration higher than 100 μM starts to deviate from a linear relation. Therefore, for higher concentrations, the sample solution was diluted before analysis<sup>56</sup>.

### 3.3.4 •OH Measurement

The concentration of •OH radical produced was determined using a “trap and trigger” method where salicylic acid was used as a scavenger to trap •OH radicals. It has been reported in previous studies that 2,3-DHBA, 2,5-DHBA, and catechol were detected as reaction products when SA was used to scavenge •OH radical<sup>57</sup>. The concentration of 2,3-DHBA is higher than 2,5-DHBA when •OH radicals are chemically produced while 2,5-DHBA is favored over 2,3-DHBA when •OH radicals are electrochemically produced, and catechol concentration has been reported to occur in very subtle quantities or to not appear at all<sup>58</sup>. UV-Vis spectroscopy was used to determine the concentration of the resulting hydroxylated products, 2,3-dihydroxybenzoic acid, and 2,5-dihydroxybenzoic acid and was then utilized to quantify the hydroxyl radicals<sup>59</sup>. Standard solutions of SA, 2,3-DHBA, and 2,5-DHBA with  $10 \times 10^{-3}$ ,  $10 \times 10^{-3}$ , and  $8 \times 10^{-4}$  M concentrations, respectively, were prepared and analysed with UV-VIS to establish the wavelength at which the maximum absorption is observed for every reagent. Standard curves with different concentrations were built for these three analytes. The molar absorption coefficient of SA, 2,3-DHBA and 2,5-DHBA was found to be 3100, 2600 and 3100  $M^{-1}cm^{-1}$  at 300, 309, and 323 nm respectively. The experiment of producing and scavenging •OH radicals was conducted in a 450 ml electrochemical cell and then determined using the method described by Peralta et al.<sup>59</sup>.

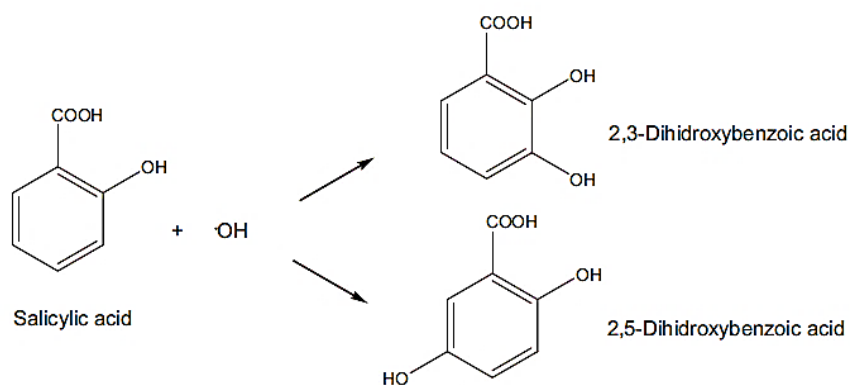


Figure 4 Formation of hydroxylated products from the reaction between salicylic acid and hydroxyl radical<sup>59</sup>.

### 3.3.5 Measurement of Fe (II), Fe (III) and Total Fe

The concentrations of Fe (II), Fe (III), and total Fe were measured analytically using Inductively Coupled Plasma-Mass Spectrometry, ICP-MS (Agilent 7500ce). The use of ICP-MS is ideal for quantifying metals and non-metals in samples from various sources as well as quantifying different species, forms, or oxidation states associated with trace elements. Ideally, ICP is an argon plasma which can reach temperatures as high as 6000°C, allowing the complete atomization of the elements in a sample and minimizing potential chemical interferences. With ICP-MS, the argon ICP generates charged ions from the elemental species within a sample that are directed into a mass spectrometer and separated according to their mass-to-charge ratio. Ions of the selected mass-to-charge ratio are then directed to a detector that determines the number of ions present. The concentration of metal ions in a sample is measured from the pre-prepared calibration curve using standard solutions of respective metals<sup>60</sup>.

A chelating resin, Ni-NTA Superflow, was used to extract the Fe species from the sample. At very low pH values (pH 1.7-2) Ni-NTA resin is capable of holding Fe<sup>3+</sup> with no retention of Fe<sup>2+</sup>. Fe<sup>2+</sup> was oxidized using H<sub>2</sub>O<sub>2</sub> and the concentration of Fe<sup>2+</sup> was determined as the difference between the two measurements. The extraction was conducted using a column chromatography method. 1 mL of Ni-NTA resin was poured into the column, and 4 mL of sample was added, with Fe<sup>3+</sup> being retained and collected by 1M HNO<sub>3</sub> elution solution. All samples were extracted twice using the same batch method for higher extraction efficiency. The same procedure was followed to detect Fe<sup>2+</sup> concentration after oxidizing by adding 50 µL of H<sub>2</sub>O<sub>2</sub>. Before and after each measurement, the resin was cleaned using 0.02 M HNO<sub>3</sub> and then DI water<sup>61</sup>. It should be mentioned that the analysis of metals at low concentration is very precarious and may be easily affected by the contaminants. Different kinds of experimental and environmental reasons may affect the results of this analysis.

## Chapter 4

### Results and Discussion

#### 4.1 Electrochemical characteristics of brewery wastewater – Cyclic Voltammetry

The cyclic voltammetry technique has received a great deal of interest for initial electrochemical studies of new systems and has proven the usefulness of these analyses in gathering information about somewhat complicated electrode reactions. Ideally, analysing the CV characteristics, a reaction can be defined as reversible or irreversible. The characteristics of reversible reactions are listed below and the deviation from these specifics can be termed as the result of an irreversible reaction<sup>62</sup>:

- The positions of peak voltage do not alter as a function of voltage scan rate,
- The ratio of the peak currents is equal to one,
- The peak currents are proportional to the square root of the scan rate.

In this study, CV analysis was carried out to obtain information on the direct oxidation of organic content in brewery wastewater on the BDD anode surface. The CV plot, Figure 5 shows that the voltage is separated between the current peaks, and the positions of the peak voltage do not change as a function of voltage scan rate, also the anodic peak current ( $I_{pa}$ ) is not equal to the cathodic peak current ( $I_{pc}$ ) i.e.  $I_{pa}/I_{pc} \neq 1$ , which implies that the electrochemical reaction in this system is irreversible. Anodic peak voltage was observed at 2.7V which confirms the presence of the higher oxidation potential agent,  $\bullet\text{OH}$  radical, with another small peak also observed in the anodic range which is attributed the presence of other oxidizing agents such as chlorine (1.36V), hydrogen peroxide (1.78V), chlorine dioxide (1.27V), and molecular oxygen (1.23V)<sup>16</sup>. It should be mentioned that the CVs in this study were performed in static mode and therefore this could limit the concentration of oxygen brought to the electrode surface<sup>63</sup>.

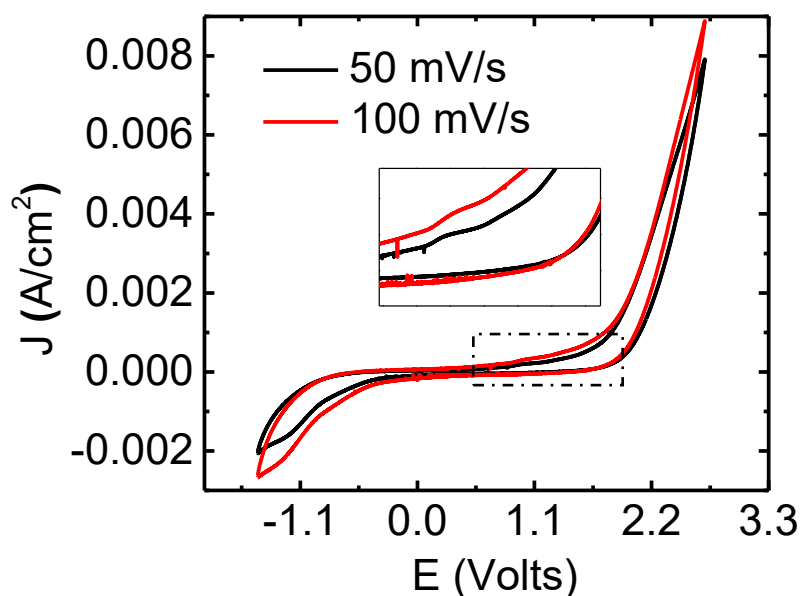


Figure 5 Cyclic voltammetry analysis of brewery wastewater as a function of applied potential. [Experimental condition: room temperature, scan rate = 50, 100 mV/s, pH = 3, working electrode = BDD, counter electrode = stainless Steel, reference electrode = Ag/AgCl, inset shows the magnified view of selected CV curve].

In the literature, several studies have looked at cathodic production of hydrogen peroxide to act as a potential agent to oxidize organics<sup>18, 64</sup>. Also, the composition of brewery wastewater has been reported to contain chloride, which may originate from intake water or the raw materials used for in beer production<sup>7-8, 33</sup>. A novel method developed by Vijayaraghavan et al. presented that chloride based sample generates hypochlorous acid in an electrolytic cell which can serve as an oxidizing agent to destroy organics present in wastewater<sup>8</sup>. Hence, it is hypothesized that a combined effect of hydroxyl radical and other potential oxidizing agents are participating in degrading organics from brewery wastewater.

## 4.2 Electro-Oxidation and Electro-Fenton degradation profiles for COD and TOC

### 4.2.1 Effect of Current density on COD reduction

In all electrochemical treatments, current density or applied electrode potential is a key experimental parameter. Electro-oxidation treatment is primarily based on the generation of hydroxyl radicals from anodic oxidation of H<sub>2</sub>O on BDD surface. The applied current intensity has a major impact on the oxidation of H<sub>2</sub>O in an electrochemical cell. As shown in Figure 6 (a), the COD concentration decreases faster and with higher removal when the current density increases. The drift of these curves with current density can be attributed to the higher production of hydroxyl radicals and other oxidants such as chlorine (1.36V), hydrogen peroxide (1.78V), chlorine dioxide (1.27V), and molecular oxygen (1.23V). COD removal efficiencies of 65, 91, and 96% were achieved for 8, 16, and 24 mA/cm<sup>2</sup> of current density respectively. From these results, 16 mA/cm<sup>2</sup> of current density was used for the rest of the studies to check the effect of other parameters individually.

### 4.2.2 Effect of Initial Fe<sup>2+</sup> dose on COD and TOC reduction

The incorporation of electro-Fenton with electro-oxidation allows the system to produce more •OH radicals by Fenton's reaction (i.e. disintegration of in situ generated hydrogen peroxide by Fe<sup>2+</sup> ion). The generation of this radical depends on the ratio of H<sub>2</sub>O<sub>2</sub> to Fe<sup>2+</sup> (Eq.1-2). Since Fe<sup>2+</sup> regenerates at the cathode (Eq.1-3), ideally the catalytic amount of Fe<sup>2+</sup> is enough to generate significant amounts of •OH radical. The faster and more efficient regeneration of the Fe<sup>2+</sup>, which is a kinetic-controlling step for hydroxyl radical generation, is an advantage of the electro-Fenton process over Fenton and photo-Fenton processes. To achieve higher efficacy of the system, Fenton's reaction must happen instantly and ceaselessly. Therefore, it is required to optimize Fe<sup>2+</sup> ion dose for total exchange of hydrogen peroxide into •OH radicals and to avoid the stimulation of any secondary b foulment through the formation and precipitation of ferric hydroxide Fe(OH)<sub>3</sub><sup>12</sup>.



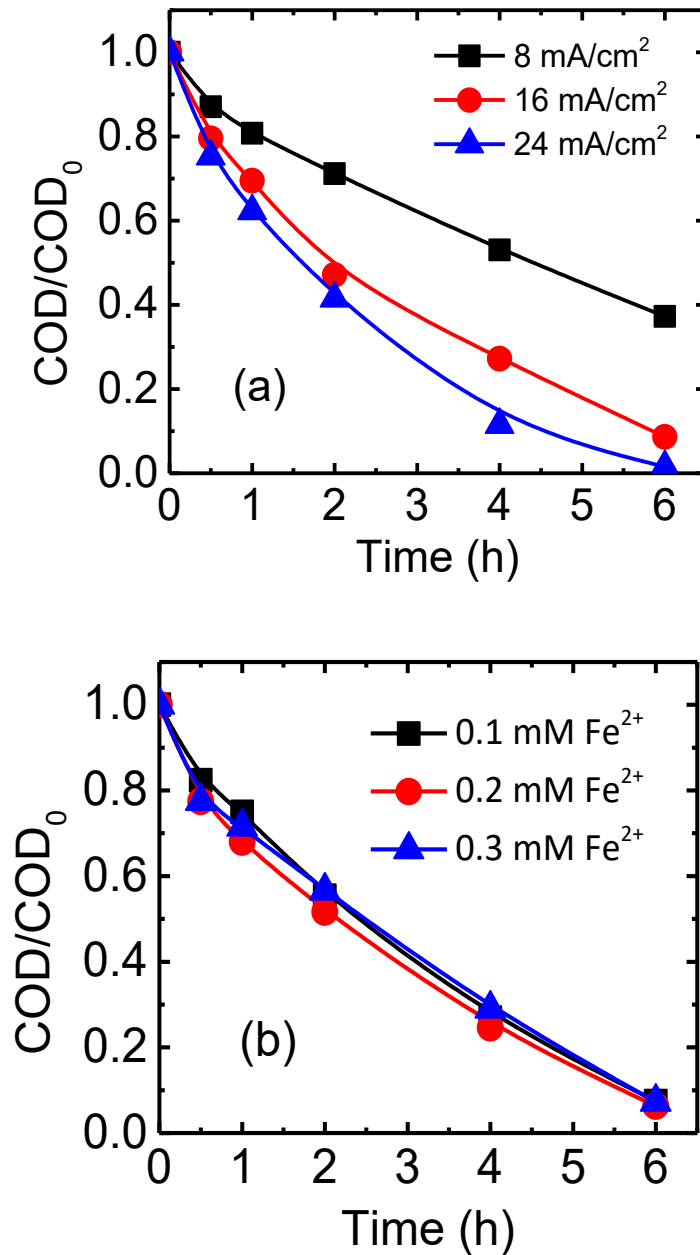


Figure 6 Degradation profile of COD over time (a) at different current densities (anodic oxidation system), (b) at different initial Fe (II) concentration (combined electro-Fenton and anodic oxidation). [Experimental condition: room temperature, pH 3, sample volume = 450 ml].

Figure 6 (b) shows the effect of Fe<sup>2+</sup> concentration on COD removal. It can be seen that both COD removal efficiency and kinetics of the reaction varies slightly with Fe<sup>2+</sup> dose. For 0.1 and 0.2 mM of initial Fe<sup>2+</sup> dose, the latter showed slightly faster rate than the former.

The change of brewery wastewater TOC concentration over time using BDD anode and graphite cathode with a current density of  $16 \text{ mA/cm}^2$  at the ideal pH 3.0 for EF process under different  $\text{Fe}^{2+}$  concentration is shown in Figure 7. It can be observed that initial  $\text{Fe}^{2+}$  concentration has a nonsignificant effect on TOC removal in terms of removal efficiency and kinetics. With  $0.1 \text{ mM Fe}^{2+}$  ion concentration, TOC concentration decreased slowly during the first hour and after that decreased rapidly. For the doses of  $0.2$  and  $0.3 \text{ mM Fe}^{2+}$  ions, the changes of TOC over time exhibit similar trends but with  $0.2 \text{ mM}$  it showed a slightly faster reaction rate than  $0.3 \text{ mM}$  for the first two hours. This can be attributed to the fact that hydroxyl radicals are being destroyed with initial  $\text{Fe}^{2+}$  doses higher than  $0.2 \text{ mM}$  hence making this dose the optimal dose for brewery BW by combined electro-Fenton and electro-oxidation and therefore, this dose was used for further study. A similar optimal dose was found for other types of industrial wastewater (e.g. photographic processing wastewater) as well<sup>12</sup>.

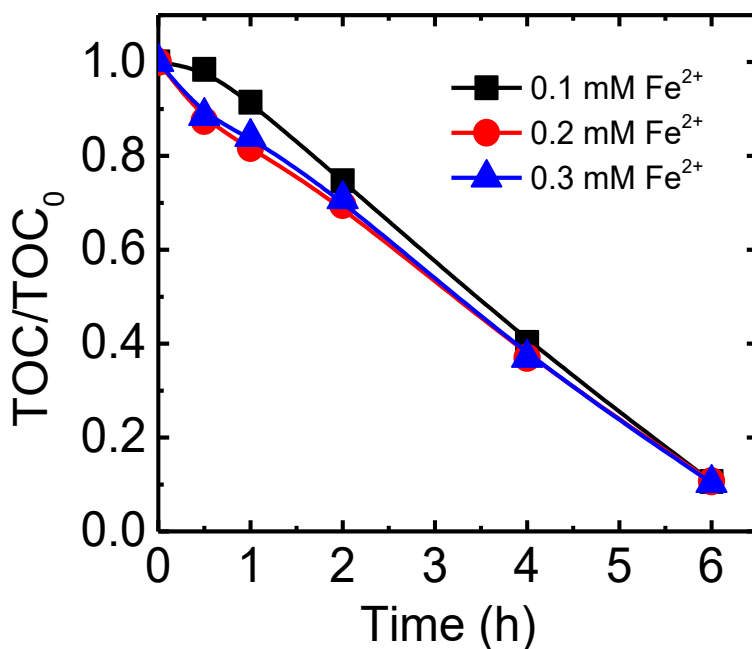
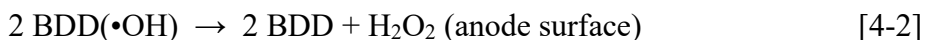
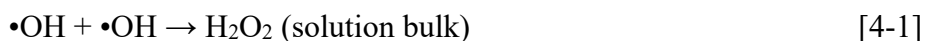


Figure 7 TOC degradation profile over time for the combined electro-Fenton and anodic oxidation system. [Experimental condition: room temperature, current density =  $16 \text{ mA/cm}^2$ , sample volume = 450 ml].

The insignificant effect of  $\text{Fe}^{2+}$  on removal efficiency can be explained by the pre-existing presence of trace amounts of  $\text{Fe}^{2+}$  in brewery wastewater which potentially comes from the raw materials used in the production cycle<sup>7, 65</sup>.

Both for COD and TOC removal, the removal rate was faster at the beginning of the experiment and then slowed down in a progressive manner. Fast removal can be explained by the formation of  $\text{Fe}(\text{OH})_3$  precipitation which coagulates organic contaminants and hence increases the removal efficiency. Since the precipitation of  $\text{Fe}^{3+}$  reduces the amount of catalyst regeneration, the removal efficiency with time was found to be reduced in the later part of electrolysis time<sup>12</sup>. Other researchers explained this by the following detail<sup>10</sup>. After a certain period of treatment (4 h for this study) the concentration of organic matter decreased, while the generation of hydroxyl radicals still advanced. This high concentration of  $\bullet\text{OH}/\text{BDD}(\bullet\text{OH})$  elevated the possibility of competing reactions, Eq.(4-1)-(4-4).

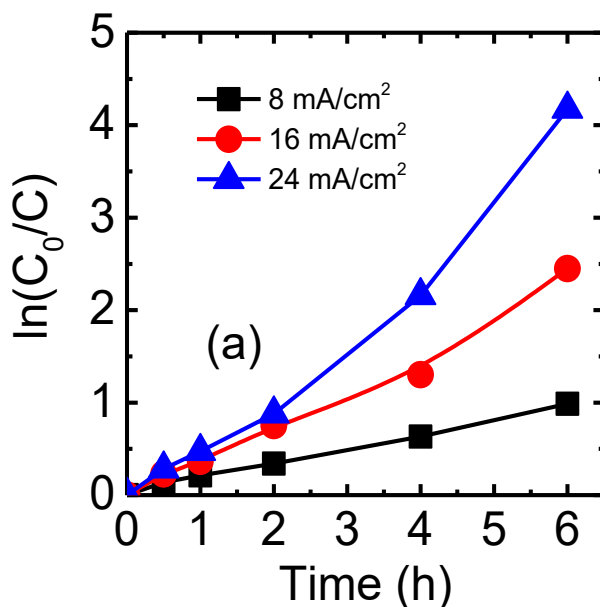


In addition, the degradation rate of the EF-BDD treatment reached up to 94 and 90% for COD and TOC respectively after 6h of electrolysis, indicating that at this stage of treatment, all aromatics were converted to short chain aliphatic carboxylic acids including complexes of  $\text{Fe}^{3+}$ , which were recalcitrant to hydroxyl radicals and hence responsible for the respective residual values<sup>10, 42</sup>. Brewery wastewater was characterized by Janhom et al. to contain aromatic compounds, the segmentation of these compounds forms short-chain carboxylic acids with low molecular weights which degrade much slower than aromatics by hydroxyl radicals, this might explain the decrease of removal rates at the final stages and be responsible for the residual TOC concentration<sup>29</sup>. Although most of these acids are classified as biodegradable, it has been reported that some of them have adverse effects to

skin and mucous membranes and hence, should be categorized before disposal<sup>66</sup>. These results offer opportunities to further treat the wastewater by integrating UV irradiation or other treatment systems with the anodic oxidation system.

### 4.2.3 Kinetic Study

In electrochemical processes, all kinds of complex intermediates are formed which makes it impossible to conduct a thorough kinetic analysis with every single reaction that occurs during these processes. It is, however, feasible to carry out a proximate kinetic analysis by using the COD value to represent the total organic pollutants content of the effluent. Thus, apparent kinetic constants can be obtained through this method to reflect the mineralization rate constant of the effluent. The gradual degradation of organic pollutants in these processes can be expressed by a simple irreversible reaction relating to COD.



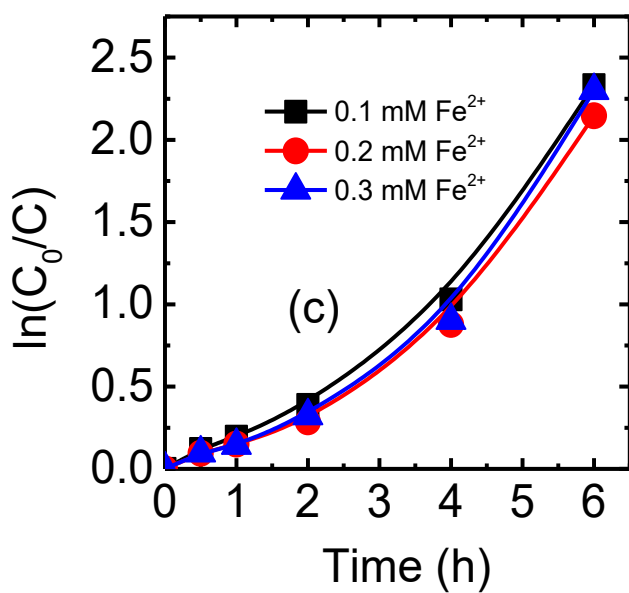
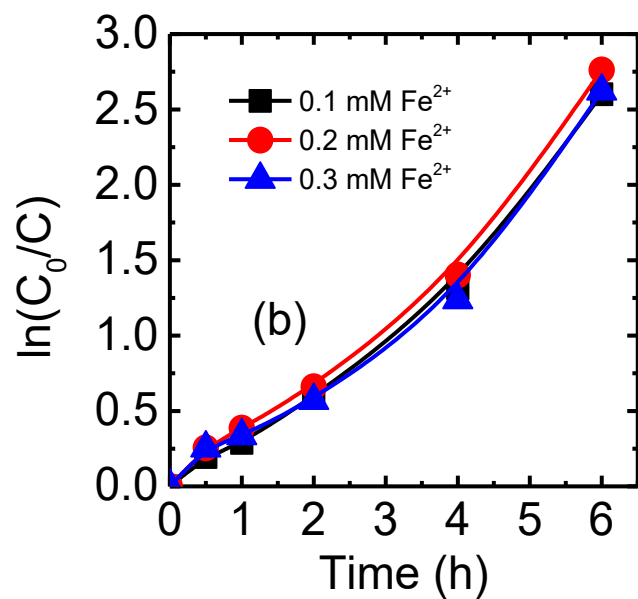


Figure 8 Kinetic study of a) COD degradation (anodic oxidation), b) COD degradation (combined electro-Fenton and anodic oxidation), and c) TOC degradation (combined electro-Fenton and anodic oxidation) [Experimental condition: room temperature, initial pH 3, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 6h, sample volume = 450 ml].

As observed in the graph, Figure 8, the chemical reactions in this system follow first order reaction kinetics when the applied current density is 8 mA/cm<sup>2</sup>. With increasing current

density, the reactions accelerate and make it difficult to carry out the kinetic study. With an applied current density of 16 mA/cm<sup>2</sup> for the first four hours, the reaction constant was found to be 0.322 sec<sup>-1</sup> and then accelerated to 0.5739 sec<sup>-1</sup>. A similar type of behaviour was observed in the case of 24 mA/cm<sup>2</sup> current density. Hence, these types of reactions can be termed a mixed reaction order reaction. Table 5 shows relevant kinetic parameters.

Table 5 Kinetic study parameters

No	Current Density, mA/cm <sup>2</sup>	Reaction Constant, sec <sup>-1</sup>	R <sup>2</sup> Value	Electrolysis Time, h	Remarks
1	8	0.1569	0.9950	0-6	First Order
2	16	0.3220	0.9928	0-4	Mixed Order
		0.5739	0.9999	4-6	
3	24	0.5317	0.9891	0-4	Mixed Order
		1.0073	0.9999	4-6	

As the concentration of organic matter decreases with time but the production of in situ generated hydrogen peroxide as well as anodic hydroxyl radical production keeps increasing, the reaction kinetics becomes more complicated and hence can be termed as mixed order reaction.

A kinetic study for COD and TOC removal with different iron (II) concentrations followed the same trend when 16 mA/cm<sup>2</sup> of current density was applied as shown in Figure 8 (b) and (c) respectively. The COD removal rate constant with catalyst addition was found to be 0.3264 sec<sup>-1</sup> for the first four hours and 0.6439 sec<sup>-1</sup> (can be termed as instantaneous rate) for the rest of the experimental time. In terms of TOC removal, for the first period the reaction rate was slower than COD removal but it increased slightly in the last two hours with numeric values of 0.2641 sec<sup>-1</sup> and 0.6517 sec<sup>-1</sup> respectively.

### 4.3 Concentration of reactive oxygen species

#### 4.3.1 In-situ generated hydrogen peroxide

The absorption spectrum of different doses of  $\text{H}_2\text{O}_2$  after reaction with the reagent solution is shown in Figure 9. The product from this oxidation reaction,  $\text{DPD}^{++}$ , shows two absorption maxima, at 511 and at 553 nm respectively. The absorption at 553 nm was used for subsequent measurements, as it is somewhat higher than at 511 nm. Table 6 shows the associated parameters from  $\text{H}_2\text{O}_2$  assay.

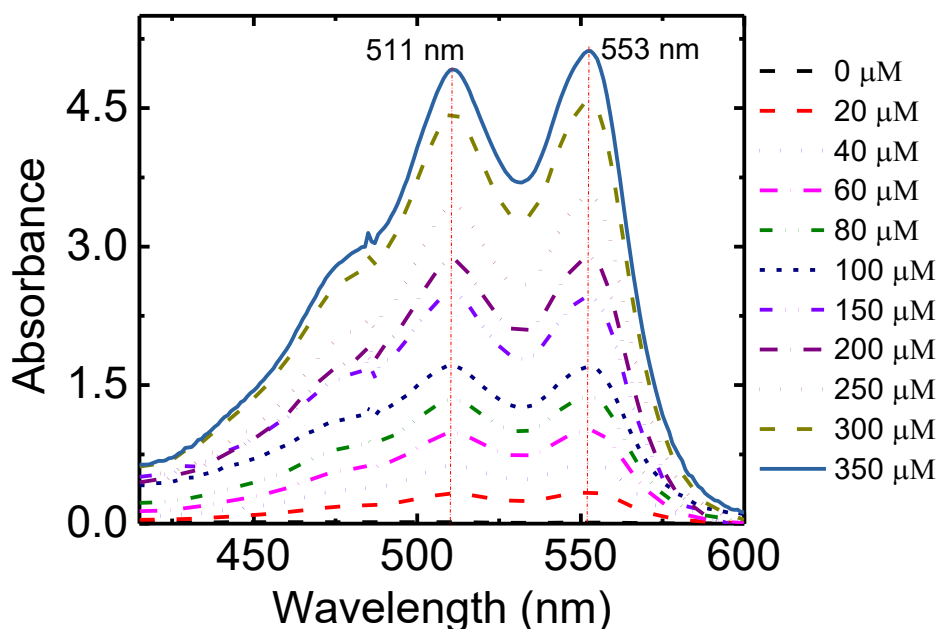


Figure 9 Absorption spectra of  $\text{DPD}^{++}$  (Product of DPD/HRP and  $\text{H}_2\text{O}_2$ ) with different  $\text{H}_2\text{O}_2$  concentrations.

The in-situ production of  $\text{H}_2\text{O}_2$  at pH 3 following a forty-minute aeration has been investigated in this study, as shown in Figure 10. It can be observed that the production of  $\text{H}_2\text{O}_2$  increased exponentially with reaction time up to 216.2  $\mu\text{M}$  after 6h of electrolysis. With the addition of 0.2 mM Fe (II) into the system, the concentration of  $\text{H}_2\text{O}_2$  produced in-situ reduced to 197.8  $\mu\text{M}$  after 6h of electrolysis. This can be explained by the

commencement of the Fenton reaction in which produced  $\text{H}_2\text{O}_2$  is consumed by Fe (II) ion and produces hydroxyl radicals, Eq.(1-2).

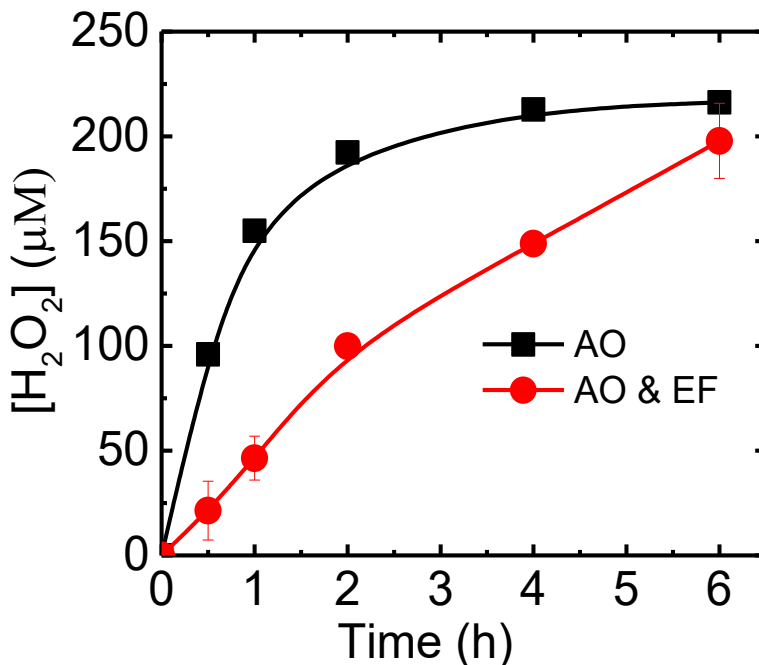
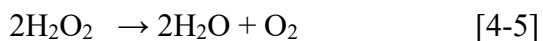


Figure 10 Cathodic  $\text{H}_2\text{O}_2$  production v/s electrolysis time in anodic oxidation and combined electro-Fenton and anodic oxidation system. [Experimental condition: room temperature, initial pH 3, current density = 16  $\text{mA}/\text{cm}^2$ , initial  $[\text{Fe}(\text{II})] = 0.2 \text{ mM}$ , sample volume = 450 ml].

Also, it can also be seen from Figure 10 that the rate of electro-reduction for  $\text{H}_2\text{O}_2$  generation reached a plateau after 4h of electrolysis for the electro-oxidation experiment whereas for combined electro-oxidation and electro-Fenton experiments the concentration of electro-generated  $\text{H}_2\text{O}_2$  kept increasing. Since the regeneration rate of  $\text{Fe}^{2+}$  slows after 4h of electrolysis (discussed in the section 4.4),  $\text{H}_2\text{O}_2$  consumption for Fenton reaction by  $\text{Fe}^{2+}$  is also reduced. The plateau region of  $\text{H}_2\text{O}_2$  generation can be explained by the commencement of side reactions Eq.(4-5)-(4-8) reported by Liu, Y.<sup>18</sup>





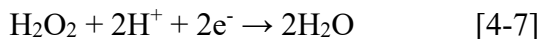
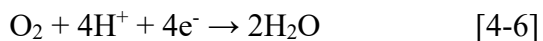


Table 6 Calibration curves equation, R<sup>2</sup> value and range of linear relations (both hydrogen peroxide and OH radicals)

Analyte	Linear Range (M)	Regression Equation	R <sup>2</sup>	Reference
H <sub>2</sub> O <sub>2</sub>	<sup>a</sup> 4×10 <sup>-5</sup> -1×10 <sup>-3</sup>	A <sup>553nm</sup> = 0.0144x + 0.1202	0.9953	This study
SA	<sup>b</sup> 6×10 <sup>-5</sup> -1×10 <sup>-3</sup>	A <sup>303nm</sup> = 3047[SA] ± 90 + 0.06 ± 0.05	0.995	Peralta et al. <sup>59</sup>
		A <sup>300nm</sup> = 3081[SA] + 0.7924	0.984	This study
2,3 - DHBA	<sup>b</sup> 6×10 <sup>-5</sup> -1×10 <sup>-3</sup>	A <sup>310nm</sup> = 2720[2,3-DHBA] ± 32.36 + 0.08 ± 0.018	0.999	Peralta et al. <sup>59</sup>
		A <sup>309nm</sup> = 2600.9[2,3-DHBA] + 0.0791	0.996	This study
2,5 - DHBA	<sup>b</sup> 6×10 <sup>-5</sup> -8×10 <sup>-4</sup>	A <sup>323nm</sup> = 3335[2,5-DHBA] ± 36.8 + 0.06 ± 0.016	0.999	Peralta et al. <sup>59</sup>
		A <sup>323nm</sup> = 3143.4[2,5-DHBA] - 0.0842	0.991	This study

<sup>a</sup>Adapted from<sup>56a</sup>, <sup>b</sup>Adapted from<sup>59</sup>

### 4.3.2 Hydroxyl Radical

A method developed by Peralta et al. was used in this study to quantify hydroxyl radical concentration<sup>59</sup>. At first, standard solutions of salicylic acid, 2,3-DHBA, and 2,5-DHBA were analyzed to set the maxima and corresponding wavelength for every analyte. The

following figure shows the absorption spectra resulting from this analysis. It can be seen that the maximum absorbance of SA, 2,3-DHBA, and 2,5-DHBA is at 300 nm, 309 nm, and 323 nm, respectively.

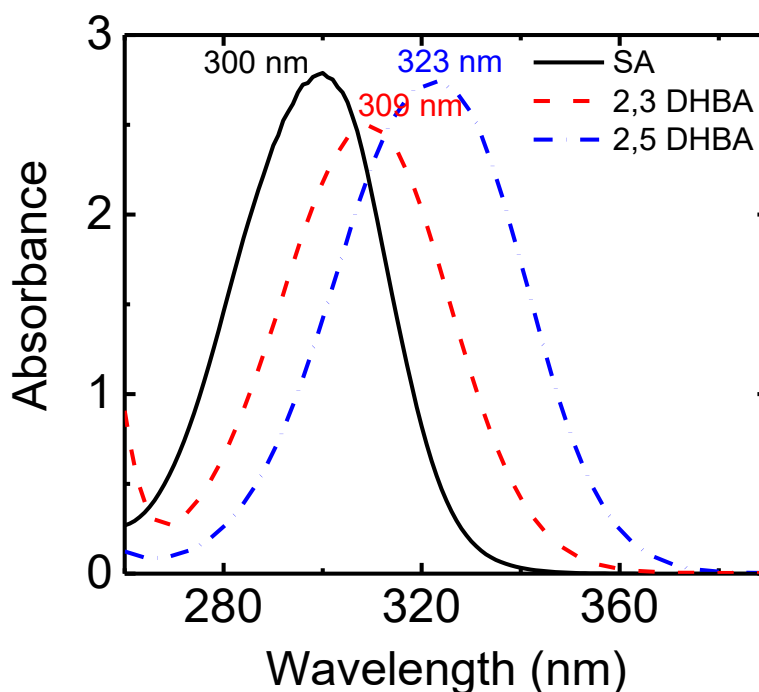


Figure 11 Absorption spectra of SA, 2,3-DHBA and 2,5-DHBA shows three different maxima at 303, 309 and 323 nm respectively.

#### 4.3.2.1 Effect of Initial SA Concentration on $\bullet$ OH production

The efficient trapping of  $\bullet$ OH radicals significantly depends on the initial concentration of salicylic acid and hence has been studied, as shown in Figure 12. It can be noticed that the production of primary derivative products of salicylic acid varies with initial SA concentration. From 0.8 mM to 5 mM initial SA concentration the production of 2,5-dihydroxybenzoic Acid (2,5-DHBA) increased rapidly. For SA initial doses of 8 mM, the production of 2,5-DHBA showed no significant difference from an initial dose of 5 mM. This can be explained by the saturation of  $\bullet$ OH radical production by this electrochemical process which does not leave enough  $\bullet$ OH radicals to scavenge by SA when the initial

concentration is higher 5 mM. For further analysis a 5 mM dose was used as the initial SA concentration for effective  $\bullet$ OH radical trapping.

#### 4.3.2.2 Effect of Reaction time for Effective trapping of $\bullet$ OH

The formation of primary hydroxylated derivatives from the reactions between hydroxyl radicals and salicylic acid is very fast. Each of these species has high rate constants, which is  $2.4 \times 10^{10}$ ,  $1.3 \times 10^{10}$  and  $2.2 \times 10^{10}$  L/mol/sec for 2,5-DHBA, 2,3-DHBA, and SA respectively<sup>58a</sup>. Though an excess of salicylic acid was added for effective radical trapping, it is required to determine the effective time to obtain sufficient amounts of primary derivatives for quantitative determination. Figure 12 presents the net formation of primary derivatives for various reaction times and it can be observed that the net formation of primary derivatives increased smoothly with time for the first 25-min. This signifies that the production and effective trapping of  $\bullet$ OH radicals for quantitative determination are under control in the studied conditions within 75-min of reaction time. A reaction time of 25-min was selected in this study for effective trapping.

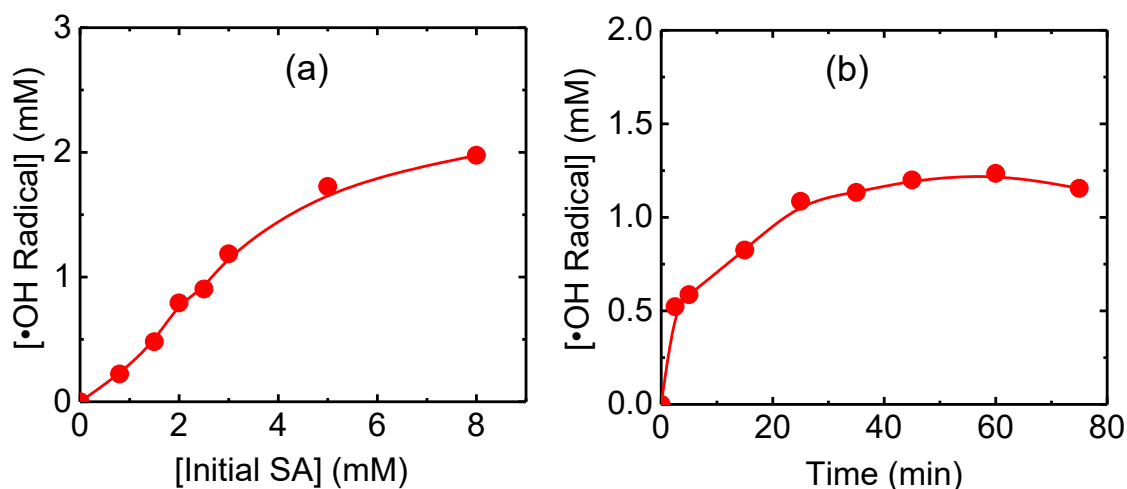


Figure 12 Effect of (a) initial [SA], (b) reaction time on effective OH radical trapping by “trap and trigger” method. [Experimental condition: reaction time = 35 min for (a), initial SA concentration = 5 mM for (b)]

### 4.3.2.3 Effect of reaction time on production of hydroxylated products of SA and COD reduction

For the quantitative determination of primary hydroxylated derivatives using this trap and trigger method, in situ generated  $\text{H}_2\text{O}_2$  and  $0.2 \text{ mM Fe}^{2+}$  via E-Fenton and anodic oxidation at pH 3 was used to produce  $\bullet\text{OH}$  radicals, and for effective trapping, salicylic acid with initial concentration of  $5 \text{ mM}$  was used for  $25 \text{ min}$  to evaluate the generation rate or the concentrations of hydroxyl radicals in the system.

To quantify hydroxyl radicals, a method described by Peralta et al. was used in this study<sup>59</sup>. In this method, SA is employed as  $\bullet\text{OH}$  scavenger to produce 2,3-DHBA and 2,5-DHBA and according to the reaction stoichiometry, the sum of the hydroxylated compound concentrations is equal to the hydroxyl radical concentration<sup>59</sup>.

Using UV-Vis, the absorbance spectra of three individual analytes is shown in Figure 11 at a different wavelength. In such a method, the total absorbance of a mixture is equal to the sum of the absorbances of each compound. The  $\bullet\text{OH}$  radical concentration is equal to the sum of 2,3-DHBA and 2,5-DHBA concentration. It can be observed from this analysis that only one of these hydroxylated products was detected. Potentially, when  $0.4 \text{ A}$  is applied to the system, both reactions may be accelerated which explains why only 2,5-DHBA was detected<sup>59</sup>.

Thus, a system with three equations was established and was solved in a matricial way (Eq. 4-9) at every reaction time. At this point it is worth noting that this method is limited to the feasibility of creating linearly independent equations. This is plausible in cases where experimentation is conducted under careful control.

$$\begin{bmatrix} A_1(t) \\ A_2(t) \\ A_3(t) \end{bmatrix} = \mathbf{b} \begin{bmatrix} \epsilon X_1 & \epsilon Y_1 & \epsilon Z_1 \\ \epsilon X_2 & \epsilon Y_2 & \epsilon Z_2 \\ \epsilon X_3 & \epsilon Y_3 & \epsilon Z_3 \end{bmatrix} \begin{bmatrix} X(t) \\ Y(t) \\ Z(t) \end{bmatrix} \quad [4-9]$$

Where,  $A$  = absorbance of mixture at 300, 309, and 323 nm wavelength,  $t$  = reaction time,  $\epsilon$  = molar Absorptivity,  $M^{-1}cm^{-1}$  at 300, 309, and 323 nm,  $b$  = cell optical length = 1 cm,  $[X]$  = molar salicylic acid concentration in the mixture,  $[Y]$  = molar 2,3-DHBA concentration in the mixture,  $[Z]$  = molar 2,5-DHBA concentration in the mixture.

The mixture absorbance was measured over time at the maximum wavelengths of every analyte and the concentrations of the analytes were also determined by solving the matrix is shown in Figure 12 (b) and Figure 13 (a). It can be observed that as soon as the electrical current is applied, the SA concentration starts decaying. It can be inferred from this that the generation of  $\bullet OH$  radical is instant. The trapping of  $\bullet OH$  radicals by SA keeps happening and hence the decaying of SA is observed. The detection/appearance of SA hydroxylated products certifies that the oxidation of SA by  $\bullet OH$  radical has commenced. In Figure 13 (a), the concentration of 2,5-DHBA reaches a maximum level after 60-min of reaction time but was smooth for the first 25-min and started to go with slow-pace after this point. The reactions might be accelerated by applying 0.4 A current and attributed to the detection of 2,5-DHBA only, which is reported by the previous study<sup>59</sup>.

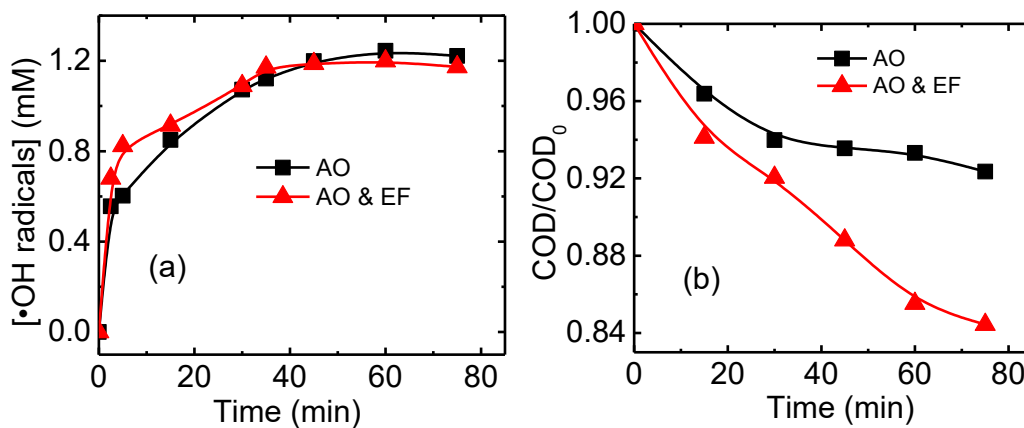


Figure 13 (a) Production of hydroxylated products, (b) Consumption of hydroxyl radical for COD reduction over time, in different electrochemical system.

The COD concentration of the sample solution was also measured to see if there are any side reactions occurring, other than oxidation of SA by  $\bullet\text{OH}$  radicals. As shown in Figure 13 (b), it can be observed that a certain degree of mineralization is happening with  $\bullet\text{OH}$  radicals. This suggests that the amount of  $\bullet\text{OH}$  radicals produced should not be only related to the acid concentration but to the degree of mineralization also. Due to this limitation, this method was reported useful to compare advanced oxidation processes with initial reaction data only. In this study, the production rate of  $\bullet\text{OH}$  radicals was found to be  $129 \times 10^{-5}$  mM/h and  $82 \times 10^{-5}$  mM/h for AO and combined AO and EF respectively at initial conditions (reaction time  $\leq 25$  minutes).

It can also be seen in Figure 13 (a) that the generation of 2,5-DHBA is slightly faster for combined AO and EF than AO only for the first 15-min, and after that no significant difference was seen. This phenomenon can be explained by the rapid reduction of COD in the sample solution by combined the AO and EF method after 15-min, Figure 13 (b). It is worthwhile to mention that in EF, it is expected that a larger fraction of  $\bullet\text{OH}$  radicals would be wasted by  $\text{Fe}^{2+}$ , along with the relative decay of anodic  $\bullet\text{OH}$ <sup>42</sup>.



#### 4.4 Total Iron and Iron (II) Concentration

The analysis of iron concentration is of paramount important in Fenton reaction based treatment systems and therefore was studied here. It can be observed from Figure 14 that after six hours of electrolysis, the concentration of total iron for the integrated anodic oxidation and E-Fenton decreased to 7.3 ppm from 10.86 ppm following the addition of 0.2 mM Fe (II) into the system. The 32.9% reduction of total iron from the system might be attributed to the adsorption of iron (II) and iron (III) species onto the electrode surface<sup>67</sup>.

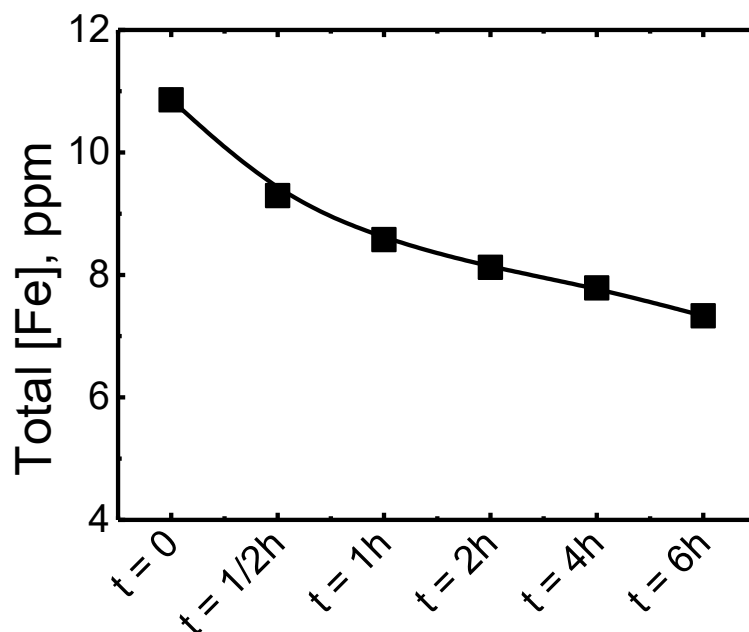


Figure 14 Trend of total iron concentration over time in an integrated electro-Fenton and anodic oxidation system.

The variation of Fe species over time in the electrolysis system has been shown in Figure 15. The reduction in Fe (II) concentration justifies the excess amount of hydrogen peroxide in the system after four hours of electrolysis in section 4.3.1. The cathodic deposition of Fe complexes can be attributed to the diminution of Fe (II) concentration. It is interesting to note here that the performance of the system was mainly attributed the Fenton-like reactions at this stage of electrolysis.

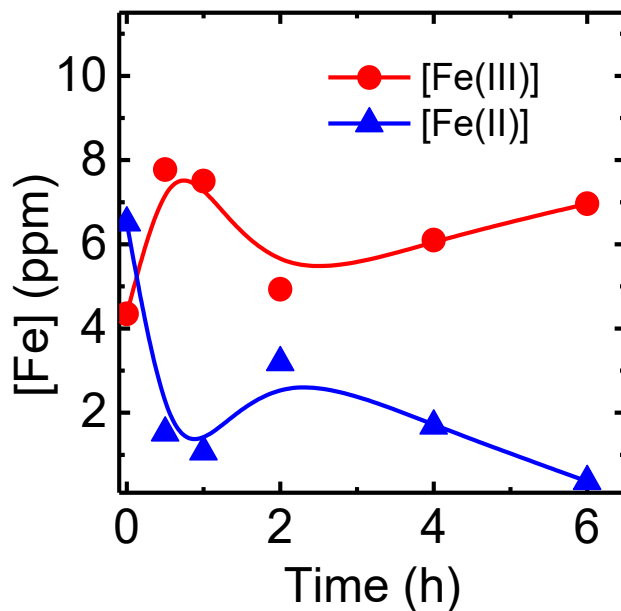


Figure 15 Variation of Fe species concentration over time in the integrated electro-Fenton and anodic oxidation system.

The rapid declination of Fe (II) concentration can also be explained by the excess amount of it in the solution, which leads to more complex formation and finally deposition on the cathode. The formation of this passivation layer on the cathode surface limits the regeneration of Fe (II) through the reduction of Fe (III).

The study of reactive oxygen species generation ( $H_2O_2$ ,  $\bullet OH$  radical) shows no influence of adding iron from external source and Fe speciation shows excess amount of iron is prone to precipitate on electrode surface. However, the concentration of pre-existed iron in the brewery sample makes the anodic oxidation system a dual performing system with high removal of organic matters.

#### 4.5 Enhancement of AO performance at different pH value with the addition of electrolytic solution

The possible enhancement of the anodic oxidation with electro-Fenton (iron source is brewery wastewater) was investigated using acidic, neutral, and basic pH ranges with the addition of electrolytes ( $Na_2SO_4$  salt). As it can be depicted from Figure 16 the variation in



pH value, as well as the addition of electrolyte, showed no improved performance. At pH 7, which is the natural pH range of brewery wastewater used in this study, showed somewhat better performance, it can be proposed that the anodic oxidation experiments can be performed without any pH adjustment.

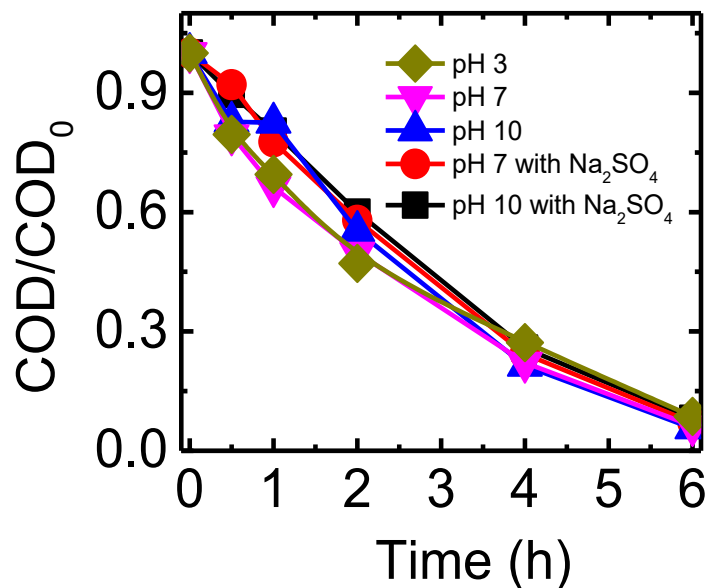


Figure 16 Effect of pH and electrolyte addition on the performance of anodic oxidation system in terms of COD removal over time. [Experimental condition: room temperature, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 6h, [Na<sub>2</sub>SO<sub>4</sub>] = 30 mM, sample volume = 450 ml].

The performance of the anodic oxidation system was then analysed in terms of total nitrogen (TN) and total phosphate (PO<sub>4</sub><sup>2-</sup>) removal. The removal of total nitrogen at each experimental condition is shown in Figure 17. The sample used in this study contained a very low concentration of total phosphate and hence, this compound was completely removed. At the end of 6 h of electrolysis, the residual TN concentrations were found to be 11, 12, 15, and 14 mg/L for respective pH 7, pH 10, pH 7 with electrolytes, and pH 10 with electrolytes at a current density of 16 mA/cm<sup>2</sup>. One possible mechanism of nitrogen compound degradation is explained by Vijayaraghavan et al. who attribute it to super chlorination<sup>8</sup>. This process occurs at close proximity to the anode surface and over the course of electrolysis over time, nitrogenic compounds are converted to monochloramines,

dichloroamines, and nitrogen trichloride and finally transformed into nitrous oxide ( $N_2O$ ) and nitrogen ( $N_2$ ) by further oxidation of chloramines.

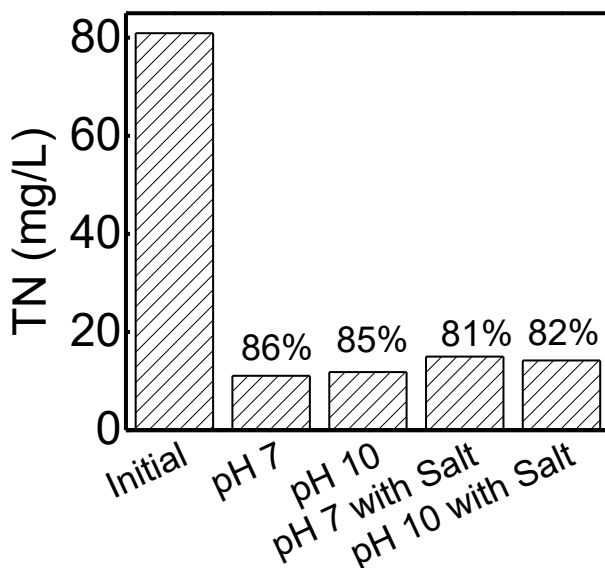


Figure 17 Total nitrogen (TN) removal at different initial pH values using the anodic oxidation system. [Experimental condition: room temperature, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 6h, [Na<sub>2</sub>SO<sub>4</sub>] = 30 mM, sample volume = 450 ml].

#### 4.6 Energy consumption and current efficiency – An analysis of relative cost

The analysis of electrical energy consumption was employed to evaluate the energy requirement of AO system. Here, energy consumption is defined by the amount of electrical energy required in kilowatt-hours to degrade pollutants of 1 m<sup>3</sup> in volume. The variation of electrical energy consumption for different current density and initial Fe (II) concentration is shown in the appendix (Figure 24-Figure 27). The graphical representation of energy requirement with different initial pH value and electrolyte addition is shown in Figure 18 (a) while (b) shows the instantaneous current efficiency (ICE) of the system in batch operation mode at a constant current. The analysis of ICE allows to check the effectiveness of electrochemical processes regarding flowing electrons throughout the system<sup>15</sup>, and by definition, the ratio of the electrical charge used for the oxidation of each compound to the total charge passed during the process<sup>44</sup>.

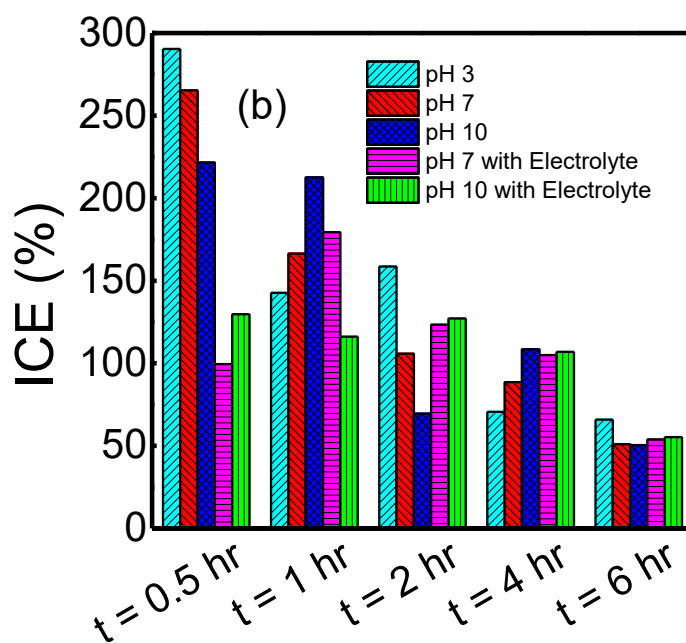
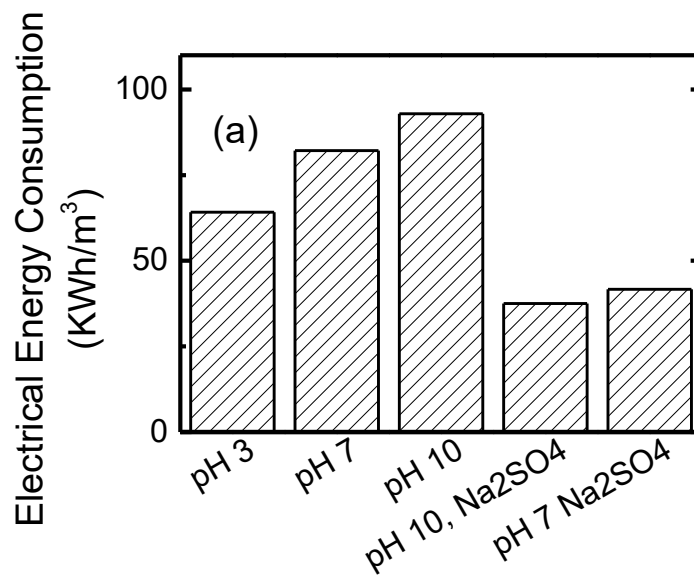


Figure 18 Effect of pH and electrolyte addition on the performance of anodic oxidation system (a) electrical energy consumption; (b) instantaneous current efficiency. [Experimental condition: room temperature, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 6h, sample volume = 450 ml].

#### 4.7 Continuous Experiment – Electrode Fouling

The continuous experiment of the anodic oxidation system using pH 7 (natural pH of the sample used in this study) was conducted to evaluate the effectiveness of the process against electrode fouling. As it can be seen in Figure 19 the system reaches steady state condition after 6 h of electrolysis and continues until ten hours of electrolysis and then starts to deteriorate slightly. This might be explained by the formation of a passivation layer on the surface of the cathode. To regenerate the performance of the system, it must go through the proper cleaning procedure (mentioned in Chapter 3).

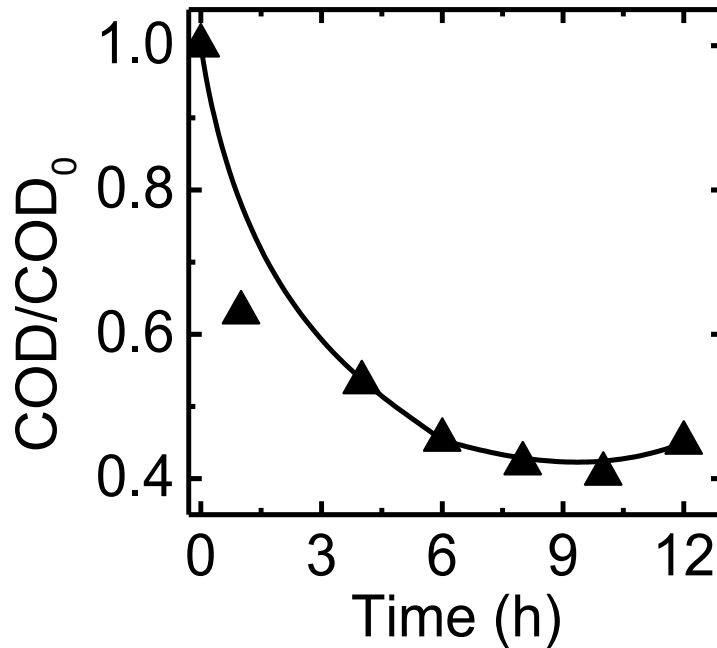


Figure 19 COD degradation profile for the continuous set of experiments. [Experimental condition: room temperature, initial pH 7, current density = 16 mA/cm<sup>2</sup>, electrolysis time = 12 h, flow rate = 0.078 L/h].

## Chapter 5

### Conclusions and Future Perspectives

In this study, anodic oxidation and electro-Fenton processes were used to degrade the organic contents of brewery wastewater. The results obtained from this work include the removal efficiency, reactive oxygen species quantification, and an evaluation of possible side reactions.

Throughout the research, the efficacy of the treatment system was evaluated using the same wastewater sample received from the Labatt brewery unless otherwise mentioned. Firstly, the sample had undergone the anodic oxidation system and with changes in applied current density, the system showed different removal efficiencies. Quantitatively, with 8, 16, and 24 mA/cm<sup>2</sup> of current density, the system showed COD removal efficiency of 65, 91, and, 96% respectively. After considering the relative energy consumption among these three densities, 16 mA/cm<sup>2</sup> was selected for the electro-Fenton experiment and the addition of Fe (II) showed insignificant effect on the sole performance of anodic oxidation. The study of reactive oxygen species showed that in an anodic oxidation system, the production of H<sub>2</sub>O<sub>2</sub> increased exponentially over time to 216.2 μM after 6h of electrolysis, while for the electro-Fenton system the amount of H<sub>2</sub>O<sub>2</sub> was measured lower at each time interval due to the commencement of the Fenton reaction. The measurement of hydroxyl radicals showed an insignificant difference in these processes. Since brewery wastewater ideally contains trace amounts of metals, it can be depicted from this study that the catalytic amount of Fe (II) was already in the sample wastewater, which made the anodic oxidation process more successful and a dual system of anodic oxidation and electro-Fenton. It is worth to mention that the concentrations of trace metals in brewery samples greatly depends on the selection of production process with a careful choice of raw materials utilized including the minor ingredients and, hence, the composition of raw wastewater would vary from sample to sample and it should be obligatory to characterize the wastewater before treating the sample specially for the scale-up systems.

While the AO system demonstrated satisfactory performance, the study encountered some limitations during the experiments: deposition of Fe species on electrodes, and a foaming phenomenon which limited the system's ability to consume O<sub>2</sub> from the ambient atmosphere and indirectly caused fouling. The study of continuous experiments supports these limitations where the AO system starts to deteriorate after 10h of electrolysis. This study suggests that the performance of continuous mode of operation in the existing system unit can be improved by incorporating an intermittent cleaning step to remove impurities from electrodes and a screening unit on top of the reactor to remove the surface scum.

Based on this research, the following recommendations can be made for future studies,

- Comprehensive study of the process to investigate the individual effect of Fenton chemistry and anodic activity on the performance of AO system in a control environment.
- To better understand the electrochemical reactions that are happening in the system, it is recommended to perform an extended characterization of the wastewater sample including trace metal ions (e.g. Mn<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup> etc.) and anions (e.g. Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>).
- Identification and toxicity evaluation – Finding a suitable way to detect the intermediate products of organics and evaluate their possible toxicity on the environment, and analysis of their time course to set a reaction mechanism of their complete mineralization (i.e. conversion into CO<sub>2</sub> and H<sub>2</sub>O).
- Performance evaluation of the existing system unit in continuous mode of operation by incorporating an intermittent cleaning step to remove impurities from electrodes and a screening unit on top of the reactor to screen off the scum.
- Pilot-scale experiments should be performed to check the amenability of anodic oxidation system to large fluctuations in organic loading.
- Analysis of energy and nutrients recovery from the system should be studied to make the system more sustainable.

## Chapter 6

### References

1. Valta, K.; Kosanovic, T.; Malamis, D.; Moustakas, K.; Loizidou, M., Overview of water usage and wastewater management in the food and beverage industry. *Desalination and Water Treatment* **2014**, *53* (12), 3335-3347.
2. Simate, G. S.; Cluett, J.; Iyuke, S. E.; Musapatika, E. T.; Ndlovu, S.; Walubita, L. F.; Alvarez, A. E., The treatment of brewery wastewater for reuse: State of the art. *Desalination* **2011**, *273* (2-3), 235-247.
3. Doubla, A.; Laminsi, S.; Nzali, S.; Njoyim, E.; Kamsu-Kom, J.; Brisset, J. L., Organic pollutants abatement and biodecontamination of brewery effluents by a non-thermal quenched plasma at atmospheric pressure. *Chemosphere* **2007**, *69* (2), 332-7.
4. Vasso Oreopoulou, W. R., *Utilization of By-Products and Treatment of Waste in the Food Industry*. Springer Science: 2007.
5. Haiping Dai, X. Y., Tingwei Dong, Yongwen Ke & Tao Wang, Engineering Application of MBR Process to the Treatment of Beer Brewing Wastewater. *Modern Applied Science* **2010**, *4* (9), 103-109.
6. Feng, Y.; Wang, X.; Logan, B. E.; Lee, H., Brewery wastewater treatment using air-cathode microbial fuel cells. *Appl Microbiol Biotechnol* **2008**, *78* (5), 873-80.
7. Chen, H.; Chang, S.; Guo, Q.; Hong, Y.; Wu, P., Brewery wastewater treatment using an anaerobic membrane bioreactor. *Biochemical Engineering Journal* **2016**, *105*, 321-331.
8. Krishnan Vijayaraghavan, D. A., and Renny Lesa, Electrolytic Treatment of Beer Brewery Wastewater. *Industrial and Engineering Chemical Research* **2006**, *45* (20), 6854-6859.
9. Santana-Martínez, G.; Roa-Morales, G.; Martín del Campo, E.; Romero, R.; Frontana-Uribe, B. A.; Natividad, R., Electro-Fenton and Electro-Fenton-like with in situ electrogeneration of H<sub>2</sub>O<sub>2</sub> and catalyst applied to 4-chlorophenol mineralization. *Electrochim. Acta* **2016**, *195*, 246-256.
10. Ganzenko, O.; Oturan, N.; Huguenot, D.; van Hullebusch, E. D.; Esposito, G.; Oturan, M. A., Removal of psychoactive pharmaceutical caffeine from water by electro-Fenton process using BDD anode: Effects of operating parameters on removal efficiency. *Separation and Purification Technology* **2015**, *156*, 987-995.

11. (a) El-Ghenymy, A.; Rodriguez, R. M.; Brillas, E.; Oturan, N.; Oturan, M. A., Electro-Fenton degradation of the antibiotic sulfanilamide with Pt/carbon-felt and BDD/carbon-felt cells. Kinetics, reaction intermediates, and toxicity assessment. *Environmental science and pollution research international* **2014**, *21* (14), 8368-78;
  - (b) Dirany, A.; Sires, I.; Oturan, N.; Oturan, M. A., Electrochemical abatement of the antibiotic sulfamethoxazole from water. *Chemosphere* **2010**, *81* (5), 594-602.
12. Bensalah, N.; Bedoui, A.; Chellam, S.; Abdel-Wahab, A., Electro-Fenton Treatment of Photographic Processing Wastewater. *CLEAN - Soil, Air, Water* **2013**, *41* (7), 635-644.
13. Ö., A., Reduction of COD in Wastewater from A textile industry by Electro-Fenton Process. *Global NEST Journal* **2014**, *16*.
14. Iglesias, O.; Mejjide, J.; Bocos, E.; Sanromán, M. Á.; Pazos, M., New approaches on heterogeneous electro-Fenton treatment of winery wastewater. *Electrochimica Acta* **2015**, *169*, 134-141.
15. Enric Brillas, I. S. s., and Mehmet A. Oturan, Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. *Chemical Reviews* **2009**, *109* (12), 6570–6631.
16. C. Barrera-Díaz, P. C., F. J. Fernández, R. Natividad, and M.A. Rodrigob, Electrochemical Advanced Oxidation Processes: An Overview of the Current Applications to Actual Industrial Effluents. *Joournal of Mexican Chemical Society* *58* (3), 256-275.
17. Jiang, C.-c.; Zhang, J.-f., Progress and prospect in electro-Fenton process for wastewater treatment. *Journal of Zhejiang University SCIENCE A* **2007**, *8* (7), 1118-1125.
18. Liu, Y.; Xie, J.; Ong, C. N.; Vecitis, C. D.; Zhou, Z., Electrochemical wastewater treatment with carbon nanotube filters coupled with in situ generated H<sub>2</sub>O<sub>2</sub>. *Environmental Science: Water Research and Technology* **2015**, *1* (6), 769-778.
19. Fergus G. Priest, G. G. S., *Handbook of brewing*. second ed.; Taylor and Francis Group: 2006.
20. (a) Hach Application - Wastewater Discharge Monitoring. <http://sea.hach.com/wastewaterdischarge> (accessed 28-11-2016);
  - (b) Wikipedia Fish Kill. [https://en.wikipedia.org/wiki/Fish\\_kill](https://en.wikipedia.org/wiki/Fish_kill) (accessed 28-11-2016).



21. Canada's Beer Industry. 2016-03-07 ed.; Agriculture and Agri-Food Canada: <http://www.agr.gc.ca>, 2016.
22. Significance of the Food and Beverage Processing Industry in Canada. 2016-03-07 ed.; Agriculture and Agri-Food Canada: <http://www.agr.gc.ca>, 2016.
23. Industrial Water Use. Environment, E. a. T. S. D., Ed. Minister of Industry: Statistics Canada, 2014.
24. *Industry Trends*; Beer Canada: [www.beercanada.com](http://www.beercanada.com), 2016.
25. Fillaudeau, L.; Blanpain-Avet, P.; Daufin, G., Water, wastewater and waste management in brewing industries. *Journal of Cleaner Production* **2006**, *14* (5), 463-471.
26. Eberts, D., To Brew or Not to Brew: A Brief History of Beer in Canada. *Manitoba Historical Society* **2007**.
27. Kanagachandran, K.; Jayaratne, R., Utilization Potential of Brewery Waste Water Sludge as an Organic Fertilizer. *Journal of the Institute of Brewing* **2006**, *112* (2), 92-96.
28. Chen, H. Optimization of Anaerobic Membrane Bioreactor Operation for Brewery Wastewater Treatment. Master's thesis, University of Guelph, 2015.
29. Janhom, T.; Wattanachira, S.; Pavasant, P., Characterization of brewery wastewater with spectrofluorometry analysis. *Journal of environmental management* **2009**, *90* (2), 1184-90.
30. Daniel Sancho, C. A. B., Isabel Caballero and Ana Pascual, Free iron in pale, dark and alcohol-free commercial lager beers. *Journal of the Science of Food and Agriculture* **2011**, *91*, 1142-1147.
31. (a) Simate, G. S.; Iyuke, S. E.; Ndlovu, S.; Heydenrych, M., The heterogeneous coagulation and flocculation of brewery wastewater using carbon nanotubes. *Water Research* **2012**, *46* (4), 1185-97; (b) Simate, G. S., The treatment of brewery wastewater for reuse by integration of coagulation/flocculation and sedimentation with carbon nanotubes 'sandwiched' in a granular filter bed. *Journal of Industrial and Engineering Chemistry* **2015**, *21*, 1277-1285.
32. Rao, A. G.; Reddy, T. S.; Prakash, S. S.; Vanajakshi, J.; Joseph, J.; Sarma, P. N., pH regulation of alkaline wastewater with carbon dioxide: a case study of treatment of brewery wastewater in UASB reactor coupled with absorber. *Bioresource Technology* **2007**, *98* (11), 2131-6.
33. Scampini, A. C. Upflow Anaerobic Sludge Blanket Reactors for Treatment of Wastewater from the Brewery Industry. Master's thesis, Massachusetts Institute of Technology, 2010.

34. (a) Wang, S. G.; Liu, X. W.; Gong, W. X.; Gao, B. Y.; Zhang, D. H.; Yu, H. Q., Aerobic granulation with brewery wastewater in a sequencing batch reactor. *Bioresource Technology* **2007**, *98* (11), 2142-7;
- (b) Wang, F.; Lu, S.; Wei, Y.; Ji, M., Characteristics of aerobic granule and nitrogen and phosphorus removal in a SBR. *Journal of Hazardous Materials* **2009**, *164* (2-3), 1223-7.
35. Adesoji T. Jaiyeola, J. K. B., Treatment technology for brewery wastewater in a water-scarce country: A review. *South African Journal of Science* **2016**, *112* (3/4).
36. Parawira, W.; Kudita, I.; Nyandoroh, M. G.; Zvauya, R., A study of industrial anaerobic treatment of opaque beer brewery wastewater in a tropical climate using a full-scale UASB reactor seeded with activated sludge. *Process Biochemistry* **2005**, *40* (2), 593-599.
37. Braeken, L.; Van der Bruggen, B.; Vandecasteele, C., Regeneration of brewery waste water using nanofiltration. *Water Research* **2004**, *38* (13), 3075-82.
38. Wang, X.; Feng, Y. J.; Lee, H., Electricity production from beer brewery wastewater using single chamber microbial fuel cell. *Water science and technology : a journal of the International Association on Water Pollution Research* **2008**, *57* (7), 1117-21.
39. Into, M.; Jönsson, A.-S.; Lengdén, G., Reuse of industrial wastewater following treatment with reverse osmosis. *Journal of Membrane Science* **2004**, *242* (1-2), 21-25.
40. Mark R. Wiesner, G. V. L., Pedro Alvarez, Dianysios Dionysiou and Pratim Biswas, Assessing the Risks of Manufactured Nanomaterials. *Environmental Science & Technology* **2006**, *40* (14), 4336-4345.
41. Oturan, M. A.; Aaron, J.-J., Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. *Critical Reviews in Environmental Science and Technology* **2014**, *44* (23), 2577-2641.
42. Guinea, E.; Arias, C.; Cabot, P. L.; Garrido, J. A.; Rodriguez, R. M.; Centellas, F.; Brillas, E., Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide. *Water Research* **2008**, *42* (1-2), 499-511.
43. Feng, Y.; Yang, L.; Liu, J.; Logan, B. E., Electrochemical technologies for wastewater treatment and resource reclamation. *Environmental Science: Water Research and Technology* **2016**, *2* (5), 800-831.

44. Cerisola, M. P. a. G., Direct And Mediated Anodic Oxidation of Organic Pollutants. *Chemical Reviews* **2009**, *109* (12), 6541–6569.
45. Carlos Barrera-Díaz, G. R.-M., Liliana Avila-Cordoba, Thelma Pavon-Silva, and Bryan Bilyeu, Electrochemical Treatment Applied to Food-Processing Industrial Wastewater. *Industrial and Engineering Chemistry Research* **2006**, *45* (1), 34-38.
46. Güven, G.; Perendeci, A.; Tanyolaç, A., Electrochemical treatment of simulated beet sugar factory wastewater. *Chemical Engineering Journal* **2009**, *151* (1-3), 149-159.
47. Guray Guven, A. P., Abdurrahman Tanyolac, Electrochemical treatment of deproteinated whey wastewater and optimization of treatment conditions with response surface methodology. *Journal of Hazardous Materials* **2008**, *157*, 69–78.
48. Radjenovic, J.; Sedlak, D. L., Challenges and Opportunities for Electrochemical Processes as Next-Generation Technologies for the Treatment of Contaminated Water. *Environmental Science & Technology* **2015**, *49* (19), 11292-302.
49. Dark beer has more iron than pale beer or non-alcoholic beer. *Science Daily* 2011.
50. Abdessamad, N.; Akrou, H.; Hamdaoui, G.; Elghniji, K.; Ksibi, M.; Bousselmi, L., Evaluation of the efficiency of monopolar and bipolar BDD electrodes for electrochemical oxidation of anthraquinone textile synthetic effluent for reuse. *Chemosphere* **2013**, *93* (7), 1309-16.
51. Wang, C. T.; Hu, J. L.; Chou, W. L.; Kuo, Y. M., Removal of color from real dyeing wastewater by Electro-Fenton technology using a three-dimensional graphite cathode. *Journal of Hazardous Materials* **2008**, *152* (2), 601-6.
52. Peter T. Kissinger, W. R. H., Cyclic Voltammetry. *Journal of Chemical Education* *60* (9), 702-706.
53. HACH, *Water Analysis Handbook*. 7th ed.; Hach Company: Loveland, Colorado, U.S.A., 2012.
54. Corporation, S. 680 °C Combustion Catalytic Oxidation Method Measurement Principles. (accessed 27 November).
55. Li, H.; Yu, Q.; Yang, B.; Li, Z.; Lei, L., Electrochemical treatment of artificial humidity condensate by large-scale boron doped diamond electrode. *Separation and Purification Technology* **2014**, *138*, 13-20.

56. (a) H. BADER, V. S. a. J. H., Photometric Method for the Determination of low concentrations of Hydrogen Peroxide by the Peroxidase Catalyzed Oxidation Of N,N-Diethyl-P-Phenylenediamine (DPD). *Water Research* **1988**, 22 (9), 1109-1115;

(b) Hsieh, H.-S.; Jafvert, C. T., Reactive oxygen species generation and dispersant-dependent electron transfer through single-walled carbon nanotubes in water. *Carbon* **2015**, 89, 361-371.

57. Wu, D.; Liu, M.; Dong, D.; Zhou, X., Effects of some factors during electrochemical degradation of phenol by hydroxyl radicals. *Microchemical Journal* **2007**, 85 (2), 250-256.

58. (a) Jen-Fon Jen, M.-F. L., Thomas C. Yang, Determination of hydroxyl radicals in an advanced oxidation process with salicylic acid trapping and liquid chromatography. *Journal of Chromatography A* **1998**, 796, 283-288;

(b) Marselli, B.; Garcia-Gomez, J.; Michaud, P. A.; Rodrigo, M. A.; Comninellis, C., Electrogeneration of Hydroxyl Radicals on Boron-Doped Diamond Electrodes. *Journal of The Electrochemical Society* **2003**, 150 (3), D79;

(c) Panchompoo, J.; Aldous, L.; Kabeshov, M.; Pilgrim, B. S.; Donohoe, T. J.; Compton, R. G., A green approach to Fenton chemistry: mono-hydroxylation of salicylic acid in aqueous medium by the electrogeneration of Fenton's reagent. *New Journal of Chemistry* **2012**, 36 (5), 1265.

59. Peralta, E.; Roa, G.; Hernandez-Servin, J. A.; Romero, R.; Balderas, P.; Natividad, R., Hydroxyl Radicals quantification by UV spectrophotometry. *Electrochimica Acta* **2014**, 129, 137-141.

60. Elmer, P., Atomic Spectroscopy - A Guide to Selecting the Appropriate Technique and System. 2011.

61. (a) Lacan, F.; Radic, A.; Jeandel, C.; Poitrasson, F.; Sarthou, G.; Pradoux, C.; Freydier, R., Measurement of the isotopic composition of dissolved iron in the open ocean. *Geophysical Research Letters* **2008**, 35 (24);

(b) Spolaor, A.; Vallelonga, P.; Gabrieli, J.; Cozzi, G.; Boutron, C.; Barbante, C., Determination of Fe<sup>2+</sup> and Fe<sup>3+</sup> species by FIA-CRC-ICP-MS in Antarctic ice samples. *Journal of Analytical Atomic Spectrometry* **2012**, 27 (2), 310-317.

62. Allen J. Bard, L. R. F., *Electrochemical Methods Fundamentals and Applications*. 2nd ed.; John Wiley & Sons, Inc.: 2001.

63. Eduardo Terrazasa, A. V., Roberto Briones, Isabel Lázaro, Israel Rodríguez, EC treatment for reuse of tissue paper wastewater: Aspects that affect energy consumption. *Journal of Hazardous Materials* **2010**, *181*, 809-816.
64. Pozzo, A. D.; Palma, L. D.; Merli, C.; Petrucci, E., An experimental comparison of a graphite electrode and a gas diffusion electrode for the cathodic production of hydrogen peroxide. *Journal of Applied Electrochemistry* **2005**, *35* (4), 413-419.
65. Eyvaz, M., Treatment of Brewery Wastewater with Electrocoagulation: Improving the Process Performance by Using Alternating Pulse Current. *International Journal of Electrochemical Science* **2016**, 4988-5008.
66. Oturan, M. A.; Pimentel, M.; Oturan, N.; Sirés, I., Reaction sequence for the mineralization of the short-chain carboxylic acids usually formed upon cleavage of aromatics during electrochemical Fenton treatment. *Electrochim. Acta* **2008**, *54* (2), 173-182.
67. Qiu, S.; He, D.; Ma, J.; Liu, T.; Waite, T. D., Kinetic Modeling of the Electro-Fenton Process: Quantification of Reactive Oxygen Species Generation. *Electrochimica Acta* **2015**, *176*, 51-58.

## Appendix

This chapter contains supporting information to better understand the system. During electrolysis period, conductivity of the sample solution increases due to the reduction of contaminants potentially induces inorganic ions into the electrolysis cell by degrading organic matters (Figure 20). Thus, the voltage requirement of the system reduced (Figure 21). Throughout the experimental period, pH of the solution remained in the acidic range potentially due to the faster oxidation of water on BDD anode surface (Figure 22). Figure 23 shows the reduction in voltage requirement upon adding electrolytes into the system.

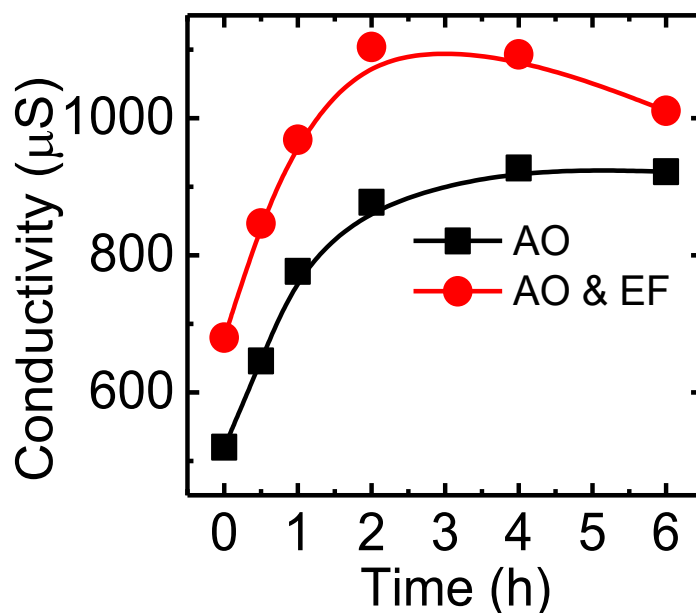


Figure 20 Change of conductivity (average) over time in different electrochemical treatment systems. [Experimental condition: room temperature, initial pH 3, sample volume = 450 ml].

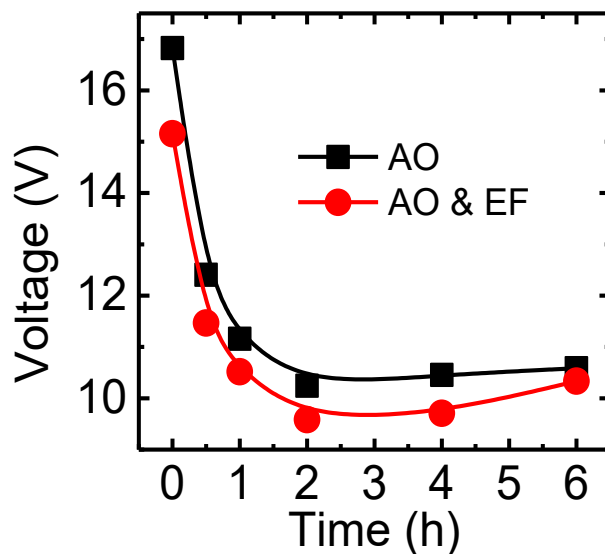


Figure 21 Change of voltage requirement (average) over time in different electrochemical treatment methods used in this study. [Experimental condition: room temperature, initial pH 3, sample volume = 450 ml].

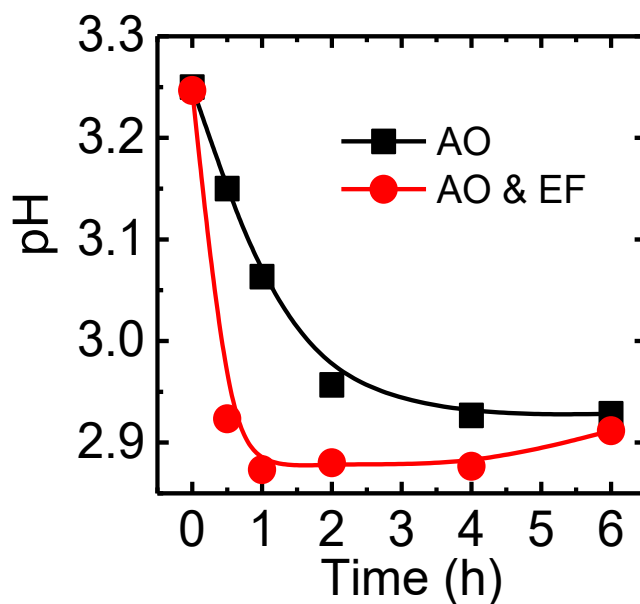


Figure 22 Change of initial pH (average) over time in different electrochemical treatment methods used in this study. [Experimental condition: room temperature, sample volume = 450 ml].

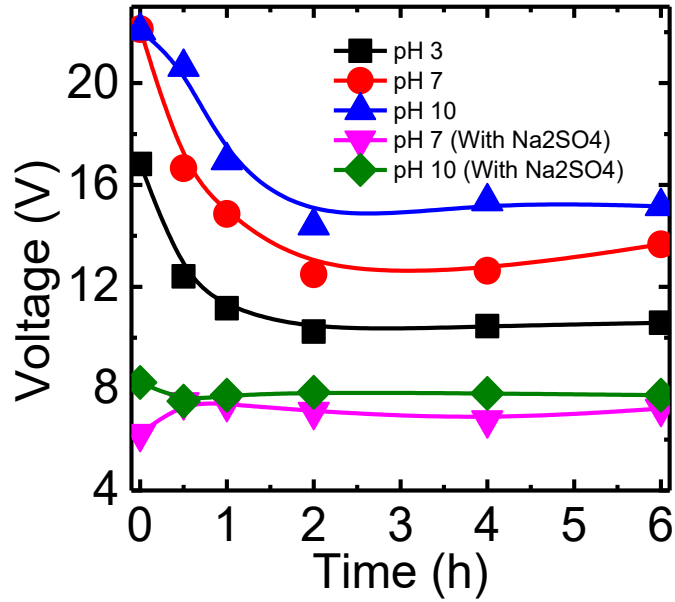


Figure 23 Effect of initial pH and electrolyte addition on the requirement of voltage over time in anodic oxidation system. [Experimental condition: room temperature, sample volume = 450 ml].

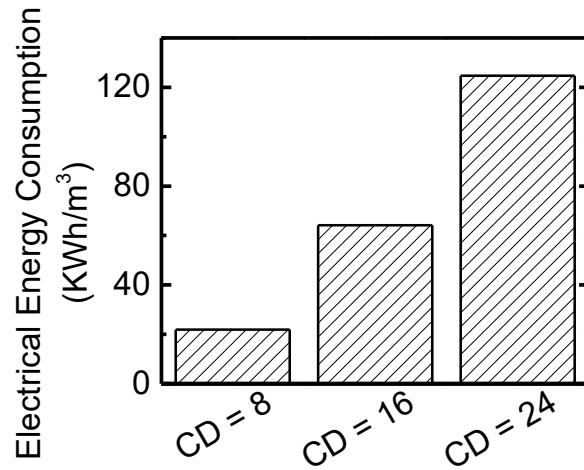


Figure 24 Electrical energy consumption as a function of current density (CD), mA/cm<sup>2</sup> for anodic oxidation system. As CD increases the energy consumption also increases where increment of CD from 8 to 16 consumes 34% more energy than the lower one and an increment from 16 to 24 consumes 51% more energy than 16 mA/cm<sup>2</sup>.



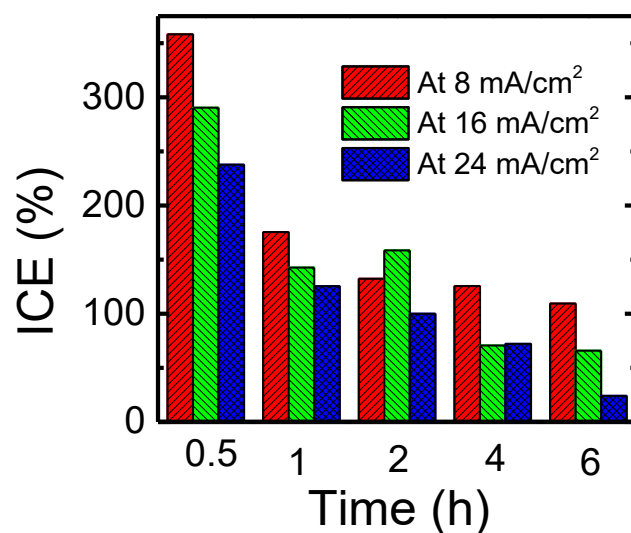


Figure 25 Changes of instantaneous current efficiency (ICE) over time at different current density. Significant difference in ICE can be observed at 0.5 and 6 hr respectively at various current density.

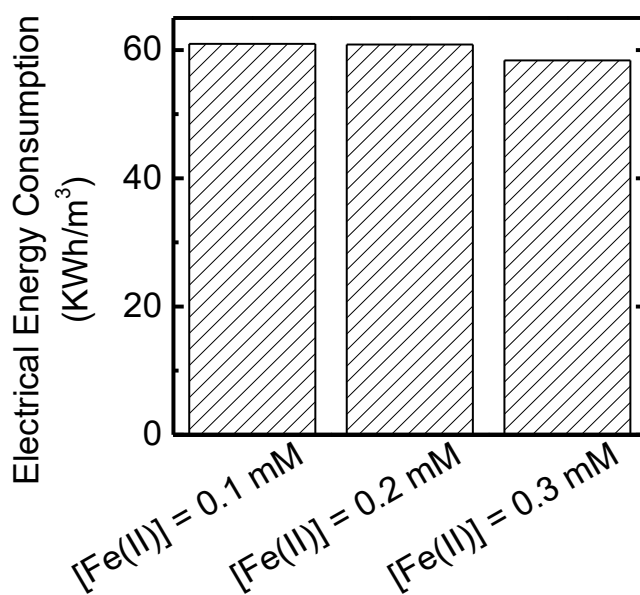


Figure 26 Electrical energy consumption as a function of current density (CD), mA/cm<sup>2</sup> for combined electro-Fenton and anodic oxidation system. The addition of Fe (II) showed no significant effect on electrical energy consumption. [Experimental condition: room temperature, initial pH 3, current density = 16mA/cm<sup>2</sup>, electrolysis time = 6 h, sample volume = 450 ml].

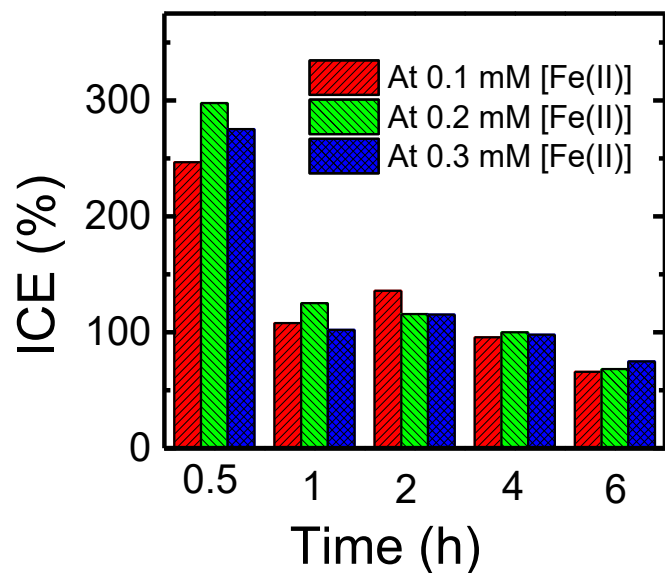


Figure 27 Changes of instantaneous current efficiency (ICE) over time at different initial iron (II) concentration. The range of concentration used in this study showed slight variation in ICE at every time interval tested. [Experimental condition: room temperature, Initial pH 3, current density = 16mA/cm<sup>2</sup>, electrolysis time = 6h, sample volume = 450 ml].