

**USING THE ELECTROCHEMICAL TREATMENT OF A
WET-AIR OXIDIZED SPENT CAUSTIC WASTE
STREAMS FOR POTENTIAL REUSE OR SAFE
DISPOSAL**

BY

SALEH N. AL-AGEEL

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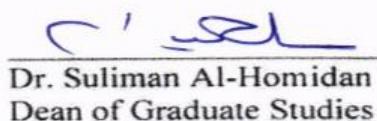
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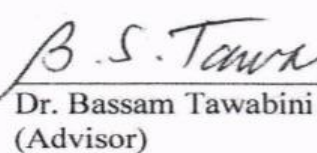
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRÂN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

This thesis, written by **SALEH AL-AGEEL** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN ENVIRONMENT**.


Dr. John Humphrey
Department Chairman

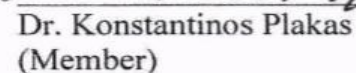

Dr. Suliman Al-Homidan
Dean of Graduate Studies

Date


Dr. Bassam Tawabini
(Advisor)

Dr. TYPE NAME
(Co-Advisor)

Dr. Basim Abussaud
(Member)


Dr. Konstantinos Plakas
(Member)



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I dedicate this thesis to my family and friends, Mohammed and Fawaz. They were the first persons to encourage me to try this subject.

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-Saleh N. AL-Ageel-

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LIST OF ABBREVIATIONS

ACF:	Activated Carbon Fiber
ACS:	American Chemical Society
BDD:	Boron Doped Diamond
CAPEX:	Capital expenditures
CAS:	Chemical Abstracts Service
CE:	Current Efficiency
CERTH:	Center for Research and Technology - Hellas
CNTs:	Carbon nanotubes
COD:	Chemical Oxygen Demand
DC:	Direct current
DSA:	Dimensionally Stable Anode
EC:	Electrocoagulation
EF:	Electro-Fenton
ETS:	Electrochemical Treatment System
GDE:	Gas Diffusion Electrodes
HMI:	Human Machine Interface
HSE:	Health, Safety, and Environment
LPG:	Liquefied petroleum gas
MEWA:	Ministry of Environment, Water and Agriculture
ORP:	Oxidation-Reduction Potential
PTFE:	Polytetrafluoroethylene
RVC:	Reticulated Vitreous Carbon

TDS: Total Dissolved Solid

Ti: Titanium

TOC: Total Organic Carbon

SCADA: Supervisory Control and Data Acquisition

SCW: Spent Caustic Wastewater

WAO: Wet Air Oxidation

WWTP: Wastewater Treatment Plants

ZEO: Zimpro Electrochemical Oxidization

ABSTRACT

Full Name : Saleh Naser AL-Ageel

Thesis Title : USING THE ELECTROCHEMICAL TREATMENT OF A WET-AIR
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In oil refining and petrochemical industrial facilities, sodium hydroxide (NaOH) solution is added to eliminate malodorous and potentially dangerous gases such as hydrogen sulfide (H_2S) and other sulfur compounds from hydrocarbon streams. The waste stream generated in the process is referred to as “spent caustic” and is considered hazardous due to the toxic, odorous, and/or corrosive nature of its components. Therefore, it needs to be treated before disposal to reduce its harmful effects on the receiving environment. Since some of the spent caustic pollutants are not biodegradable, meeting effluent regulations may be challenging. In addition to biological treatment, acid neutralization, incineration, and wet air oxidation (WAO), are used for the treatment of spent caustic streams. However, the characteristics of spent caustic treated by such methods, such as WAO, may not meet the strict environmental discharge limit of COD 50 mg/L. Therefore, a post-treatment step is needed to lower the COD below the allowable limits. In this study, an ethylene plant spent caustic effluent pre-treated by wet air oxidation was further treated using a Fenton-based Electrochemical Advanced Oxidation Process (F-EAOP). The study aimed to identify the optimum operational parameters of authentic spent caustic treatment such as initial COD concentration, pH, conductivity, electric current, circulation flow rate, airflow rate, addition of iron, and electrolysis time. The study

was conducted with the aid of an electrochemical treatment pilot system equipped with Boron Doped Diamond and Gas Diffusion Electrodes (BDD/GDE). Under the near optimum operational conditions, COD was reduced from 860 mg/L to 57 mg/L in 4 hours of electrolysis time, at pH 4, current density (150 mA/cm^2), and spent caustic circulation rate of $0.2 \text{ m}^3/\text{h}$. The addition of iron (II) and air did not affect the COD abatement.

ملخص الرسالة

الاسم الكامل: صالح ناصر العقيل

عنوان الرسالة: استخدام المعالجة الكهرو كيميائية لتدفقات النفايات الكاوية المستهلكة والتي تم اكسبتها عن طريق تقنية الهواء الرطب لإعادة الاستخدام المحتمل أو التخلص الآمن

التخصص: علوم البيئة

تاريخ الدرجة العلمية: مايو 2023

في منشآت تكرير النفط ومصانع البتروكيماويات، تُستخدم محاليل هيدروكسيد الصوديوم (NaOH) للتخلص من الغازات الكريهة والتي يحتمل أن تكون خطرة مثل كبريتيد الهيدروجين (H_2S) ومركبات الكبريت الأخرى من تيارات الهيدروكربون. يُطلق على المخلفات التي تم الحصول عليها اسم "المواد الكاوية المستهلكة" والتي تحتاج إلى المعالجة قبل التخلص منها بسبب آثارها الضارة جدًا على البيئة. قد يكون التخلص من النفايات الخطرة "المواد الكاوية المستهلكة" أمرًا صعبًا بسبب المكونات السامة و / أو الرائحة و / أو المسببة للتآكل. لذلك، يجب معالجتها قبل التخلص منها لتقليل آثارها الضارة على البيئات المستقبلية لها. ونظرًا لأن بعض الملوثات الكاوية المستهلكة غير قابلة للتحلل البيولوجي، فقد يكون تلبية لوائح التعامل مع النفايات السائلة أمرًا صعبًا. بالإضافة إلى المعالجة البيولوجية، فإن معادلة الحمض، والحرق، وأكسدة الهواء الرطب (WAO) تُستخدم تقليديًا للتخلص من هذه المواد. ومع ذلك، فإن خصائص المادة الكاوية المستهلكة المعالجة بمثل هذه الطرق مثل WAO قد لا تفي بمعايير التصريف البيئي المحلي الصارمة الأخيرة لـ COD البالغة 50 مجم / لتر. لذلك، هناك حاجة إلى خطوة ما بعد المعالجة لخفض COD إلى ما دون الحدود المسموح بها. في هذه الدراسة، تمت معالجة النفايات السائلة الكاوية الناتجة من مصنع الإيثيلين والتي تمت معالجتها مسبقًا بواسطة (WAO) باستخدام عملية الأكسدة الكهروكيميائية المتقدمة المعتمدة على الفينتون (F-AEOP).

هدفت الدراسة إلى تحديد المعايير التشغيلية المثلى للمعالجة المواد الكاوية المستهلكة الأصلية مثل تركيز COD الأولي ، ودرجة الحموضة ، والتوصيل ، والتيار الكهربائي ، ومعدل تدفق السائل ، ومعدل تدفق الهواء ، وإضافة الحديد ووقت التحليل الكهربائي. أجريت الدراسة من خلال نظام تجريبي للمعالجة الكهروكيميائية مزود بأقطاب

Boron Doped Diamond and Gas Diffusion Electrodes (BDD / GDE) في ظل ظروف التشغيل

شبه المثالية، تم خفض تركيز COD من 860 مجم / لتر إلى 57 مجم / لتر في 4 ساعات من وقت التحليل الكهربائي،

عند درجة الحموضة 4، والتيار الكهربائي (15 أمبير أو 150 مللي أمبير / سم 2) ومعدل دوران بمقدار 0.2 متر مكعب / ساعة. لم تؤثر إضافة الحديد (II) والهواء على خفض تركيز COD من المادة الكاوية المستهلكة.

CHAPTER 1
INTRODUCTION

Many industries generate wastewater streams during manufacturing and production processes, which is an ongoing challenge for their treatment. This is because, if the industrial wastewater is not treated effectively, it can result in severe contamination of receiving water bodies and cause serious health effects to humans and other living species. Among the industrial wastewaters that have treatment and disposal challenges, is spent caustic effluents.

1.1 What is Spent Caustic?

Spent caustic is an industrial caustic waste solution generated from either petroleum refineries or olefins plants (Bahadori, 2016). In the process, caustic solution (NaOH) is used to remove contaminants such as sulfides, carbonates, and small fractions of organic compounds that are exhausted and will be no longer useful. That is why it is referred to as spent.

Sulfides are highly odorous, even at $\mu\text{g/L}$ (ppb) levels; hence, spent caustic effluents are a substantial source of odor. It is also alkaline, with a pH of around 14 (Sun, 2016). Furthermore, the COD load in spent caustic is extremely high, typically in the tens of thousands $\text{mg O}_2/\text{L}$. This is due to entrained polymer oil during the ethylene plant operation process, which can significantly raise the total organic carbon (TOC) and, as a result, the COD of spent caustic. This may cause problems with the spent caustic treatment system's operation. Sodium hydroxide (NaOH) is one of the common types of caustics that are utilized to remove contaminants in refineries and ethylene industries before being spent. Spent caustic is usually classified depending on its pollutant's composition (Table 1) (Veerabhadraiah, G. et. al., 2001) as follows:

- Sulfur compounds are mainly sulfides produced during the scrubbing of straight-run gaseous hydrocarbons.

- Phenolic compounds are mainly phenol, xylene, and cresols with sulfides produced during the scrubbing of fractured gases/gasoline.
- Naphthenic compounds are naphthenic acids produced during the scrubbing and mercaptan extraction of middle distillates.

Table 1: Typical spent caustic formulations Veerabhadraiah, G. et. al., 2001

Component (wt. %)	Sulfidic	Phenolic	Naphthenic
Sodium Hydroxide	2 - 10	10 - 15	1 - 4
Inorganic Sulphide as S	0.5 - 4	0 - 1	0 - 0.1
Mercaptide as S	0.1 - 4	0 - 4	0 - 0.5
Cresylic Acid	-	10 - 25	0 - 3
Naphthenic Acids	-	-	2 - 15
Carbonate as CO ₃	0 - 4	0 - 0.5	-
pH	13 - 14	12 - 14	12 - 14
Free Oil	Vary up to 20% in raw/unskimmed Content		

1.1.1 Types of Spent Caustic

1.1.1.1 Ethylene Cracker Spent Caustic

In ethylene cracker facilities, caustic (such as Sodium Hydroxide) is used to scrub the cracked gas generated from ethylene crackers. Usually, this solution is made using a caustic scrubbing column to scrub the contaminants (H₂S (g) and CO₂ (g) and some traces of oil, olefins, and polymers). As a result, NaHS (aq) and Na₂CO₃ (aq) will be produced and caustic consumed. The effluent (spent caustic) is combined with sulfate and carbonates, as well as a small number of organic compounds. A typical composition of ethylene plant spent caustic is shown in Table 2, where NaSR is Sodium Sulfide and R stands for any group of carbon or hydrogen atoms (Maugans, 2010).

Table 2: Typical composition of ethylene plant spent caustic (Maugans, 2010)

Compound	Concentration
Sodium Hydrosulfide	0.5-6 %
Sodium Bicarbonate	1-5 %
Sodium Hydroxide	1-4 %
NaSR (Mercaptans)	0-0.2 %
Soluble oil	50-150 ppm
TOC	50-1500 ppm
COD	Usually in tens of thousands ppm
Benzene	20-100 ppm

1.1.1.2 Refinery Spent Caustic

It is produced by the Meroux processing of gasoline, Liquefied petroleum gas (LPG), and kerosene. Organic acids and sulfides are present in these streams, and they are removed in the scrubber by caustic such as sodium hydroxide. Caustic will be consumed and then wastewater (spent caustics) will be generated as follows: Sulfidic from LPG, Naphthenic from kerosene, and Cresylic from gasoline. Therefore, the spent caustic will have a high percentage of organic acids, sulfides, carbonates, and other contaminants.

1.1.2 Treatment Methods of Spent Caustic

It is crucial to choose the optimal treatment process, especially when it comes to overall waste management. Environmental regulations governing emissions and discharges are often the driving force behind it. Accordingly, off-site disposal is usually expensive in terms of meeting environmental and legal obligations, leading most refineries and ethylene facilities to have a preference for on-site treatment.

Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) levels in spent caustic streams from the oil and gas industry are quite high in addition to various other dangerous pollutants such as sulfate, mercaptan, sodium salts, and others. These wastewaters are difficult to remediate and particularly damaging to the environment because of the pollutants in refinery spent caustic. As a result, spent caustic wastewater treatment can be difficult and costly.

Depending on the waste stream volume, its content, the design of the whole process facility, as well as the toxicity threshold limits of downstream treatment systems, a variety of treatment procedures can be used. Physical separation and oxidation processes are the two basic types of processes applied (Table 3). Chemical, thermal, or biological treatment options are available for spent caustic. Additional classifications can be made based on the operational parameters of the systems and the chemicals employed in the oxidation processes (Table 4).

Table 3 briefly summarizes the physical separation and oxidization of spent caustic treatment and Table 4 explains the oxidation of spent caustic on-site treatment technologies (Clark, M., 2017).

Table 3: Physical separation and chemical oxidation of spent caustic:

Category	Process	Advantage	Disadvantage
Physical separation	Acid oil can be separated from the aqueous phase by adding enough strong acid, generating a floating oil layer. It is then skimmed and collected to be disposed of off-site or blended into low-grade hydrocarbon products.	It aids in the removal of a substantial amount of COD.	Volatile materials will be released at low pH, which is particularly corrosive and causes odor as well as health, safety, and environmental (HSE) problems. In addition, it necessitates a lot of maintenance. More treatment is required before it may be disposed of in an acid gas flare or a sulfur recovery plant. Sulfidic, cresylic, and naphthenic chemicals that remain will be difficult to break down biologically, posing considerable operating issues for wastewater treatment plants (WWTP). In addition, the aeration basin is creating stink and foaming.
Oxidation processes	Sulfides are converted to sulfate salts by oxidation, and mercaptan is converted to sulfonic acids by oxidation. Organic acid molecules are also converted into carbon dioxide and water, as well as organic acids with lower molecular weights. Oxidation approaches include incineration, biological, chemical, wet air oxidation, and now electro-oxidation.	Generally, • It can convert it to a harmless material, with neither odor nor HSE issues depending on the used technology. • The treated material can easily be biodegradable. In Table 4, there are more details of the advantages.	In Table 4, there are more details of the disadvantages of the oxidation processes.

Table 4: Oxidation of spent caustic

Category	Process	Advantage	Disadvantage
Caustic waste is discharged directly into a biological WWTP	Bacteria are used in biological treatments to break down organic wastes through normal cellular processes.	Organic content removal	Because of the modest amounts of caustic used, it is unappealing because it requires facilities to commit substantial throughput capabilities for dilution. Controlling smells, corrosion, foaming, toxicity, and oil springing requires constant monitoring.
Chemical advanced oxidation	Hydrogen peroxide catalyzed by ferrous iron is commonly used. Ozone or chlorine can also be utilized as oxidants. The better the results, the more an oxidant is employed.	It is widely used for WWTPs.	- Even handling modest volumes of spent caustic is expensive. - It necessitates the storage of large quantities of powerful oxidizers. - It results in a low pH, which leads to the formation of acid oils and the liberation of sulfate and mercaptan. - There are safety issues with oxidants combined with undissolved oil.
Incineration	Uses thermal treatment to oxidize organic matter contained in the spent caustic.	It is capable of properly removing spent caustic.	- Because spent caustic cannot satisfy the heat requirements of the incineration process, it requires a large amount of fuel. - It must be built specifically to withstand high salt concentrations. - Its refractory material will need to be replaced frequently, making it an expensive solution.
WAO	It uses heat and pressure to oxidize the aqueous phase of spent caustic with oxygen from the air.	- It can convert sulfur species to more benign forms like sodium sulfate. - Complex chemical molecules are being oxidized to carbon dioxide and biodegradable short-chain organic compounds.	- In a traditional on-site WWTP, the oxidized spent caustic may require additional treatment. - It may lead to additional costs and risks due to the requirement to store powerful oxidizing chemicals on-site. - The greater the temperature, the more biodegradable the effluent, which means more energy, and therefore cost, to attain the optimum.

Electrochemical oxidation	The electrodes create extremely reactive hydroxyl radicals from the water molecules in the spent caustic aqueous solution using DC electricity as the oxidizing agent. The electrodes do this by splitting a hydrogen ion from the H ₂ O molecule.	• There are fewer safety concerns. • It allows complying with a WWTP, sea or ocean discharge regulatory requirements. • It can avoid more costs and hazards as there is no need to store strong oxidizing chemicals onsite.	• If the electrode is unable to tolerate the hostile environment of spent caustic, such as corrosion resistance and lifetime utilization, it will be commercially impracticable. • It is ideally suited to low flow rates and COD loads.
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Wet Air Oxidation (WAO), is a method of oxidizing wastewaters such as spent caustic at high pressure and temperature with O₂. The primary goal of this hydrothermal process is to transform organic contaminants into easily biodegradable compounds or mineralize them. Since WAO can lower the COD of the effluent, it is frequently used to pre-treat used caustic before biological treatment. (Forbess, B., et. al., 2011). In this study, electro-oxidation will be evaluated as a cost-effective alternative to biological treatment.

The following reactions take place within the WAO process as indicated by equations Eq.1 to Eq. 8.

For Sulfide



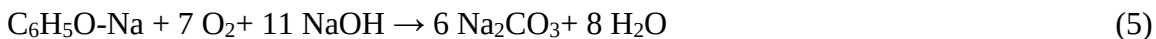
For Thiosulfate



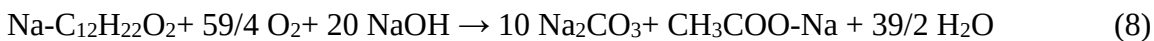
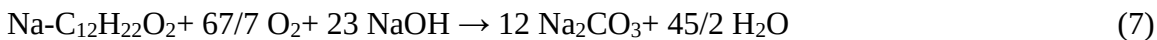
For Mercaptan



For Cresylic Acids



For Naphthenic Acids



The temperatures can range from 180°C to 315°C, and pressures can range from 2 MPa to 20 MPa depending on the contaminant load. There are three types of oxidation, namely low-temperature oxidation, middle-temperature oxidation, and high-temperature oxidation. Typically, spent caustic is oxidized at low temperatures in the 120°C-220°C range in the ethylene plant (Tungler, A., et. al., 2017). Figure 1 shows that the WAO process involves continuously supplying air (or oxygen) as well as the required operating pressure and temperature (energy source such as steam) in the reactor where the exothermic oxidation reaction occurs. The effluent will then travel through a separator, which will separate the effluent from the off-gases. The organic components are oxidized mainly to carbon dioxide and short-chain organic compounds which are biodegradable, and the sulfur is oxidized to sulfate, which is present in the basic solution as sodium sulfate.

Specific process elements can be assessed to guarantee effective and successful operations as follows (Maugans, C., et. al. 2009):

1. Spent caustic is heated up before entering the caustic tower.
2. In the caustic tower, antifouling additives or skim loops are utilized to control the formation of red oil.

3. Red oil precursors and entrained oils are removed by utilizing a gasoline wash.
4. The spent caustic is kept in a tank covered with a nitrogen blanket. The oil is skimmed frequently and the tank is drained from time to time to remove the sludge.
5. For all dilution and flush streams, low-mineral water is used.

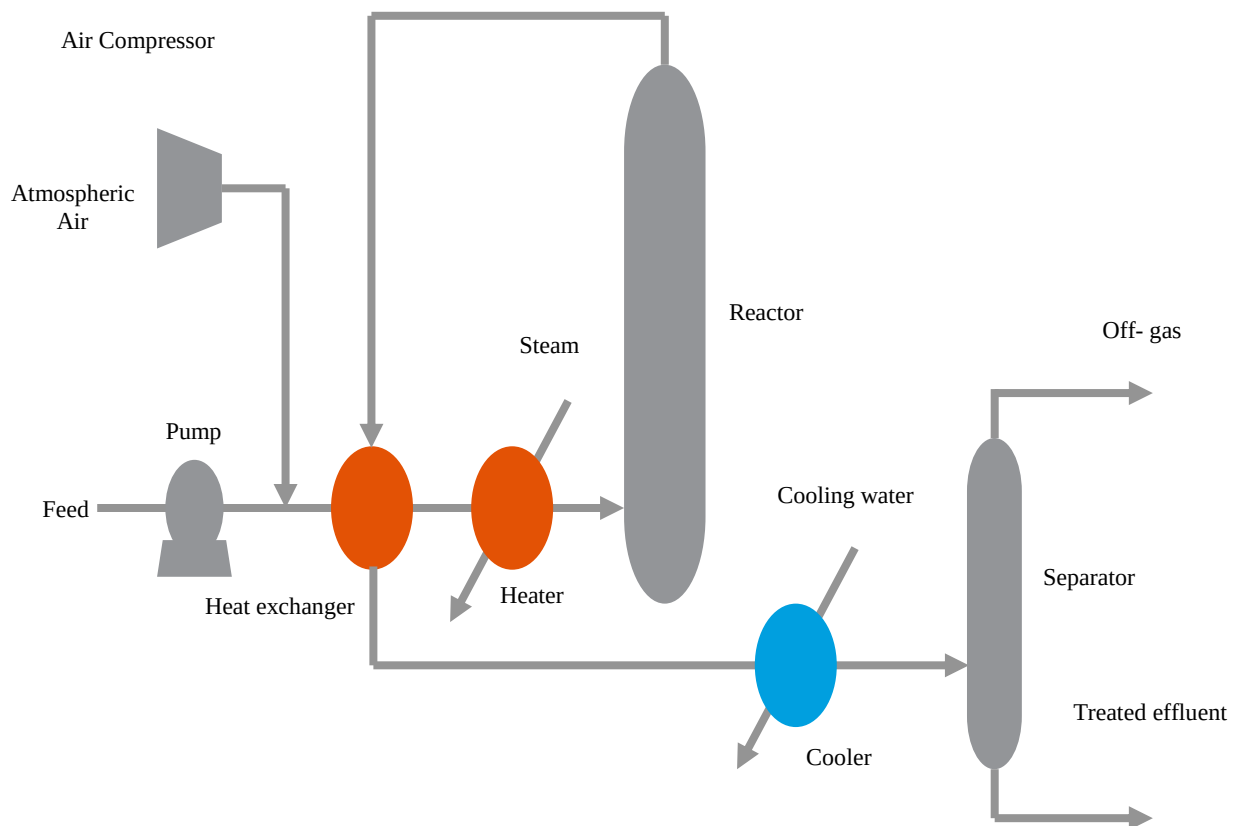


Figure 1 Typical flow diagram of WAO (Tungler, A., et al., 2015)

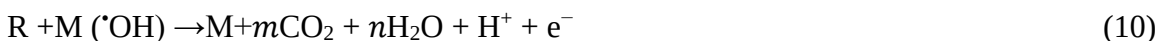
Although WAO is a great method for treating caustic, there are some disadvantages. The biggest one is the cost which is mostly influenced by the feed strength-related operation circumstances (Alnaizy, R., 2008). The strength of the feed requires more stringent operating conditions, which raises the plant's operating costs (Ellis, C., 1998).

The electrochemical oxidation method can be used for wastewater treatment to remove organic contaminants (Seyedin, S., et. al.2018), non-selectively and with a very high efficiency (Medel, A., et. al., 2015).

During the electrolysis process, organics with electron-rich moieties are directly oxidized on the electrode surface of the anode and/or indirectly by oxidants in the bulk that are *in situ* electro-generated by electrode reactions on the cathode and anode electrodes (Roudsari, M., et. al, 2017).

The most common cathode materials used include graphite, gas diffusion electrodes (GDEs), activated carbon fiber (ACF), carbon felt, and reticulated vitreous carbon (RVC) while, graphite, boron-doped diamond (BDD), Pt, and metal oxides are common choices for anodes (Brillas, E., et. al., 2009).

The electrochemical oxidation reaction of organic matter is carried out at the electrode/solution interface, and the anode materials directly affect the efficiency and selectivity of the organic mineralization process. Specifically, the oxidation of the organic compounds can take place directly or indirectly. Direct oxidation is the oxidation removal of organic matter by adsorption of organic pollutants on the anode surface in the form of electron transfer. According to the degree of oxidation, it can also be divided into electrochemical conversion and electrochemical combustion. Indirect oxidation is the oxidation removal of organic pollutants by producing active intermediates or high oxidizing metal oxides on the anode surface.



The production of hydroxyl radicals ($\cdot\text{OH}$) and metallic hydroxyl radicals ($\text{M}(\cdot\text{OH})$) by the water oxidation (Eq. 9), results in a total mineralization of contaminants to CO_2 and water (Eq. 10), with high current efficiencies.

Also, the Electro-Fenton (EF) method relies on the continual electrogeneration of H_2O_2 at an appropriate cathode in the presence of air supply or oxygen, as well as an iron catalyst added to form $\cdot\text{OH}$ in the bulk by Fenton reaction as per the following equation:



The following are the main benefits of the indirect electro-oxidation process:

- (i) The ability to adjust the pace of degradation kinetics to enable mechanistic investigations.
- (ii) The possibility of producing H_2O_2 on-site.
- (iii) Due to the ongoing regeneration of Fe^{2+} at the cathode, the degradation rate of organic pollutants will be higher which also reduces sludge creation.
- (iv) If the operation parameters are tuned, the feasibility of total mineralization at a reasonably low cost is possible (Brillas, E., et. al., 2009).

The development of anode materials that can economically and efficiently degrade organic wastewater has always been the research focus in the field of electrochemical oxidation.

There are two types of anodic materials investigated, active anodes (low generation of hydroxyl radicals) and inactive anodes (high generation of hydroxyl radicals). Since the hydroxyl radicals are the core reagent for the elimination of any recalcitrant to biodegradable organics to carbon dioxide and water, the utilization of inactive anodes is preferred (Comninellis, C., 1994).

There are many types of anodes; however, in this study, we focused on BDD (boron-doped diamond) electrodes. This is because of their distinctive attributes such as high resistance against corrosion, low adsorption of organic compounds, production of strong oxidizing species (O_3 , H_2O_2 , and $\cdot OH$), and high potential for oxygen production.

A typical flow diagram of an electrochemical oxidation process is shown in Figure 2 below. In this study, we tested the electrochemical oxidation as a post-treatment of spent caustic effluent treated with wet air oxidation (WAO). The experimental work was conducted with authentic (real) samples of spent caustic effluents that originated from an ethylene plant after their pretreatment with WAO. Fenton-based Advanced Electrochemical Oxidation Process (F-AEOP) was evaluated for its efficiency of constituents removal by measuring the Chemical Oxygen Demand (COD) of the treated wastewater.

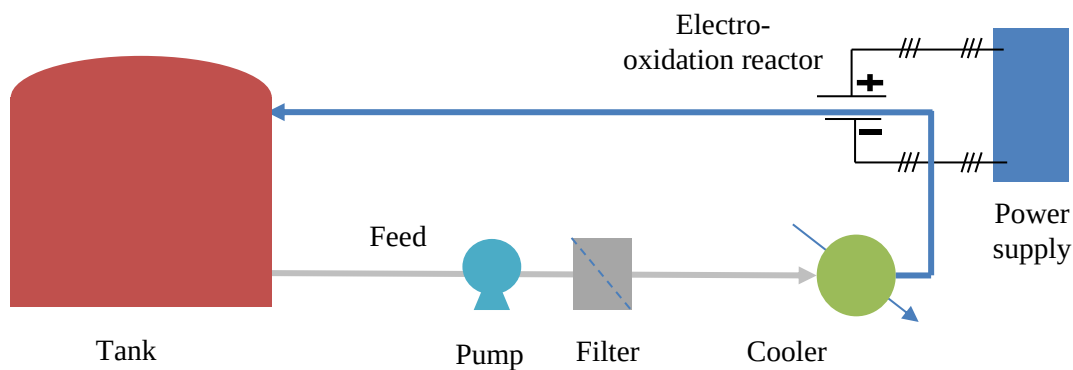


Figure 2: Typical flow diagram of electrooxidation process

1.2 Problem Description

Worldwide, spent caustic effluents generated from scrubbing towers to remove contaminants and Meroux processing of gasoline are a challenge for ethylene plants and petroleum refineries, respectively, due to their hazardous nature in terms of safety, environment, and health. Although there are global technologies available today in the market to treat spent caustic effluents, they still present a major challenge, especially with strict regulatory requirement and cost optimization. In addition, spent caustic effluent from the wet air oxidization treatment phase may not meet the strict allowable limits, and therefore, further enhancement of the treatment of spent caustic is needed.

1.3 Objective

The main objective of this study was to prove the technical feasibility of utilizing an electrochemical oxidization treatment on spent caustic effluent from ethylene plants as a second treatment following a wet air oxidization unit. The treatment was carried out by the Electrochemical Treatment Pilot System using a real sample of spent caustic from an olefin factory. To do that, sub-objectives were set as follows:

1. Collection and characterization of batches of wet air oxidized ethylene plant spent caustic effluents.
2. Evaluation of the efficiency of COD removal under various conditions of current, circulation rate, air flow rates, pH, and Fe content with air.
3. Identification of the optimum treatment conditions.

CHAPTER 2

LITERATURE REVIEW

With stricter environmental regulations and a strong desire to achieve a balance between economics and environmental preservation, the hunt for ways to decrease environmental effects and optimize materials continues. The solution search space is often too complex and extensive, resulting in sub-optimal methods to recycle spent caustic, mostly from the treatment of TOC, COD, and TDS parameters. Iterative heuristics, on the other hand, have proven to be extremely helpful in finding acceptable solutions to such issues in the past.

A subset of these searches refers to the above-mentioned treatment technologies, either alone or in comparison to one another, or combining two or more technologies, such as catalytic oxidation and biological treatment. Furthermore, electrochemical technology is one of the most promising methods for treating waste caustic. The caustic recovery was the main emphasis of the recovery phase. However, the study in this thesis focuses on combining wet air oxidization and electrochemical technologies to reduce organic components to an acceptable level for potential reuse of the respective treated wastewater.

(Alnaizy, R., 2008) in his work reported that sodium hydroxide (caustic) is still one of the most common reagents used to remove organic acids, mercaptan, and hydrogen sulfide from hydrocarbon streams in refineries and petrochemical facilities. Discarded caustics (5000 m³) comprising naphthenic and cresylic chemicals had accumulated at a local refinery. Before treatment, chemical oxygen demand (COD) concentrations shall be reduced to less than 1 g/L. Fenton's reagent procedure removed more than 95 per cent of the COD from spent caustic on a bench scale, and COD was less than 1 g/L. The procedure was carried out at atmospheric pressure and a temperature of less than 80°C. This resulted in a lower capital expenditure (CAPEX) than the WAO process, which operates at 28 bar and 200°C. The exporting cost of spent caustic to a company with full-service was \$1.21

per gallon in the United States, which was competitive with individual generation sites of short-term treatment.

(Delnavaz, M., et. al., 2021) investigated the remediation of organic pollutants in naphthenic spent caustic from petroleum refineries using an electrocoagulation (EC) procedure in which carbon nanotubes (CNTs) were used to modify graphite cathodes. The findings demonstrated the significance of CNTs on the cathode electrode by showing that in coated samples, hydrogen release not only takes place sooner but also uses less energy, resulting in a higher current intensity. In general, the procedure is completely acceptable as a commercial option for pretreating industrial wastewaters in the future, such as those from petroleum refinery plants, according to cost and energy consumption estimates.

(Elmi, R., et. al., 2021) reported that caustic soda is a material used in oil refineries, gas plants, and petrochemical plants to sweeten hydrocarbon products. During the process of eliminating contaminants such as mercaptan, sulfate, and nitrates, caustic soda-generated salts are increasingly created, which eventually leave the processing system via spent caustic discharge. Because of the presence of organic and poisonous chemicals, sulfate salts, mercaptan, and a high chemical oxygen demand (COD), the release of spent caustic into the environment is forbidden, highlighting the necessity to treat such effluents.

The goal of their research was to use a catalytic wet air oxidation process to treat spent caustic effluent from the refinery and then optimize the variables involved. The experiments were carried out in a batch reactor (500 ml). The box-Behnken design was used to optimize catalyst concentration, residence time, and stoichiometric airflow parameters. According to the findings, 123 mg/L catalyst concentration, 3 h residence time, and 4.1 l/h stoichiometric airflow were the best for this process, with the highest reduction

of spent caustic of around 42.2 per cent of COD. Design Expert 11 software was used to examine the outcomes of optimization experiments, and the results showed that the three variables stated above had the largest impact on minimizing COD of spent caustic. The COD elimination rate was unaffected by increasing the residence time. To predict spent caustic COD changes, a polynomial equation was presented based on the above variables. In this treatment approach, the accessible hazardous chemicals were reduced to less than 1 mg/L, in addition to a significant decrease in COD.

(Clark, M., 2017) did a comparison on on-site spent caustic treatment technologies considering performance and relative prices as highlighted below in Table 5.

Table 5: Comparison of on-site spent caustic treatment technologies (Clark, M., 2017)

Technology	Eliminates odor	Reduces COD	Destroys acid oils	Produces biodegradable effluent	Produces byproducts requiring disposal	Capital cost	Operating cost	Maintenance cost
Acid springing	No	Yes	No	No	Yes	Medium	Medium	Medium
Chemical advanced oxidation	Yes	Yes	Yes	Yes	Yes for some and /No for the other	Low	Very High	Medium
Low temp WAO	Mostly	Yes	No	Dependent upon load & WWTP*	No	Medium /High	Low	Low
Medium temp WAO	Yes	Yes	Yes	Yes	No	Medium /High	Low	Low
High temp WAO	Yes	Yes	Yes	Yes	No	High	Low	Low
ZEO*	Yes	Yes	Yes	Yes	No	Medium	Medium	Low

* WWTP= wastewater treatment plant. ZEO= Zimpro electrochemical oxidization, Zimpro brand name

Medel and his co-worker found that the larger part of spent caustic treatment studies were considered with only synthetic samples and there are only a few studies that have been conducted with real samples from refineries and ethylene plants. Even though there are large numbers of studies regarding Electrochemical Oxidization with synthetic samples,

only a few studies have been reported that utilized this technology to treat spent caustic samples from ethylene plants.

They assessed the electrochemical oxidation, utilizing boron-doped diamond with titanium (Ti/BDD) as substrate in spent caustic electrolysis from different refineries to check the ability to execute the electrochemical mineralization in an acidic medium of spent caustics. They reported a TOC removal of >80% as shown in Table 6. As a result, the hydrocarbons in spent caustic effluents were mineralized to CO₂ and water effectively.

Table 6: Electrochemical treatment of spent caustics mixture (Medel, A. et. al, 2015)

Sample	COD (mg/L)	COD removal (%)	TOC (mg/L)	TOC removal (%)
Without treatment	98,750	0	20,137.5	0
Chemical treatment	24,533	75.15	15,700	22.03
Electrochemical treatment	2,333	90.40	2,322	85.21

Davarnejad and his team (2017) treated spent caustic wastewater from an olefin plant using the electro-Fenton process in order to minimize COD and sulfide. Laboratory-scale tests were conducted. The effectiveness of the process is affected by a number of parameters, including pH, current density in mA/cm², reaction time, H₂O₂/Spent Caustic (ml/l), and H₂O₂/Fe²⁺ molar ratio (Table 7):

Table 7: Outcomes of electro-Fenton process on spent caustic (Davarnejad, R, et al., 2017)

Responses	pH	Reaction time (min)	Molar ratio (H ₂ O ₂ /Fe ²⁺)	Removal Observed %	Removal Predicted %
COD removal	2.96	70.67	3.47	81.20	82.93
Sulfide removal	2.87	65.52	3.21	99.9998	100

Clark and his co-workers (2017) treated refinery spent caustic with the aid of an electro-oxidation pilot system and they managed to reduce sulfides and mercaptans to undetectable levels. In a mixed spent caustic that is both organic and sulfidic, the sulfides can be entirely oxidized without totally oxidizing the COD. While COD levels can be decreased to extremely low levels of about 100 mg/L for organic-only materials and to values of about 20 mg/L for total organic carbon (TOC).

A study of different industrial spent caustic wastewater treatment technologies was conducted by Zahra, A., et. al, 2020. They compared various techniques for treating spent caustic waste in terms of their effectiveness and cost. They concentrated on the mechanisms and the significant variables that influence COD reduction (Table 8):

Table 8: Comparison between technologies for industrial spent caustic (Zahra, A., et. al, 2020).

Treatment	biological and membrane systems	WAO	Fenton reagent in an electrochemical cell
Efficiency	80–98 %	70–96 %	90–99 %
Remark	• Low energy consumption and easy design. • Costly due to membrane cleaning	• High efficiency • Due to the difficult working conditions, it is not advised.	• Electricity is the energy source that improves the effectiveness of processes

From specialized literature review, the major outcomes are as follows:

- Most of the research studies were on spent caustic generated from refineries with few studies on ethylene spent caustic.

- Limited treatment studies utilizing AEOP technology for the ethylene spent caustic by a pilot plant.
- Most studies were done using synthesized spent caustic rather than real samples.
- Based on the outcomes from the above research so far, the combined treatment effect of WAO and EO was not studied before.

CHAPTER 3

MATERIAL AND METHODS

3.1 Material

3.1.1 Spent Caustic

The spent caustic used was obtained from one of the ethylene plants in Jubail Industrial City, Saudi Arabia. A 40 L sample was obtained after spent caustic has been treated by Wet Air Oxidation for further treatment by an electrochemical pilot scale plant. The characteristics of WAO-treated spent caustic are represented in Table 9.

Table 9: Spent caustic characteristics used in the pilot plant

Parameters	Value	Unit
COD	670	mg/L
TOC	251	mg/L
pH	10	pH
Conductivity	36,000	us/cm
Ammonia	1.7	mg/L
Na	10042	mg/L
K	ND*	mg/L
Mg	31	mg/L
Ca	322	mg/L
F	ND*	mg/L
Cl	18	mg/L
NO ₂	ND*	mg/L
Br	ND*	mg/L
NO ₃	32	mg/L
PO ₄	ND*	mg/L
SO ₄	28191	mg/L
Li	ND*	mg/L
NH ₄	ND*	mg/L
Phenolphthalein alkalinity	0	mg of CaCO ₃ /L
Total alkalinity	527.36	mg of CaCO ₃ /L
Bicarbonate	527.36	mg of CaCO ₃ /L
Carbonate	0	mg of CaCO ₃ /L
Turbidity	9.66	NTU

* ND: not deducted

3.1.2 Chemicals and Solutions

Mercury (II) sulfate was purchased (CAS# 7783-35-9) from Alfa Aesar, ACS grade, 98%, powder. Sulfuric acid (H_2SO_4) (CAS# 7664-93-9) was purchased from VWR Chemicals BDH®, ACS grade, 98%, liquid. Potassium hydrogen phthalate (CAS# 877-24-7) was purchased from Bahadurgarh Haryana, 99.5 %, liquid. Iron (II) sulfate (CAS# 7782-63-0) was purchased from PanReac AppliChem, ACS grade, 99%, powder.

The following solutions were prepared:

Chloride can affect the results of COD readings at a level of more than 1000 mg/L. In order to make sure there is no chloride in the sample, a solution of 1g of Mercury sulfate in 100 ml of deionized water was prepared. Then, a few drops of the prepared solution were added to the spent caustic sample. The color was checked and the result was not cloudy which means a negligible amount of chloride.

To check the ions (anions and cations) of spent caustic, 1 ml of spent caustic solution was diluted to 100 ml with deionized water. Samples were prepared in duplicate for QC/QA and placed in the autosampler device in addition to other samples of deionized water only.

For calibration, a COD Stock of 850 mg Potassium hydrogen phthalate was prepared and diluted with 1000 ml of deionized water. COD stock solutions of 1000, 500, 250, 100, 50, 25, 10, and 0 mg/L were prepared and the recorded readings are shown in Table 10. The Calibration curve obtained for COD measurements is shown in Figure 3.

Table 10: Different concentrations of COD stock solution for calibration

S.N.	COD Stock Solution (mg/L)	Intensity
1	1000 mg/L	535
2	500 mg/L	257
3	250 mg/L	107
4	100 mg/L	23
5	50 mg/L	6
6	25 mg/L	0
7	10 mg/L	0
8	Blank	0

The above calibration is for the medium range, which is from 50 mg/L to 1000 mg/L. In case of a low range from 0 to 50 mg/L, 2 ml of Digestion solution and 4 ml of spent caustic sample were taken. For digestion, the first solution (solution 1) composed of 5.1 g $K_2Cr_2O_7$ (oxidized agent), 82.5g H_2SO_4 and was diluted with deionized water till 500 ml. Then, the second solution (solution 2) was prepared by mixing 400 ml of solution 1 and 600 ml of H_2SO_4 . The respective analytical method is discussed below

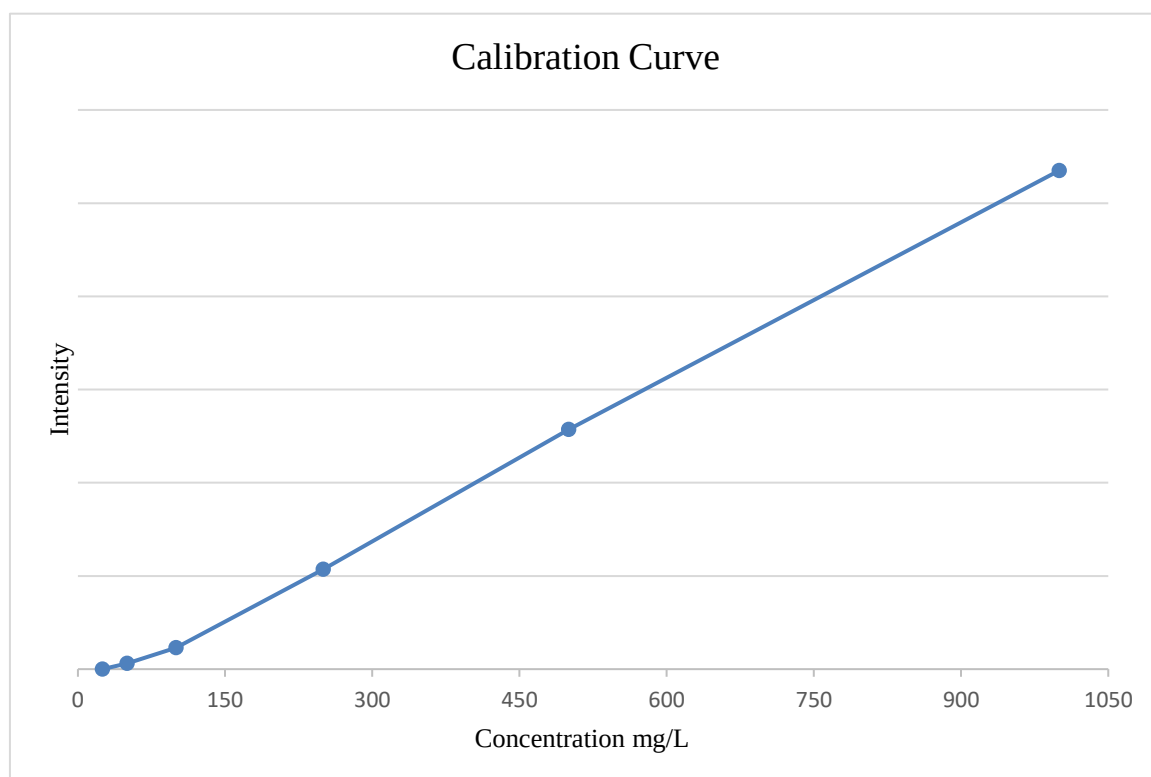


Figure 3: The COD calibration curve

3.1.3 Instrumentation

Conductivity and pH of the spent caustic sample were measured with the aid of a conductivity meter (PCD 650) (Figure 4). The concentration of anions and cations were measured by using dual column Metrohm 850 Professional IC (Metrohm, Switzerland) (Figure 5) equipped with 858 professional sample processor (Figure 6). COD was measured by utilizing HANNA, HI 83224 photometer (Figure 7) equipped with a COD reactor (HANNA 839800) (Figure 8).

TOC was measured by using Analytikjena multi N/C analyzer model 3100 equipped with auto-sampler and software. This device uses the combustion method to analyze TOC by using oxygen as inlet gas (Figure 9).

Finally, the other parameters were measured by using a PC-BOD Multi-parameter analyzer from MANTECH. These parameters include: alkalinity, turbidity, and conductivity. (Figure 10).



Figure 4: (PCD 650) Multiparameter



Figure 5: 850 professional IC

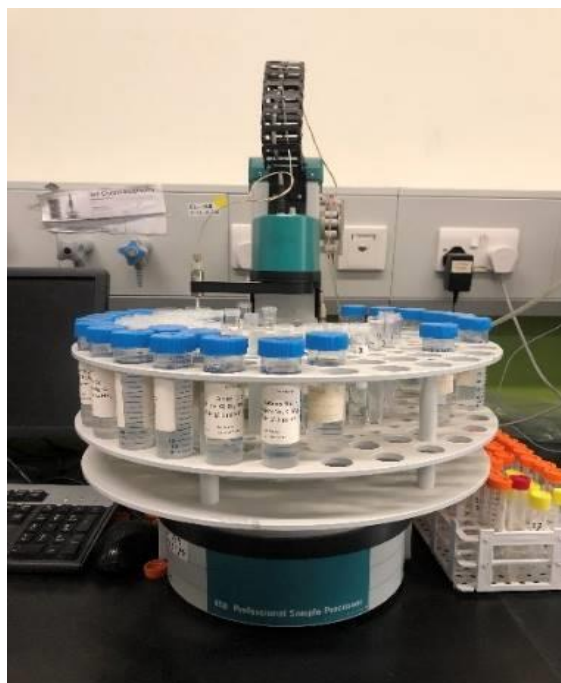


Figure 6: 858 professional sample processor 650)

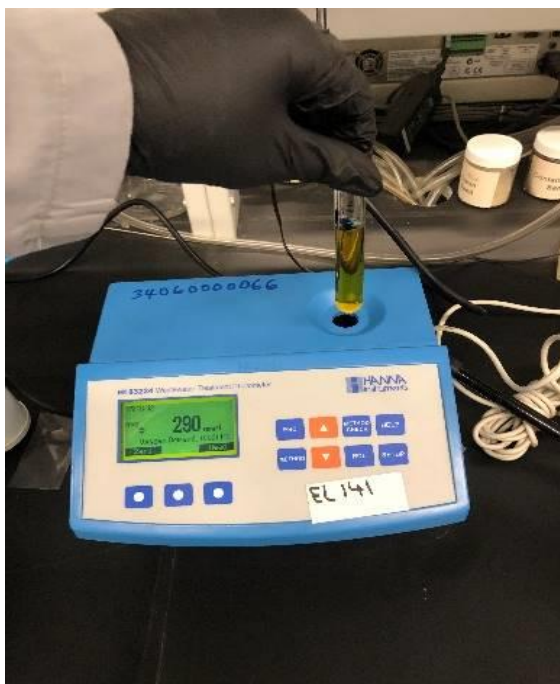


Figure 7: HANNA, HI 83224 photometer



Figure 8: HANNA 839800 COD Reactor



Figure 9: Analytikjena multi N/C analyzer model 3100



Figure 10: PC-BOD multiparameter analyzer

To conduct the treatment of spent caustic electrochemically, a laboratory-scale pilot Electrochemical Treatment System (ETS) was employed in this investigation. It was designed and constructed by the Center for Research and Technology - Hellas (CERTH). Figure 11 displays front and back images of the ETS unit.

The pilot unit consists of an Electro MP Cell from ElectroCell Co. in Denmark, a versatile plate-and-frame electrochemical cell that may be set up in divided or undivided cell mode. The cell has carbon-PTFE GDE as the cathode and a BDD electrode as the anode. Each one has a 0.01 m² effective area.



Figure 11: Electrochemical Treatment System (ETS) pilot plant

The tests were conducted with a power supply at constant current from (SM 3300-series, Netherlands) Delta Electronika with maximum 22 A and 70 V. At the ETS unit's input and output are sensors that monitor operational factors like conductivity, pH, temperature, pressure, and oxidation-reduction potential (ORP). A Supervisory Control and Data Acquisition (SCADA) system is equipped in the plant to control the pilot plant via a PLC unit. A Human Machine Interface (HMI) touch screen and other expansion electronic modules are also installed in the system. This system was used to collect and record the above operating parameters. Electrochemical cell (plate-and-frame), a compressed air system, a source of DC power, a horizontal multistage pump, an inlet tank, and a number of sensors measuring various operating variables are all included in the electrochemical treatment system pilot plant schematic diagram (Figure 12).

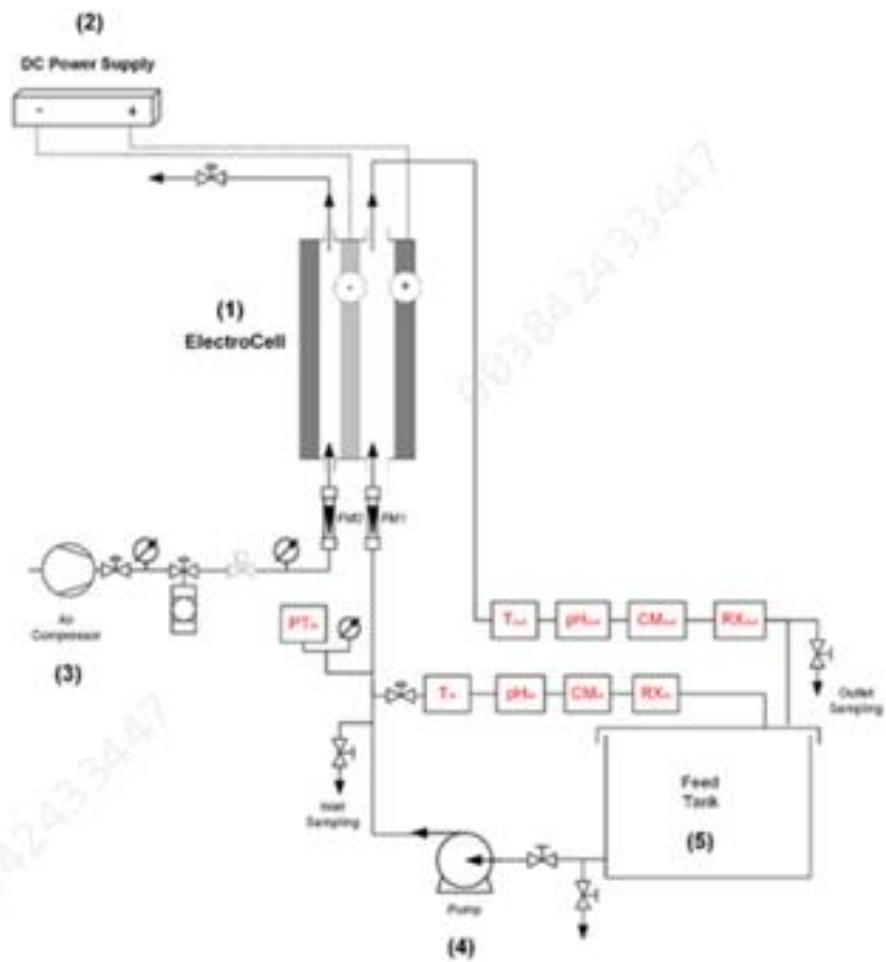


Figure 12: Schematic diagram of the electrochemical treatment system pilot plant

To supplying air to the cathode (GDE), an air compressor (maximum pressure of 8 bar and maximum airflow rate 180 NL/min) was used. To control and monitor the pressure and airflow, a regulator valve, a check valve, an airflow meter, a relief valve, and pressure gauge are connected to the air system. An inverter-controlled horizontal multistage pump with a maximum flow rate of 2 m³/h at a head of 50 m was used to circulate the spent caustic solution from the tank (volume 20 L) to the cell. A float-type flow meter was used to measure the liquid flow rate.



Figure 13: Setting process parameter screen

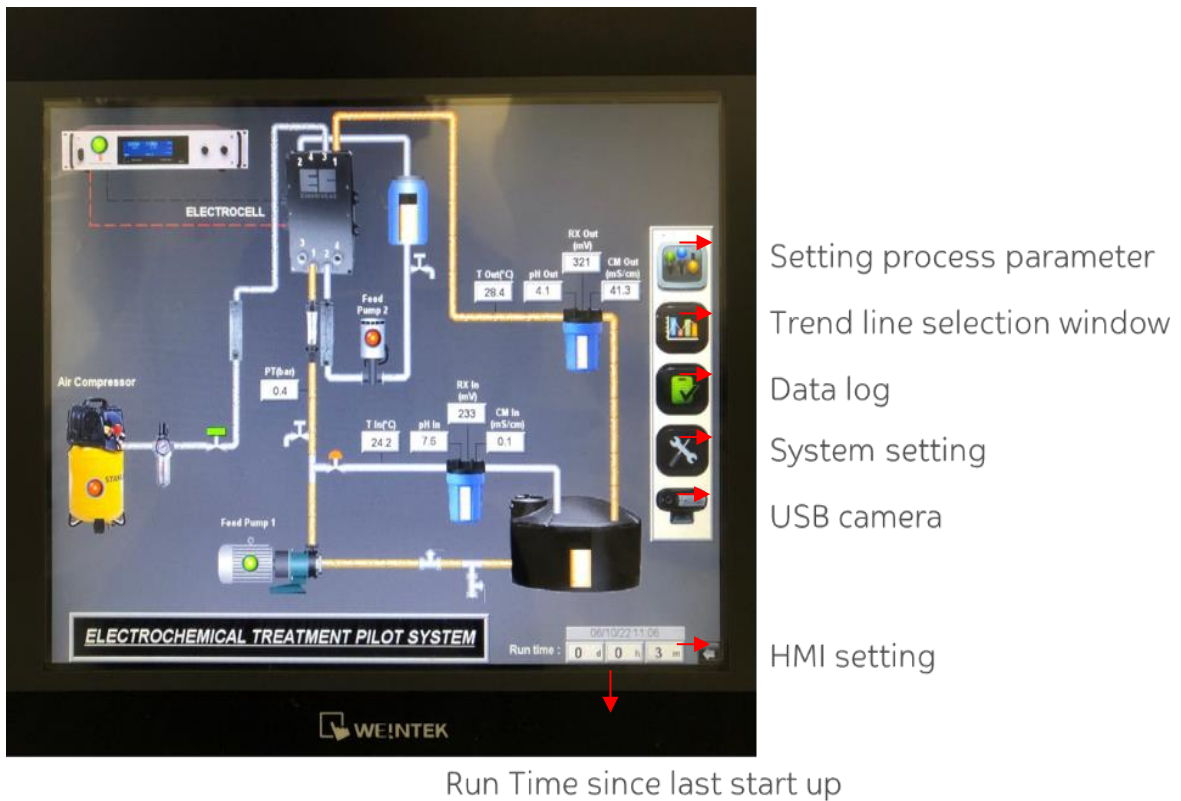


Figure 14: Main screen

3.1.4 Experimental procedure

Before starting the treatment of spent caustic in the ETS pilot plant, the system was first subjected to flushing by water. Then, drain the system totally to add the spent caustic sample. This step was repeated after each experiment to ensure that the results of the experiments are reliable.

To determine the practicality of the procedure for high COD spent caustic, all experiments were carried out in the range of 2.2 to 2.5 L of the spent caustic sample at a time that was fed to the feed tank. The samples were collected from WAO-treated effluent spent caustic from the ethylene plant and stored at room temperature in the lab under an exhaust hood.

For homogenization, initially, the feed solution was recirculated within the cell for a short period of time at a flow rate of 0.2 m³/h. The power source was switched on (with the appropriate current values), then the experiment started after the pH conductivity, and ORP readings in the cell's inlet and outlet became steady (time zero of the experiment). The physicochemical characteristics (pH, conductivity, COD) of all samples collected (time 0, 30, 60, 120, 180 min) were characterized after the termination of each experiment. These parameters will be used as the initial set point for the electrochemical treatment. In each batch experiment, the following variables were adjusted, current density (mA/cm²), pH, circulation rate of the wastewater sample (m³/hr), airflow rate (NL/min), and Fe dosage (mM), with the aim to identify the optimum operational conditions. The respective design of experiments is presented in detail in Table 11. The percentage removal of COD was determined in all samples collected to determine the kinetic analysis of the organic

removal, during the batch operation of the ETS. In addition, quality control techniques and statistical analysis of the results were carried out.

3.1.5 Analytical methods

In order to evaluate the samples, COD digestion vials were used. These vials which hold 0.35 g of Mercury Sulfate were added to participated chloride if any, 5 mL of digestion solution (see material and apparatus section for solution 2), and 0.2 mL of treated spent caustic. Then, placed the digestion vials in a reactor heater (HANNA 839800) as shown in Figure 8 to heat the sample at 150 °C for 2 hours. The COD was then determined after allowing digestion vials to naturally cool to room temperature. The vials are then placed in a wastewater treatment photometer (HANNA, HI 83224) as shown in Figure 7, which is used to compare the results to a COD digestion vial blank generated with COD-free water.

3.1.6 Design of experiments

The objective of the experiments was to treat undiluted spent caustic (WAO-treated effluent) collected from an ethylene production plant to achieve a maximum COD reduction under (near) optimum range of operating conditions. The operating variables investigated for their effect on COD removal were:

- 1 pH
- 2 Applied electric current.
- 3 Effluent circulating rate.
- 4 Fe (II) dosage.
- 5 Rate of air supply.

The design of experiments was based on a sequential approach, investigating the effect of a single parameter for the selection of its optimum value, which was next adopted for the subsequent series of experiments (Table 11).

Table 11: Design of experiments

Sr.No.	Description	pH	Current density (mA/cm ²)	Circulation rate (m ³ /hr)	Fe Dosage (mM)	Air rate (NL/min)	Time (min)
1	Blank	initial pH	0	0.2	0	0	0-180
2	Effect of pH	4	150	0.2	0	0	0-180
3	Effect of pH	7	150	0.2	0	0	0-180
4	Effect of pH	10	150	0.2	0	0	0-180
5	Effect of current	Optimum pH	100	0.2	0	0	0-180
6	Effect of current	Optimum pH	150	0.2	0	0	0-180
7	Effect of current	Optimum pH	200	0.2	0	0	0-180
8	Effect of circulation rate	Optimum pH	Optimum current	0.1	0	0	0-180
9	Effect of circulation rate	Optimum pH	Optimum current	0.2	0	0	0-180

10	Effect of circulation rate	Optimum pH	Optimum current	0.3	0	0	0-180
11	Effect of iron dosage	Optimum pH	Optimum current	Optimum circ. rate	5	0	0-180
12	Effect of iron dosage	Optimum pH	Optimum current	Optimum circ. rate	10	0	0-180
13	Effect of iron dosage	Optimum pH	Optimum current	Optimum circ. rate	15	0	0-180
14	Effect of air rate	Optimum pH	Optimum current	Optimum circ. rate	Optimum Fe	1	0-180
15	Effect of air rate	Optimum pH	Optimum current	Optimum circ. rate	Optimum Fe	2	0-180
16	Effect of air rate	Optimum pH	Optimum current	Optimum circ. rate	Optimum Fe	3	0-180
17	Effect of other types of anode	Optimum pH	Optimum current	Optimum circ. rate	0	0	0-180
18	Effect of other types of anode	Optimum pH	Optimum current	Optimum circ. rate	Optimum Fe	0	0-180
19	Effect of other types of anode	Optimum pH	Optimum current	Optimum circ. rate	Optimum Fe	Optimum Air	0-180
20	Effect of time	Optimum pH	Optimum current	Optimum circ. rate	Optimum Fe	Optimum Air	0-240

After the completion of 16 pilot experiments, the optimum values of pH, applied electric current, circulation rate, Fe dosage, and air supply rate could be identified. Next, three additional experiments were conducted under the optimum conditions using a lesser active BDD anode (DSA, Dimensionally Stable Anode). The first one was conducted without Fe (II) dosage to explore the effect of the *in situ* generated H₂O₂ (by the cathode) on COD removal efficiency (in the absence of strong BDD([•]OH) formed during the BDD anodic oxidation). The second was conducted with the addition of Fe (II) and the third was conducted with the addition of Fe (II) and air supply with the aim to explore the effect of possible electro-Fenton reactions in the system (*in situ* generation of hydroxyl radicals by the reaction between the H₂O₂ formed in the cathode with the dissolved Fe²⁺). Finally, the optimum parameters (Exp.# 2) were repeated for 4 hours in order to check the COD decay at a larger treatment time.

According to the following equation, the efficiency of the pilot ETS system was evaluated in terms of COD removal:

$$\%R = ((C_i - C_t) / C_i) \times 100\% \quad (12)$$

where C_i and C_t are the initial and final concentrations of COD at electrolysis time t, and %R is the proportion of COD (% COD) eliminated.

The average current efficiency (%CE) for each treated solution at a particular time t (s) was computed using the COD data (Brillas, E., et. al., 2009):

$$\%CE = ((\Delta COD)_t F V_s) / 8 I t \times 100 \quad (13)$$

where ΔCOD is the corresponding decays in COD (mg O₂/L) at time t (s), F is the Faraday constant (96487 C/mol), V_s is the solution volume (L), the constant 8 is the oxygen equivalent mass (g eq⁻¹), and I is the applied current (A).

The following equation was used to calculate the energy consumption (EC) per unit COD mass at a specific electrolysis time, t (h) (Brillas, E., et. al., 2009):

$$EC = (E_{cell} It) / ((\Delta COD)_t V_s) \quad (14)$$

where E_{cell} is the average cell voltage (V), t is the electrolysis time (h), and $(\Delta COD)_t$ is the solution COD decay (mg O₂/L).

CHAPTER 4

RESULTS AND DISCUSSIONS

Table A1 in Appendix A summarizes the key experimental parameters and findings from a collection of 18 pilot investigations. In the beginning, the possible losses of COD were monitored (Exp. # 1) because of adsorption or volatilization during the recirculation of the wastewater in the pilot system, in the absence of an electric field. The losses after 3 hours of feed water recirculation were negligible since the COD removal percentage was approx. 1.5% (Figure 15).

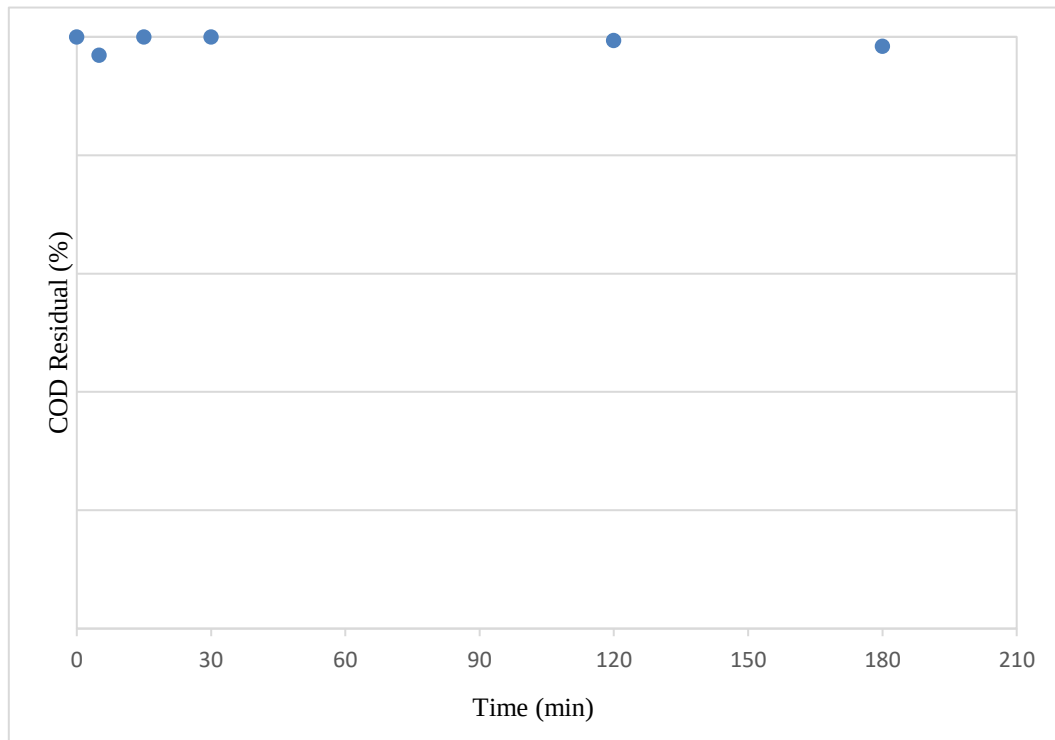


Figure 15: Removal of COD of spent caustic due to circulation only (blank run)

CODi = 569 mg/L, current density = 0 mA/cm², pH = 9.5, circulation rate = 0.2 m³/h

Next, the impact of applied electric current on process efficiency was examined and the optimal value (150 mA/cm^2) was chosen, with the exception of two experiments Exp. # 5 and 6 for the ensuing series of experiments to determine the impact of the following process performance parameters: pH, circulating rate, Fe (II) dosage, and air rate. Except for Exp. # 7 and 8, for which different flow rates were used, all experiments were conducted at a solution flow rate of $0.2 \text{ m}^3/\text{h}$.

4.1 Effect of pH

At the beginning, the role of the pH on the removal of COD was investigated by carrying out three studies using acidic (pH 4), neutral (pH 7), and alkaline (pH 10) spent caustic solutions. pH was adjusted by 98% sulfuric acid.

As shown in Figure 16, the best % COD removal was at pH 4 (approx. 91%) compared to pH 7 and 10. The results show that the BDD oxidation of the spent caustic solution can take place in a wide pH range since the efficiency of the process was not dramatically affected by the pH. The better efficiency at acidic pH is probably attributed to the speciation of the dissolved organics (which may differ with the pH) and the formation of sulfate radicals (due to the addition of the sulfuric acid) which can synergistically oxidize the organics. Considering the larger COD removal and the higher current efficiency, pH 4 was selected as the optimum for the conduction of the next series of experiments.

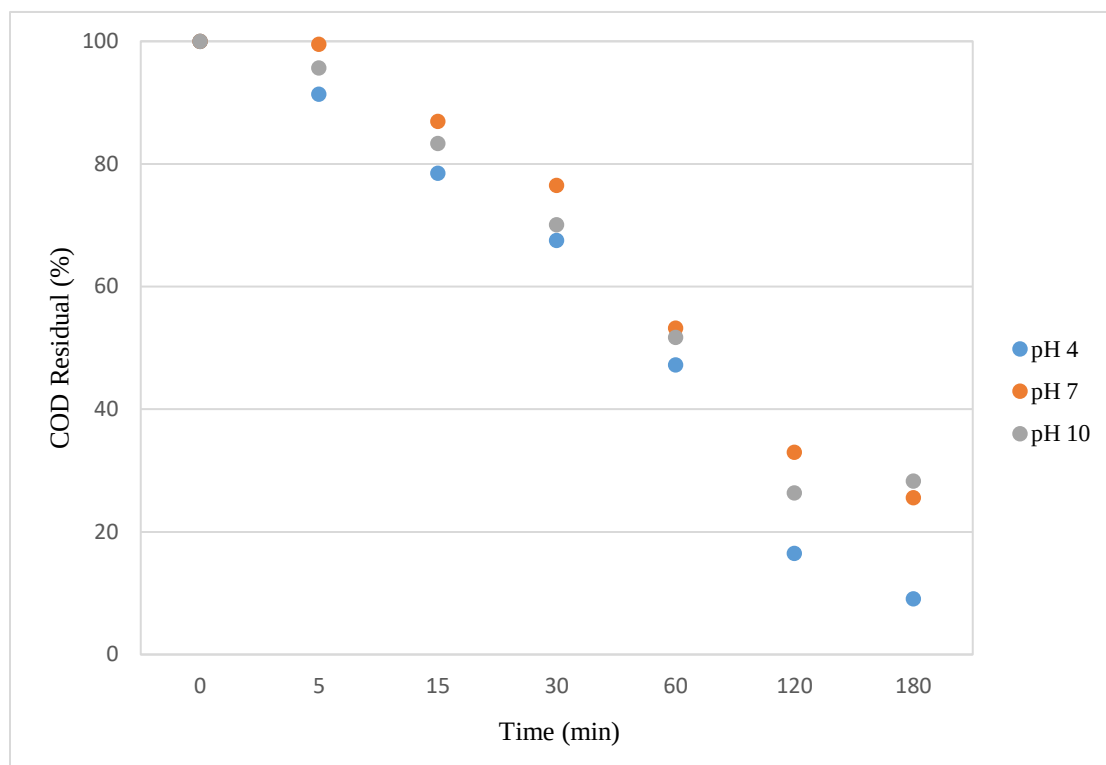


Figure 16: Effect of pH on COD removal

CODi = 650 – 750 mg/L, current density = 150 mA/cm², circulation rate 0.2 m³/hr, Fe²⁺ = 0 mM and air flowrate = 0 NL/min)

4.2 Effect of applied electric current

The effect of the applied electric current on COD removal was studied at pH 4 according to the experimental conditions summarized in Table 11.

The results obtained at 15 A and 20 A were very similar showing that the system has already reached its maximal oxidation power at around 15 A. This pattern is consistent with the literature since parasitic reactions like oxygen evolution can cause current efficiency to decrease at high applied currents (Brillas, E., et. al., 2009).

Figure 17 indicates that, approx. 91% of the organic compounds were oxidized in the cell after 3 hours due to the high oxidation power of the heterogeneously generated hydroxyl radicals (BDD($\cdot$ OH)), (Eq. 15).



It is noted that COD removal presents a linear decrease up to 120 min of electrolysis, after which oxidation reaches a plateau. (Brillas, E., et. al., 2009)

The (15 A or 150 mA/cm²) current value was adjusted for the ensuing set of studies in light of the above findings and the need for lowering the running costs.

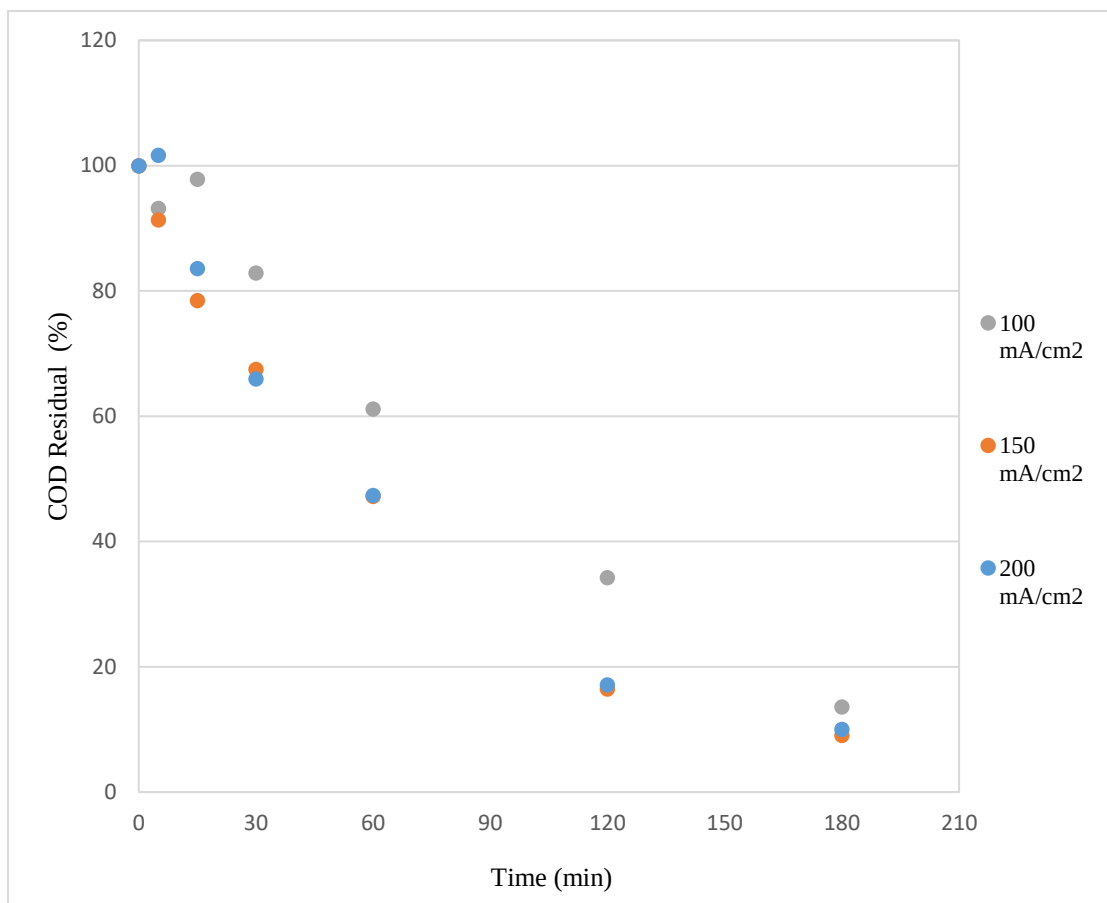


Figure 17: Effect of applied electric current on COD removal

COD_i = 650 – 750 mg/L, pH = 4, circulation rate 0.2 m³/hr, Fe²⁺ = 0 mM and air flowrate = 0 NL/min)

4.3 Effect of the circulating rate

In these experiments, the effect of spent caustic effluent circulation rate was studied to see its effect on COD removal. As shown above, the best COD percentage removal was obtained in Exp. # 2 (pH 4, current density (150 mA/cm^2) and circulation rate $0.2 \text{ m}^3/\text{h}$). Therefore, two additional experiments (Exp. #7 and 8) were performed to investigate the effect of circulation rate on process efficiency ($0.1 \text{ m}^3/\text{h}$ and $0.3 \text{ m}^3/\text{h}$) (Figure 18).

For batch processes, such as the one carried out in this study, a change in the recirculation flow rate may have an impact on the residence time within the cell and may accelerate the mass transit of organic molecules to the anode, facilitating their direct oxidation. In fact, the COD removal was not enhanced when the flow rate was adjusted to lower ($0.1 \text{ m}^3/\text{h}$) or higher ($0.3 \text{ m}^3/\text{h}$) values. At a flow rate of $0.2 \text{ m}^3/\text{h}$, it was still at a high enough level to quickly homogenize the treated solutions and improve reactant mass transfer to the electrodes, which produces the highest rates of electrode reactions.

During the first five minutes of treatment, the relative CE% values (Table A2) varied greatly, with the final values being equal to 16%, 46%, and 2% for recirculation flow rates of 0.1 , 0.2 , and $0.3 \text{ m}^3/\text{h}$, respectively.

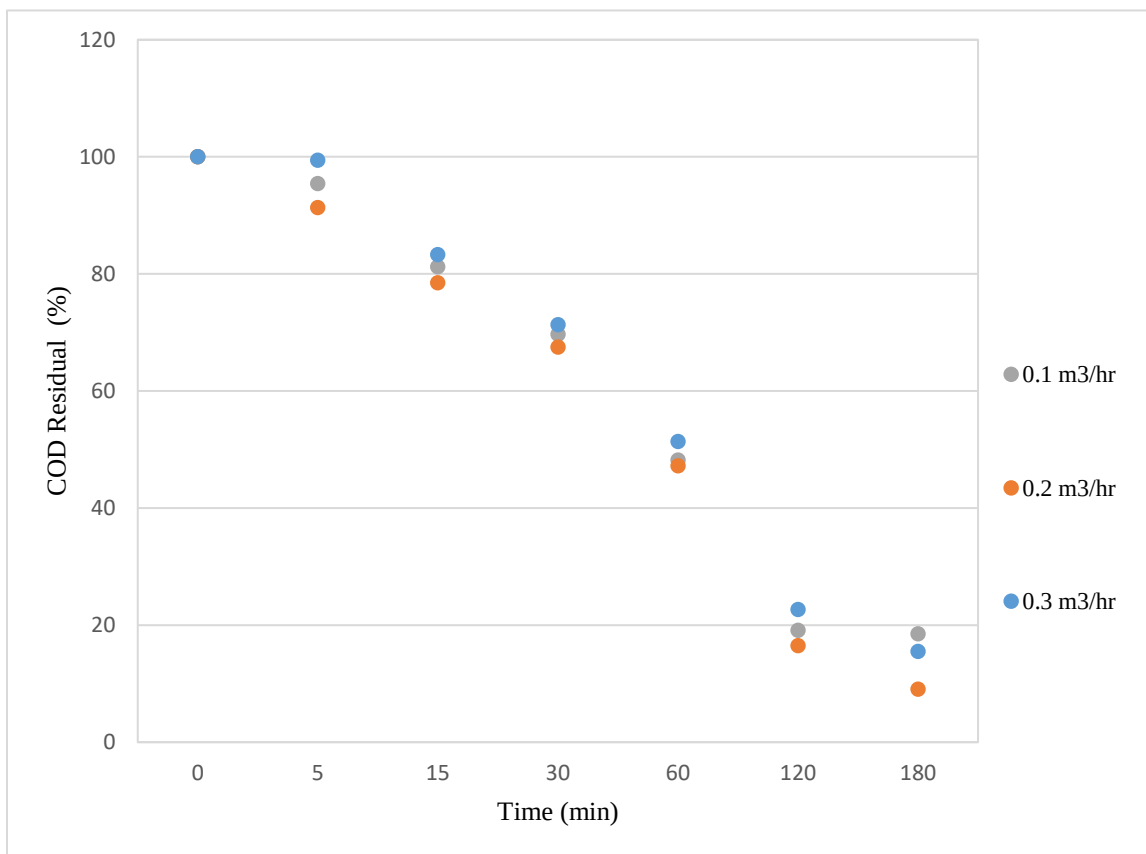


Figure 18: Effect of circulating rate on COD removal

COD_i = 550 – 750 mg/L, pH = 4, current density = 150 mA/cm², Fe²⁺ = 0 mM and air flowrate = 0 NL/min)

4.4 Effect of Fe (II) dosage

Fenton's reaction can yield $\cdot\text{OH}$ at the bulk level from the reaction of the in situ generated H_2O_2 at the GDE cathode (when fed with air) and the presence of an iron catalyst in the treated water (Eq. 16). According to Salmerón et al. (2019), the homogenous $\cdot\text{OH}$ generated by this process, known as electro-Fenton (EF), works together with BDD ($\cdot\text{OH}$) to increase the oxidation potential of the system.

To start the Fenton reaction, ferrous iron concentration is important. Hydrogen peroxide's hydroxyl radicals are produced with the addition of ferrous sulfate.



According to Table 11 and from the above experimental results, a set of three experiments were performed at pH 4, electric current density 150 mA/cm^2 , and circulation rate $0.2 \text{ m}^3/\text{h}$, with the addition of ferrous sulfate as follows: 0.695 g (0.5 mM), 1.39 g (1 mM) and 2.085 g (1.5 mM), in the absence of air supply (the effect of air is investigated in the next section).

From Figure 19, it is apparent that the removal of COD was not improved by the addition of ferrous ions to spent caustic with pH set to 4 (Fe^{2+} highest availability in the reaction medium at low pH). On the other hand, for all three iron doses used, the reaction rate of COD elimination was decreased to a similar extent.

This may occur as a result of the ferrous ion's scavenging effect due to parasitic reactions, according to the equation below.



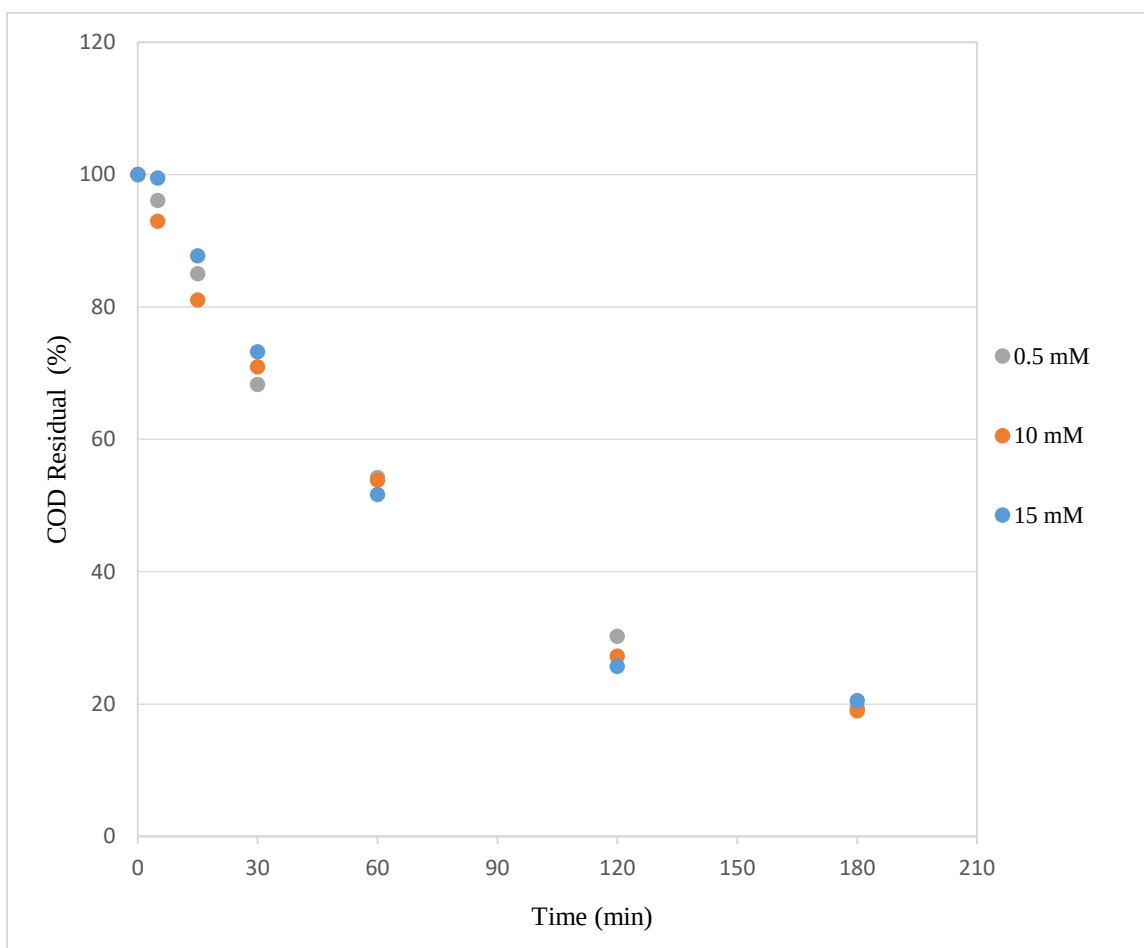


Figure 19: Effect of Fe (II) dosage on COD removal

COD_i = 550 – 650 mg/L, pH = 4, current density = 150 mA/cm², circulation rate 0.2 m³/hr and air flowrate = 0 NL/min)

4.5 Effect of air rate

The last parameter studied was the airflow rate as per the experiment layout. In these experiments, pH, applied electric current, and circulation rate were fixed at 4, 15 A (or 150 mA/cm²), and 0.2 m³/h, respectively. Fe (II) dosage was also fixed with the minimum at 0.5 mM as an outcome of the previous experiment to maintain the lower cost. Airflow rate varied at 1, 2, and 3 (NL/min) respectively, by feeding compressed air into the GDE electrode's air chamber.

The system's oxidation power can be significantly improved by an excessive air supply due to the increased electrogeneration of hydrogen peroxide (H₂O₂), (Salmerón et al. 2019).

From Figure 20, the COD decay was similar without and with air feeding. This result demonstrates that the excess air may not always enhance the combined EO/EF treatment's ability to treat spent caustic. This is may be due to the excess oxygen in the bulk that prevents the direct anodic oxidation of the intermediate organic compounds.

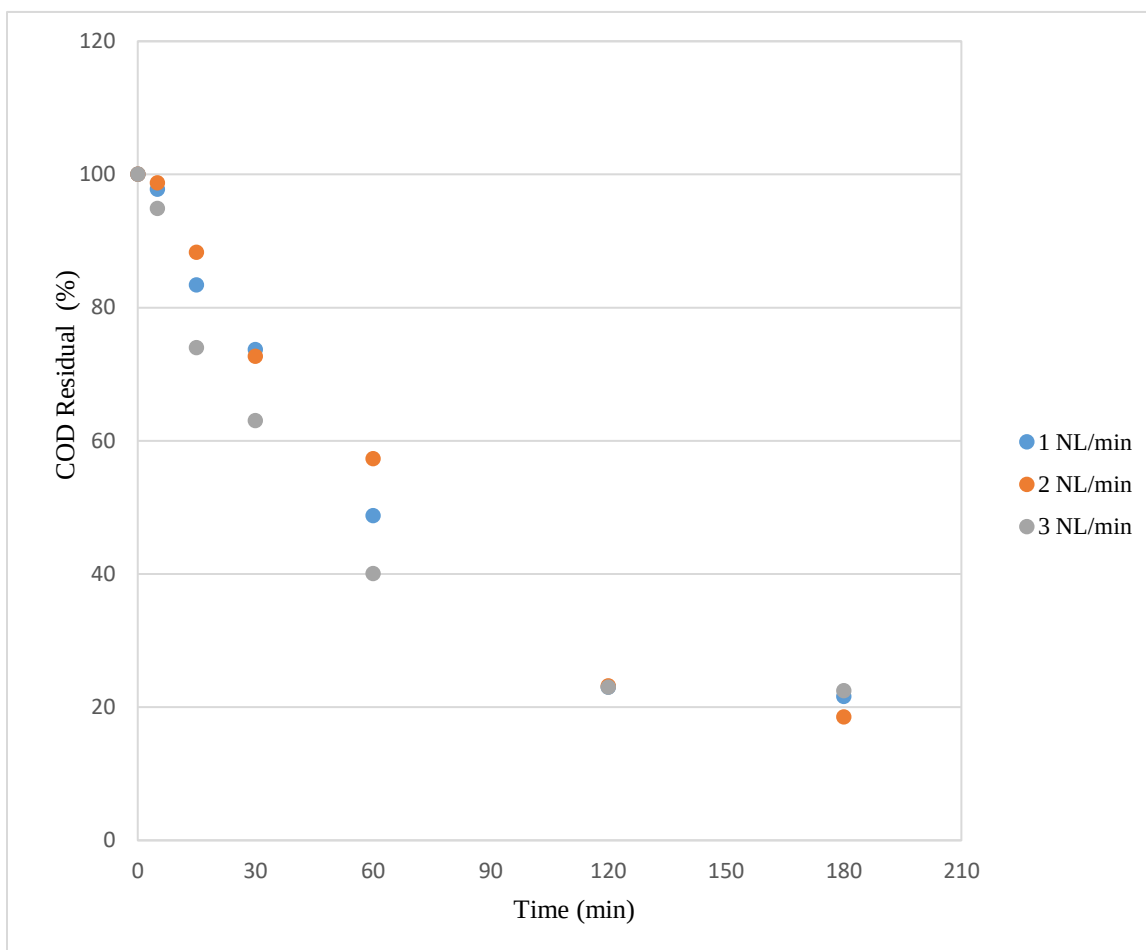


Figure 20: Effect of air rate on COD removal
COD_i = 600 – 700 mg/L, pH = 4, current density = 150 mA/cm², circulation rate 0.2 m³/hr and Fe²⁺ = 0.5 mM,

4.6 COD Removal with DSA Anode

Three (3) experiments were conducted in addition to the above experiments with a less active anode (Dimensionally Stable Anode, DSA). The first one was conducted without Fe dosage to explore the effect of the *in situ* generated H_2O_2 (by the cathode), and the lack of BDD ($\cdot\text{OH}$) on COD removal (the contribution of BDD anodic oxidation). The second was conducted with Fe (II) dosage and the third with Fe (II) dosage and air to explore the effect of the *in situ* generated hydroxyl radical due to electro-Fenton reaction (reaction between the H_2O_2 formed in the cathode with the dissolved Fe^{2+}) as shown in Figure 21.

According to Figure 21, the process took more than 15 minutes to have a positive COD removal. Also, it was observed that oxidization was mainly attributed to the direct anodic oxidation on the BDD electrode, since the indirect oxidation by the H_2O_2 or the hydroxyl radicals generated *in situ* by the porous GDE cathode (due to electro-Fenton reaction) was rather less important.

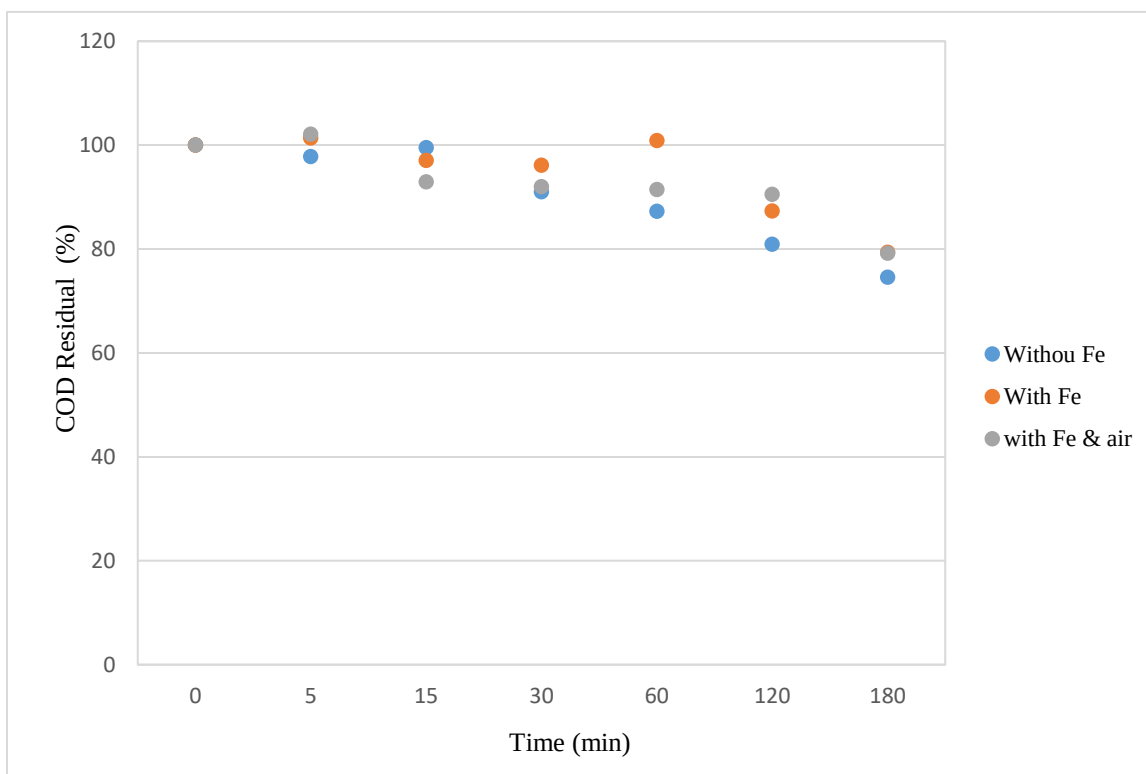


Figure 21: Effect of DSA anode on COD removal

CODi = 600 – 800 mg/L, pH = 4, current density = 150 mA/cm², circulation rate 0.2 m³/hr, Fe²⁺ = 0 – 0.5 mM, air flowrate = 0 – 1 NL/min)

4.7 Effect of time for the optimum parameters

The last experiment Exp. # 18 was conducted to evaluate the effect of the treatment time on process efficiency. The optimum parameters (Exp.# 2) was repeated for a longer electrolysis time (4 hours) and the results are shown in Figure 22:

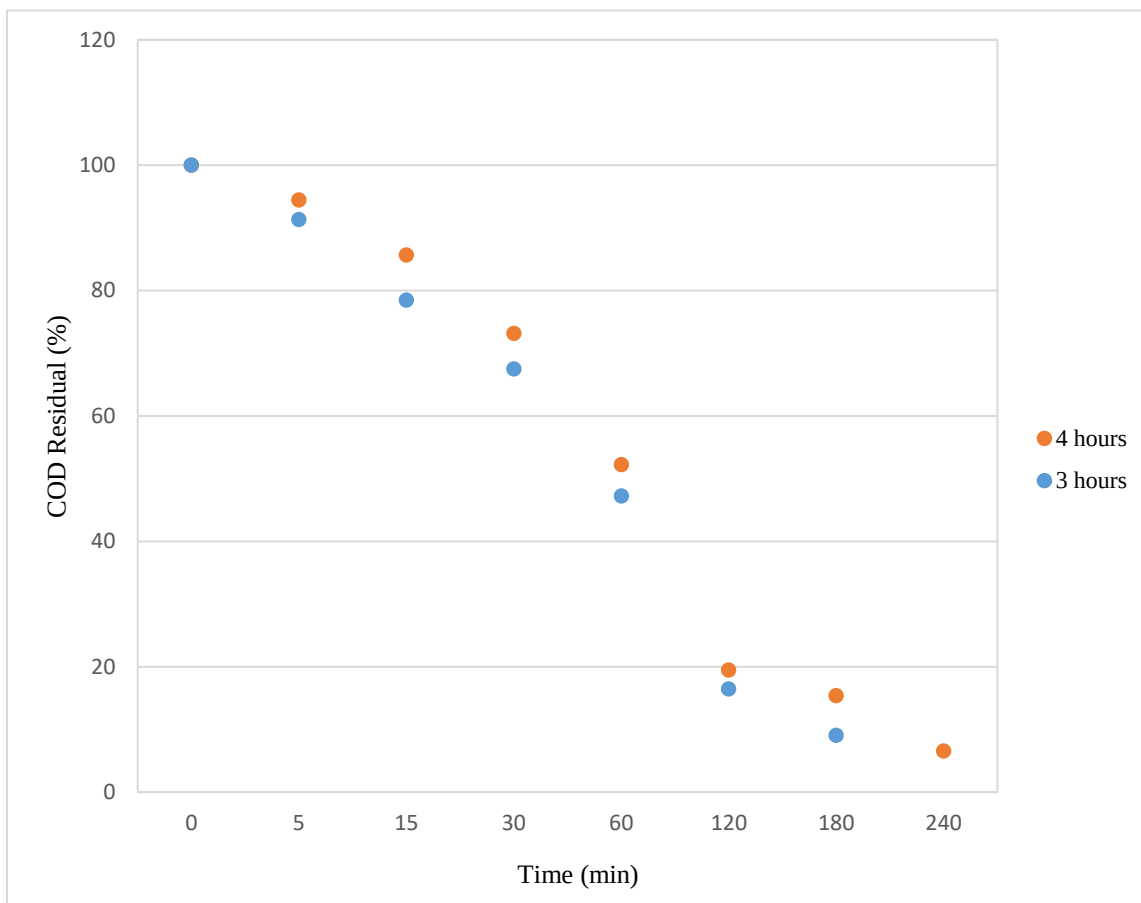


Figure 22: Effect of time on COD removal

CODi = 750 - 800 mg/L, pH = 4, current density = 150 mA/cm², circulation rate 0.2 m³/hr, Fe²⁺ = 0 mM and air flowrate = 0 NL/min)

4.8 Kinetic Analysis and Current Efficiency (%)

To determine the reaction order of the involved reaction from Exp. # 18 (which was the optimum one), the kinetics of this reaction has also been investigated. These data have made it possible to investigate the kinetic behavior of treated contaminants and suggest potential pathways for their degradation. Therefore, kinetic analysis for optimum experimental conditions (pH = 4, current density = 150 mA/cm², circulation flow rate = 0.2 m³/h, Fe (II) dosage = 0 mM and air flow rate = 0 NL/min. (Exp. #18, Table A1)), has been conducted according to the following equations:

Zero order

$$C_a = C_0 - kt \quad (18)$$

First order

$$\ln C_0 / C_a = kt \quad (19)$$

Second order

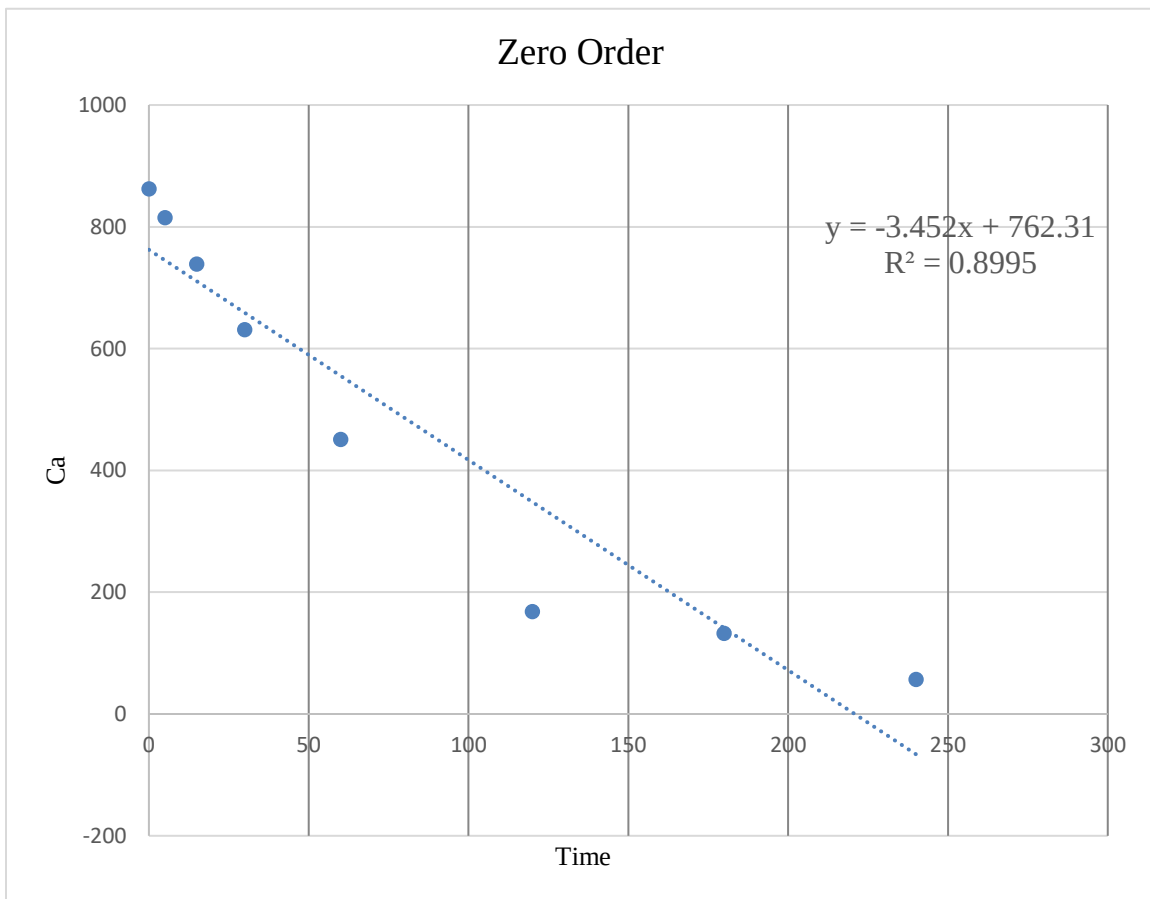
$$1/C_a - 1/C_0 = kt \quad (20)$$

where C_0 and C_a are the initial and final concentrations of COD at time “t”, respectively. k is the order rate constant.

Table 12 provides the results of the kinetics data for the removal of COD and Figures 23, 24, and 25 indicate the fitting of experimental data for reaction orders.

Table 12: Kinetics parameters of COD removal

Zero order		First order		Second order	
t	Ca	t	ln (Ca)	t	1/Ca
0	862	0	6.8	0	0.001159
5	815	5	6.7	5	0.001227
15	739	15	6.6	15	0.001354
30	631	30	6.4	30	0.001585
60	451	60	6.1	60	0.002219
120	168	120	5.1	120	0.005955
180	133	180	4.9	180	0.007543
240	57	240	4.0	240	0.017672

**Figure 23: Zero order**

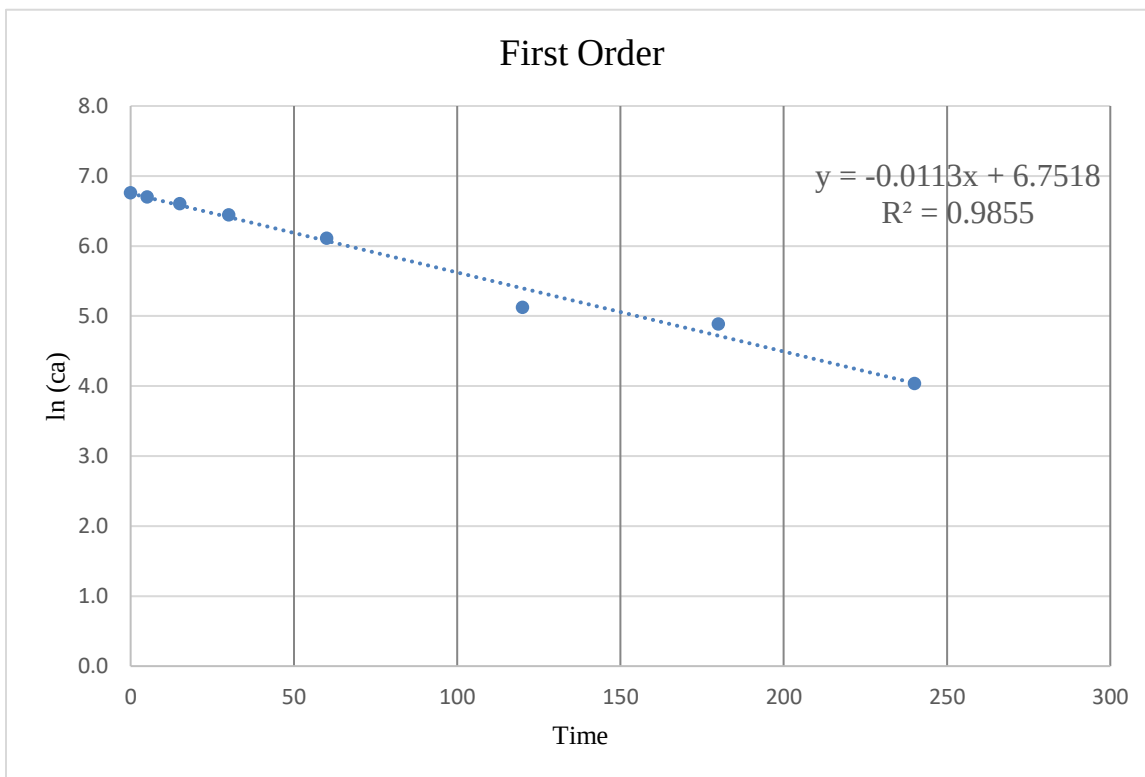


Figure 24: First order

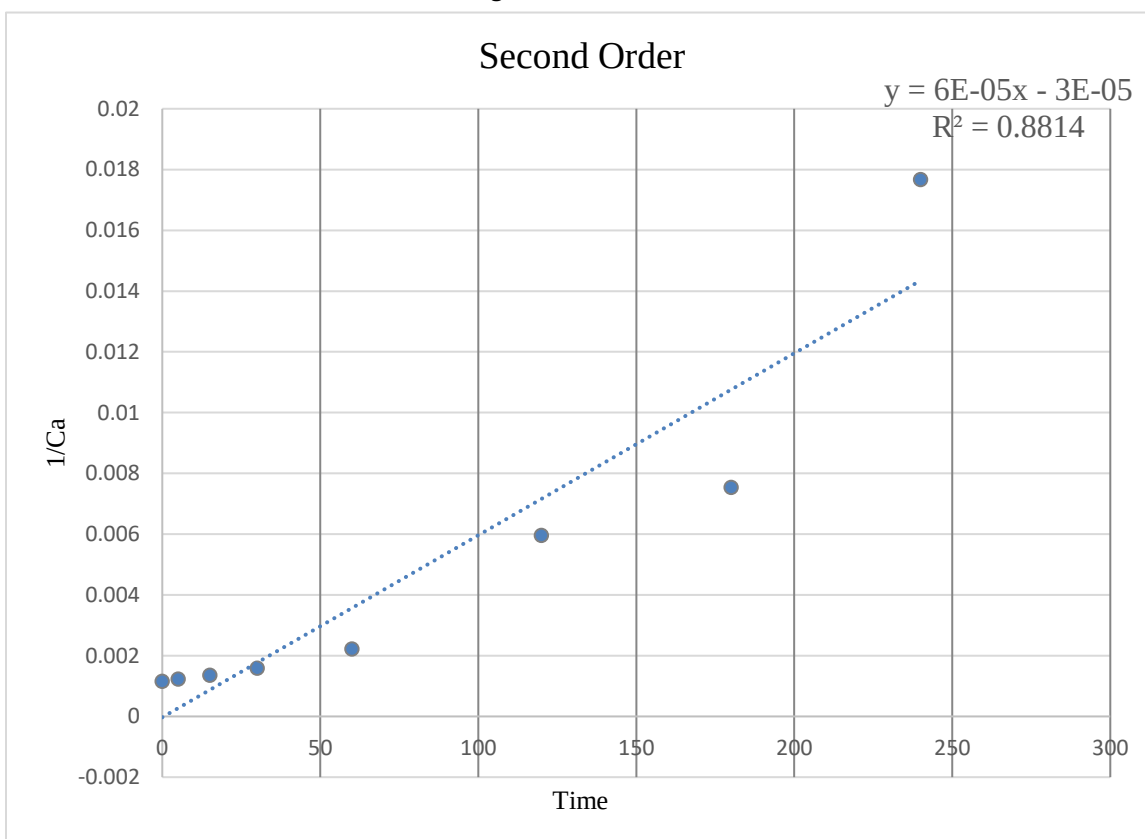


Figure 25: Second order

From the above, the reaction behaves as a first-order reaction since R^2 (0.9855) is the highest and close to 1.

For current efficiency, the beginning of the reaction was determined to have the fastest COD decay kinetics. In contrast, it took 4 hours of treatment to reach the maximum removal with a 93% COD elimination rate.

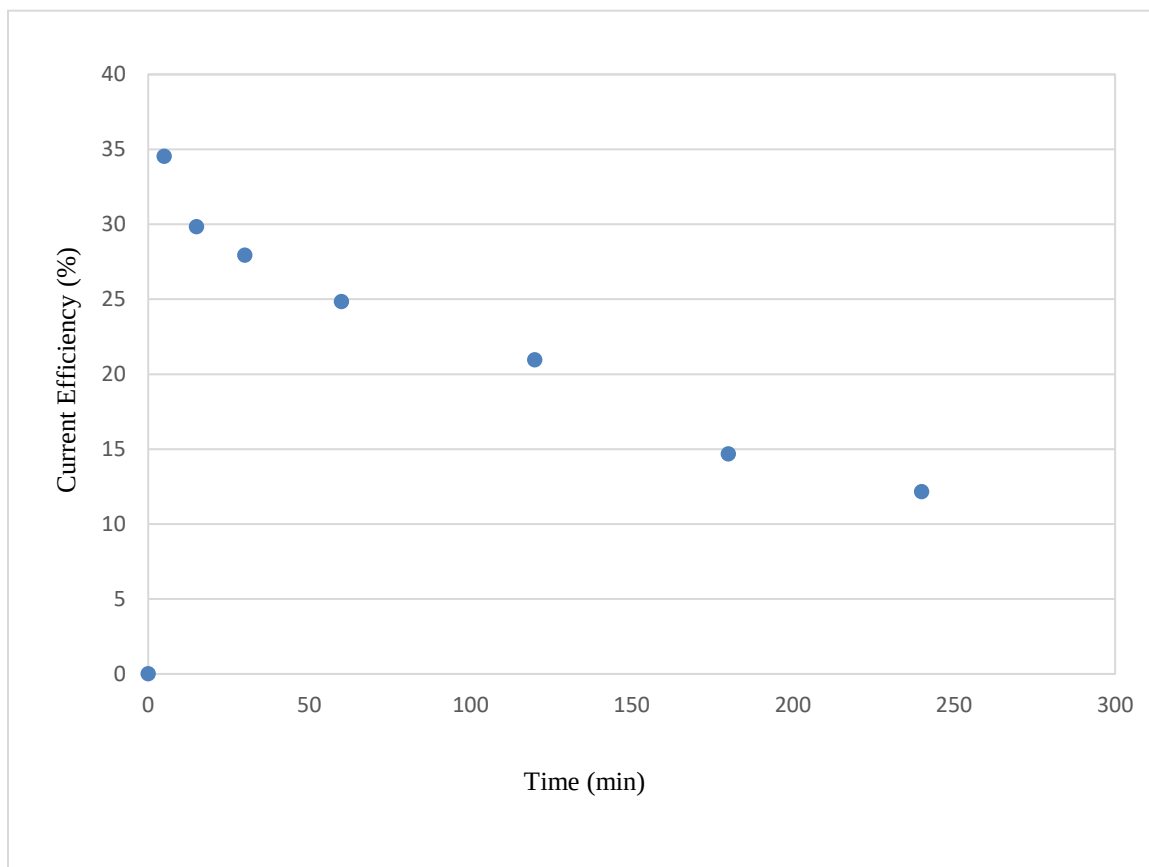


Figure 26: COD removal decay with the corresponding current efficiency (%)

4.9 Electrical energy consumption and cost

The cost has been taken into account in previous experiments, to evaluate the feasibility of overall treatment, most of the operation parameters were optimized to achieve the best current efficiency and at the same time lowest energy cost (Table A3). The average current efficiency for a specific electrolysis period in batch operation mode at a constant current is defined by Eq. 13 and energy consumption (EC) can be defined by Eq. 14.

$$EC = (E_{cell} It) / V_s * R \quad (21)$$

Where R is the current KSA price per unit of electricity for business, which is 0.018 SAR (about 0.0048 USD/kWh). Table A3 provides a summary of the outcomes.

According to Table A3, the cost of electrical energy (CE) ranged from 0.41 to 1.14 (USD/ m³) depending on the average cell voltage. For the optimum parameters (Exp. # 2), the cost was 0.81 USD/ m³. Under the same conditions and longer electrolysis time (4 hours), the cost increased to 0.89 USD/ m³.

In addition to the electrical energy cost, another one should be added also which is the cost of the sulfuric acid. It was added for adjusting the pH of the solution (to be acidic). In the pilot test, around 2 to 3 ml of 98% sulfuric acid was used to reach pH 4. (Table 13).

Table 13: Summary of the treatment cost

Run time	98% Sulfuric acid (mL)	Spent caustic volume (L)	98% Sulfuric acid USD/ mL	Cost of electrical energy (USD/ m ³)	Total treatment cost of 1 m ³ of spent caustic (USD)
3 hours	2.5	2.7	0.07	0.81	0.88
4 hours	2.5	2.7	0.07	0.89	0.96

Note: the above price of 98% Sulfuric acid is considered for industries utilization quantities (Merck, 2022).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Spent caustic is industrial wastewater that is generated from ethylene plants and oil refineries. The collected spent caustic samples that have undergone WAO from an ethylene plant were treated further by an electrochemically advanced oxidation method that combines anodic oxidation (AO) with electro-Fenton (EF).

The objective of the electrochemical oxidation was to reduce COD to a level that can meet the restricted regulations for safe discharge and to determine whether this approach can be used for spent caustic treatment.

The pilot-scale study was conducted using a pilot plant of electrochemical treatment system equipped with an undivided plate-and-frame cell. As cathode and anode, a carbon-PTFE gas diffusion electrode type (GDE) and a boron-doped diamond (BDD) electrode were used, respectively. All experiments were conducted in batch mode.

To identify the optimum operation conditions, the experiments included a wide range of important process parameter values such as pH, applied current, flow circulation, Fe (II) dosage, and airflow.

Results showed that the determined parameters for COD removal were pH and the applied current. The acidic conditions resulted in larger efficiencies than the normal and basic solutions. As expected, the higher the applied current, the higher the removed COD, up to a specified level (15 A or 150 mA/cm²), however, after that, no significant change was observed. The circulating rate did not affect the removal of COD with the value of 0.2 m³/h being the optimum. This is probably the result of a balance between time resistance and

the mass transfer of reactants toward the electrodes. On the other side, Fe (II) dosage and air did not affect the process efficiency.

The anode type had a dramatic effect on the process since the use of the less active anode (DSA) did not remove the COD effectively, in comparison to BDD.

The best results obtained were a residual COD of approx. 67 mg/L (91% COD removal) at pH 4, 150 mA/cm² current density, 0.2 m³/h circulation flow after 3 hours of electrolysis, in the absence of Fe (II) dosage and airflow. Under the same operating conditions but after 4 hours, the treated effluent had a residual COD of 57 mg/L (93% COD removal).

The running cost at the optimum treatment conditions (3 hours) and and run time of 4 hours, were 0.88 USD/m³ (0.0031 USD/ gal) and 0.96 USD/m³ (0.0034 USD/ gal), respectively. These costs include the current applied and the chemical used (there are also other costs associated with the operation of the plant, such as utility and labor costs). The operational cost of EO is significantly less expensive than the expense of transferring the spent caustic wastewater to the USA for treatment when compared to the 1.23 \$/gal cost. (Alnaizy, R., 2008)

The comparison of COD removal results after WAO and EO were as follows; WAO can reduce the initial COD of spent caustic effluent (approx. 2,500 mg/L) by 70%, down to approx. 700 mg/L. As a second treatment step, EO can further reduce COD up to a level for safe discharge (57-67 mg/L).

5.2 Recommendations

Since EO treatment reached almost the required COD limit (50 mg/L as per MEWA regulation limit of discharging to seawater in KSA), the following recommendations for future research are made:

- 1 Experiments should be conducted at smaller intervals of pH in order to avoid the overuse of chemicals for the correction of the effluent pH, as well as the need for non-corrosive materials in the EST system. Also, safety concerns will be lesser.
- 2 Increase the electrolysis time of treatment by more than 4 hours.
- 3 A hybrid process that combines EO with activated carbon adsorption for removing the COD traces (<50 mg/L).
- 4 If the site has a wastewater stream with low COD concentration, the EO-treated effluent can be diluted with this stream making sure the discharge limit is met.

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Appendix

Table A1: Experimental parameters and findings

Exp.#	Description	Initial COD (mg/L) @ 0 min	pH	Current density (mA/cm ²)	Circulation rate m ³ /hr	Fe Dosage ml	Air rate NL/min	Time (min)	Final COD (mg/L) @ 180 min	% COD Removal	Remark
1	Blank	569	≈ 9.5	0	0.2	0	0	180	560	1.55	
2	Effect of pH	741	4	15	0.2	0	0	180	67	91	Optimum pH
3	Effect of pH	691	7	15	0.2	0	0	180	177	74	
4	Effect of pH	732	≈ 9.5	15	0.2	0	0	180	180	72	
5	Effect of Current	650	4	10	0.2	0	0	180	88	86	
2	Effect of Current	741	4	15	0.2	0	0	180	67	91	Optimum current applied
6	Effect of Current	742	4	20	0.2	0	0	180	74	90	
7	Effect of circulation rate	583	4	15	0.1	0	0	180	108	82	
2	Effect of circulation rate	741	4	15	0.2	0	0	180	67	91	Optimum circulation rate
8	Effect of circulation rate	592	4	15	0.3	0	0	180	92	84	
9	Effect of Iron Dosage	590	4	15	0.2	5	0	180	115	80	
10	Effect of Iron Dosage	578	4	15	0.2	10	0	180	110	81	
11	Effect of Iron Dosage	647	4	15	0.2	15	0	180	133	81	
12	Effect of air rate	638	4	15	0.2	5	1	180	138	78	

13	Effect of air rate	679	4	15	0.2	5	2	180	126	82	
14	Effect of air rate	693	4	15	0.2	5	3	180	156	78	
15	Less active anode	808	4	15	0.2	0	0	180	603	25	
16	Less active anode	781	4	15	0.2	5	0	180	620	21	
17	Less active anode	578	4	15	0.2	5	1	180	458	21	
18	Effect of time	862	4	15	0.2	0	0	240	57	93	

Table A2: Summary of current efficiency

			% Current Efficiency					
Time	0	5	15	30	60	120	180	240
Exp. 1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
Exp. 2	0	46	38	29	24	19	14	
Exp. 3	0	2	20	18	18	13	10	
Exp. 4	0	19	24	22	17	13	9	
Exp. 5	0	44	5	19	21	18	16	
Exp. 6	0	-7	23	24	18	14	10	
Exp. 7	0	16	22	17	15	12	8	
Exp. 8	0	2	19	17	14	11	8	
Exp. 9	0	14	18	19	14	10	8	
Exp. 10	0	24	22	16	13	10	8	
Exp. 11	0	2	16	17	15	12	8	
Exp. 12	0	8	21	16	16	12	8	
Exp. 13	0	5	16	18	14	13	9	
Exp. 14	0	21	35	40	20	13	9	
Exp. 15	0	10	1	7	5	4	3	
Exp. 16	0	-6	5	3	0	2	3	
Exp. 17	0	-7	8	5	2	1	2	
Exp. 18	0	35	30	28	25	21	15	18

Table A3: Summary of energy consumption and cost of electrical energy

Exp. No	Ecell (V)	I (A)	Time (h)	Vs (L)	Δ COD (mg/L)	EC (kWh/g COD)	CEE (USD/m ³)
1	0	0	3	2.2	0	0.00	0.00
2	10.1	15	3	2.7	674	0.25	11.45
3	10.05	15	3	2.5	514	0.35	12.30
4	9.4	15	3	2.2	552	0.35	13.07
5	7.2	10	3	2.5	562	0.15	5.88
6	11.1	20	3	2.8	668	0.36	16.17
7	9.75	15	3	2.2	475	0.42	13.56
8	9.1	15	3	2.2	500	0.37	12.66
9	9.4	15	3	2.25	475	0.40	12.78
10	9.4	15	3	2.2	468	0.41	13.07
11	9.4	15	3	2.2	514	0.37	13.07
12	9.6	15	3	2.2	500	0.39	13.35
13	9.6	15	3	2.2	553	0.36	13.35
14	9.95	15	3	2.2	537	0.38	13.84
15	8	15	3	2.2	205	0.80	11.13
16	7.85	15	3	2.2	161	1.00	10.92
17	8.05	15	3	2.2	120	1.37	11.20
18	8.35	15	4	2.7	805	0.23	12.62

Vitae

Name : Saleh AL-Ageel

Nationality : Saudi Arabia

Date of Birth : 06/06/1986

Email : slooo741@gmail.com

Permenant Address : Saudi Arabia, Jubail Industrail City, 35821

Academic Background :

- Master degree in Environmental Sciences, KFUPM, Dhahran, Saudi Arabia (expected graduated June 2023).
- Bachelor in Chemical Engineering, Al-Jubail Industrial College, Jubail Industrail City, Suadi Arabia. (June 2012)
- Diploma in Chemical Engineering, Al-Jubail Industrial College, Jubail Industrail City, Suadi Arabia. (June 2008)

Experaince :

Total work experience: 14 years

SABIC-Coorprate, Jubail Industrail City, Suadi Arbaia

- (Environment Engineer) (October 2022- now)

SABIC-KEMYA, Jubail Industrail City, Suadi Arbaia

- (Environment Manager) (February 2018- October 2022)
- (Environment Engineer) (Aug 2013- February 2018)
- (Raw Material Coordinator) (Oct 2012 – Aug 2013)
- (Utility plant / Operation) (Feb 2009- Oct 2012)

Qulicication :

- IEMA Associate Certificate in Environmental Management (International)
- NEBOSH Certificate in environment management