



Faculty of Resource Science and Technology

**Coating of ZnO/Zn Photoanode Using Electrochemical Deposition (ECD) Method
and Optimization of Dual Chamber Photocatalytic Fuel Cell (DCPFC) in Treating
Organic Wastewater and Power Generation**

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Coating of ZnO/Zn Photoanode Using Electrochemical Deposition (ECD) Method and
Optimization of Dual Chamber Photocatalytic Fuel Cell (DCPFC) in Treating Organic
Wastewater and Power Generation

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DECLARATION

I declare the work in this thesis was carried out in accordance with the regulation of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted for any other degree.

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Coating of ZnO/Zn Photoanode Using Electrochemical Deposition (ECD) Method and Optimization of Dual Chamber Photocatalytic Fuel Cell (DCPFC) in Treating Organic Wastewater and Power Generation

ABSTRACT

Due to the rapid economic development, the photocatalytic fuel cell (PFC) could be one of the alternatives for wastewater treatment and power generation. The PFC technology remained in laboratory scale as the power generation and wastewater treatment rate were insufficient for daily application despite showing great effectiveness. In this project, the ZnO/Zn photoanode was produced via electrochemical deposition (ECD) method to investigate the performance of treating methyl red dye solution and palm oil mill effluent (POME). Besides, a dual chamber photocatalytic fuel cell (DCPFC) was fabricated to study the performance in treating methyl red dye solution and POME. In the study, 10 ppm methyl red dye solution at pH 4 and 250 mL/L of NaClO solution concentration in DCPFC showed the highest degradation rate (138 minutes) and power density (209.83 mW/cm^2) using ECD method prepared ZnO/Zn photoanode compared to ultrasonic method prepared ZnO/Zn photoanode (217 minutes and 134.67 mW/cm^2). The study continued by replacing the methyl red dye solution with POME. From the study, the DCPFC using ECD method prepared ZnO/Zn photoanode showed complete degradation of pH 4 25% POME and sulphuric acid added as additive at the 8th hour with the power density at 236.312 mW/cm^2 . The ECD method prepared ZnO/Zn photoanode and DCPFC provided a new insight into the real application of PFC with greater performance.

Keywords: Advanced oxidation process, electrochemical deposition, photocatalytic fuel cell, POME, power generation, wastewater treatment

Lapisan ZnO/Zn Fotoanod dengan Cara Penedapan Elektrokimia dan Pengoptimuman Sel Bahan Api Fotokatalisis Dua Ruang (DCPFC) dalam Rawatan Air Sisa Organik dan Penjanaan Elektrik

ABSTRAK

Dengan pembangunan ekonomi yang pesat, sel bahan api fotokatalisis (PFC) boleh dijadikan sebagai satu alternatif dalam proses rawatan air dan menjana elektrik. Teknologi PFC masih kekal dalam skala makmal kerana skala rawatan dan penjanaan elektrik masih tidak memuaskan walaupun telah menunjukkan prestasi yang tinggi. Dalam projek ini, ZnO/Zn fotoanod telah dibuat dengan cara penedapan elektrokimia dan digunakan dalam proses rawatan larutan pewarna merah metil dan efluen kelapa sawit. Selain daripada ZnO/Zn fotoanod, sel bahan api fotokatalisis dua ruang (DCPFC) dihasilkan untuk mengakses prestasi rawatan air sisa dan penjanaan elektrik. Dalam kajian ini, 10 bahagian per juta larutan pewarna merah metil dengan pH 4 dan 250 mL/L kepekatan larutan NaClO telah menunjukkan penjanaan elektrik (209.83 mW/cm^2) dan melengkapkan degradasi dalam 138 minit. Kajian diteruskan dengan menggantikan larutan pewarna merah metil dengan larutan efluen kelapa sawit. Hasil kajian dengan menggunakan larutan efluen kelapa sawit pada kepekatan 25%, pH 4, dan sulfuric asid sebagai bahan tambahan telah menunjukkan penjanaan elektrik sebanyak 236.312 mW/cm^2 dan melengkapkan degradasi dalam 8 jam. Dengan cara penedapan elektrokimia dalam penyediaan ZnO/Zn fotoanod dan DCPFC akan memberi pandangan baharu mengenai penggunaan PFC dengan prestasi yang lebih baik.

Kata kunci: *Penjanaan tenaga, penedapan elektrokimia, proses pengoksidaan lanjut, POME, rawatan air sisa, sel bahan api fotokatalis.*

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LIST OF ABBREVIATION

ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
BOD	Biochemical Oxygen Demand
CB	Conduction Band
COD	Chemical Oxygen Demand
DC	Direct Current
DCMFC	Dual Chamber Microbial Fuel Cell
ECD	Electrochemical Deposition
EDX	Energy Dispersive X-ray
FAS	Ferrous Ammonium Sulphate
FE-SEM	Field Emission Scanning Electron Microscope
HRTEM	High Resolution Transmission Electron Microscope
IC	Integrated Circuit
MB	Methylene Blue
MFC	Microbial Fuel Cell
MG	Malachite Green

MO	Methyl Orange
MOH	Metal Hydroxide
PDS	Peroxydisulfate
PFC	Photocatalytic Fuel Cell
PL	Photoluminescence
PMS	Peroxymonosulfate
POME	Palm Oil Mill Effluent
PV	Photovoltaic
ROS	Reactive Oxygen Species
SAR	Sulphuric Acid Reagent
SCMFC	Single Chamber Microbial Fuel Cell
TRPL	Time Resolved Photoluminescence
TSS	Total Suspended Solid
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible Light
VB	Valence Band

CHAPTER 1

INTRODUCTION

1.1 Background

Wastewater treatment remains a challenge for sustainable environmental practices and resource utilization. With the rapid industrialization and city developments, small and medium industries, as well as heavy industries, have been found to release partially treated or untreated wastewater into water bodies. Majority of the wastewater contains high amount of heavy metals and organic-rich pollutants which could lead to a series of irreversible environmental impacts (Ahmed et al., 2014; Tang et al., 2019).

Currently, water pollution is one of the major obstacles caused by rapid economic growth around the globe (Li et al., 2019). In view of this, advanced and effective wastewater treatment technologies are required immediately to cater for the increase volume of wastewater discharges daily. Due to non-biodegradable nature of some organic-based pollutants, the discharge of untreated wastewater from textile, pharmaceutical, and manufacturing industries has possessed threat to both human and aquatic life (Nahyoon et al., 2019). To ensure the demand of clean water resources is sufficient, recycling of wastewater from industries is crucial (Kee et al., 2018). With high concentration of organic-based pollutants in wastewater, coagulation and flocculation, adsorption, and membrane filtration has shown ineffectiveness in complete removal or degradation of pollutants due to high complexity and hence post-treatment are required for complete removal of pollutants (Khalik et al., 2018; Vasseghian et al., 2020). Thus, by expanding insight and research into

the latest technologies such as fuel cells with higher efficiency in wastewater treatment, the wastewater treatment rate could be enhanced.

The process during electrical energy generation is considered one of the culprits that contribute to environmental pollution due to the burning of coal and the release of wastewater. As the demand for electricity increases daily due to the burst of economic activity, the global fossil fuel consumption for electricity generation increased steadily which caused in the increment of global carbon dioxide (CO₂) emissions (Ding et al., 2021; Dong et al., 2020). In order to reduce the impact of fossil fuel consumption and carbon footprint, solar energy (Han et al., 2021; Sharif et al., 2021), hydro energy (Blakers et al., 2021), wind energy (Nazir et al., 2019), and geothermal energy (Lund & Toth, 2021) are potential alternative for generating electrical energy while conserving the environment. Electricity generation via hydro energy, solar energy, and wind energy are usually labelled as green and eco-friendly. However, such alternatives indirectly increased the damage to the environment. Despite massive power generation from hydropower plant, the constructing of hydropower plant significantly affected the surrounding environment as flooding a huge forest area results in landscape alterations (Bagher et al., 2015). Furthermore, the electrical energy generated via wind and solar energy indirectly contributes to global CO₂ emissions and carbon footprint during the manufacturing of the components for wind turbines and solar panels. Thus, alternatives for green electrical energy generation from various sources are required immediately.

In this context, the combination of photocatalysis process and fuel cell technology could give rise to an advanced exploration into simultaneous wastewater treatment and power generation. Photocatalyst such as zinc oxide (ZnO), titanium dioxide (TiO₂), and iron oxide (Fe₂O₃) plays a vital role in wastewater treatment with the production of free radicals

via photoexcitation for initiation of advanced oxidation process (AOP) (Kanakaraju et al., 2018; Pandey et al., 2021). Moreover, the photocatalytic fuel cell (PFC) could be one of the alternatives to hydroelectric, solar power, as well as wind power for cleaner and greener electricity production by utilizing photocatalytic process. In this manner, the combination between the photocatalytic capabilities of photocatalysts and energy conversion of fuel cell technologies contributes to the potential of PFC in foreshadowing a sustainable pathway for simultaneous wastewater treatment and renewable energy production.

1.2 Electrochemical Deposition (ECD) Method

Electrochemical deposition (ECD) is a type of coating method that utilizes electricity to deposit a thin layer of materials onto the surface of a conductive object. Currently, the ECD coating method is widely implemented in the production of several types of electronic components. According to Mbugua et al. (2020), using ECD coating process brings several types of advantages including low initial investment with higher production rate, ease of production with sizes as small as 10 nm, products can be used immediately after ECD without further processing, and minimal technological barriers which can be used in any fields. Moreover, the ECD coating method granted precise control of mass and thickness which further enhances the performance of final products (Bocchetta et al., 2019). Typically, the ECD coating method takes place in an electrolytic cell which consists of electrolyte solution, anode, cathode, and a direct current (DC) supply unit. (Figure 1.1).

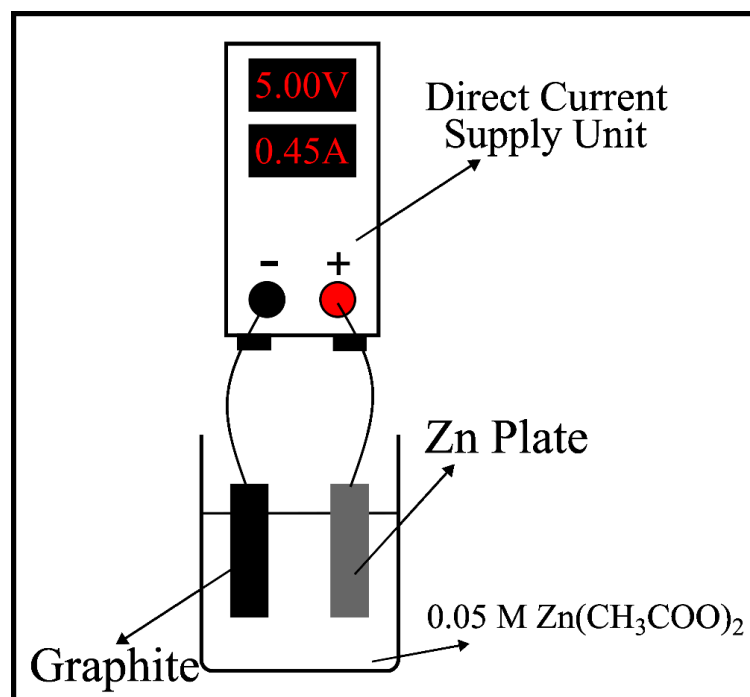


Figure 1.1: Electrochemical deposition (ECD) method of ZnO/Zn photoanode preparation

In this project, the ZnO/Zn photoanode will be prepared via ECD method. During the process, the surface of the zinc plate will be coated with a thin layer of ZnO, which is one of the most commonly used photocatalyst in PFC for wastewater treatment and electricity generation.

1.3 Problem Statement

The photocatalytic system has proven its effectiveness in the study done by researchers in organic-based wastewater treatment and power generation using single chamber PFC. However, the concept of PFC remains in laboratory scale as the scale for wastewater treatment and power generation from the PFC was insufficient for actual implementation. In order to meet the requirements for daily wastewater treatment scale and power generation, the upscaling of PFC is necessary. As increasing the scale of PFC, researchers have to face a series of challenges including the photocatalyst coating method as well as the design of the PFC to ensure that the performance is equivalent to the conventional wastewater treatment method.

Despite thousands of photocatalysts application related research and publications, the photoanode coating method is rarely getting attention as coating method directly influence the performance of PFC in wastewater treatment as well as the power generation. The photoanode synthesized using hydrothermal, ultrasonicate, sol-gel method and etc. showed excellent efficiency in degradation of organic wastewater and power generation. However, those methods of preparation often require long preparation duration, high cost, and long reaction duration. Ultrasonicate coating method for photocatalyst on the electrode is the most commonly applied method due to ease of handling and lower cost but the uneven coating, poor adhesion on surface, and produced different crystalline structure of photocatalyst greatly reduced the performance of the photoanode in PFC. Therefore, a new approach such as using ECD method which is easier to operate and lower cost yet producing a photoanode that is on par with the commonly applied method is necessary.

Furthermore, in the voyage of PFC research, the majority of the researchers focused on the modification of photocatalyst, however, the modification of PFC design has gained less attention. With appropriate design of PFC such as dual chamber PFC, the wastewater degradation and power generation efficiency of PFC would significantly increase under the optimal operating conditions such as pH, concentration, volume, and additives of the solution.

1.4 Objectives

The objectives of the project are:

1. To fabricate and characterize the ZnO/Zn photoanode using electrochemical deposition (ECD) method.
2. To fabricate a dual chamber photocatalytic fuel cell (DCPFC) for methyl red dye solution degradation and power generation using ECD method prepared ZnO/Zn photoanode compared to ultrasonicate coating method.
3. To investigate the degradation efficiency and power generation of dual chamber photocatalytic fuel cell (DCPFC) using ECD method prepared ZnO/Zn photoanode in treating palm oil mill effluent (POME) solution under different pH, concentration, and volume of POME solution as well as the different additives added.

1.5 Scope of Study

The study focuses on the fabrication of ZnO/Zn photoanode using ECD coating method and the fabrication of DCPFC. The fabricated ZnO/Zn photoanode using ECD coating method was compared with the ultrasonicate coating method for ZnO/Zn photoanode in DCPFC using methyl red dye as targeted synthetic dye solution. The purpose of choosing the ZnO as the photocatalyst in this project is the ease of preparation, low cost, non-toxic, and the characteristics of the ZnO are well studied. The surface structure of ECD method prepared and ultrasonicate method prepared ZnO/Zn photoanode observed under Field Emission Scanning Electron Microscope (FE-SEM). Besides, the energy dispersive X-ray (EDX) analysis was performed for the confirmation of ZnO formation on ECD method prepared ZnO/Zn photoanode. Furthermore, the degradation of methyl red dye solution using ECD method and ultrasonicate method prepared ZnO/Zn photoanode in DCPFC performed under different pH value as well as the concentration of sodium hypochlorite (NaClO) solution. After obtaining the optimum operating conditions for the degradation using ECD method prepared ZnO/Zn photoanode and DCPFC, the project continues by replacing methyl red dye solution with POME solution. The performance of the dual chamber PFC was accessed, with the optimization study aimed at investigating the optimum conditions such as pH, concentration, volume, and additives added to the POME solution for best degradation efficiency and power generation.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

2.1.1 Dye Industrial Wastewater

With the rapid growth of textile industries, the discharge of dye-containing effluent has been increased resulting in severe environmental issues that ultimately harm the living organisms. Especially for aquatic ecosystem, the released of dye wastewater severely disrupt the photosynthetic activity for aquatic plants as well as the bioaccumulation of toxins that released from the degraded dyes (Donkadokula et al., 2020; Premaratne et al., 2021). Generally, the dyes are classified into their own group based on the chromophore such as azo dye, anthraquinone dye, cyanine dye, diarylmethane dye, triarylmethane dye, triphenylmethane dye and etc. (Mehra et al., 2021; Premaratne et al., 2021). As shown in Table 2.1, the pH value for dye wastewater commonly falls between 6 to 11 while for both biological oxygen demand (BOD) and chemical oxygen demand (COD), the highest concentration is at 6,000 mg/L and 30,000 mg/L, respectively. As for the total suspended solid (TSS) in dye wastewater, the value falls between 15 to 800 mg/L. Although textile wastewater has generally lower COD and BOD compared to other types of wastewaters such as palm oil mill effluent (POME), domestic wastewater, or municipal solid wastewater, the high complexity of chemical structure of dye increased the difficulties in the treatment process.

Table 2.1: General characteristics of textile wastewater (Shindhal et al., 2021; Yaseen & Scholz, 2019)

Parameter	Range
pH	6 – 11
BOD	80 – 6,000 mg/L
COD	150 – 30,000 mg/L
TSS	15 – 800 mg/L

According to Sudarshan et al. (2023), triphenylmethane dye and azo dye are the types of dye that generally applied in textile industries, manufacturing industries, as well as food and beverages industries. Malachite green (MG) (Figure 2.1a) is often used in food, textiles, leather, paint, and paper production. However, MG dyes are highly cytotoxic and carcinogenic to mammalian cells. Sudarshan et al. (2023) also mentioned that although methylene blue (MB) (Figure 2.1b) generally used in as medicine, over dosage of MB will increase the blood pressure, and myocardial depression. Oladoye et al. (2022) also mentioned that high concentration of MB will also increase the risk of serotonin toxicity. Zafar et al. (2022) and Alsukaibi (2022) also mentioned that azo dyes such as methyl orange (MO) (Figure 2.1c) that often used in the industries mostly carcinogenic, mutagenic, and genotoxic. The long exposure of human body to azo dyes will increase the risk of vital organs such as liver, kidney, brain, and heart suffer from irreversible damage resulting in failure of respiratory system, immune system, as well as reproductive system (Slama et al., 2021).

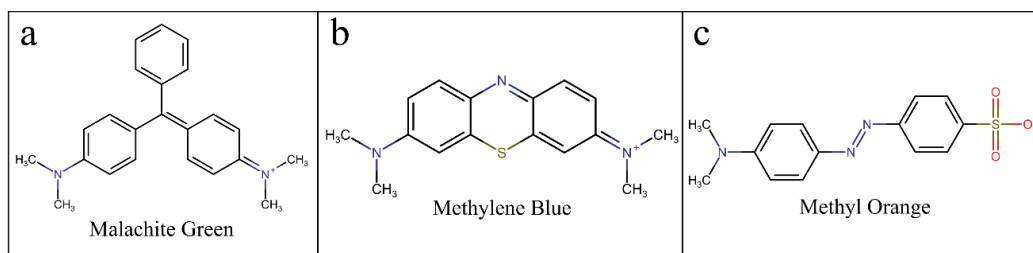


Figure 2.1: Chemical structure of commonly used dye in various industries

2.1.2 Palm Oil Mill Effluent (POME)

Palm oil is one of the main exports as well as backbone of economy among the countries in Southeast Asia which predominated by Malaysia and Indonesia (Lokman et al., 2021; Nawaz et al., 2021). About 28% of world palm oil production and 33% of world palm oil exports was contributed by Malaysia according to Lokman et al. (2021). The demand for palm oil increased gradually due to the increase of biodiesel and consumption demand. According to Low et al. (2021), the palm oil products have been found brings several health benefits such as decreasing cholesterol level, boosting brain health, and reducing oxidative stress. Although palm oil related industries have greatly contributed to the economy to our country, the palm oil industries often highly associated with deforestation, forest fragmentation, water pollution, and climate change (Ayompe et al., 2021). No doubt, one of the wastes produced from the palm oil mill, namely palm oil mill effluent (POME) is well known as the major pollutant source to the environment. This is due to its escalated level of organic pollutants which can be characterized by high COD, BOD, TSS, as well as oil and grease content as shown in Table 2.2 (Tan & Lim, 2019).

Table 2.2: The characteristics of raw POME (Mahmod et al., 2023; Saputera et al., 2021)

Parameter	Range
pH	3.4 – 5.2
Oil and grease	130 – 18,000 mg/L
BOD	10,000 – 44,000 mg/L
COD	15,000 – 100,000 mg/L
TSS	5,000 – 54,000 mg/L

From Figure 2.2, the raw POME typically is a highly viscous brownish liquid and often emits bad odor due to high concentration of crude palm oil, carotene, pectin, tannin, phenolic compounds, and lignin. Therefore, the raw POME requires tremendous treatment before discharged to the environment (Saputera et al. 2021).



Figure 2.2: Appearance of raw POME

Despite POME is known as the major pollution source to the environment, the high organic content in POME is an excellent fuel source for electricity generation in PFC (Selihin & Tay, 2022). Due to high concentration of organic pollutants, POME has attracted our attention to explore the possibility of harvesting energy sources from POME through the application of PFC.

2.2 Wastewater Treatment Method

The process of wastewater treatment in textile industries as well as palm oil manufacturing is crucial for pollutants removal to ensure the safety of discharging into the environment or the recycling of water for consumption. The treatment methods for textile wastewater and POMW generally fall into three broad categories, which are physical, chemical, and biological treatment. To effectively remove the organic-based contaminants from wastewater, industries often implemented a combination of physical, chemical, and biological treatment to completely remove the pollutants.

2.2.1 Biological Treatment

The biological treatment utilizes different microorganisms in degrading the organic-based pollutants during the treatment process. Due to high effectiveness, cost effective, and ecologically safe, biological method in wastewater treatment widely used treatment method in textile wastewater and POME degradation. Table 2.3 summarizes the application of various microorganisms applied in the biological treatment of dye containing wastewater and POME.

Table 2.3: List of microorganisms applied in the biological treatment for textile wastewater and POME

Microorganisms	Sources	Removal	Duration	Reference
<i>Aeromonas hydrophilia</i> LZ-MG14	Malachite Green (MG)	96.8% removal	12 hours	Shindhal et al. (2021)
<i>Chlorella vulgaris</i>	Textile dye wastewater	69.9% COD removal	N.A.	Premaratne et al. (2021)
<i>Gloeocapsa pleurocapsoides</i>	Acid red 97	100% removal	N.A.	Singh et al. (2019)
<i>Halomonas sp.</i> A55	Reactive red 184	>85% removal	N.A.	Wang et al. (2020)
<i>Bacillus cereus</i>	Reactive black 5	97% removal	120 hours	Khan et al. (2023)
<i>Bacillus megaterium</i> KY848339.1	Acid red 337	100% removal	24 hours	Moyo et al. (2022)
<i>Oscillatoria limnetica</i>	Basic Fuchsin dye	90.23% removal	7 days	Al-Tohamy et al. (2022)
<i>Staphylococcus cerevisiae</i>	POME	91% BOD removal	55 hours	Lokman et al. (2021)
<i>Chlorella vulgaris</i>	POME	74% COD removal	N.A.	Nur et al. (2021)
<i>Nannochloropsis sp.</i>	POME	71% COD removal	N.A.	Emparan et al. (2020)
<i>Haematococcus pluvialis</i>	POME	50.9% COD removal	N.A.	Fernando et al. (2021)
<i>Chromochloris sofigiensis</i>	POME	44.8% COD removal	N.A.	Fernando et al. (2021)

N.A. = Not Available

2.2.2 Physical Treatment

Meanwhile, physical treatment consists of various treatment methods which include sedimentation, screening, filtration, adsorption, and so on. Among these methods, filtration is considered as the most efficient and widely applied method in conventional wastewater treatment plants due to ease of installation, maintenance, and affordability. The filtration system of wastewater treatment often utilizes sand or biochar to effectively remove the pollutants from the wastewater. Besides, membrane filtration also showed excellent removal efficiency in dye-containing wastewater as well as POME according to Moyo et al. (2021). Physical treatments that are applied in various wastewater sources are summarized in Table 2.4.

Table 2.4: Wastewater treatment via physical treatment

Materials	Source	Removal	Reference
Ceramic microfiltration membrane	Dye effluent	75% COD removal	Donkadokula et al. (2020)
Polyether sulfone membrane ES404	Reactive brilliant blue	99.5% removal	Cao et al. (2020)
Polyether sulfone (PES)	Dye effluent	80% - 100% removal	Shindhal et al. (2021)
Sand filtration	Dye wastewater	61 ± 12% removal	Kaetzi et al. (2020)
Micro zeolite	Textile dye wastewater	97% COD removal	Badawi & Zaher (2021)
Zeolite imidazolate framework (ZIFs)	Malachite Green	99.2% removal	Abdi & Abedini (2020)
Ultrasound-assisted $Ti_3C_2T_x$ MXene	Methylene blue	>80%	Jun et al. (2020)
Ultrafiltration	POME	90% removal	Lee et al. (2019)
Biochar	POME	49.5% COD removal	Razali & Kamarulzaman (2020)
Microfiltration	POME	68.5% COD removal	Saad et al. (2020)
Polydopamine (PPA)/polyethyleneimine based zwitterion (Z-PEI)	POME	81.75% colour removal	Abdullah et al. (2023)

2.2.3 Chemical Treatment

Besides physical and biological treatment applied in textile wastewater and POME, chemical treatment which includes coagulation and flocculation, electrocoagulation, and advanced oxidation process (AOP) are widely employed in wastewater treatment. Generally, chemicals such as aluminium sulphate $[Al_2(SO_4)_3]$ or iron chloride ($FeCl_3$) are added to the wastewater as a coagulant for wastewater treatment (Table 2.5). During coagulation process, the pollutants' molecules react and coagulate with the coagulant, forming precipitates trapping the pollutants. Once the precipitate has settled down to the bottom of the reactor tank, the precipitate is removed by filtration or decantation. As shown in Table 2.5, coagulation and flocculation process showed excellent removal efficiency in various wastewater which typically more than 90% removal rate of dyes wastewater and POME.

Table 2.5: Coagulation and flocculation process in wastewater treatment

Materials	Sources	Removal	Reference
Iron chloride ($FeCl_3$)	Acid orange 7	98% removal	Al-Tohamy et al. (2022)
Pectin	Textile wastewater	54.2% removal	Ishak et al. (2020)
Chitosan	Congo red	94.5% removal	Ishak et al. (2020)
Iron chloride ($FeCl_3$)	Acid red 119	96.53% removal	Solayman et al. (2023)
Chloride-anionic polyacrylamide	POME	90% removal	Lee et al. (2019)

The traditional coagulation method that utilized chemical or natural coagulant and adsorbent has few major flaws including long treatment period and generating large amount of sludge especially in the treatment of organic-rich wastewater (Nasrullah et al., 2022). As mentioned by Nasrullah et al. (2022), electrocoagulation wastewater treatment method was applied to overcome the drawbacks from the conventional coagulation method due to its'

faster removal rate and lower sludge production (Table 2.6). In the electrocoagulation process, the metal hydroxide (MOH) which is used as the coagulant spontaneously produced from anode when electrical current is applied, destabilized, and adsorbed the organic pollutants. With the smaller particle size and larger surface area of coagulant formed, the organic pollutants effectively adsorbed.

Table 2.6: Electrocoagulation process for POME treatment

Electrodes	Removal rate	Conditions	Duration	Reference
Iron	94.2% colour removal 69.9% COD removal	10 V	60 minutes	Saad et al. (2020)
Steel wool	97.21% COD removal	19.07 A	44.97 minutes	Nasrullah et al. (2022)
Aluminium	71.31% COD removal	40.21 mA/cm ²	45.67 minutes	Bashir et al. (2019)
Aluminium	44% COD removal	6 V	7 hours	Sia et al. (2020)
Aluminium	91.68% COD removal	N.A.	8 hours	Mohamad et al. (2022)
Aluminium and Iron	96% COD removal 97% colour removal	30 mA/cm ² at pH 5	10 minutes	Khongkliang et al. (2023)

N.A. = Not Available

Wastewater treatment via adsorption process also one of the most implemented methods in conventional wastewater treatment plant due to easy operational conditions, low production cost, wide pH tolerance, excellent metal binding capacity, and less toxic by-products (Jun et al., 2020; Thotagamuge et al., 2021). Based on Abdi and Abedini (2020) study, the synthesized PES/ZIF-8/ZIF-67 beads shows great removal efficiency of 20 mg/L malachite green dye solution with the maximum removal efficiency of 99.2% under the optimized conditions of solution at pH 7. In addition, the adsorbent, FS@CS-PAA, synthesized by Zheng et al. (2020) showed maximum removal rate of 98% for crystal violet

(CV), 86% for copper (Cu) ion, and 75% for nickel (Ni) ion at pH 4 to pH 10. In the study done by Mustapha et al. (2020), the synthesized kaolin/ZnO nanocomposite has successfully removed 93%, 96%, and 91% of COD, BOD, and chlorides, respectively from tannery wastewater. Moreover, in Mustapha et al. (2020) study also found out that the maximum removal rate of the Cr and Fe has achieved 75% and 69%, respectively using kaolin/ZnO nanocomposite. Due to higher surface area of chitosan-based adsorbent as mentioned in Alyasi et al. (2023), the maximum removal percentage of 20 mg/L methyl orange dye achieved was 98.8%. However, according to Alyasi et al. (2023), as the initial concentration of MO dye increased, the removal percentage of MO dye decreased due to unavailability of active site for higher concentration of MO.

Currently, microbial fuel cell (MFC) is one of the prime interests for wastewater treatment as the wastewater was treated biologically while producing electricity by harvesting sunlight. The MFC has two general designs which are single chamber MFC (SCMFC) and double chamber MFC (DCMFC). The SCMFC is comprised of a single chamber with both anode and cathode electrodes placed in the same chamber (Figure 2.3).

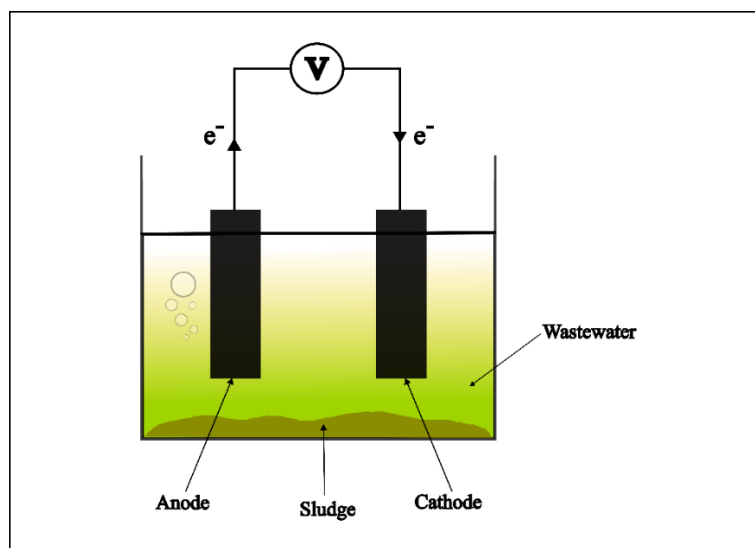


Figure 2.3: Single chamber microbial fuel cell setup

On the other hand, DCMFC was made up of two separate chambers namely anode chamber and cathode chamber connected through a salt bridge where a membrane was used to separate the solution in each compartment (Figure 2.4). The MFC is a bio-electrochemical system that generates bio-electricity with the help of biocatalytic reaction (Jaiswal et al., 2020). According to Flimban et al. (2019), the electron generates from metabolic activity of microbes transfer and collected at the surface of anode by cytochromes or redox-active protein then passed to cathode (Figure 2.4).

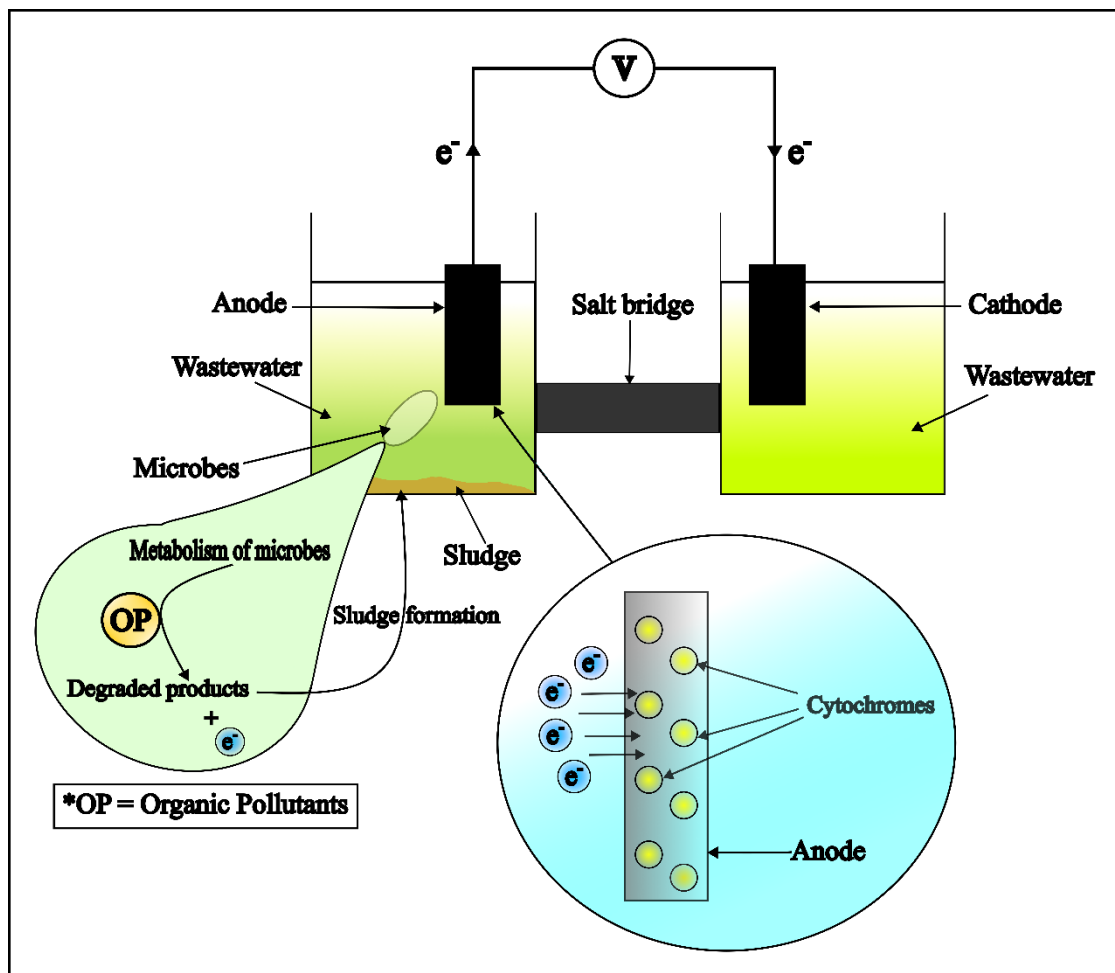


Figure 2.4: Double chamber microbial fuel cell and the illustration of transfer of electron generated from the microbial metabolic activity

Table 2.7 showed the application of different types of microbial in microbial fuel cells for wastewater treatment as well as generating power. Despite MFC having higher efficiency in high complexity wastewater treatment, the application of MFC in wastewater treatment is still yet to satisfy the wastewater treatment plant due to the scale of the application.

Table 2.7: Wastewater treatment via microbial fuel cell

Microbes	Sources	Removal rate	Duration	Power generation	Reference
<i>Shewanella algae</i> (MTCC-10608)	POME	92.21% COD removal	286 hours	141 mA/m ² 50 mW/m ²	Choudhury et al. (2021)
<i>Synechococcus sp.</i>	Kitchen wastewater	N.A.	N.A.	41.5 ± 1.2 mW/m ²	Naina Mohamed, Thomas et al. (2020)
Biofilm	Municipal solid wastewater	80.55% COD removal	N.A.	2.76 mA 0.76 mW	Rashid et al. (2021)
<i>Scenedesmus quadricauda</i> SDEC-8	Domestic wastewater	80.2%	N.A.	62.93 mW/m ²	Yang et al. (2018)
<i>Nitzschia palea</i>	Modified f/2 growth medium	N.A.	N.A.	12.62 mW/m ²	Khan et al. (2022)
Anaerobic sludge	Rice mill wastewater	85.22% COD removal	N.A.	15.92 mA	Raychaudhuri & Behera (2020)
Anaerobic sludge	Synthetic wastewater	84% COD removal	N.A.	50.7 mW/m ² 570 mA/m ²	Rahmani et al. (2022)
Microbe complex	Methyl orange	94.04 ± 2.87% COD removal	N.A.	148.29 mW/m ² 544.6 mA/m ²	Mittal et al. (2022)
Inoculum	Industrial wastewater	87% COD removal	N.A.	260 mW/m ² 364 mA/m ²	Karuppiah et al. (2022)
Mix algae	Landfill leachate	26% COD removal	60 hours	303 mV	Nguyen & Min (2020)

N.A. = Not Available

2.2.4 Advantages and Limitation of Conventional Wastewater Treatment

Wastewater treatment remains a huge challenge to humanity due to the adverse effects on the environment and living organisms. Recent years, several wastewater treatment technologies including physical, biological, and chemical method have been reported but the best treatment method has yet to be found as each wastewater treatment holds its specific benefits. However, each wastewater treatment method also has its own challenges including environmental impact, sludge production, and cost effectiveness. Table 2.8 summarizes the advantages and limitations of various wastewater treatment methods.

Table 2.8: Advantages and limitations of wastewater treatment methods

Wastewater Treatment Method	Advantages	Limitation	Reference
Adsorption	1. Isolation of specific contaminant 2. Fast and highly effective 3. High treatment capacity	1. Accumulation of cyanotoxin 2. High operation cost due to consumption and regeneration of chemicals	Ahmed et al. (2021) Younas et al. (2021) Nasrollahi et al. (2022)
Membrane-based	1. Wide range application 2. Filtration based on particle size and type	1. Membrane fouling 2. High energy consumption 3. Low cost effectiveness	Ahmed et al. (2021) Nasrollahi et al. (2022) Srivastava et al. (2021)
Biological Treatment	1. High effectiveness 2. Easily coupling with other treatment methods 3. Low operational cost 4. Efficient in the treatment of high organic loading 5. Methane production as alternative energy source	1. Long retention period 2. Inefficient in removing inorganic pollutants 3. Microbes community affected by surrounding conditions 4. High capital cost	Ahmed et al. (2021) Nasrollahi et al. (2022) Srivastava et al. (2021) Zieliński et al. (2023)
Chemical Treatment	1. High efficiency 2. Less sludge production	1. High operation cost 2. High maintenance cost	Srivastava et al. (2021) Younas et al. (2021)

2.3 Advanced Oxidation Process (AOP)

Among the pollutants removal technologies, advanced oxidation process (AOP) is considered as one of the main researched solution due to its benefits i.e., high reaction rate, efficiency, and low toxic by-products generation during various wastewater treatment for achieving water sustainability (Giwa et al., 2021; Pandis et al., 2022). Generally, AOP is an oxidation process where reactive oxygen species (ROS) generated for wastewater degradation by attacking organic compounds via hydrogen abstraction, combination or addition of radicals, and electron transfer (Garrido-Cardenas et al., 2020). As stated by Pandis et al. (2022), AOP can be categorized into UV-hydrogen peroxide (UV/H₂O₂) process, Fenton and photo-Fenton process, ozone-based process, photocatalysis process, and sonolysis process which shared a common characteristic of producing ROS during the process.

2.3.1 Ultraviolet/ Hydrogen Peroxide (UV/H₂O₂) Process

In the UV/H₂O₂ process, the H₂O₂ was photoactivated yielding hydroxyl radical (Equation 2.1) showed in Figure 2.5 as mentioned in Ganiyu et al. (2022) study. The regeneration of H₂O₂ occurred as shown in Equation 2.2 was due to the reaction between the unpaired electrons in hydroxyl radical.



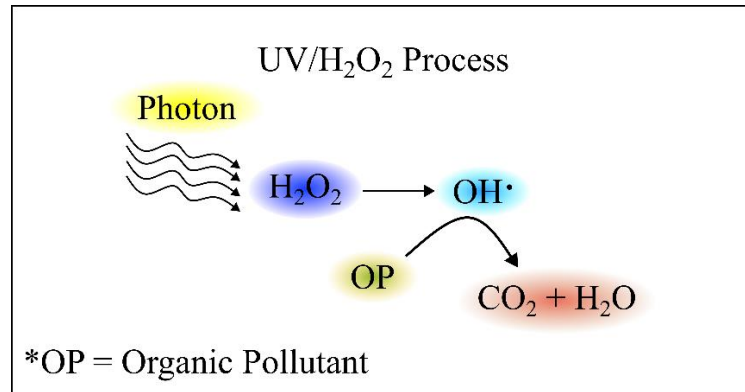


Figure 2.5: UV/H₂O₂ process

2.3.2 Ozone-based Process

As for the ozone-based process showed in Figure 2.6, the ozone (O₃) was photoactivated via photon producing hydroxyl radical when reacted with water (Brillas, 2022). Equation 2.3 showed the general equation for hydroxyl radical production via ozone-based process.

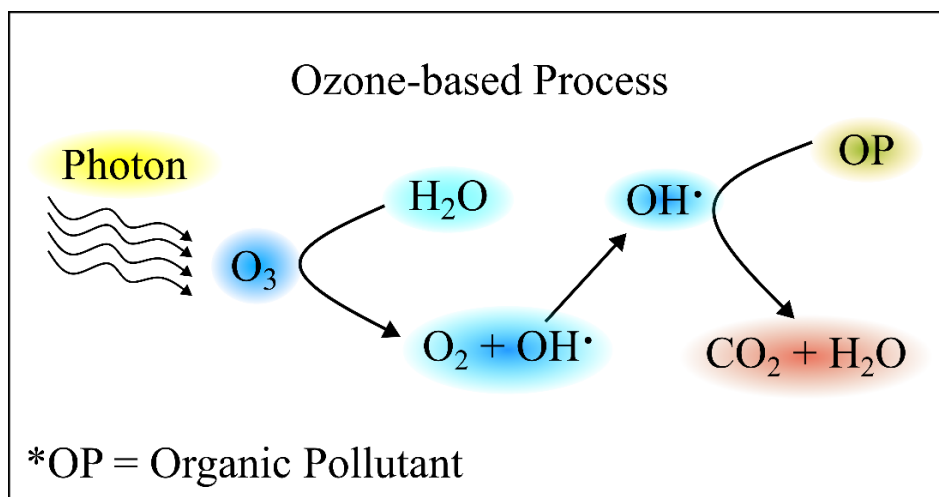


Figure 2.6: Ozone-based process

2.3.3 Fenton Process

In addition, the Fenton process shown in Figure 2.7 utilized Fe_2O_3 in the process of hydroxyl radical formation. Due to the nature of iron (Fe) in changing its oxidation state from Fe^{2+} to Fe^{3+} or vice versa via redox reaction (Equation 2.4), the electrons released from the redox reaction reacted with the H_2O_2 forming hydroxyl radical (Equation 2.5) whereas hydroperoxyl radical ($\text{HO}_2\cdot$) produced resulted from the reaction of Fe^{3+} ion with H_2O_2 (Equation 2.6).

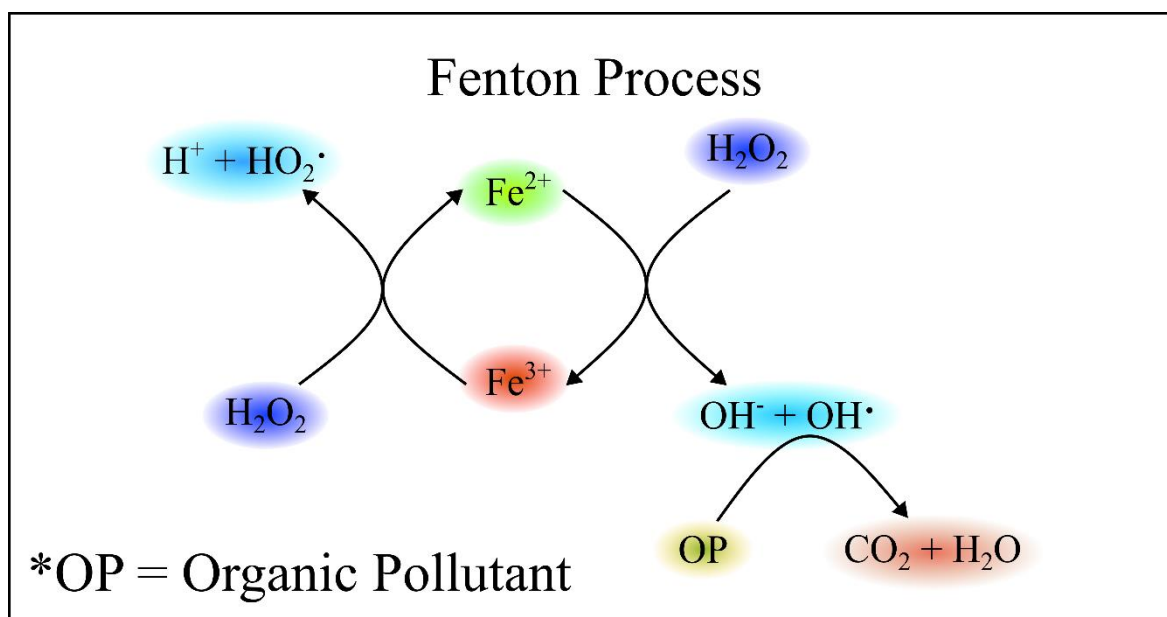


Figure 2.7: Fenton process

2.3.4 Photo-Fenton Process

A photo-Fenton process utilized the Fe_2O_3 photocatalyst for wastewater treatment. Unlike the typical Fenton process, a photo-Fenton process utilized the photocatalytic properties of Fe_2O_3 for radicals generation. As shown in Figure 2.8, the hydroxyl radical produced via photoexcitation of electrons from Fe_2O_3 (Equation 2.7) (Fawzi Suleiman Khasawneh & Palaniandy, 2021). The photogenerated hole from Fe_2O_3 reacted with OH^- ion or H_2O forming hydroxyl radical (Equation 2.8 and Equation 2.9).

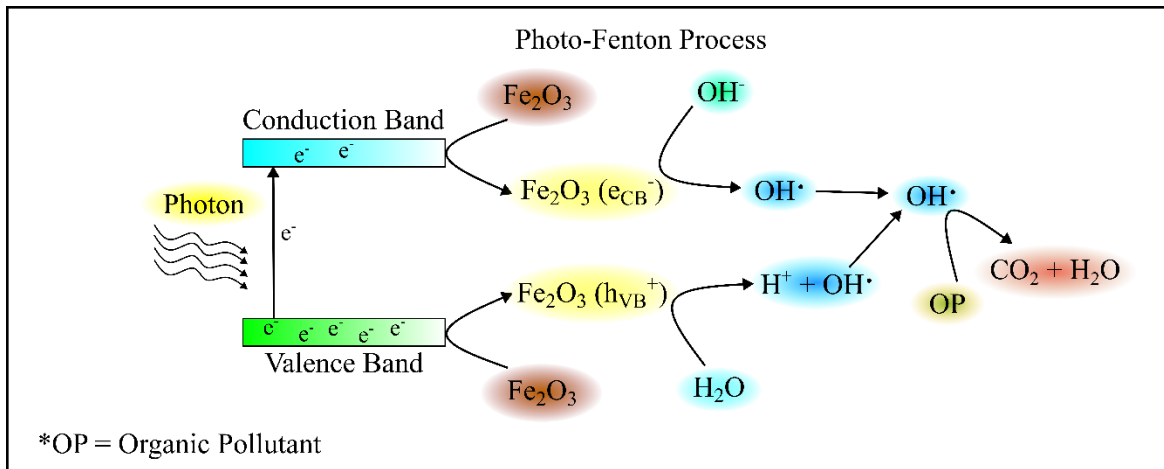


Figure 2.8: Photo-Fenton process

2.3.5 Sonolysis Process

As indicated by Dehghani et al. (2023), in sonolysis process (Figure 2.9), the hydroxyl radical produced through the growth and implosion of microbubbles. During the implosion of microbubbles process, high temperature (5000 K) and pressure (1500 atm) generated which further induced various chemical, mechanical, or physical reactions in water and hence leading to the generation of hydroxyl radical (Equation 2.10).

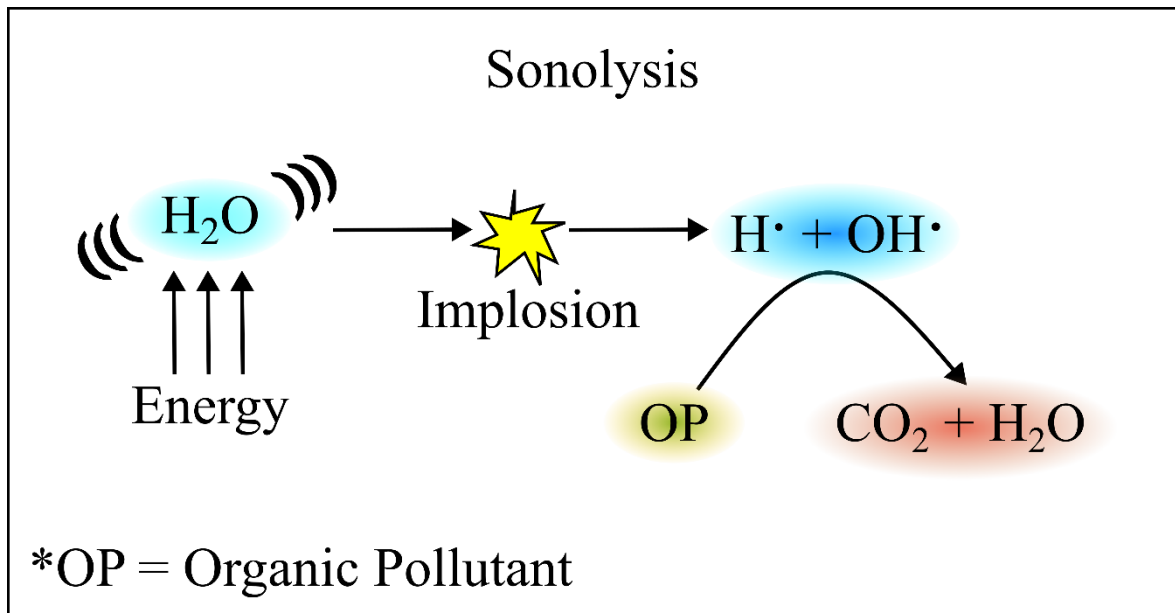
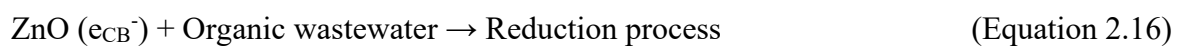


Figure 2.9: Sonolysis process

2.3.6 Photocatalysis Process

By harnessing the advantage of sunlight, the PFC with photocatalysts undergo photocatalysis process which simultaneously convert chemical energy to electrical energy while consuming wastewater as a fuel source (Figure 2.10) (Roy et al., 2023). For example, the most commonly used photocatalyst, ZnO, due to low cost and low toxicity, the general photocatalytic reaction begins with the photoexcitation of ZnO as the electron from the valence band (VB) excited to conductance band (CB) and hence producing electron-hole pair (Equation 2.11) (Wetchakun et al., 2019). The photogenerated hole from ZnO later reacts with water (Equation 2.12) or hydroxide (OH⁻) ion (Equation 2.13) forming hydroxyl radical (OH•) (Al-Mamun et al., 2019). As stated by Al-Mamun et al. (2019), the excited electron from ZnO further reacts with oxygen (O₂) molecules (Equation 2.14) producing superoxide anion (O₂^{•-}). The superoxide anion has two standard redox potential which acts as both reductant [E' (O₂/O₂^{•-}) = 0.33 V] and oxidant [E' (O₂^{•-}/H₂O₂) = 0.93 V] (Andrés et al., 2023; Collin, 2019). According to Mishra et al. (2023), the photogenerated electrons and holes from the photocatalyst also aided in the wastewater degradation through oxidation process (Equation 2.15) and reduction process (Equation 2.16).



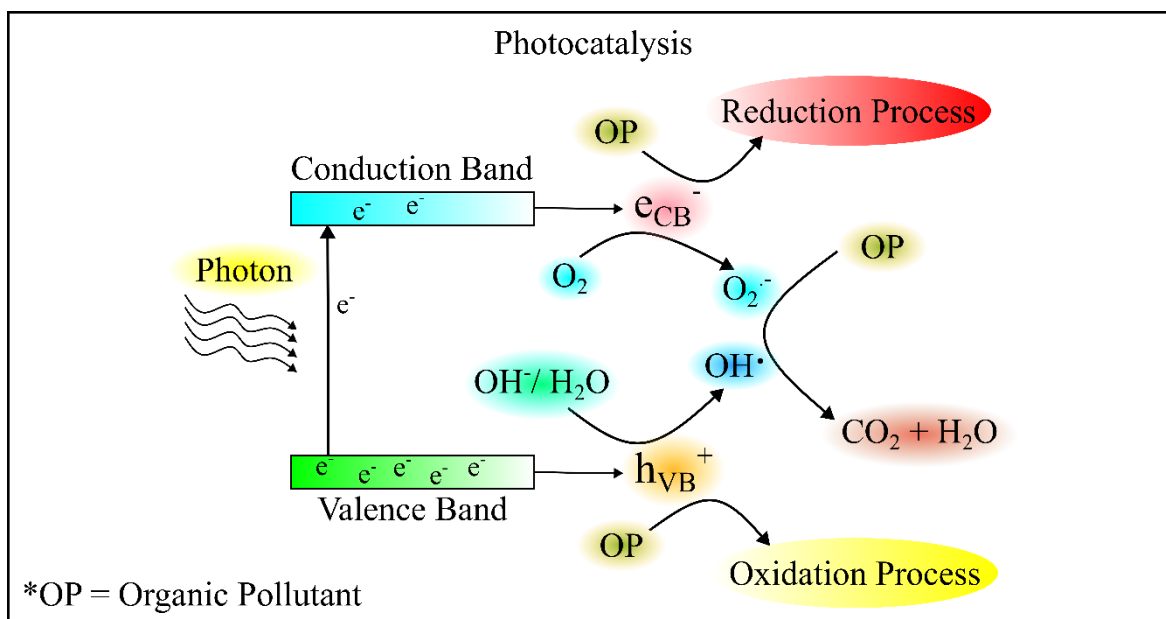


Figure 2.10: Photocatalysis process

2.4 Application of Photocatalysis Process in Wastewater Treatment

Among the materials, semiconductors such as silicon (Si) and germanium (Ge) were typically applied in photovoltaic (PV) applications such as solar cell due to the presence of bandgap. Conductors, generally metals, have overlapped bandgap showed in Figure 2.11(a) where the valence band (VB) and conduction band (CB) overlapped allowing the maximum electron transfer rate between VB and CB hence inducing current formation (Yang et al., 2023). Semiconductors otherwise have separated bandgap shown in Figure 2.11(b) where the bandgap is between 0.5 eV to 3.5 eV. With separated VB and CB, the electrons from VB required heat or light energy for excitation to CB while leaving a hole in VB. Due to the electron-hole pair formation, the semiconductor often applied in various electrical applications such as transistors, integrated circuits (ICs), and microchips, as well as employed in photocatalytic fuel cells. As shown in Figure 2.11(c), insulator was not a

suitable material for photocatalyst with the existence of VB and CB due to bandgap energy more than 3.5 eV which impossible for excitation as it requires huge amount of energy (Yang et al. 2023).

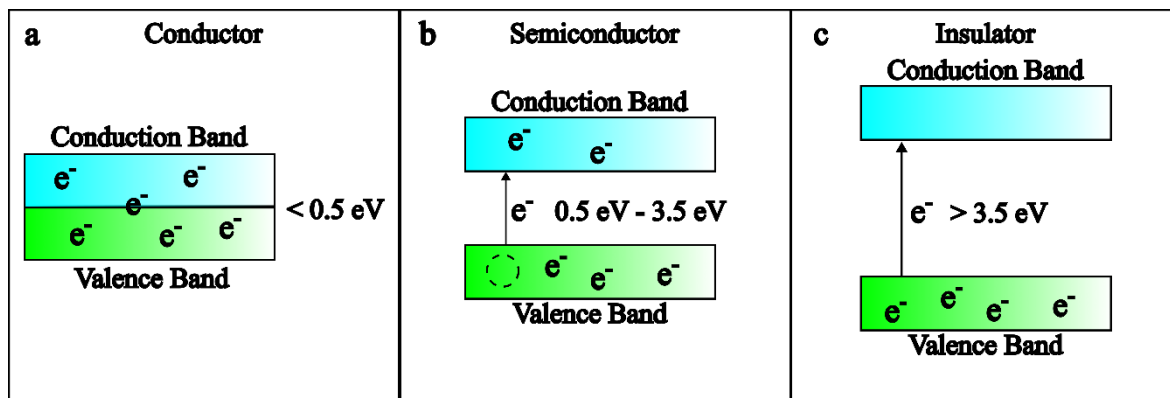


Figure 2.11: Bandgap of conductor, semiconductor, and insulator

Since the discovery of water splitting via TiO_2 by Fujishima and Honda in 1972, the application of transition metal oxide (MO) as photocatalysts had been extensively researched and reviewed (Guillard & Robert, 2024). Due to excellent stability, low cost, TMO electronic structure, light absorption characteristic, photo-corrosion resistance, and charge transport, TMOs are widely applied in solar cell as well as PFC (Krishnan et al., 2024). Transition metal alone is a conductor, thus oxygen as a point defect was introduced to the transition metal to increase the bandgap between VB and CB (Pastor et al., 2022). According to Pastor et al. (2022), the bandgap formation on the transition metal was due to the formation of hybridization of $2p$ orbital from oxygen and the s or d orbital from transition metal. For example, the partially filled valence d orbital, such as Fe_2O_3 , bonded with oxygen $2p$ orbital resulting in lowered bandgap. As stated by Pastor et al. (2022), with the higher oxidation state of transition metal and fewer electrons in d orbitals, the valence electrons from d orbitals strongly bonded to the $2p$ orbitals of oxygen results in increased oxygen-metal hybridization. Therefore, the higher bandgap of ZnO (3.34 eV) was due to the fully filled d

orbitals causing a hindrance in the electrons resulting in weakened oxygen-metal hybridization. As the comparison, Fe_2O_3 only required visible light for strongly activation while ZnO required UV irradiation in which UV only accounted for 4% of total solar spectrum (Suleiman et al., 2021; Hitam & Jalil, 2020). Moreover, the higher energy bandgap of the photocatalyst, the recombination rate of electron-hole pairs increased hence leading to reduction in overall performance as mentioned by Suleiman et al. (2021) and Hitam et al. (2020). Table 2.9 shows the application of ZnO-based photocatalyst in the treatment of various wastewater.

Table 2.9: Application of ZnO-based photocatalyst in wastewater treatment

Photocatalyst	Sources	Removal	Duration	Reference
ZnO	Methylene blue	49% COD removal	60 minutes	Raizada et al. (2019)
ZnO with graphene oxide	Methylene blue	98.5% COD removal	15 minutes	Raizada et al. (2019)
ZnO/BiOBr/C-Dots	Rhodamine blue	100% removal	2 hours	Goktas & Goktas (2021)
ZnO	Methyl orange	98% removal	40 minutes	Ong et al. (2018)
Ag@ZnO/BiOCl	Antibiotic pollutants	80.4% COD removal	80 minutes	Zhang et al. (2021)
ZnO	Spiramycin	95 – 99%	80 minutes	Vignati et al. (2021)

The photocatalyst, ZnO, used in this project due to its non-toxic, abundance, high stability, high charge carrier, and highly active photocatalyst according to Abdullah et al. (2022) and Dihom et al. (2022). However, due to its high bandgap of ZnO at about 3.34 eV, the efficiency of ZnO as photocatalyst is reduced as it requires UV for activation according to Dihom et al. (2022). Hence, modification such as doping for ZnO is necessary to lower the bandgap for performance enhancement.

2.5 Photocatalytic Fuel Cell (PFC)

A photocatalytic fuel cell (PFC) is a type of fuel cell that operates on the principle of photocatalysis process where the chemical reaction was initiated by a light source, for example sunlight or ultraviolet (UV) light on the surface of a semiconductor catalyst. Due to affordability, higher stability, and carbon monoxide (CO) poisoning resistance, metal oxides photocatalyst were commonly utilized in PFC instead of noble metal catalyst (Qian et al., 2020). As the strong oxidizing ability of free radical produced during the photocatalysis reaction, PFC majority applied in wastewater treatment. Generally, a PFC was fabricated in two general designs, particularly single chamber, and dual chamber. A single chamber PFC (Figure 2.12a) was fabricated by placing both electrodes in a single chamber whereas a dual chamber PFC (Figure 2.12b) was fabricated based on the design on standard model of dual chambered proton membrane fuel cell. A dual chamber PFC assembled with two chambers, anode chamber and cathode chamber, which separated by a membrane (Mishra et al., 2021).

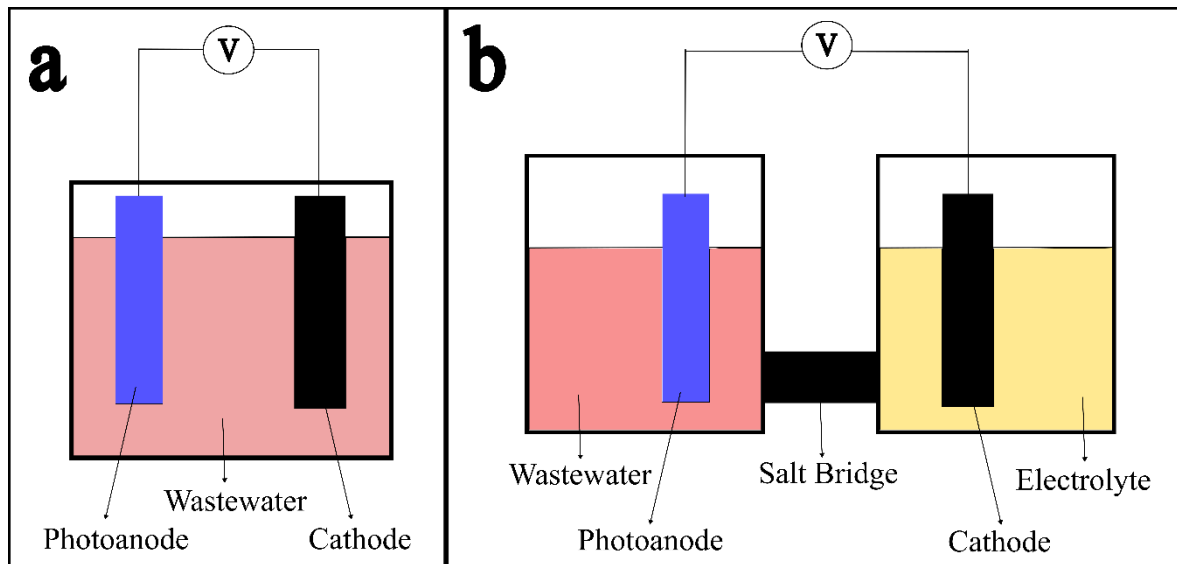


Figure 2.12: Schematic diagram of (a) single chamber and (b) dual chamber PFC

In the case of PFC, the anode chamber in dual chamber PFC is added with organic-based wastewater while the cathode is added with electrolyte solution. In addition, ordinary cathodes such as platinum (Pt), graphite, graphene, or carbon cloth will be used or replaced by a photocathode to pair with a photoanode for enhancing the performance of dual chamber PFC for its degradation rate and power generation. Usually, the *n*-type semiconductor will be used as a photoanode as the photogenerated electron-hole pair are prompt to oxidation according to Oli et al. (2022). While the photogenerated electrons from photocathode which are usually *p*-type semiconductors are majority for reduction as stated by Oli et al. (2022). Due to high stability and highly active photocatalyst characteristics for ZnO, the photoanode made by ZnO-based photocatalyst showed great pollutants removal efficiency as well as power generation (Table 2.10).

Table 2.10: Application of PFC in wastewater treatment

Electrodes	Sources	Removal	Power generation	Duration	Reference
MoO ₃ /ZnO/Zn (Anode) Pt-loaded carbon cloth (Cathode)	Phenol (Anode) CuSO ₄ •5H ₂ O (Cathode)	73.6% COD removal for phenol 85.0% Cu ²⁺ removal	0.005 mW/cm ²	N.A.	Lam et al. (2021)
ZnO/BaTiO ₃ (Anode) Pt-loaded carbon (Cathode)	Reactive red 120	93.67% removal	0.5284 mW/cm ²	N.A.	Ong et al. (2019)
ZnO/Zn (Anode) CuO/Cu (Cathode)	Methyl green	92% colour removal 66% COD removal	0.2203 mA/cm ² 0.0380 mW/cm ²	4 hours	Kee et al. (2018)
ZnO/CF (Anode) Pt-loaded carbon (Cathode)	Batik wastewater	74.4 ± 34.9% COD removal (pH 9) 19.4 ± 8.7% COD removal (pH 3)	985 mW at 250 Ω	6 hours	Khalik et al. (2018)

Table 2.10 Continue

ZnO/Zn (Anode) Pt-loaded carbon (Cathode)	Reactive green 19	92% COD removal 100% colour removal	2.64 mA/cm ² 1.2696 mW/cm ²	8 hours	Lee et al. (2016)
ZnO/Ni (Anode)	Reactive red 120	>95% colour removal	0.0788 ± 0.0033 mA/cm ² 9.1799 ± 0.5142 μW/cm ²	N.A.	Ong et al. (2020)
NiFe ₂ O ₄ /ZnO (Anode) CuO/Cu ₂ O (Cathode)	Rhodamine blue (RhB) Real printing effluent	85.2% colour removal for RhB 60.5% COD removal	0.539 mW/cm ² (RhB) 0.5181 mW/cm ² (Real printing effluent)	N.A.	Lam et al. (2023)
ZnO/Zn (Anode) Pt wire (Cathode)	Palm oil mill effluent (POME)	74% COD removal	35.85 μW/cm ²	N.A.	Moksin et al. (2021)

Based on Table 2.10, with the modification of ZnO such as doping or introducing different photocatalyst has shown major improvement in the wastewater treatment as well as power generation under different conditions of wastewater.

2.6 Photoelectrode Coating Method

The performance of PFC in wastewater treatment and power generation is directly influenced by the quality of the photocatalyst coated on the electrodes. Usually, a thin layer of photocatalyst was applied on the surface of an electrode via hydrothermal method, sol-gel method, ultrasonicate method, dip coating method, and spin coating method. With the coating method applied, the photocatalyst attached to the surface of the electrodes which slightly altered the properties of the electrodes hence forming a photoelectrode.

During the photocatalytic process, the photoelectrodes serve as an active site for the photocatalytic reaction between the pollutants and photocatalyst. Therefore, high specific surface area, uniformity, shape, and size of the photocatalyst is significantly important to ensure high performance of the photoelectrodes. Table 2.11 summarizes the advantages and disadvantages of different commonly used coating method in photoelectrodes production.

Table 2.11: Advantages and disadvantages of different coating method used for photoelectrode production

Coating method	Advantages	Disadvantages	Reference
Hydrothermal	1. Lower reaction temperature 2. Uniform particle shape and size 3. Good dispersion of materials	1. Long reaction time 2. Difficult to control final morphology of photocatalyst 3. Hard to achieve single layer nanosheet	Sankar & Kumar (2021) Zhang et al. (2022)
Sol-gel	1. High porosity 2. High yield production 3. Low processing temperature 4. Cost effective	1. No uniform particle shape and size 2. Require calcination 3. Poor adhesion on the surface 4. Long preparation cycle	Deshmukh et al. (2020) Gu et al. (2020) Jaafar et al. (2020)
Ultrasonicate	1. Uniform particle coating 2. Increase vacancy defect 3. Highly efficient 4. Cost effective	1. Low scalability 2. Requires high frequency acoustic wave 3. Increase cost for better equipment to run experiment	Li et al. (2023) Meroni & Bianchi (2022) Qi et al. (2022) Wang et al. (2023) Qiang et al. (2021)
Dip Coating	1. Controllable coating thickness 2. Uniform particle shape and size 3. Cost effective 4. Large scale production	1. Variance in surface smoothness 2. Poor adhesion on surface 3. High annealing temperature	Butt (2022) Ojstrsek et al. (2022) Ritwik et al. (2022) Wang et al. (2021)
Spin Coating	1. Time efficient 2. Cost effective 3. Uniform coating 4. Controllable coating thickness	1. Difficult to control surface morphology 2. Only for flat surface 3. Special instrument required 4. Material waste	Butt (2022) Lukong et al. (2022) Moreira et al. (2021) Wang et al. (2021)

From this literature review, the application of photocatalyst in wastewater treatment has shown its effectiveness in wastewater degradation and power generation. By utilizing the photocatalytic ability of photocatalyst, organic-rich wastewater including POME, municipal wastewater, pharmaceutical wastewater, and industrial wastewater can be easily treated.

Nevertheless, the conventional wastewater treatment method holds its position as the cost effectiveness in treating large volumes of wastewater. In contrast, the PFC technology currently yet to be implemented in industries as there are several obstacles notably materials used for photoanode fabrication, photocatalyst coating method, and design of PFC as discussed in the literature review, noble metal such as silver (Ag) was included in some of the high performance photocatalyst would increase the operation cost especially when the scale increased.

Therefore, it is worth noticing that several strategies have to be developed to increase the performance of PFC. The strategies include development of methods for photoelectrode fabrication, materials used to synthesize the photocatalyst, and new design for PFC. For example, in this project, dual chamber PFC was used rather than a single chamber PFC. In addition, the development of a new coating method namely electrochemical deposition (ECD) to coat ZnO on Zn plate for photoanode fabrication. All the results of the enhancement of PFC are reported and discussed in detail in Chapter 4 Results and Discussion.

CHAPTER 3

METHODOLOGY

3.1 Materials

The materials used in the projects are ferrous ammonium sulphate [$\text{Fe}(\text{NH}_4)_2\text{SO}_4 \bullet 6\text{H}_2\text{O}$, 99.9%], ferroin indicator, hydrochloric acid (HCl, 37%), methyl red ($\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$, 99.99%), mercury sulphate (HgSO_4 , 99.99%), nitric acid (HNO_3 , 68%), phosphoric acid (H_3PO_4 , 85%), potassium chloride (KCl, 99.99%), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, 99.9%), potassium hydrogen phthalate (KHP) ($\text{C}_8\text{H}_5\text{KO}_4$, 99.9%), silver sulphate (Ag_2SO_4 , 99.99%), sodium carbonate (Na_2CO_3 , 99.97%), sodium chloride (NaCl, 99.98%), sulphuric acid (H_2SO_4 , 96%), zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2$, 99.99%], zinc oxide (ZnO, 99.9%), and zinc foil (Zn, 99.999%) were purchased from Bendosen, Fisher, Fluka, HmbG, JT Baker, Merck, R&M Chemicals, and UniChem in high purity and used without further purification. The sodium hypochlorite (NaClO) solution with concentration at 2.5% was purchased from a local store and used without further purification. Graphite plates with the size of 20 cm^2 and 100 cm^2 with the thickness of 0.25 cm were purchased and used without further treatment.

3.2 ZnO/Zn Photoanode Fabrication

3.2.1 Ultrasonicate Coating Method

For the ultrasonicate coating method, the Zn plate was cut 10.0 cm long by 2.0 cm wide and polished with P400 grit sandpaper. Later, the surface of the polished Zn plate was rinsed with distilled water to remove the zinc dust produced during the polishing process. Then, the Zn plate was immersed in the ZnO suspension and sonicated in a sonicator (Brand: Elma Schmidbauer GmbH, Model: Elmasonic Easy 30H) for at least 1 hour. The ZnO suspension solution was prepared by suspending 1.0 g of ZnO powder per 100 mL of distilled water. After 1 hour of sonicating, the ZnO coated plate was rinsed with distilled water to remove excess ZnO precipitate on the surface and dried in oven for 24 hours at 120 °C.

3.2.2 Electrochemical Deposition (ECD) Coating Method

As for the electrochemical deposition (ECD) method, the Zn plate was cut into 10.0 cm long by 2.0 cm wide then polished with P400 grit sandpaper. After polishing, the surface of Zn plate was rinsed with distilled water to remove the dust produced. Later, the Zn plate was connected to cathode of a direct current (DC) supply unit (Brand: Longwei, Model: LW-K3010D) while a graphite plate was connected to anode. Both electrodes were dipped into 150 mL of 0.05 M $\text{Zn}(\text{CH}_3\text{COO})_2$ solution 10% weight per volume (w/v) KCl salt added as supporting electrolyte to increase the conductivity of the solution. The ECD process was carried out for 5 minutes at 5 V with constant stirring. Then, the coated Zn plate was rinsed with distilled water to remove excess precipitation from the surface. Then ZnO coated plate later dried in oven for at least 2 hours at 120 °C.

3.2.3 ZnO/Zn Photoanode Surface Observation

The surface for both ultrasonicate coating method prepared and ECD coating method prepared ZnO/Zn photoanode was examined by using Field Emission-Scanning Electron Microscope (FE-SEM) (Brand: JOEL, Model: JSM-IT500HR) at 1,000 times, 10,000 times, and 25,000 times magnification. The energy dispersive X-ray (EDX) spectroscopy was performed to confirm the ZnO formation on the surface for ECD method prepared ZnO/Zn photoanode.

3.3 Dual Chamber Photocatalytic Fuel Cell (DCPFC)

3.3.1 Dual Chamber Photocatalytic Fuel Cell (DCPFC) Fabrication

The dual chamber PFC was set up according to Figure 3.1 with two 1.2 L plastic containers connected using a polyvinyl chloride (PVC) tee-connector as a salt bridge. One of the containers was filled with methyl red dye solution as anode chamber while the other was filled with diluted sodium hypochlorite (NaClO) solution as cathode chamber. The salt bridge was filled with approximately 120 mL of 1.0 M KCl solution prepared by dissolving 74.5 g of KCl solution in 1 L of distilled water. The 0.45 μm cellulose acetate membrane filter (Brand: Sartorius Stedim) was placed in between salt bridge and containers acts as a separator for KCl solution, methyl red dye solution, and NaClO solution. The use of cellulose acetate membrane filter was to increase the ion exchange rate between both anode and cathode chamber. Later, the ultrasonicate method prepared ZnO/Zn photoanode was inserted into the anode chamber while the graphite plate was inserted into cathode chamber. The cathode chamber was aerated with an air pump (Brand: Aquaspeed, Model: AP-446). The purpose of aeration in cathode chamber was to increase the amount of dissolved oxygen in

the solution for enhancing the performance of DCPFC. Both electrodes were connected to an external circuit consisting of a variable resistor box (Brand: DoMore, Model:ZX21d) with resistance ranging from 1 Ω to 1,000,000 Ω . A multimeter (Brand: AVOSKY, Model: XL830L) was connected parallel to the circuit to measure the voltage produced from the DCPFC. An LED light bulb (Brand: Wishful 40W, 220 – 240 V, 6500K) was used for illuminating the anode chamber during the experiments.

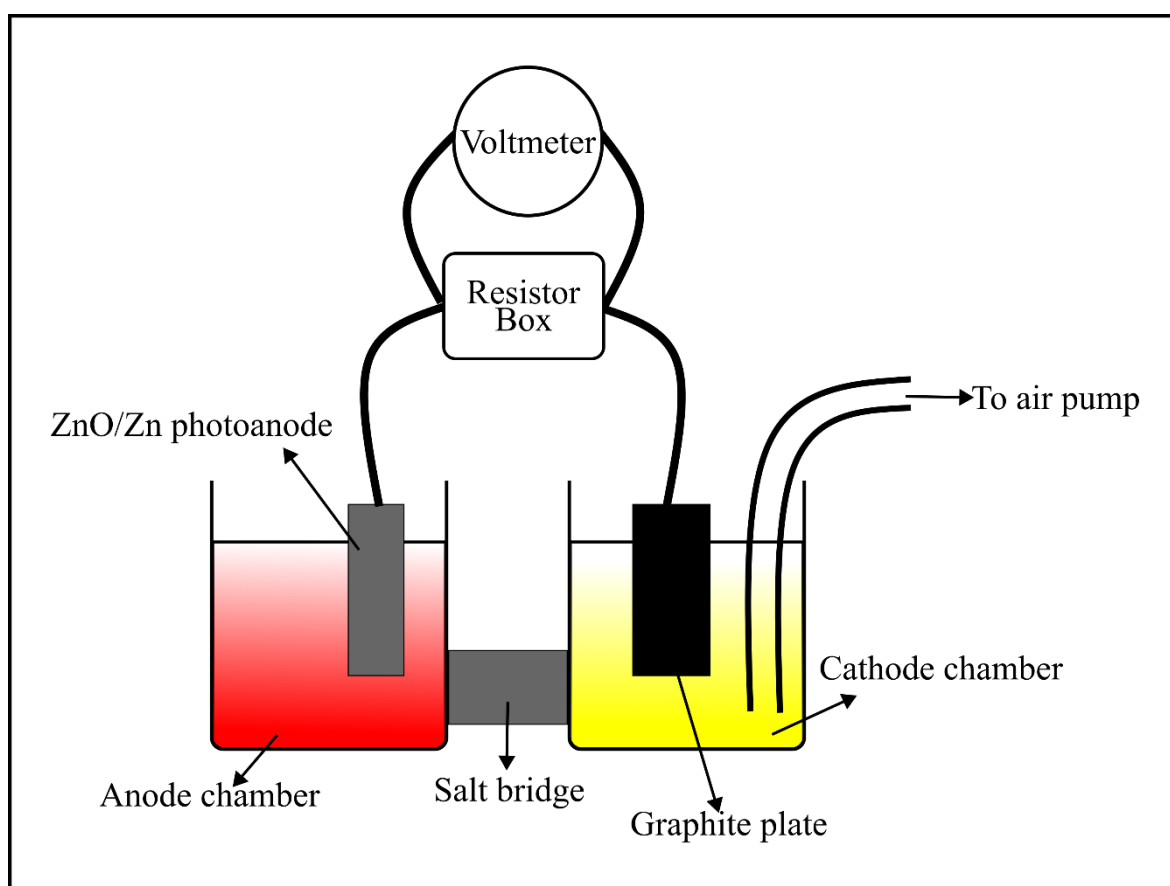


Figure 3.1: Dual chamber photocatalytic fuel cell (DCPFC) setup

3.3.2 Optimization of Dual Chamber Photocatalytic Fuel Cell (DCPFC) Using Methyl Red Dye Solution

The DCPFC was tested for the degradation of organic-based wastewater efficiency and the power generation using methyl red dye solution. The methyl red dye was selected as it was characterized as an azo dye due to the presence of N=N bond in its chemical structure (Figure 3.2). Azo dye is a common dye used in textile industries which can cause detrimental effects to living organisms and interferes with the aquatic ecosystem if left untreated (Ikram et al., 2022). In this experiment, the degradation efficiency of 10 ppm methyl red dye solution as well as power generation of DCPFC using ultrasonicate method and ECD method prepared ZnO/Zn photoanode were accessed under different NaClO solution concentration, pH value of methyl red dye solution, and volume of DCPFC.

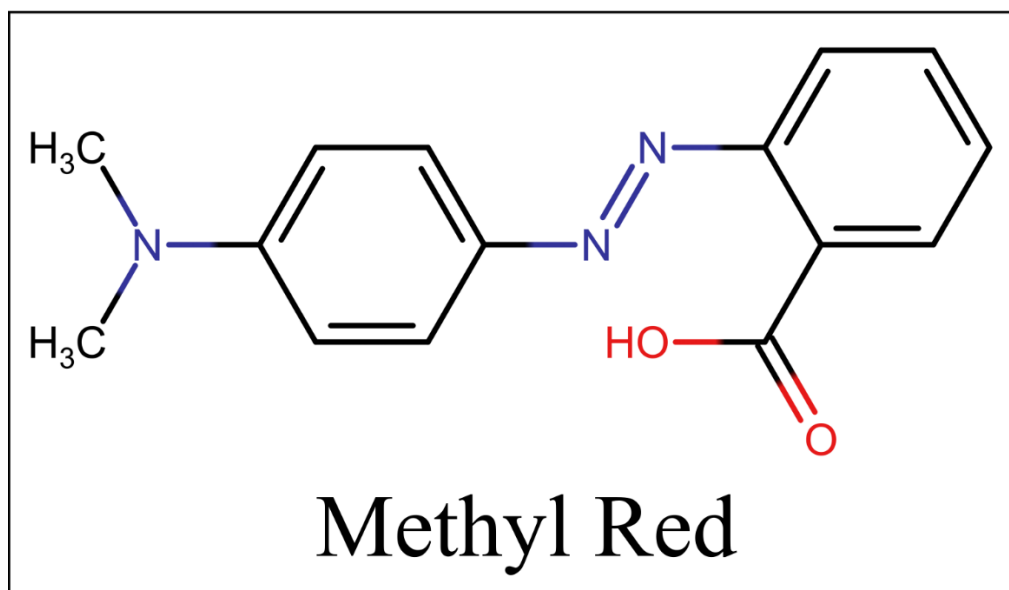


Figure 3.2: Chemical structure of methyl red dye

3.3.2.1 Methyl Red Dye Solution Preparation and Concentration Determination

A 100 mL stock solution of 1000 parts per million (ppm) methyl red dye solution was prepared by dissolving 0.10 g of methyl red powder in 95 mL distilled water and 5 mL of 10% volume per volume (v/v) HCl solution was added to the solution. The addition of HCl to the solution was to ensure all the methyl red powder was fully dissolved. To prepare a 1 L of 10 ppm methyl red dye solution for the DCPFC experiment, 10.0 mL of stock solution was carefully pipetted out and added to approximately 990.0 mL of distilled water.

The methyl red dye solution concentration with the maximum peak at 520 nm was determined by using Ultraviolet – Visible Light (UV-Vis) spectrophotometer (Brand: Agilent, Model: Cary 60 UV-Vis Spectrophotometer). Thus, a standard calibration curve was required for concentration determination. The standard methyl red dye solution was prepared by dissolving 0.01 g of methyl red powder in 95 mL distilled water and 5 mL of 10% v/v HCl solution where added to ensure the complete dissolve of methyl red powder, which the final concentration of the methyl red dye solution was 100 ppm. For the preparation of 10 mL of 2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm, and 12 ppm solution from 100 ppm stock solution, the volume required is shown in Table 3.1. The standard calibration solution was freshly prepared before the analysis as the methyl red dye tends to degrade when exposed to light, hence affecting the accuracy and precision of analysis.

Table 3.1: Preparation of standard methyl red dye solution

Concentration	Volume pipetted	Distilled water added	Final Volume
2 ppm	0.2 mL	9.8 mL	10.0 mL
4 ppm	0.4 mL	9.6 mL	10.0 mL
6 ppm	0.6 mL	9.4 mL	10.0 mL
8 ppm	0.8 mL	9.2 mL	10.0 mL
10 ppm	1.0 mL	9.0 mL	10.0 mL
12 ppm	1.2 mL	8.8 mL	10.0 mL

After the calibration curve of the known methyl red dye concentration against the absorbance was plotted, a general equation was obtained as shown in Equation 3.1.

$$y = mx \quad (\text{Equation 3.1})$$

Where y represented as the absorbance obtained, m is the gradient of calibration curve, x represented as the concentration of methyl red dye solution in ppm.

3.3.2.2 Concentration of Sodium Hypochlorite (NaClO) Solution

The design of PFC is a dual chamber PFC, hence the concentration of NaClO solution in cathode chamber directly affected the performance of a DCPFC. To investigate the effect of concentration of NaClO solution in the cathode chamber, the experiment was carried out by filling the anode chamber with 1 L of 10 ppm methyl red dye solution at pH 4, whereas the cathode chamber was filled with diluted NaClO solution which prepared according to Table 3.2.

Table 3.2: Preparation of different concentration of NaClO solution

NaClO : Distilled Water	Amount of NaClO Solution	Amount of Distilled Water	Final Concentration
1:8	125 mL	875 mL	125 mL/L
1:4	250 mL	750 mL	250 mL/L
3:8	375 mL	625 mL	375 mL/L

The ZnO/Zn photoanode prepared with ultrasonicate method was placed in the anode chamber while the graphite plate was placed in the cathode chamber. The degradation reaction of methyl red dye solution started immediately after both electrodes were inserted into the anode and cathode chamber. The power generated from the DCPFC was recorded using a multimeter as voltage (V) for every hour at 100 Ω resistance until the methyl red dye solution

was completely degraded. The time taken for the methyl red dye solution to complete degradation was recorded. The experiment was repeated for each NaClO solution concentration. Furthermore, the experiment was repeated for at least 3 times by replacing the ultrasonicate method prepared ZnO/Zn photoanode to ECD method prepared ZnO/Zn photoanode to compare its degradation efficiency and power generation in different concentration of NaClO solution.

3.3.2.3 pH Value of Methyl Red Dye Solution

The experiment was then performed by altering the pH value of the 10 ppm methyl red dye solution to pH 3, pH 4, pH 5, pH 7, and pH 8 while the concentration of NaClO solution was maintained at 250 mL/L. The pH value of the 10 ppm methyl red dye solution was determined using a bench top pH meter (Brand: Thermo Scientific, Model: Eutech pH 700).

The acid used for the adjustment of the pH value of methyl red dye solution was prepared by adding 10 mL of 37% HCl concentrated solution into 90 mL of distilled water, where the concentration of the HCl solution was 10% volume by volume (v/v). The base solution of Na₂CO₃ was prepared by dissolving 10 g of Na₂CO₃ powder in 90 mL of distilled water, where the final concentration of Na₂CO₃ solution is 10% weight by volume (w/v).

The anode chamber of DCPFC was filled with 1 L of 10 ppm of pH 3 methyl red dye solution while the cathode chamber was filled with 1 L of 250 mL/L NaClO solution. The power generation from DCPFC using ultrasonicate method prepared ZnO/Zn photoanode was recorded for every hour using a multimeter as voltage (V). The experiment was repeated at least 3 times for each pH value. Then, the ultrasonicate method prepared ZnO/Zn

photoanode was replaced by the ECD method prepared ZnO/Zn photoanode to compare the degradation efficiency and power generation for DCPFC under different pH values.

3.3.2.4 Volume of Dual Chamber Photocatalytic Fuel Cell (DCPFC)

The experiment continued by adjusting the volume of DCPFC from 1 L to 2 L and 4 L while maintaining the 10 ppm methyl red dye solution at pH 4 and the concentration of NaClO solution at 250 mL/L.

For the volume of DCPFC, the initial 1 L DCPFC was scaled up to 2 L and 4L in the volume of anode chamber and cathode chamber. With the increase of both anode and cathode chamber, the size of ZnO/Zn photoanode was increased to 28 cm² for 2 L volume and 56 cm² for 4 L volume of methyl red dye solution. While the size of the graphite plate was increased from 20 cm² to 40 cm² for 2 L and 80 cm² for 4 L. The experiment was repeated at least 3 times for each volume of DCPFC. The determination of degradation efficiency and power generation of DCPFC for different volumes was repeated by replacing the ultrasonic method prepared ZnO/Zn photoanode with ECD method prepared ZnO/Zn photoanode.

3.4 Optimization of Dual Chamber Photocatalytic Fuel Cell (DCPFC) With Palm Oil Mill Effluent (POME)

For the optimization of DCPFC with POME solution, the solution in anode chamber was filled with diluted POME solution obtained from the second clarifier tank while the cathode chamber was filled with 250 mL/L NaClO solution. In this experiment, the photoanode used was ECD method prepared ZnO/Zn photoanode. To investigate the performance of DCPFC using POME solution under different conditions, the pH, concentration, and volume of POME solution were altered.

3.4.1 Chemical Oxygen Demand (COD) Concentration Determination of Palm Oil Mill Effluent (POME)

3.4.1.1 American Society of Testing and Material (ASTM) Method of Chemical Oxygen Demand (COD) Determination

The chemical oxygen demand (COD) of POME solution was determined using ASTM 5220D, namely closed reflux, colorimetric method. The digestion solution for COD determination was prepared by dissolving accurately 10.216 g of $K_2Cr_2O_7$ and 33.3 g of $HgSO_4$ in 167 mL of concentrated H_2SO_4 in a 1 L volumetric flask then the solution was topped up with distilled water to the 1 L marking on the volumetric flask. To ensure all the solids were fully dissolved, the solution was sonicated for at least 30 minutes. Since the mixing process of digestion solution was extremely exothermic, the digestion solution was cooled to room temperature before used. The digestion solution was prepared weekly to ensure its accuracy. In addition to the digestion solution, sulphuric acid reagent (SAR) was

prepared by adding 5.5 g of Ag_2SO_4 for every kg of concentrated H_2SO_4 weight. The SAR solution was stirred for at least 1 day for homogenization.

The standard COD calibration solution was prepared by dissolving 0.851 g of KHP powder which previously dried in oven for 2 hours at 120 °C in 1 L volumetric flask. The prepared standard calibration KHP solution has the theoretical COD concentration of 1,000 mg/L. The prepared KHP standard calibration solution was used as stock solution for prepared of lower COD concentration standard solution. The lower concentration COD standard solution was prepared according to Table 3.3 with the final volume of 10 mL. Similar to digestion solution, the standard solution was prepared weekly to ensure its accuracy.

Table 3.3: Preparation of different concentrations of KHP standard calibration solution from 1,000 mg/L stock solution

Desired Concentration	Volume Pipetted from Stock Solution	Distilled Water	Total Volume
200 mg/L	2 mL	8 mL	10 mL
400 mg/L	4 mL	6 mL	10 mL
600 mg/L	6 mL	4 mL	10 mL
800 mg/L	8 mL	2 mL	10 mL

It is worth highlighting that the micropipette used for COD determination must be checked using a calibrated balance scale prior being used. This is because the volume transferred by the micropipette may vary from the actual desired volume after certain usage.

For COD concentration determination, the dimension of digestion vessels used was 16 mm x 100 mm according to ASTM 5220D. About 1.5 mL of freshly prepared digestion solution was pipetted precisely using a calibrated micropipette (Brand: Eppendorf) into the digestion vessel followed by 2.5 mL of samples. Then, 3.5 mL of SAR solution was added

to the mixture. The solution was inverted gently 3 to 4 times to ensure the solution was fully mixed. Shaking of solutions was prohibited as this will induce precipitation. After that, the digestion vessel was inserted into the COD reactor (Brand: Hanna Instrument, Model: HI839800) which was pre-heated to 150 °C. The digestion process was carried out for 2 hours at 150 °C. Later, the digestion vessel was removed from the COD reactor and cooled to room temperature before analysis.

Since the ASTM 5220D method of COD determination was performed using UV-Vis spectrophotometer, a standard calibration curve was required before sample analysis. A standard calibration curve was plotted by analyzing the known COD concentration of KHP standard calibration solution to obtain its specific absorbance at 420 nm and 600 nm. The standard calibration solution was prepared according to Table 3.3 from 1,000 mg/L COD concentration stock solution. However, different instruments used resulted in a slight deviation in wavelength obtained compared to ASTM 5220D method is inevitable. Therefore, the absorbance at 420 nm, 440 nm, 600 nm, and 610 nm were taken and an ANOVA Sidak's multiple comparison test as well as Two Tail t-test were performed to determine the suitable wavelength used for COD concentration determination.

After the standard calibration curve was plotted, the equation and regression of the curve was obtained. The standard calibration process was repeated if the regression obtained was less than 0.95 and the standard deviation is more than 5%. If the problem persists, the previously prepared digestion solution, SAR solution, and KHP standard calibration solution were discarded, a new solution will be prepared. After the standard calibration curve was obtained, the COD concentration of POME solution can be determined by calculating from the equation obtained by using the absorbance of digested POME solution in the digestion solution.

3.4.1.2 American Public Health Association (APHA) Method of Chemical Oxygen Demand (COD) Determination

To ensure the reliability of ASTM 5220D method, the traditional American Public Health Association (APHA) method, namely closed reflux, titration method was performed to compared with ASTM 5220D. The digestion solution was prepared by dissolving 14.709 g of $K_2Cr_2O_7$ with distilled water in 1 L volumetric flask. About 33.3 g of $HgSO_4$ was added into the 1 L volumetric flask followed by 167 mL of concentration H_2SO_4 . Later, the solution was topped up to the 1 L marking with distilled water. The solution was sonicated for at least 30 minutes to ensure all the solids were completely dissolved. The prepared digestion solution has a theoretical molarity of 0.05 M according to APHA method.

The ferrous ammonium sulphate (FAS) solution was prepared by dissolving 3.92 g of FAS powder in 1 L volumetric flask with distilled water. About 20 mL of concentrated H_2SO_4 was added to the solution. The prepared FAS solution has a theoretical molarity of 0.01 M. The prepared FAS solution was standardized using the prepared digestion solution to obtain the exact molarity. The standardization of FAS solution was performed by adding 5 mL of digestion solution to 10 mL of distilled water in an Erlenmeyer flask. About 1 to 2 drops of ferroin indicator were added to the solution and immediately starts the titration. The molarity of FAS solution was calculated based on Equation 3.2.

$$\text{Molarity of FAS, } M = \frac{\text{Volume of Digestion Solution}}{\text{Volume of FAS Solution used}} \times 0.1 \text{ (Equation 3.2)}$$

To compare with the ASTM 5220D, the COD concentration of 200 mg/L was selected as the standard reference for both methods. About 1.5 mL of digestion solution was added to the digestion vessel followed by 2.5 mL of 200 mg/L KHP standard calibration solution and 3.5 mL of SAR solution. The solution was inverted gently several times to

ensure the solution was fully mixed. Later, the digestion vessel was inserted into the COD reactor and digested for 2 hours at 150 °C. After the digestion process, all the solution in the digestion vessel were transferred into an Erlenmeyer flask followed by 1 drop of ferroin indicator, and immediately starts the titration with FAS solution. The titration stopped when the colour of the solution changed from red to pale-blue and the volume of FAS solution used was recorded. The COD concentration was calculated with Equation 3.3. According to Equation 3.3, the volume of FAS solutions used for blank solution sample titration was required. The blank solution sample was prepared by replacing the 2.5 mL of 200 mg/L KHP standard calibration solution with distilled water and titrated with FAS solution to obtain the volume of FAS solution used for the blank sample.

$$\text{COD, mg/L} = \frac{(A-B) \times M \times 8000}{\text{Volume of sample (mL)}} \quad (\text{Equation 3.3})$$

Where A is the volume of FAS used for blank (mL), B is the volume of FAS used for sample (mL), and M is the molarity of the FAS solution (M).

3.4.2 Degradation Efficiency and Power Generation of Dual Chamber Photocatalytic Fuel Cell (DCPFC) Using Palm Oil Mill Effluent (POME) Solution

3.4.2.1 pH of Palm Oil Mill Effluent (POME) Solution

The pH of the 25% concentration of POME solution in the anode chamber of DCPFC was adjusted to pH 3, pH 4, and pH 5 using 10% v/v H_2SO_4 solution and 10% w/v Na_2CO_3 solution to investigate the degradation efficiency as well as power generation. Besides the pH adjusted POME solution, the degradation efficiency and power generation for unadjusted POME solution have also been investigated.

In the DCPFC, the anode chamber was filled with 1 L of pH adjusted POME solution while the cathode chamber was filled with 1 L of 250 mL/L NaClO solution. For the power generation of DCPFC, the voltage output was recorded for 8 hours at 1 hour interval. As for the degradation efficiency, the POME solution sample was collected for 8 hours at 1 hour interval. Then, the collected POME solution samples were digested in the digestion solution for COD concentration determination. The experiment was repeated at least 3 times for each pH value of the POME solution while maintaining the concentration of NaClO solution at 250 mL/L.

3.4.2.2 Concentration of Palm Oil Mill Effluent (POME) Solution

To investigate the effects of concentration of POME solutions to the degradation efficiency and power generation, the concentration of POME solution from second clarifier tank was adjusted in anode chamber while maintaining the pH of the solution at pH 4 and 250 mL/L of NaClO solution concentration in cathode chamber. The POME solution was diluted to 25% v/v by adding 250 mL of raw POME solution to 750 mL of distilled water.

Similar to 25% v/v of POME solution concentration, the 50% and 75% v/v POME solution concentration were adjusted by adding 500 mL and 750 mL of raw POME solution to 500 mL and 250 mL of distilled water, respectively.

The COD concentration and power generation for DCPFC of concentration adjusted POME solution was collected for 8 hours at 1 hour interval. The experiment was conducted repeatedly at least 3 times to ensure the accuracy of the result obtained.

3.4.2.3 Volume of Palm Oil Mill Effluent (POME) Solution

The volume of the POME solution was adjusted from 1 L to 2 L and 4 L while maintaining the pH of the POME solution at pH 4 and 25% v/v POME solution concentration. To prepare 2 L and 4 L of 25% v/v POME solution concentration, about 500 mL and 1 L of raw POME solution was added to 1.5 L and 3 L of distilled water, respectively. As the volume of the POME solution increased, the size of the ECD method prepared ZnO/Zn photoanode increased from 14 cm² to 28 cm² then finally to 56 cm². The data for power generation and degradation efficiency was recorded at 1 hour interval for 8 hours. The experiment for each volume was repeated at least 3 times with ECD method prepared ZnO/Zn photoanode.

3.4.2.4 The Anion Additives to Palm Oil Mill Effluent (POME) Solution

The next experiment was studying the impact of different anions added in the anode chamber to the power generation and degradation efficiency of DCPFC. Different acids produce different anions when dissociated in water. Hence, the acid used for pH adjustment for POME solution was changed from 10% v/v H₂SO₄ solution to 10% v/v HNO₃ solution, 10% v/v H₃PO₄ solution, and 10% v/v HCl solution. The different 10% v/v acid solution was prepared as shown in Table 3.4.

Table 3.4: Preparation of 10% v/v acids

Acids	Volume from concentrate acids	Distilled water added	Anion produced when dissociated
H ₂ SO ₄	10 mL	90 mL	SO ₄ ²⁻
HNO ₃	10 mL	90 mL	NO ₃ ⁻
H ₃ PO ₄	10 mL	90 mL	PO ₄ ³⁻
HCl	10 mL	90 mL	Cl ⁻

The idea of this experiment was initiated by single chamber PFC where different performance resulted when different salts were used as the electrolyte. In other words, the impact of anion present in the anode chamber was investigated in this experiment. The conditions used were adopted from the optimal conditions from the previous experiments, namely, pH of the POME solution was adjusted to pH 4 using respective acids, the concentration was fixed at 25% v/v and the NaClO solution concentration was fixed at 250 mL/L in cathode chamber. The degradation efficiency and power generation of DCPFC using ECD method prepared ZnO/Zn photoanode were conducted for 8 hours. Both the degradation efficiency and power generation from DCPFC was recorded at 1 hour interval for 8 hours.

3.5 Power Generation from Dual Chamber Photocatalytic Fuel Cell (DCPFC)

The power generation from the DCPFC was calculated based on the voltage reading obtained from the multimeter connected parallelly to the DCPFC. The current (mA) and power (W) obtained from the DCPFC were calculated based on the voltage reading at specific resistance using Equation 3.4 and Equation 3.5, respectively.

$$I = \frac{V}{R}$$

(Equation 3.4)

Where V represents as voltage (V) obtained from the multimeter and R represents as resistance (Ω).

$$P = VI \quad \text{(Equation 3.5)}$$

Where P represents power (W).

As for the power density (W/cm^2), the calculated power obtained from the DCPFC were divided by the surface area of the photoanode used, which in this project is about 14 cm^2 (Equation 3.6).

$$\text{Power density} = \frac{W}{\text{surface area of photoanode}} \quad \text{(Equation 3.6)}$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 ZnO/Zn Photoanode

The degradation efficiency and power density obtained from DCPFC can be explained through the coating method as different coating method produced different crystal structures. The ECD method and ultrasonic method prepared ZnO/Zn photoanode was observed under FE-SEM and the results are shown in Figure 4.1.

Figure 4.1(a) shows the surface structure of freshly prepared ZnO/Zn photoanode by ultrasonic method at 1,000 times magnification. Several types of ZnO structure can be observed from Figure 4.1(a) are in the shape of rock, flakes, and hexagonal rod structures (Lam et al., 2021). The hexagonal rod ZnO structure can be observed clearly under 10,000 times magnification [Figure 4.1(b)] alongside with rock shape ZnO structure. Meanwhile Figure 4.1(c) shows the surface of ECD method prepared ZnO/Zn photoanode at 1,000 times magnification. The surface of ZnO/Zn photoanode mostly shown flower-like or petal-like shape structures (Qiao et al., 2019). A clearer image of the structure can be observed under 10,000 times magnification as shown in Figure 4.1(d). Besides, Figure 4.2 shows the EDX analysis for ECD method prepared ZnO/Zn photoanode. The two peak intensities at 0.53 and 1.01 keV indicated the oxygen (O) and zinc (Zn) formation on the ZnO/Zn photoanode surface (Figure 4.2).

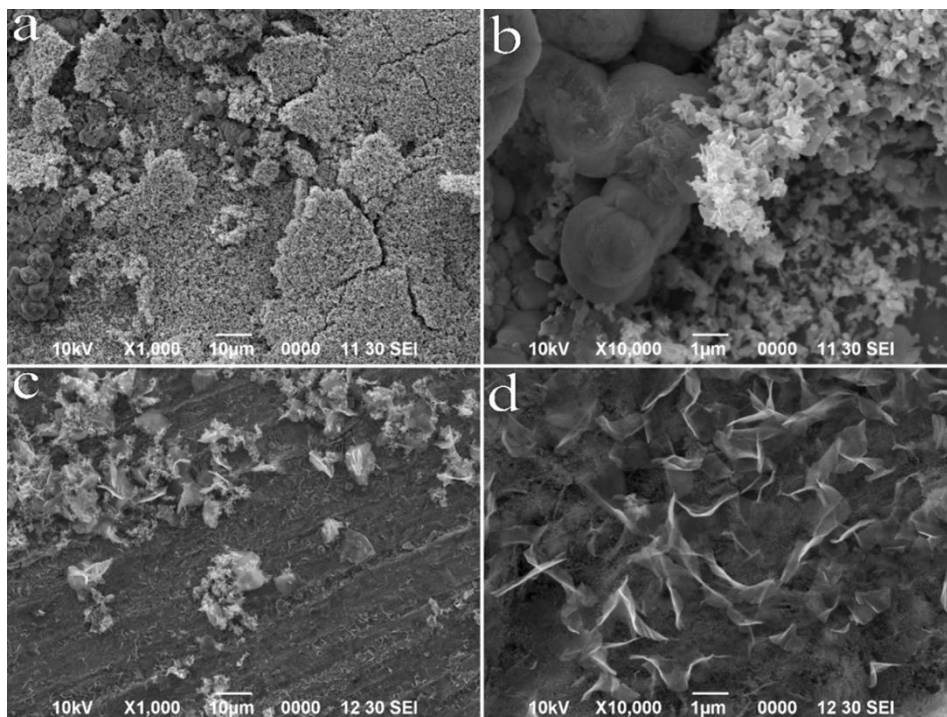


Figure 4.1: Surface structure of ZnO/Zn photoanode using (a), (b) ultrasonic method, and (c), (d) ECD method under 1,000 times and 10,000 times magnification, respectively

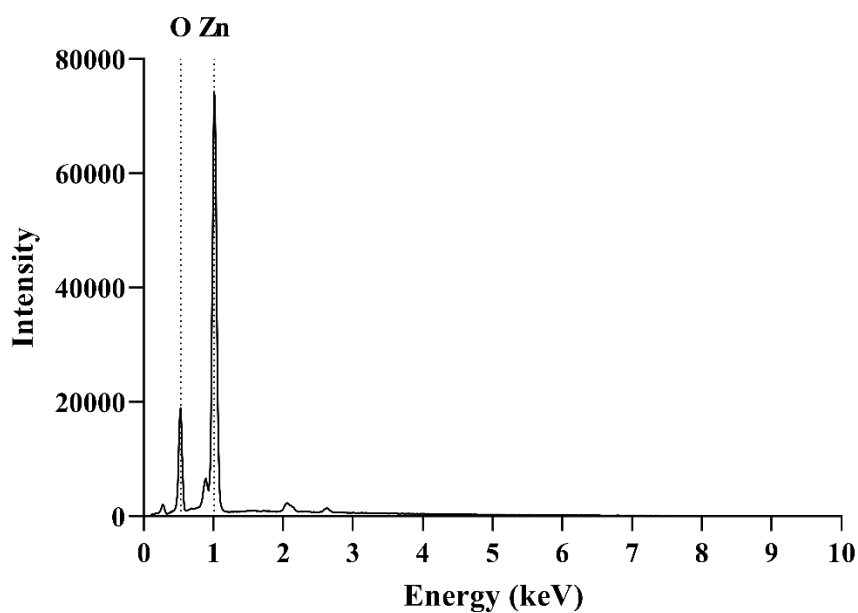


Figure 4.2: EDX spectrum for ZnO/Zn photoanode prepared by ECD method

The EDX elemental analysis showed that the composition of ECD method prepared ZnO/Zn photoanode comprises of $81.08 \pm 9.12\%$ of Zn and $15.09 \pm 0.04\%$ of O (Figure 4.3).

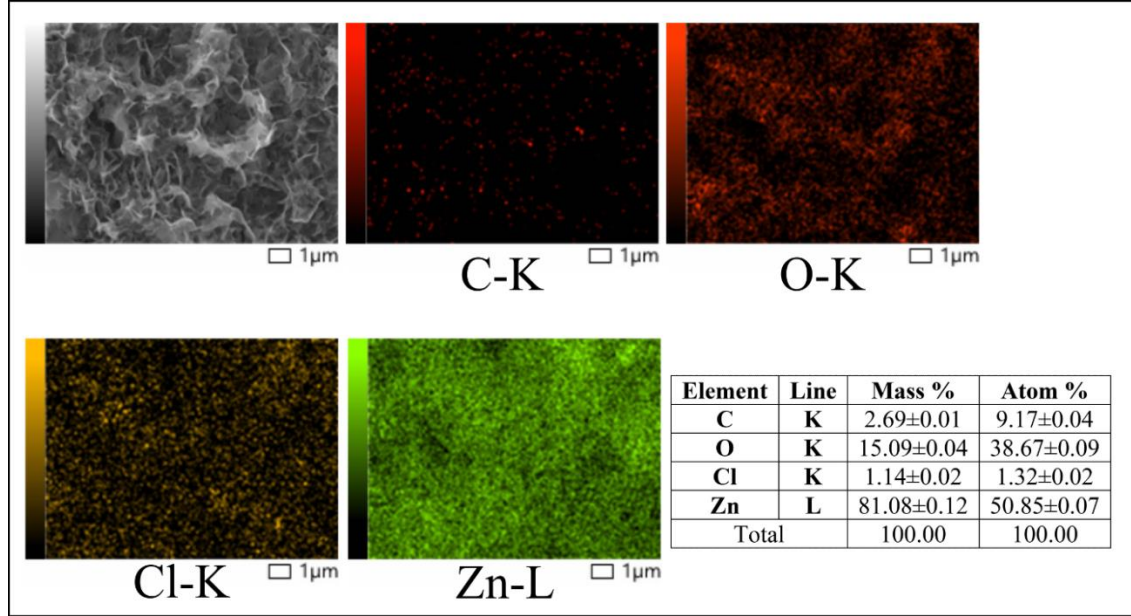
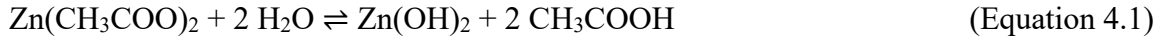


Figure 4.3: Elemental map for ZnO/Zn photoanode fabricated using ECD method

Under ultrasonic method, the formation of different ZnO structure on the Zn plate surface was probably due to the random collision between each ZnO particles during the ultrasonic process. Thus, the specific effective surface area reduces due to different structure formation and hence decreases the effective adsorption on the photoanode surface. Unlike ultrasonic method, the ZnO forms on the surface of Zn plate were electrochemically grew through the ECD method. The $\text{Zn}(\text{CH}_3\text{COO})_2$ solution acts as the precursor for the growth of ZnO particles. Through the ECD coating process, $\text{Zn}(\text{CH}_3\text{COO})_2$ reacts with water producing zinc hydroxide, $\text{Zn}(\text{OH})_2$, and acetic acid, CH_3COOH (Equation 4.1). Then, $\text{Zn}(\text{OH})_2$ further decomposed to ZnO and H_2O (Equation 4.2) (Henni et al., 2019; Romero et al., 2016).



By comparing methods of ZnO/Zn photoanode preparation, the ultrasonicate method comprised of 3 types of ZnO microstructure [Figure 4.1(b)] while ECD method comprised only one type of microstructure [Figure 4.1(d)]. The uneven coating of ZnO using ultrasonicate method has decreased the surface area to volume (SA/V) ratio according to Li et al. (2020) and Pattadar et al. (2019) hence directly affects the performance of DCPFC in degradation efficiency and power generation. In contrast to the ultrasonicate method, the ECD method prepared ZnO/Zn photoanode provided an even coating, which believed that enhanced the power generation and degradation of organic pollutants in wastewater.

4.2 Factors Affect the Degradation Efficiency and Power Generation in a Dual Chamber Photocatalytic Fuel Cell (DCPFC)

4.2.1 Effect of pH Value on Methyl Red Dye Solution

In order to access the removal efficiency of 10 ppm methyl red dye solution using ultrasonicate method and ECD method prepared ZnO/Zn photoanode in dual chamber PFC, the pH of the 10 ppm methyl red dye solution was adjusted to pH 3, pH 4, pH 5, pH 7, and pH 8 with the concentration of NaClO solution in cathode chamber at 250 mL/L. Figure 4.4 show the highest power density (mW/cm^2) of DCPFC with ZnO/Zn photoanode prepared via ultrasonicate method and ECD method, respectively, at different pH values.

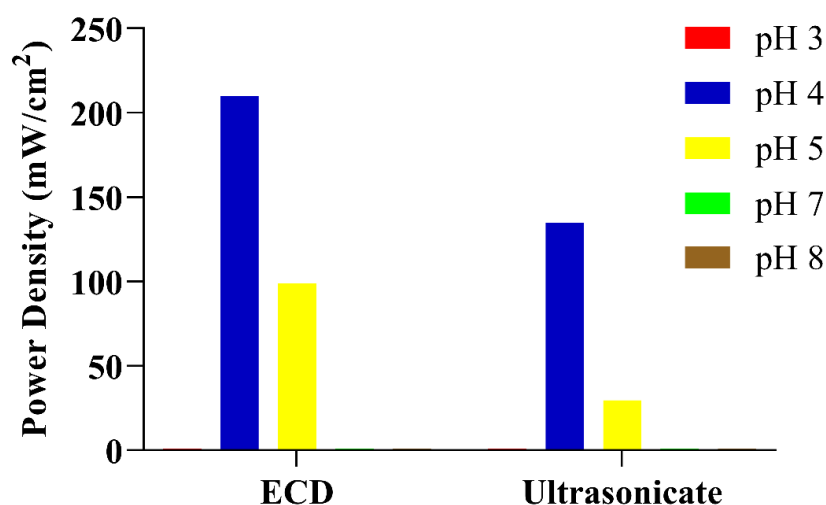


Figure 4.4: Power density obtained from photoanode prepared via ECD method and ultrasonic method under different pH value of 10 ppm methyl red dye solution.

Table 4.1 summarizes the increment percentage of ECD method prepared ZnO/Zn photoanode compared to ultrasonic method prepared photoanode. By using the ECD method, the power generation from the DCPFC drastically increased compared to the ultrasonic method. The increment percentage of power density for ECD method prepared ZnO/Zn photoanode compared to ultrasonic method at pH 4 is 55.81% whereas at pH 5, the increment in power density is 233.94%. However, the power density for pH 7, and pH 8 were not available as the power generation from the DCPFC is too low rendering it unable for detection. As for the pH 3, no result was determined as the ZnO/Zn photoanode was checked using FE-SEM and found that the ZnO as well as Zn plate was dissociated (Figure 4.5). The drastic increase in power density as shown in Table 4.1 was probably due to the effect of pH of methyl red dye solution and the surface area of ZnO/Zn photoanode prepared by ECD method.

Table 4.1: Power density increment percentage of DCPFC using ECD method and ultrasonic method prepared ZnO/Zn photoanode

pH	NaClO solution concentration	Power Density (mW/cm ²)		Increment %
		ECD method	Ultrasonic method	
3	250 mL/L	N.A.	N.A.	N.A.
4	250 mL/L	209.83	134.67	55.81
5	250 mL/L	98.85	29.601	233.94
7	250 mL/L	N.A.	N.A.	N.A.
8	250 mL/L	N.A.	N.A.	N.A.

N.A. = Not Available

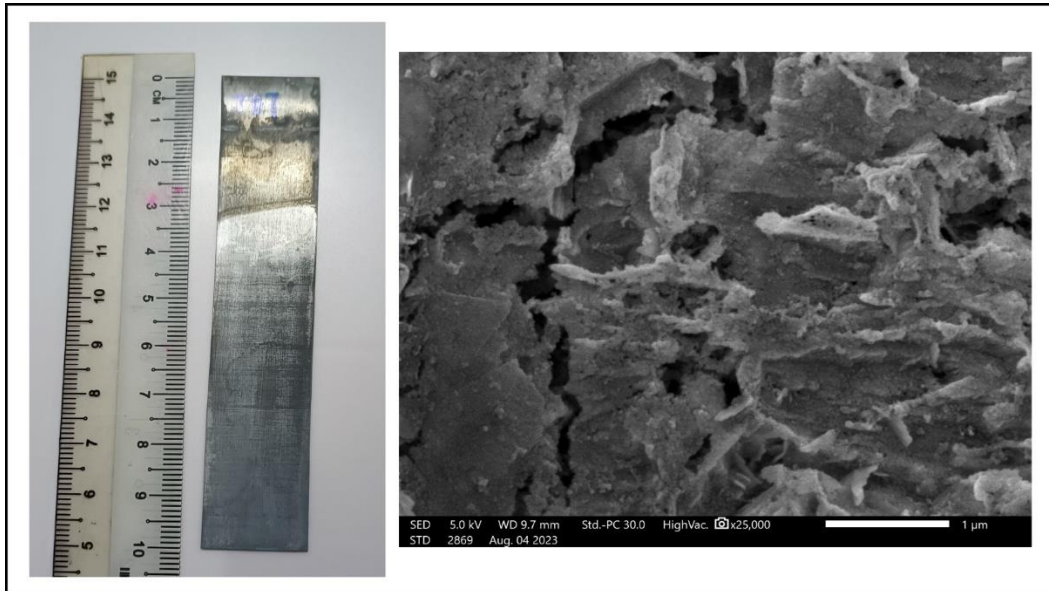


Figure 4.5: Condition of ZnO/Zn photoanode after used under pH 3

The pH value of the methyl red dye solution in anode chamber greatly affected the power generation of the DCPFC as shown in Figure 4.4 and Table 4.1. High power generation from DCPFC was due to the increases of hydrogen (H^+) ion in the solution. The pH of the solution was adjusted by using 10% v/v HCl solution, hence the increase of H^+ ion in the solution enhances the performance of DCPFC by increasing the mass transfer of electron. Moreover, the increase in H^+ ion in the solution also resulted in more Zn^{2+} ion formation. The Zn^{2+} ion will then react with OH^- ion and water to form $[Zn(OH)_4]^{2-}$ ion

(Equation 4.3 and Equation 4.4). As the pH value of methyl red dye solution decreased from pH 4 to pH 3, more $[\text{Zn}(\text{OH})_4]^{2-}$ ion form which significantly affected the performance of DCPFC as the more ZnO from the photoanode dissociated.



As the pH of the methyl red dye solution increased to pH 7, and pH 8, there was no power generation as well as no degradation occurred in the DCPFC. This phenomenon was probably due to the transfer of electrons almost reaching equilibrium in the DCPFC system as the pH of NaClO solution in the cathode chamber is about pH 8 after dilution. At higher pH values, the methyl red dye solution in anode chamber contains higher concentration of hydroxide (OH^-) ion. The pH value of both chambers is almost the same, hence reducing the transfer of ions in between anode and cathode chambers. Therefore, the transfer of electrons in the DCPFC system is at minimum causing the reduction in power generation as well as the degradation efficiency of DCPFC.

Furthermore, the 10 ppm methyl red dye was completely removed by using DCPFC with ECD method and ultrasonicate method prepared ZnO/Zn photoanode for pH 4 and pH 5. Therefore, in order to investigate the efficiency of the DCPFC, the duration of complete removal of 10 ppm methyl red dye solution at pH 4 and pH 5 were recorded. At pH 4, the ECD method prepared ZnO/Zn photoanode showed the fastest removal duration (138 minutes) compared to the ultrasonicate method prepared ZnO/Zn photoanode (217 minutes). While at pH 5, similar to pH 4, the ECD method prepared ZnO/Zn photoanode has faster removal duration (153 minutes) compared to ultrasonicate method (195 minutes). The faster removal duration was probably due to the larger effective surface area of photoanode

prepared using ECD method. As shown in Figure 4.1, ECD method prepared ZnO/Zn photoanode has generally smaller crystal size compared to ultrasonicate method. Moreover, the even coating as well as single crystal formation also enhanced the performance of ZnO/Zn photoanode.

4.2.2 Effect of Concentration of NaClO Solution in Cathode Chamber

The experiment continued by altering the concentration of NaClO solution in cathode chamber as it is equally important in affecting the performance of DCPFC. The concentration of NaClO solution was diluted to 125 mL/L, 250 mL/L, and 375 mL/L using distilled water. Figure 4.6 shows the power density obtained from the DCPFC with ECD method and ultrasonicate method prepared ZnO/Zn photoanode under different concentration of NaClO solution and different pH value of 10 ppm methyl red dye solution.

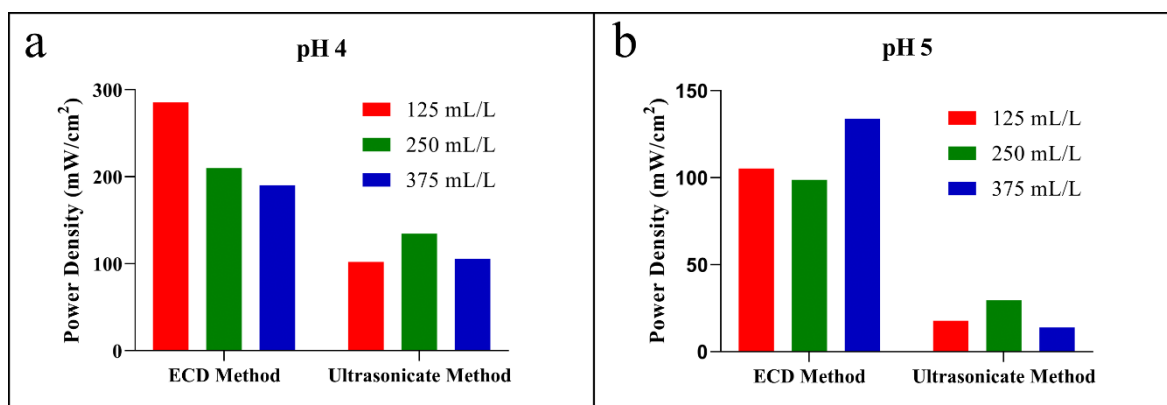


Figure 4.6: Power density of DCPFC under different concentration of NaClO solution at (a) pH 4 and (b) pH 5

As the concentration of NaClO solution increased from 125 mL/L to 375 mL/L, the power density obtained from the DCPFC using ECD method and ultrasonicate method prepared ZnO/Zn photoanode generally decreased. Table 4.2 shows the power density obtained from DCPFC under 125 mL/L, 250 mL/L, and 375 mL/L NaClO solution concentration.

Table 4.2: Power density obtained from DCPFC using ECD method and ultrasonicate method prepared ZnO/Zn photoanode under different NaClO solution concentration

pH	NaClO Concentration	Power Density (mW/cm ²)	
		ECD method	Ultrasonicate method
pH 4	125 mL/L	285.31	102.083
	250 mL/L	209.83	134.67
	375 mL/L	190.18	105.6
pH 5	125 mL/L	105.33	17.864
	250 mL/L	98.85	29.601
	375 mL/L	133.92	13.94

At pH 4, when the NaClO solution concentration increased from 125 mL/L to 375 mL/L, the power density obtained from the DCPFC using ECD method prepared ZnO/Zn photoanode decreased from 285.31 mW/cm² to 190.18 mW/cm². Whereas for the power density from DCPFC using ultrasonicate method prepared ZnO/Zn photoanode slightly increased from 102.083 mW/cm² to 105.6 mW/cm². As for pH 5, the power density obtained from DCPFC using ECD method prepared ZnO/Zn photoanode increased from 105.33 mW/cm² to 133.92 mW/cm² while for ultrasonicate method prepared ZnO/Zn photoanode, the power density obtained was decreased from 17.864 mW/cm² to 13.94 mW/cm² when the NaClO solution concentration increased from 125 mL/L to 375 mL/L.

Moreover, the degradation duration for 10 ppm methyl red dye solution in DCPFC using ECD method and ultrasonic method prepared ZnO/Zn photoanode generally decrease as the concentration of NaClO solution increased from 125 mL/L to 375 mL/L (Table 4.3 and Figure 4.7). At pH 4, the degradation duration for 10 ppm methyl red dye solution has decreased from 325 minutes to 157 minutes for ECD method prepared ZnO/Zn photoanode and from 354 minutes to 193 minutes for ultrasonic method prepared ZnO/Zn photoanode. Similar to pH 4, at pH 5, the degradation duration also reduced significantly when the NaClO solution concentration has increased from 125 mL/L to 375 mL/L.

Table 4.3: Degradation duration of methyl red dye solution under different concentration of NaClO solution

NaClO concentration	Degradation Duration (minutes)			
	ECD method		Ultrasonic method	
	pH 4	pH 5	pH 4	pH 5
125 mL/L	325	231	354	233
250 mL/L	138	153	217	195
375 mL/L	157	183	193	172

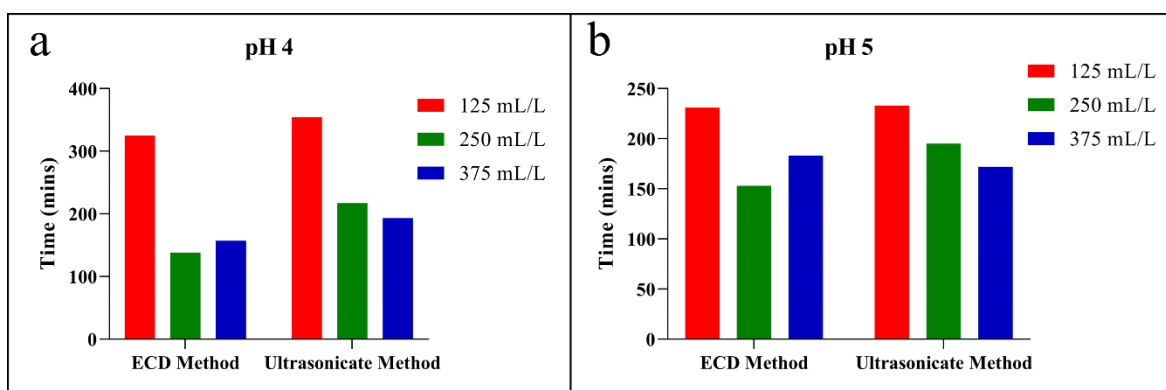


Figure 4.7: Degradation duration of methyl red dye solution at (a) pH 4 and (b) pH 5 using ECD method and ultrasonic prepared ZnO/Zn photoanode in DCPFC with different concentration of NaClO solution.

Although from Table 4.3, the result showed that when increasing the NaClO solution in cathode chamber significantly reduced the degradation duration of 10 ppm methyl red dye solution, the power density obtained from DCPFC (Table 4.2) reduced drastically. This could be due to the reaction of the hypochlorite ion (ClO^-) in the cathode chamber that utilized the electrons produced from the anode chamber in the production of OH^- ion (Equation 4.5).



However, from the result shown in Table 4.2 and Table 4.3, the highest removal efficiency and power density of 10 ppm methyl red dye solution was at pH 4 with 250 mL/L NaClO solution concentration with the power generation at 209.83 mW/cm^2 while using ECD method prepared ZnO/Zn photoanode. Similarly, while using ultrasonicate method prepared ZnO/Zn photoanode, the highest removal efficiency and power density from DCPFC also at pH 4 with 250 mL/L NaClO solution concentration with the power generation at 134.67 mW/cm^2 .

4.2.3 Effect of Volume on DCPFC while Using ECD Method Prepared ZnO/Zn Photoanode

Along with the study, the upscaling of DCPFC from 1 L to 2 L and 4 L was conducted to investigate the performance of DCPFC in increased capacity for 10 ppm methyl red dye solution. As the increased in the capacity of DCPFC from 1 L to 2 L and 4 L, the size of the photoanode was increased from 14 cm² to 28 cm² and 56 cm² for 2 L and 4 L, respectively. The conditions of the methyl red dye solution and NaClO solution concentration were adapted from the previous experiment in which the methyl red dye solution was maintained at 10 ppm concentration and pH 4 while the concentration of NaClO solution was at 250 mL/L.

When the volume of methyl red dye solution increased from 1 L to 2 L, the removal rate decreased significantly from 100% to 49.72% while the power density obtained also reduced from 209.83 mW/cm² to 122.62 mW/cm². Besides, further increase in volume of DCPFC to 4 L yielded lower degradation efficiency at only 42.88% with the power density at 103.86 mW/cm². Not only the power generation and degradation duration also greatly affected (Table 4.4). As the increase in the capacity of DCPFC, the degradation duration significantly increased from 2 hours to 7 hours and 8 hours for 2 L and 4 L, respectively.

Table 4.4: The performance of DCPFC using ECD method prepared ZnO/Zn photoanode at different volume

Volume of DCPFC	Removal Rate	Degradation Duration (hours)	Power density (mW/cm ²)
1 L	100%	2	209.83
2 L	49.72%	7	122.62
4 L	42.88%	8	103.86

The decrease in overall performance of DCPFC when the volume increased was due to the decrease in the energy for ZnO/Zn photoanode activation. As the volume of methyl red dye solution increased, most of the photons from the irradiation of light bulb was absorbed by the solution hence there were less photons reached the photoanode. The decrease in overall performance of DCPFC when the volume increased was probably due to the incomplete activation of ZnO/Zn photoanode. Thus, the production of free radical species decreased and resulted in reduced degradation efficiency for methyl red dye solution. Moreover, the power generation for DCPFC decreased when the volume of methyl red dye solution increased due to the increased resistance of the solution. With increased resistance, most of the energy produced is lost due to overcoming the resistance of the solution.

4.2.4 Degradation Rate of Methyl Red Dye Solution in DCPFC

In terms of degradation rate, the ECD method prepared ZnO/Zn photoanode has faster degradation rate while using 10 ppm methyl red dye solution at pH 4 with 250 mL/L NaClO solution concentration at cathode chamber compared to ultrasonicate method prepared ZnO/Zn photoanode (Figure 4.8).

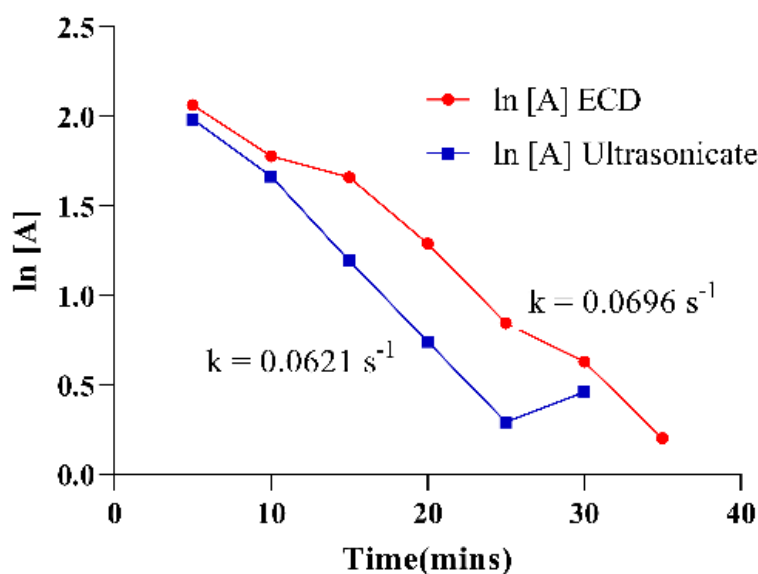


Figure 4.8: Degradation rate of methyl red dye solution in DCPFC using ECD method and ultrasonic method prepared ZnO/Zn photoanode

The degradation rate for ECD method prepared ZnO/Zn photoanode was 0.0696 min^{-1} whereas the k value of ultrasonic method was 0.0621 min^{-1} . From Figure 4.6, the kinetic order of methyl red dye degradation in DCPFC was pseudo first kinetic order. Although both ECD and ultrasonic prepared ZnO/Zn photoanode degradation rates have slight differences, the methyl red solution was completely degraded within 40 minutes. This result was parallel with a study reported by Li et al. (2020) where the group investigated the kinetic study of the degradation of RhB dye using $\text{gC}_3\text{N}_4/\text{Ag}/\text{GO}$ (CNAG) nanocomposite catalyst, where gC_3N_4 is a metal-free graphite carbon nitride polymeric organic semiconductor and GO is the graphene oxide. The kinetic model that the group obtained was a pseudo-first order kinetic model.

4.2.5 Role of Sodium Hypochlorite (NaClO) as Oxidizing Agent in DCPFC

In the DCPFC system, there is an ion exchange and electron transfer between anode chamber and cathode chamber. The electron transfers from the anode chamber cathode chamber through the external circuit then transfers back to the anode chamber through the salt bridge. However, the electron transfers cannot be performed in a single chamber PFC as the additional oxidizing agent could affect the hydroxyl radicals formation at the photoanode since the anode and cathode electrodes are placed in the same chamber. Hence, the separation of anode and cathode chamber is an advantage of a DCPFC compared to single chamber PFC where the oxidizing agent can be used to further improve the efficiency of a PFC.

The purpose of using NaClO solution in cathode chamber is due to its strong oxidizing effect (Trautmann et al., 2021). The NaClO solution in cathode chamber used to produce electrons for enhancing the photocatalytic degradation, with the electron (e^-) produced from the HCl solution added in the anode chamber, the hypochlorite (ClO^-) ion reaction can be initiated.

The addition of HCl solution to the methyl red dye solution not only to adjust the pH value of the solution, but also to increase the conductivity of the solution. The addition of the HCl solution to the methyl red dye solution resulted in the production of e^- from the dissociation of HCl (Equation 4.6) which later reacted with chloride ion (Cl^-) in the cathode chamber to produce chlorine (Cl_2) (Equation 4.7).

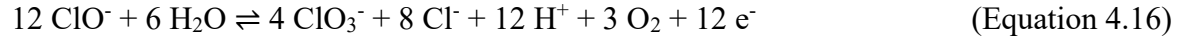


When NaClO was added with water, NaClO dissociates into sodium hydroxide (NaOH) and hypochlorous acid (HOCl) (Equation 4.8). Hypochlorous acid dissociates into H^+ ion and ClO^- ion (Equation 4.9). Due to the presence of NaOH in the solution, the Cl^- ion reacts with OH^- ion in the solution producing ClO^- ion (Equation 4.10) and ClO_2^- ion (Equation 4.11). Furthermore, Cl^- ion also reacted with water producing ClO_3^- ion (Equation 4.12). Furthermore, the ClO_3^- ion reacted with OH^- ion yielding ClO_4^- ion (Equation 4.13). With the aid of electrons, the formation of OH^- ion increased (Equation 4.14). The formation of OH^- ion helps in enhancing the reaction in cathode chamber as well as the performance of the DCPFC.



According to Yi et al. (2019), the ClO^- ion reacted with water molecules producing Cl^- ion and OH^- ion (Equation 4.15). With sufficient water, ClO^- ion continues to react, producing chlorine trioxide (ClO_3^-) ion, Cl^- ion, H^+ ion, oxygen (O_2), and e^- (Equation 4.16). The ClO_3^- ion further reacts with H_2O producing Cl^- ion and OH^- ion (Equation 4.17), chloride dioxide (ClO_2^-) ion (Equation 4.18), or perchlorate (ClO_4^-) ion (Equation 4.19) and

lastly the ClO_2^- ion continues to react with water resulting in reformation of ClO^- ion (Equation 4.20).



The performance of DCPFC using NaClO solution in cathode chamber as oxidizing agent significantly increased due to the production of electrons based on the Equation 4.8 to Equation 4.20.

4.3 The Degradation Efficiency and Power Generation Using Palm Oil Mill Effluent (POME) in a Dual Chamber Photocatalytic Fuel Cell (DCPFC)

The palm oil mill effluent (POME) used in DCPFC was obtained from an advanced treatment pond of a palm oil mill located in Bau, Sarawak. Table 4.5 shows the characteristics of POME solutions used in this project. The COD concentration of the POME solution was 399.352 ± 39.885 mg/L, and the pH was 8.495 ± 0.02799 with the conductivity of 5.002 ± 0.00789 mS/cm. Despite the POME sample obtained from the advanced treatment pond, the organic pollutant content was still around 400 mg/L indicating the typical biological ponding system was not efficient to treat POME. Nevertheless, the biological ponding system managed to remove the TSS in POME where the TSS value of POME sample was 12.8 ± 1.989 mg/L.

Table 4.5: The characteristics of POME sample

Parameter	Value
pH	8.495 ± 0.0279
COD	399.352 ± 39.885 mg/L
Conductivity	5.002 ± 0.0789 mS/cm
Total Suspended Solid (TSS)	12.8 ± 1.989 mg/L

It was found that the power density obtained from DCPFC using POME has significantly increased compared to methyl red dye solution under the similar conditions which is pH 4 with 250 mL/L NaClO solution concentration in cathode chamber. However, the degradation rate significantly decreased when the POME solution was used in the DCPFC. With the high amount of organic-based pollutants presence in the POME, the degradation duration drastically increased which further increased the power generation of DCPFC (Figure 4.9).

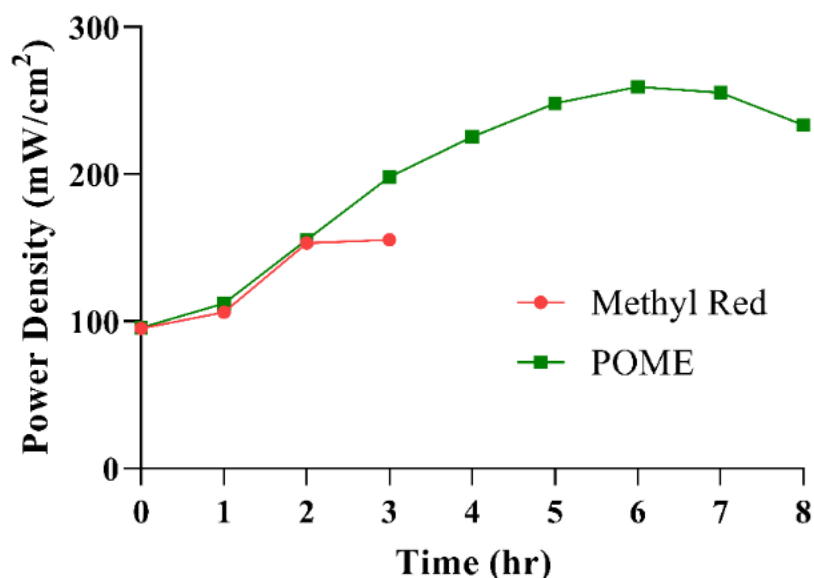


Figure 4.9: Power generation of 10 ppm methyl red dye solution and 25% concentration of POME solution at pH 4

4.3.1 Chemical Oxygen Demand (COD) Assurance and Verification Test using ASTM Method and APHA Method

Chemical oxygen demand (COD) is an important parameter to measure the concentration of organic pollutants present in a water sample. The determination of COD is based on the colour change of hexavalent chromium (Cr^{6+}) ion to trivalent chromium (Cr^{3+}) ion in which the colour changes from orange to apple green and lastly to cyan. The deeper cyan colour in the final solution, the higher concentration of organic pollutants presents in the water sample. Due to the obvious colour change can be observed, COD can be determined using either titration or colorimetric methods. Although COD determination is not a research subject in the project, it is a water quality parameter used in the project in

order to determine the removal efficiency of photocatalytic fuel cell (PFC) that we fabricated. Hence, it is very important to ensure the accuracy of COD determination in water samples to avoid miss-leading results obtained.

In this project, the colorimetric method was applied to determine COD concentration presented in palm oil mill effluent (POME). This method was adopted from the American Society for Testing and Materials (ASTM) 5220D namely closed reflux, colorimetric method. To ensure the reliability of ASTM 5220D method, a repetitive testing with standard potassium hydrogen phthalate (KHP) calibration solution was conducted and compared with the standard method adopted from American Public Health Association (APHA) namely closed reflux, titration method.

The working principle of COD concentration determination using ASTM 5220D is by analyzing the absorbance of chromium ions i.e., Cr^{6+} and Cr^{3+} with ultraviolet-visible light (UV-Vis) spectrophotometer. During the digestion process of organic pollutants, the Cr^{6+} ion was reduced to Cr^{3+} ion (Equation 4.21).



The Cr^{6+} ion has a distinctive orange colour with an absorbance maximum at 420 nm while Cr^{3+} with cyan colour has an absorbance maximum at 600 nm. As the concentration of organic substances increased, more Cr^{6+} ion was reduced to Cr^{3+} ion and hence the colour of digestion solution changes from orange to apple green and lastly to cyan. Thus, the absorbance of the digestion solution changed with respect to the changes of both chromium ions' concentration, and concentration organic pollutants in the water sample can be calculated. Figure 4.10 shows the change of absorbance at 440 nm and 610 nm as the COD concentration increased in the digestion solution. As the COD concentration increased from

200 mg/L to 1,000 mg/L, the absorbance at 440 nm decreased, whereas at 610 nm, the absorbance increased when the COD concentration increased. From Figure 4.8, the peak absorbance has shifted to 440 nm instead of the reported 420 nm, and 610 nm instead of 600 nm according to ASTM 5220D method. Therefore, the absorbance from 420 nm, 440 nm, 600 nm, and 610 nm were analyzed prior to obtaining the best estimation of COD concentration using ASSTM 5220D method.

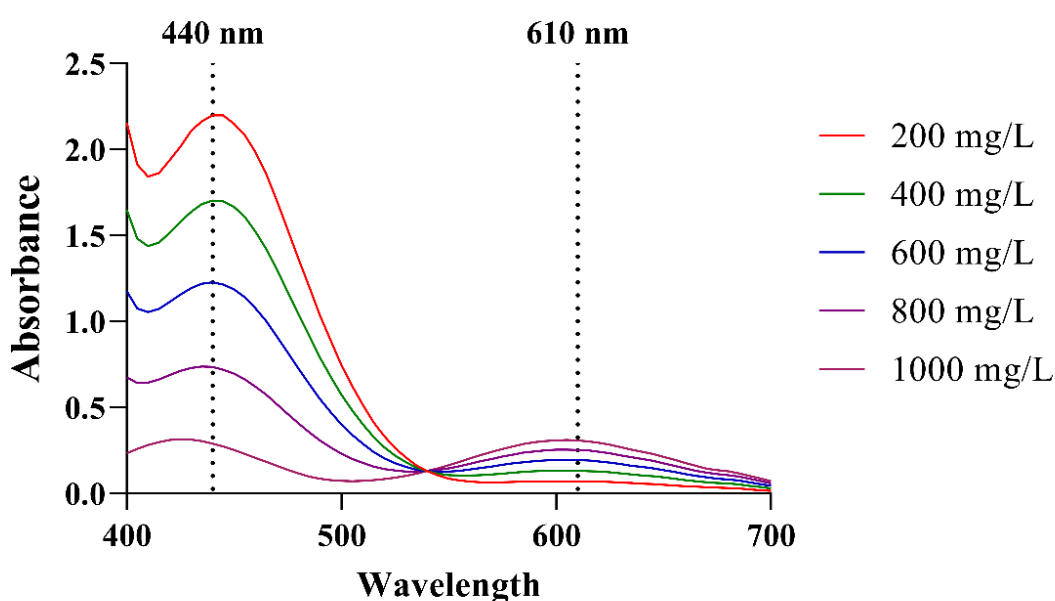


Figure 4.10: Absorbance of COD standard calibration solution at different concentrations

For the colorimetric method, a simple linear regression was used to determine the COD concentration. By using the standard KHP solution with the fixed concentrations of 200, 400, 600, 800, and 1000 mg/L COD, the solutions were prepared and digested. Lastly, the absorbance (ABS) of the $\lambda_{\max}$ at 420 and 440 nm were recorded. For absorbance at 420 nm and 440 nm, the fitted regression model was shown in Figure 4.9(a) with the equations. The regression, r^2 , calculated for 420 nm was 0.9944 whereas 0.9960 for 440 nm. Both fitted regression models have differences at their slope where 420 nm (0.002058) was steeper than

440 nm (0.002414). In contrast, the fitted regression model for 600 nm and 610 nm shows negligible differences in their r^2 which are 0.9928 and 0.9925, respectively. The slope for 600 nm and 610 nm were no significant difference shown in Figure 4.11(b).

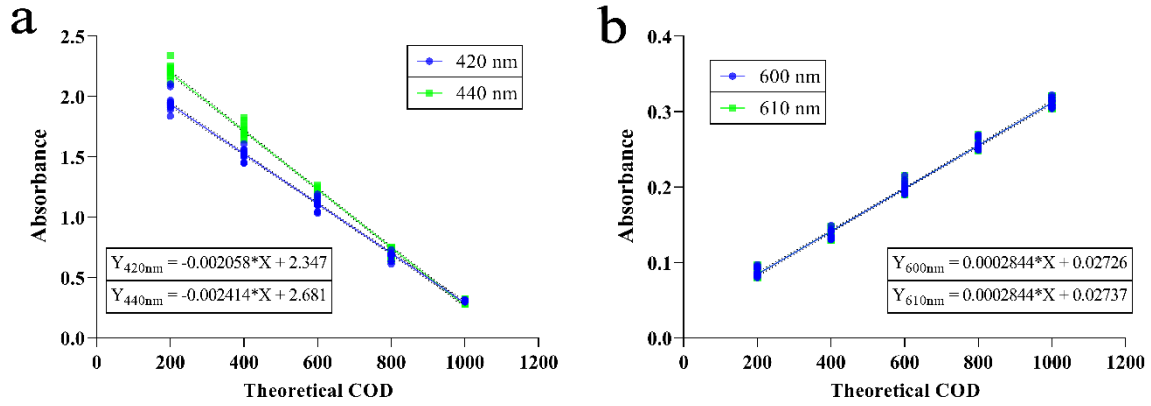


Figure 4.11: Linear plot for obtained absorbance at (a) 420 nm and 440 nm and (b) 600 nm and 610 nm

From Table 4.6, the one-way ANOVA Sidak's multiple comparison test for the 420 nm and 440 nm pair shows that there is significant difference ($p = < 0.0237$) between the absorbance obtained at 420 nm and 440 nm. On the other hand, there is no significant difference ($p = 0.9675 - 0.9999$) between absorbance obtained at 600 nm and 610 nm as the p -values obtained for COD concentrations were higher than the significant level of 0.05. To further confirm the ANOVA Sidak's multiple comparison test for significant difference, two-tail t-test were carried out for 420 nm and 440 nm pair, and 600 nm and 610 nm pair. The two-tail t-test result shows that there is significant difference between the absorbance obtained at 420 nm and 440 nm. The t-value obtained for each COD concentration was 17.785 (200 mg/L), 15.659 (400 mg/L), 9.9629 (600 mg/L), 4.6136 (800 mg/L), and 2.599 (1000 mg/L) which is significantly higher than the critical t-value of 1.96. For the 600 nm and 610 nm pair, there is no significant difference between both obtained absorbance as the

t-value for COD concentration of 200, 400, 600, 800, and 1000 mg/L was 0.00448, 0.03558, 0.01348, 0.1377, and 0.2291, respectively, lies between the critical t-value of -1.96 and 1.96.

Table 4.6: Average absorbance, standard deviation, p-value, and t-value for each theoretical COD concentration and $\lambda_{\max}$

COD concentration (mg/L)	$\lambda_{\max}$ (nm)	Average absorbance	p-value	t-value
200	420	1.949 ± 0.06625	0.0001	17.785
	440	2.214 ± 0.04923		
	600	0.08760 ± 0.015527	0.9999	0.00448
	610	0.08767 ± 0.005589		
400	420	1.516 ± 0.04405	0.0001	15.659
	440	1.718 ± 0.04923		
	600	0.1357 ± 0.006127	0.9992	0.03558
	610	0.1361 ± 0.006875		
600	420	1.108 ± 0.04392	0.0001	9.9629
	440	1.211 ± 0.03449		
	600	0.1920 ± 0.02579	0.9999	0.01348
	610	0.1981 ± 0.008083		
800	420	0.6815 ± 0.03074	0.0001	4.6136
	440	0.7192 ± 0.03120		
	600	0.2569 ± 0.007053	0.9881	0.1377
	610	0.2558 ± 0.006419		
1000	420	0.3080 ± 0.005267	0.0237	2.599
	440	0.2994 ± 0.01537		
	600	0.3114 ± 0.005569	0.9675	0.2291
	610	0.3122 ± 0.005936		

To further proof that the ASTM 5220D method, the obtained absorbance from 420 nm, 440 nm, 600 nm, and 610 nm were converted to respective COD concentration value by using the fitted regression model from Figure 4.2. The one-way ANOVA Sidak's multiple comparison test and two-tail t-test were performed for significant difference between each average COD concentration at the expected COD concentration of 200, 400, 600, 800, and 1000 mg/L. Table 4.2 shows the average COD concentration and standard deviation for each $\lambda_{\max}$ alongside with their respective p-value and t-value.

As shown in Table 4.7, the one-way ANOVA Sidak's multiple comparison test for COD value at 420 nm shows significant differences between expected COD values and average actual COD value. As the p -value obtained for each expected COD value being less than the significant level of 0.05 which is 0.0270 (200 mg/L), and 0.0001 (400 mg/L to 1000 mg/L) as shown in Table 4.7. Furthermore, the two-tail t-test also showed a significant difference between the expected COD value and average COD value with the t-value of 3.5625 (200 mg/L), 5.2634 (400 mg/L), 4.7706 (600 mg/L), 6.767 (800 mg/L), and 5.0922 (1,000 mg/L). The obtained t-value for each average COD value is higher than the critical t-value of 1.96. Thus, it was concluded that the ASTM 5220D method of COD determination using absorbance at 420 nm was not accurate due to the p -value obtained is less than $\alpha = 0.05$, and t-value obtained more than critical t-value of 1.96.

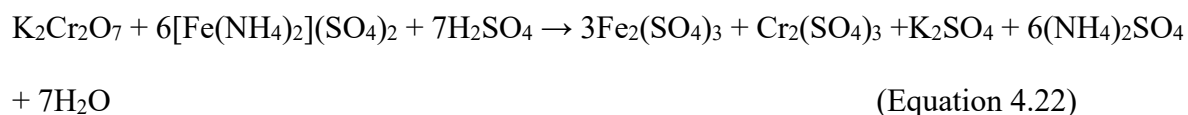
Table 4.7: Average COD concentration, standard deviation, p -value, and t-value for each theoretical COD concentration and $\lambda_{\max}$

Expected COD (mg/L)	$\lambda_{\max}$ (nm)	Average actual COD (mg/L)	p -value	t-value
200	420	227.15 ± 32.192	0.0270	3.5625
	440	203.95 ± 19.420	0.9759	0.5179
	600	212.17 ± 19.432	0.3862	1.5966
	610	212.01 ± 19.652	0.3986	1.5766
400	420	437.69 ± 21.463	0.0001	5.2634
	440	409.08 ± 20.395	0.6087	1.2678
	600	381.34 ± 21.544	0.0440	2.6060
	610	382.48 ± 24.172	0.0659	2.4472
600	420	635.97 ± 21.341	0.0001	4.7706
	440	619.29 ± 14.288	0.0498	2.5578
	600	600.23 ± 25.788	0.9999	0.0311
	610	600.34 ± 28.421	0.9999	0.0451
800	420	843.01 ± 14.935	0.0001	6.7670
	440	823.02 ± 12.923	0.0022	3.6229
	600	807.52 ± 24.800	0.6671	1.1840
	610	803.18 ± 22.571	0.9789	0.4998
1000	420	1024.5 ± 2.5595	0.0001	5.0922
	440	996.94 ± 6.3675	0.9498	0.6361
	600	999.20 ± 19.581	0.9997	0.1558
	610	1001.5 ± 20.072	0.9966	0.3097

To sum up, the COD determination using ASTM 5220D method namely closed reflux, colorimetric method, the most suitable absorbance for COD value estimation is 440 nm for COD value lower than 400 mg/L with higher accuracy and precision. Although higher COD concentration can be estimated at the absorbance at 440 nm, the accuracy and precision in estimation of COD value is lower. Besides, higher COD concentration starting from 400 mg/L to 1000 mg/L could be estimated using the λ_{max} at 600 nm and 610 nm with higher accuracy and precision. The COD concentration determined at 600 nm and 610 nm for 200 mg/L, the average actual COD value shows no difference according to both *p*-value and *t*-value. However, the COD estimation was not suitable according to Table 4.6 on their absorbance at 600 nm (0.08760) and 610 nm (0.08767) as the sensitivity of UV-Vis spectrophotometer where sometimes there is no peak detected for absorbance lower than 0.1.

To ensure the ASTM 5220D closed reflux, colorimetric method is accurately estimating the COD concentration compared to traditional closed reflux, titration method as stated in APHA, the COD concentration estimation was repeated for 200 mg/L using closed reflux, titration method.

As mentioned before, COD concentration usually is determined by using the APHA titration method. Hence, the APHA method was used as a standard reference method to ensure the ASTM colorimetry method was compatible to determine the COD concentration in this project. After the digestion process, the solution was back titrated with ferrous ammonium sulphate (FAS) solution to determine the unused $\text{Cr}_2\text{O}_7^{2-}$ ion in the digestion solution. The equation of the titration reaction is shown in Equation 4.22. After obtaining the volume of FAS solution used, COD concentration can be calculated. To increase the accuracy of the titration method, the concentration of FAS solution was reduced from 0.10 M to 0.01 M and the titration was repeated at least 10 times.



The average actual COD value obtained for repeated testing was 199.550 ± 6.6776 mg/L for APHA closed reflux, titration method. By comparing both ASTM 5220D method and APHA method of COD concentration estimation, the *p*-value calculated was 0.4409 and *t*-value was 0.7932. The calculated *p*-value (0.4409) was higher than the significant level ($\alpha = 0.05$) whereas the calculated *t*-value (0.7932) was lower than the critical *t*-value (1.96) indicates that there is no significant difference between both methods of COD concentration estimation. In spite of that, ASTM 5220D closed reflux, colorimetric method was chosen for the determination of COD concentration in this project due to reduce chance of contamination from the solutions' preparation. As the number of steps in the APHA method is more than the one in ASTM method, the chance of contamination occurring also can be higher than the ASTM method. To minimize the contamination, ASTM 5220D closed reflux, colorimetric method was the suitable method as the digestion solution was analyzed directly after the digestion process was completed and cooled to room temperature. Moreover, the wastewater produced from ASTM 5220D method was significantly less than APHA method. This is due to the use of mercury sulphate (HgSO_4) in the digestion solution. It is important to reduce the mercury (Hg) based wastewater produced from each analysis because mercury is harmful to the environment and also humans. Although both methods used HgSO_4 , the wastewater produced from APHA titration method was significantly higher than the ASTM colorimetric method because the volume of titrant (i.e. FAS) has turned into waste after the titration was performed. Therefore, ASTM 5220D method of COD concentration estimation is a suitable method for this project. The wavelength used was 440 nm for the COD concentration determination.

4.3.2 Effect of pH Value of Palm Oil Mill Effluent (POME) on DCPFC Using ECD Method Prepared ZnO/Zn Photoanode

The pH value of the POME solution was adjusted to pH 3, pH 4, and pH 5 in the anode chamber while the cathode chamber was filled with NaClO solution with the concentration of 250 mL/L. The power density obtained at the 8th hour for pH 3 was 174.878 mW/cm², pH 4 was 236.312 mW/cm², and pH 5 was 164.826 mW/cm². As for the unadjusted pH, which is about 8.495 for POME solution, the power density obtained at the 1st hour is 6.607 mW/cm² then slowly reduced to about 0.00507 mW/cm² at the 8th hour. As shown in Figure 4.12, the power density obtained at the 8th hour for pH 3, pH 4, and pH 5 was higher compared to the power density obtained at the 1st hour. The continuous increase in the power density was due to the degradation reaction of the organic-based molecules presence in the POME solution, hence releasing electrons. The increment in the power density for each pH is summarized in Table 4.8. The power density obtained from DCPFC using the ECD method prepared ZnO/Zn photoanode achieved the maximum output when the POME solution was adjusted to pH 4 which was the same result obtained from the study using methyl red dye solution.

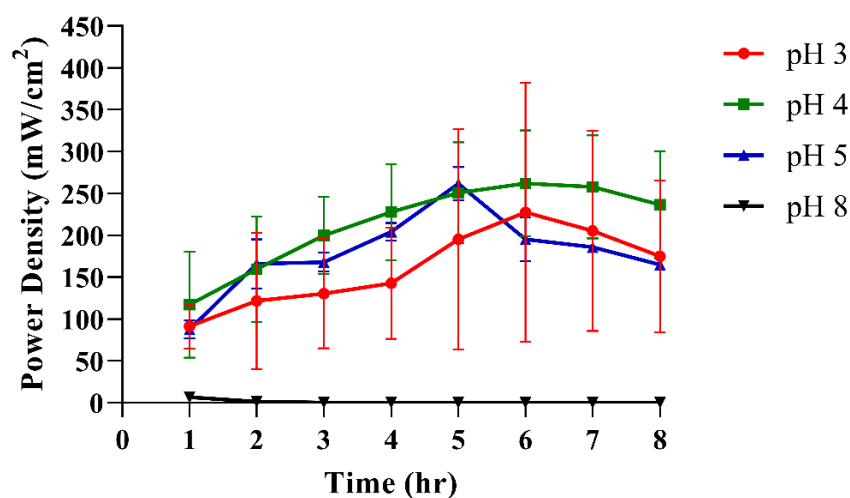


Figure 4.12: Average power density obtained from DCPFC at different pH values of POME solution

Table 4.8: Increment in average power density obtained from DCPFC under different pH values

pH	Power Density (mW/cm ²)		
	1 st hour	8 th hour	Increment %
pH 3	91.179	174.878	91.796
pH 4	117.289	236.312	101.478
pH 5	87.73	164.826	87.878
pH 8	6.607	0.00507	-99.923

Figure 4.13 shows the degradation trend of POME at pH 3, pH 4, and pH 5. At the 8th hour, the 25% concentration POME solution was completely degraded at pH 3 and pH 4, but at pH 5, the degradation does not occur on the POME solution. From Figure 4.13, the COD concentration gradually increased for pH 5 until the 5th hour then decreased after reaching the maximum COD concentration. For pH 3 and pH 4, the COD concentration slightly increased at the 2nd and 3rd hour, respectively. Compared to the adjusted pH, the unadjusted pH of 25% POME solution also did not show degradation throughout the 8th hour

experiment. Although the POME solution was completely degraded at 7th hour for pH 3, the pH value of pH 4 was chosen as the optimal pH for degradation and power generation in this study due to the power density obtained for pH 4 (236.312 mW/cm²) was higher than pH 3 (174.878 mW/cm²) at the 8th hour.

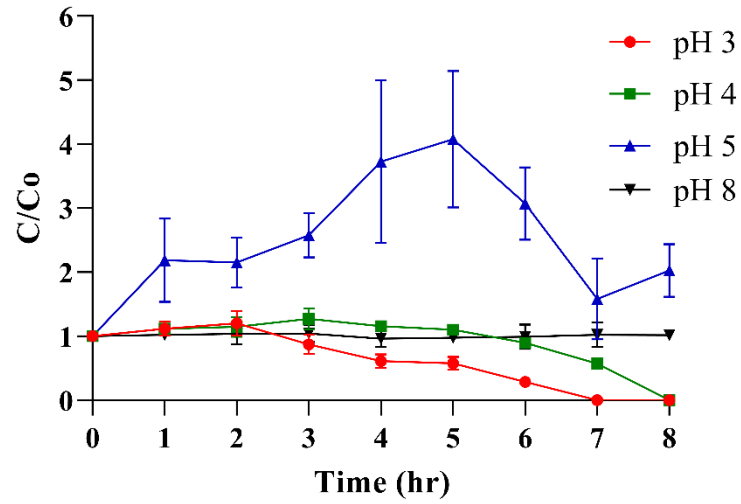


Figure 4.13: Average degradation of POME solution at pH 3, pH 4, pH 5, and pH 8

4.3.3 Effect of Concentration of Palm Oil Mill Effluent (POME) on DCPFC Using ECD Method Prepared ZnO/Zn Photoanode

In this experiment, the concentration of POME solution was altered to 25%, 50%, and 75% from the original POME solution. The higher the percentage of the solution, the higher the POME concentration is. The COD concentration of pH 4 POME solution at 25%, 50%, 75%, and 100% was 180.184 ± 10.786 mg/L, 165.042 ± 20.236 mg/L, 198.539 ± 2.646 mg/L, and 324.072 ± 1.578 mg/L respectively. The condition of the POME solution in anode chamber was fixed at pH 4, and the concentration of NaClO solution in cathode chamber was fixed at 250 mL/L. Figure 4.14 shows the power density obtained from the DCPFC at 25%, 50%, 75%, and 100% POME solution. From Figure 4.14, the power density obtained for 25%, 50%, and 75% POME solution gradually increased from 1st hour to 8th hour. However, the power density obtained for 100% POME solution significantly decreased from the 1st hour to the 8th hour. The reducing of power density was due to the oil and grease that deposited on the ZnO/Zn photoanode surface which prevented the photocatalysis reaction (Figure 4.15). Table 4.9 summarizes the increment of power density obtained from different POME concentrations.

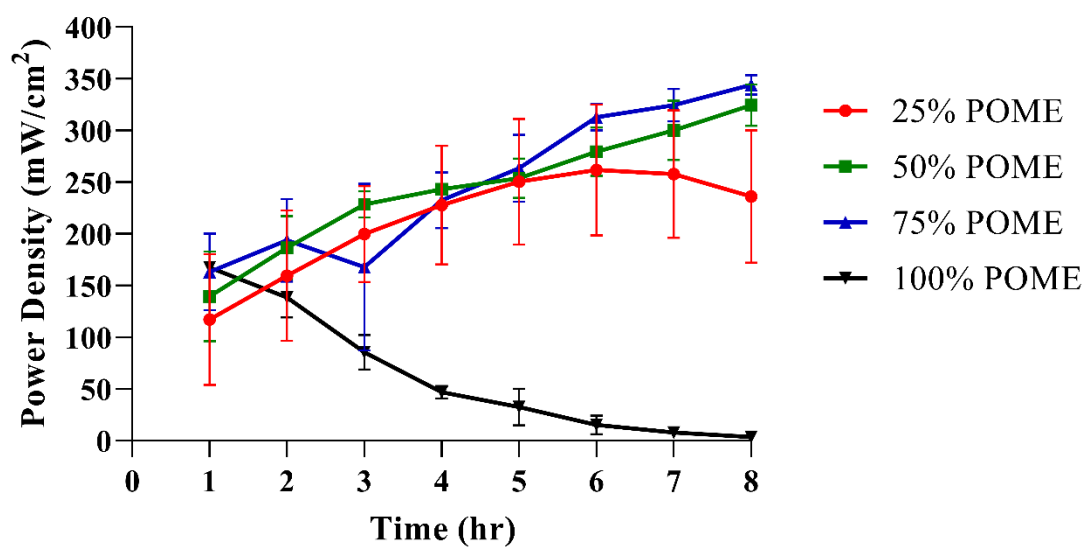


Figure 4.14: Power density obtained from DCPFC at different POME solution concentrations



Figure 4.15: Surface condition of ZnO/Zn photoanode in 100% POME solution after 8th hour

Table 4.9: Increment in power density obtained from DCPFC at different POME solution concentrations

POME concentration	Power Density (mW/cm ²)		Increment %
	1 st hour	8 th hour	
25%	117.289	236.312	101.478
50%	139.35	324.373	132.776
75%	163.028	344.069	111.049
100%	230.965	3.649	-622.954

In Figure 4.16, the degradation of 50%, 75%, and 100% POME solution were slower than the 25% POME solution. The reduction in the degradation rate could be due to the increased concentration of organic pollutant in the POME solution. As the high concentration of organic pollutant content limits the light penetration in DCPFC allowing less light reaching the surface of ZnO/Zn photoanode and reducing the photocatalysis reaction.

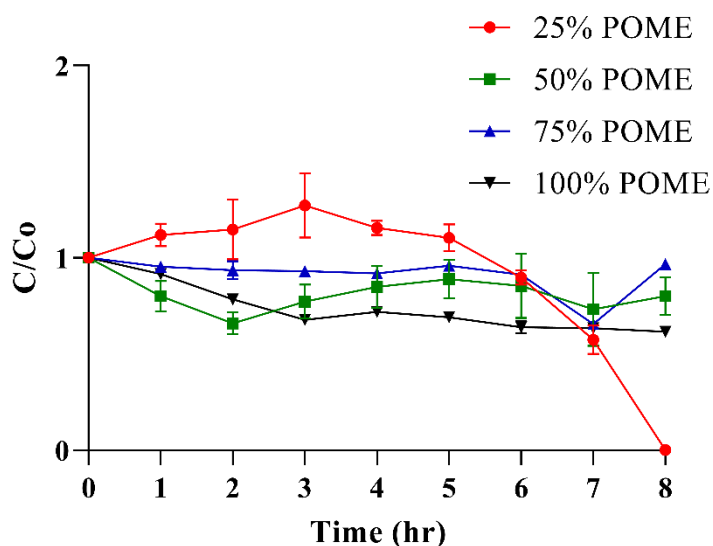


Figure 4.16: Average degradation of POME solution at different concentrations

As the increase in the POME solution concentration, the degradation rate for POME solution decreased. Despite the slower degradation rate observed in 50%, 75%, and 100% POME solution compared to 25% POME solution, the power density obtained for 50%, 75%, and 100% POME solution were higher than 25% POME solution as shown in Figure 4.14 and Table 4.9.

The increase in power generation of DCPFC at the first hour as the concentration of POME increased from 25% to 75% was due to the increase in ion and electron concentration in the solution hence reducing the overall resistance of the POME solution. With the degradation of POME continued, the amount of available electrons in the solution increased, hence increasing the electron transfer between anode and cathode chamber. The reduced resistance of the solution and the increased electron concentration resulted in rapid electron transfer rate between anode and cathode chamber.

The increment in organic pollutant concentration resulted in the increased reaction rate between the radical species and the pollutants. However, as the concentration of POME solution increased further to 100% concentration, the surface of the ZnO/Zn photoanode was deposited with thick layer of organic pollutants which reduced the overall efficiency of ZnO/Zn photoanode. The thick layer of the deposited pollutants decreased the active site of the ZnO/Zn photoanode thus the degradation efficiency of the POME solution reduced as the concentration of POME solution increased.

The vary in degradation efficiency of POME solution when the concentration of POME solution has increased from 25% to 100% similar to the study done by Moksini et al. (2021). In Moksini et al. (2021) study, the concentration of POME solution was increased from 1:100 to 1:50, the degradation rate reduced from $35.8 \pm 0.57\%$ to $17.42 \pm 0.64\%$. The

power density obtained has decreased from $2.442 \mu\text{W}/\text{cm}^2$ to $0.676 \mu\text{W}/\text{cm}^2$ when the concentration of POME solution increased from 1:200 to 1:50.

4.3.4 Effect of Volume of Palm Oil Mill Effluent (POME) on DCPFC Using ECD Method Prepared ZnO/Zn Photoanode

This experiment was conducted to investigate the performance of DCPFC when the capacity has increased from 1 L to 2 L and 4 L. The conditions of POME solution in the anode chamber were adjusted to pH 4 and 25% POME solution while the concentration of NaClO solution in cathode chamber maintained at 250 mL/L. From Figure 4.17, the power density obtained from 1 L volume has the highest power density at $236.312 \text{ mW}/\text{cm}^2$ where only $86.219 \text{ mW}/\text{cm}^2$ was obtained for 2 L volume and $8.065 \text{ mW}/\text{cm}^2$ for 4 L volume at the 8th hour.

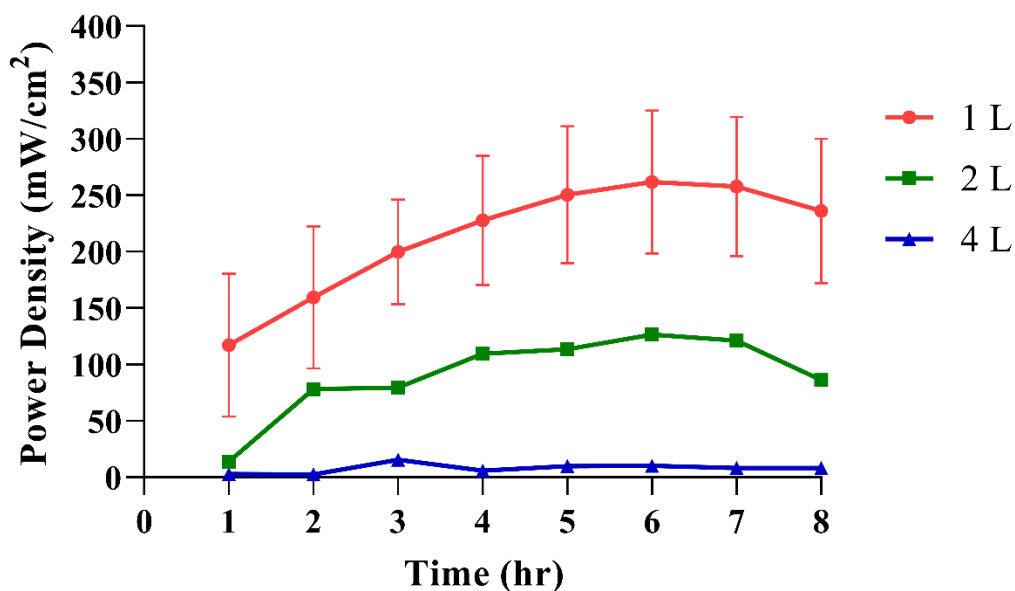


Figure 4.17: Power density obtained from DCPFC at 1 L, 2 L, and 4 L

Not only in power density, the 2 L and 4 L capacity of DCPFC, the degradation rate of 2 L and 4 L capacity gave lower degradation rate compared to 1 L capacity (Figure 4.18). At the 8th hour, the 1 L DCPFC completed the degradation of POME solution while 2 L and 4 L DCPFC showed increased COD concentration.

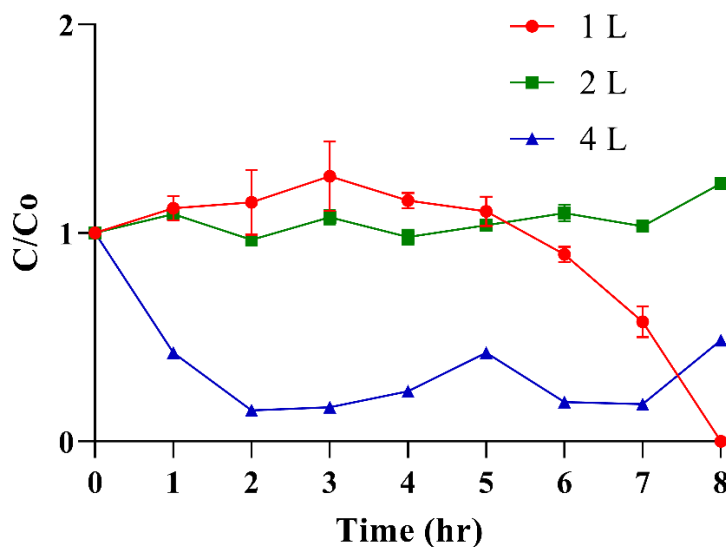


Figure 4.18: Average degradation of POME solution at 1 L, 2 L, and 4 L capacity of DCPFC

The drastic reduction in power density and the degradation rate as the volume of POME solution increase was due to the effective collision between the radical species and the organic pollutants reduced. When the volume increased while the concentration of POME solution was kept constant, the space in between each molecule increased thus reducing the possibility of effective collision. Due to the reduction in effective collision, the degradation rate of the POME reduced as well as lesser electron production. Hence, the power generation and degradation efficiency decreased when the volume of DCPFC increased.

4.3.5 Effect of Additives in Palm Oil Mill Effluent (POME) Solution on DCPFC Using ECD Method Prepared ZnO/Zn Photoanode

The next experiment was to investigate the effect of additives added to the POME solution in the anode chamber. The idea of this experiment was initiated by single chamber PFC where different performance resulted when different salts were used as the electrolyte in single chamber PFC. In other words, the impact of anion present in the anode chamber was investigated in this experiment. In the experiment, the acids used were sulphuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), and phosphoric acid (H_3PO_4) which dissociates into sulphate ion (SO_4^{2-}), nitrate ion (NO_3^-), chloride ion (Cl^-), and phosphate ion (PO_4^{3-}), respectively. The condition of the POME solution was fixed at pH 4 with 25% POME solution in anode chamber and the concentration of NaClO solution was maintained at 250 mL/L.

The highest power density obtained from DCPFC at 8th hour was sulphuric acid (236.312 mW/cm²) (Figure 4.19), then followed by nitric acid (148.342 mW/cm²), phosphoric acid (96.529 mW/cm²), and then lowest power density obtained was hydrochloric acid (7.371 mW/cm²).

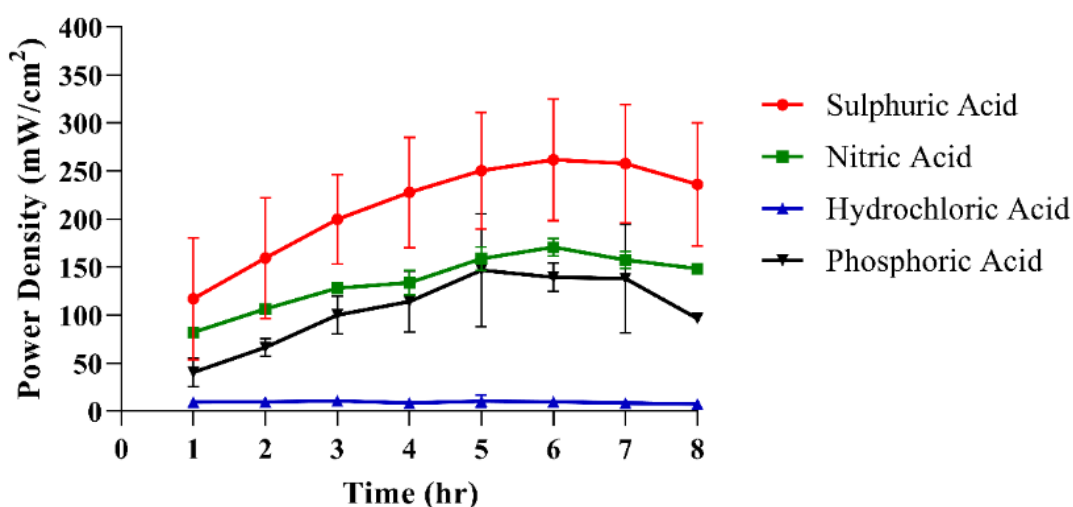


Figure 4.19: Average power density obtained from DCPFC with different acids added to POME solution

Table 4.10 showed the overall increment in power density of DCPFC using POME with different acids added. The power density for POME solution with H_2SO_4 , HNO_3 , and H_3PO_4 added showed gradually increased from 1st hour to 8th hour. Meanwhile, for the POME solution with HCl added, the power density significantly reduced from 9.433 mW/cm^2 (1st hour) to 7.371 mW/cm^2 (8th hour).

Table 4.10: Increment in average power density of DCPFC with different acids added

Acids	Power Density (mW/cm^2)		Increment %
	1 st hour	8 th hour	
H_2SO_4	117.289	236.312	101.478
HNO_3	82.108	148.342	80.667
H_3PO_4	40.335	96.529	139.318
HCl	9.433	7.371	-21.859

Furthermore, the degradation of POME solution with H_2SO_4 added showed the highest degradation efficiency where the 25% POME solution completely degraded at the 8th hour (Figure 4.20) alongside the highest power density generated. The POME solution

with H_3PO_4 added was the second highest degradation efficiency and followed by POME solution with HCl and HNO_3 added. The difference in degradation efficiency in POME solution with different acids added was probably due to the effect of the anion produced during the dissociation of the acids.

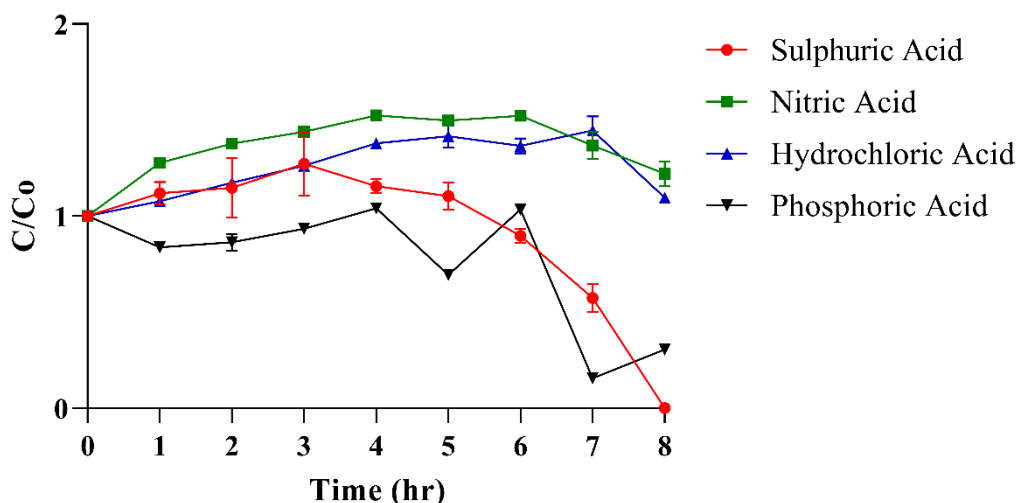


Figure 4.20: Degradation of POME solution with different acids added

This result was in-line with the research done by Barisci and Suri (2020) where the degradation of perfluorocarboxylic acid experienced 50% increment when Na_2SO_4 solution were used as electrolyte. The authors also mentioned that the use of Na_2SO_4 electrolyte in the solution decreased the solution's resistance, resulting in greater potential difference in the solutions which ultimately enhanced the degradation of perfluorocarboxylic acid solution. In the experiment, H_2SO_4 was added to the solution has produced higher power density and greater degradation efficiency compared to HCl , HNO_3 , and H_3PO_4 due to high ionic conductivity of H_2SO_4 solution which further enhanced the electrochemical performance (Fischer et al., 2022).

The maximum power generation from ECD method prepared ZnO/Zn photoanode in methyl red dye solution and POME treatment showed approximately 5,000 times higher than the power obtained from the studies (Table 4.11). The significant increase in power generation showed that the DCPFC and ECD method prepared ZnO/Zn photoanode significantly improved the performance of the reported PFC.

Table 4.11: Power generation from PFC using different photoanode in various wastewater treatment

Photoanode	Sources	Power Generation	Reference
ECD method prepared ZnO/Zn photoanode	POME	236.312 mW/cm ²	In this study
ECD method prepared ZnO/Zn photoanode	Methyl red dye	209.83 mW/cm ²	In this study
UiO66-NH ₂ -TiO ₂ /NiF	Antibiotic wastewater	16.98 μ W/cm ²	Abbasnia et al. (2023)
ZnO/C	Amaranth Dye	1.2211 μ W/cm ²	Thor et al. (2021)
W-BiVO ₄ /V ₂ O ₅	N.A.	0.84 mW/cm ²	Andrade et al. (2021)
MoO ₃ /ZnO/Zn	Real plating wastewater	0.005 mW/cm ²	Lam et al. (2021)
TiO ₂	o-chlorophenol	301 mW/m ²	Wang et al. (2022)
RuO ₂ -TiO ₂	N.A.	0.5 mA/cm ²	Jiang et al. (2022)
NiFe ₂ O ₄ /ZnO	Printing wastewater	0.6 mW/cm ²	Lam et al. (2023)
ZnO/BiOBr/UiO-66-NH ₂	Tetracycline wastewater	29.26 μ W/cm ²	Ghorbani et al. (2023)
BiVO ₄	Chromium (VI) wastewater	1.35 mW/cm ²	Tan et al. (2023)
Polyaniline/g-C ₃ N ₄ /Bi ₂ O ₃ /Ti	Rhodamine B	4.78 μ W/cm ²	Dong et al. (2023)

N.A. = Not Available

4.3.5.1 The Effect of SO_4^{2-} Ion in POME Solution

With the addition of H_2SO_4 solution in the POME solution, the power density and degradation rate increased. It was believed due to the formation of sulphate radical ($\text{SO}_4^{\bullet-}$) by the activation of persulfate in the solution via photocatalyst (T. Jiang et al., 2023). When H_2SO_4 solution was added to the POME solution in DCPFC, the energy sufficient environment causes a series of reaction on SO_4^{2-} ion which leads to the production of peroxymonosulfate (PMS) and peroxydisulfate (PDS) (Sun et al., 2023). The formation of PMS and PDS was summarize in Equation 4.23 to Equation 4.25.

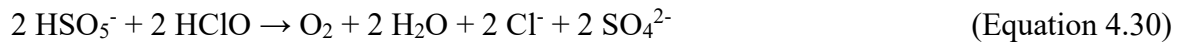


The PMS and PDS formed in during the process considered as strong oxidizer which capable for self-activation or activated via photons or heat into $\text{SO}_4^{\bullet-}$ radicals (Equation 4.26 and Equation 4.27) (Qin et al., 2023). According to Wang and Wang (2020), the sulphate radical has the redox potential between 2.5 V to 3.1 V only second to fluoride (F^-) ion. Moreover, the SO_4^{2-} ion reacts readily with $\bullet\text{OH}$ radical to form $\text{SO}_4^{\bullet-}$ radical (Equation 4.28) (Chen et al., 2023).



In the experiment, the effect of SO_4^{2-} ion was promoted by the addition of Cl^- ion from the cathode chamber which indicated by the increased power generation and

degradation efficiency. According to Oyekunle et al. (2021) and Ren et al. (2020), the Cl^- ion reacts with the PMS forming SO_4^{2-} ion and HOCl (Equation 4.29). The HOCl produced also reacted with PMS yielding oxygen (O_2), Cl^- ion, and SO_4^{2-} ion (Equation 4.30) according to Oyekunle et al. (2021). The regeneration of SO_4^{2-} ion by Cl^- ion induced the generation of more electrons in the solution which directly increased power generation. The Cl^- ion reacts with the $\bullet\text{OH}$ radicals forming chlorine radical ($\bullet\text{Cl}$) and OH^- ion (Equation 4.31) (Zhang et al., 2021). Later, the $\bullet\text{Cl}$ radical reacts with the SO_4^{2-} ion producing $\text{SO}_4^{\bullet-}$ radical (Equation 4.32).



4.3.5.2 The Effect of PO_4^{3-} Ion in POME Solution

From Figure 4.18, the addition of H_3PO_4 in POME solution resulted in a higher degradation rate compared to HNO_3 and HCl . This is due to the PO_4^{3-} ion strongly bond to photoanode surface and thus lead to a strong interaction with ZnO and the organic pollutants in POME (Ong et al., 2020). Attested by Ong et al. (2020), the zinc phosphate $[\text{Zn}_3(\text{PO}_4)_2]$ formation (Equation 4.33) was due to some of the PO_4^{3-} ion trapped by the Zn^{2+} ion. The formation of $\text{Zn}_3(\text{PO}_4)_2$ on the photoanode enhanced the degradation of POME due to its photocatalytic effect. The result obtained for POME degradation in this project was parallel to the results reported by Chennah et al. (2021) and Naciri et al. (2018), where the groups

used $\text{Zn}_3(\text{PO}_4)_2$ coated photoanode for the degradation of Rhodamine B (RhB) wastewater. The degradation efficiency of RhB wastewater by $\text{Zn}_3(\text{PO}_4)_2$ was about 99% under UV irradiation. However, the degradation of POME solution with H_3PO_4 added shown in Figure 4.18 was lower compared to H_2SO_4 because it was the mixture of ZnO and $[\text{Zn}_3(\text{PO}_4)_2]$ in our DCPFC instead of pure $[\text{Zn}_3(\text{PO}_4)_2]$.



4.3.5.3 The Effect of Cl^- Ion in POME Solution

As shown in Figure 4.17 and Figure 4.18, the power generation and degradation rate of DCPFC for POME solution is the lowest when HCl was added compared to H_2SO_4 , HNO_3 , and H_3PO_4 . This is due to the saturation of Cl^- ion, as Cl^- ion is presented in both salt bridge and cathode chamber. The formation of $\bullet\text{Cl}$ radicals during the degradation process has higher selectivity than $\bullet\text{OH}$ radicals especially in the reaction with aromatic pollutants despite $\bullet\text{OH}$ radicals has higher redox potential than $\bullet\text{Cl}$ radicals (Nikraves et al., 2020). Therefore, the reduced degradation rate of POME solution was due to the competitive reaction between $\bullet\text{Cl}$ radicals and $\bullet\text{OH}$ radicals. Based on the study done by Nur et al. (2021), the major phenolic compounds existed in POME were gallic acid, p-hydroxybenzoic acid, protocatechuic acid, caffeic acid, syringic acid, and vanillic acid. Besides the mentioned phenolic compounds, the tannins, humic acid, and melanoidins which contributed to the brown coloration of POME are majority phenolic or aromatic compounds (Khongkliang et al., 2023).

Moreover, with the addition of Cl^- ion in anode chamber disturbed the electrons transfer reaction from cathode chamber to anode chamber. Without the introduction of Cl^-

ion in the anode chamber, there was a flow of Cl^- ion and electrons from cathode chamber by diffusion and initiating a series of reaction in anode chamber. As the addition of Cl^- ion in anode chamber, the equilibrium between anode chamber and cathode chamber established faster resulting in lower or halted diffusion rate. Thus, the degradation rate and power generation of DCPFC is lower as shown in Figure 4.17 and Figure 4.18.

4.3.5.4 The Effect of NO_3^- Ion in POME Solution

Although the nitrate radical ($\bullet\text{NO}_3$) has redox potential stronger than $\text{SO}_4^{\bullet-}$ radicals, the addition of HNO_3 in POME was inferior to the one using H_2SO_4 (Figure 4.15) (Hering et al., 2015). The production of $\bullet\text{NO}_3$ radicals started with the photoactivation of NO_3^- ion to excited-state nitrate ion $[\text{NO}_3^-]^*$ (Equation 4.34) (Xie et al., 2023). Under acidic conditions, the peroxyxynitrous acid (ONOOH) was produced via a series of isomerization reactions with water (Equation 4.35). Besides production of ONOOH , the nitrite radicals ($\bullet\text{NO}_2$) were formed via the decomposition of $[\text{NO}_3^-]^*$ under irradiation as well as formation of singlet oxygen ($\text{O}^{\bullet-}$) (Equation 4.36). Xie et al. (2023) also mentioned that the $\bullet\text{NO}_2$ radical formed further reacted with water and singlet oxygen yielding $\bullet\text{NO}_2$ radical, $\bullet\text{OH}$ radical, and OH^- ion (Equation 4.37). In acidic conditions, the ONOOH dissociated to ONOO^- and H^+ ion where the ONOO^- ion further reacted with $\bullet\text{OH}$ radical producing nitric radical ($\bullet\text{NO}$) (Equation 4.38) according to Xie et al. (2023).





Although the $\bullet\text{NO}_2$ radicals have stronger oxidizing potential than hydroxyl radical, the degradation of POME solution in DCPFC remained low. This was due to the competitive reaction of $\bullet\text{NO}$ radicals with $\bullet\text{OH}$ radicals where both radicals reacted together producing nitrous acid (HNO_2) (Equation 4.39) (Tang et al., 2021; Wu et al., 2020).



Besides competitive reaction between $\bullet\text{OH}$ radical, the $\bullet\text{NO}_2$ radical and NO_2^- ion are also significantly affected by the Cl^- ion or $\bullet\text{Cl}$ radical in the solution. The nitrate radicals scavenging activity was inhibited by the presence of Cl^- ion diffused from salt bridge and cathode chamber in DCPFC. The inhibition of scavenging activity was due to the formation of nitryl chloride (ClNO_2) (Equation 4.40) from reaction between NO_2^- ion produced via the dissociation of HNO_2 and hypochlorous acid (HOCl) (Ao et al., 2024). The diffused Cl^- ion from salt bridge and cathode chamber reacted with water according to Yu et al. (2004) resulted in the formation of HOCl (Equation 4.41). The favorable reaction of Cl^- ion with $\bullet\text{NO}_2$ radical as mentioned by Wang et al. (2021) causing in reduced in amount of available reactive species. Hence, the degradation of POME solution with HNO_3 added exhibits a lower rate (Figure 4.18).



It is worth mentioning that the power generation from the DCPFC with HNO_3 added POME solution has the second highest power density compared to POME solution with HCl

and H_3PO_4 added (Figure 4.17). According to Ao et al. (2024), the secondary pathway of the nitrate ion related reaction producing more electrons contributing to mass transfer of electrons from anode chamber to cathode chamber via external circuit.

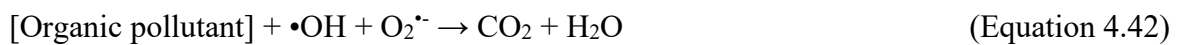
4.4 Radicals Reaction in Dual Chamber Photocatalytic Fuel Cell (DCPFC)

The degradation of POME as shown in Figure 4.11, Figure 4.14, Figure 4.16, and Figure 4.18 have demonstrated an increase-then-decrease pattern. The increase-then-decrease pattern of organic pollutants removal also exhibited in the research done by Li et al. (2021). According to Li and co-workers, the increased organic pollutants' concentration at the initial stage was due to the continuous release of organic substances from the removal process where the substances are harder to remove or oxidized to CO_2 . In this context, the POME degradation pattern observed in Figure 4.11, Figure 4.14, Figure 4.16, and Figure 4.18 resembled the research done by Li et al. (2021). However, the exact mechanism of photocatalytic degradation was not well understood as the strong scavenging ability of free radical produced from ZnO/Zn photoanode reacted with the organic compounds at any possible position. The higher entropy in the irreversible free radical reaction increased the difficulty in predicting the degradation rate of organic molecules especially with various types of organic molecules existing in the solution.

Due to the production of free radical species during the photocatalytic degradation, the photocatalytic reaction followed the free radical reaction where typically consists of three major steps specifically initiation step, propagation step, and termination step (Faroux et al., 2020). The initiation step for the free radical reaction through photocatalyst is the production

of free radical including $\bullet\text{OH}$ radical and $\text{O}_2^{\bullet-}$ anion via photoactivation on the surface of ZnO/Zn photoanode.

The $\bullet\text{OH}$ radical and $\text{O}_2^{\bullet-}$ anion produced are extremely reactive and unstable, thus it was utilized for oxidizing most of the organic pollutants to CO_2 and H_2O (Equation 4.42) (Ganiyu et al., 2022). The oxidization process of organic pollutants via free radicals in DCPFC continued by propagating the radical species to a non-radical species. The propagation of radical's unpaired electron to organic pollutant summarized as shown in Equation 4.43 to Equation 4.46 (Bule Mozar et al., 2023). Considering the nature of radicals, the transfer of unpaired electron from radical species to organic pollutant occurs at any possible position hence it is capable to produce different fragment of alkyl radicals (Equation 4.50) stated by Bule Mozar et al. (2023). The propagation reaction continued as the alkyl radicals formed reacted with another organic molecule until a stable and non-reactive species produced. The continuous propagation of radical species is also known as free radical chain reaction. During the free radical chain reaction, more alkyl radicals species formed with different length formed as the alkyl radicals species continued to propagate (Equation 4.51).



The alkyl radicals produced then reacted with H^+ ion in the anode chamber forming a stable alkyl species (Equation 4.47). Due to the smaller fragment of organic compound as a result of free radical splitting, the degradation rate of organic molecules increased. As shown Figure 4.11, the pH value of POME solution decreased resulting in faster POME degradation. This is due to the increase of H^+ ion as pH value decreased had promoted the formation of smaller yet stable organic molecules. A slight increase in COD value for pH 3 and pH 4 was due to the increase in organic substances in POME solution.



Nevertheless, the increase in pH value resulting in reduced degradation rate because the alkyl radical tends to react with the OH^- ion (Equation 4.48) yielding organic compound with hydroxide group (-OH). With the reaction between alkyl halide resulted from the reaction of alkyl radical and halide ion (Equation 4.49), with $O_2^{\bullet-}$ anion, alkylperoxy radical ($ROO\bullet$) formed (Equation 4.50). and further produced peroxy anion due to one-electron reduction (Andrés et al., 2023). The ROO^- anion reacted with H^+ ion forming either peroxy acid ($RO-OOH$) (Equation 4.51) or carboxylic acid ($ROOH$) (Equation 4.52) according to Andrés et al. (2023).



The formation of peroxy acid intermediates contributed to the complexity of the degradation process as the peroxy acid considered as one of the most versatile organic compounds which utilized in wide range of specific oxidation reactions (Kaur & Kishore, 2014). Therefore, as increased in pH value, the degradation rate of organic-based wastewater reduced due to the contribution of OH^- ion and $\text{O}_2^{\bullet-}$ anion in formation of various oxygenated compounds.

However, as the degradation period increased for POME solution in DCPFC, the formation of smaller yet unstable intermediates and fragments of organic compounds increased. Those organic compounds were gradually degraded by ROS and free radicals into simplest molecules such as CO_2 and H_2O .

Last but not least, the termination step during the free radical reaction occurred when two radical species reacted together forming a new organic molecule. However, the production of stable compounds via termination step will significantly affected the photocatalytic degradation (Liu et al., 2020). This is due to the chemically stable compounds that are able to withstand various chemical reactions including photocatalytic redox reaction which increased the difficulties in degradation. Liu et al. (2020) added, it is important to prevent the termination step during the photocatalytic degradation while promoting the chain reaction of initiation and propagation.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this project, the ZnO/Zn photoanode was successfully prepared using electrochemical deposition (ECD) and ultrasonic method. The surface morphology of both ECD method and ultrasonic method prepared ZnO/Zn photoanode was observed under FE-SEM. From the result, the ultrasonic method prepared ZnO/Zn photoanode showed several types of ZnO crystal form while ECD method prepared ZnO/Zn photoanode only presence of one type of ZnO crystal (Figure 4.1). Besides, the formation of ZnO on the ECD method prepared ZnO/Zn photoanode was confirmed by using EDX analysis (Figure 4.3) where the analysis showed the photoanode consisted of $81.08 \pm 0.12\%$ of Zn as well as $15.09 \pm 0.04\%$ of oxygen. Moreover, the EDX spectrum (Figure 4.2) showed two peak at 0.53 and 1.01 keV which represented the peak for oxygen and Zn formation on the ZnO/Zn photoanode surface.

Furthermore, the DCPFC was successfully fabricated by connecting two containers with a PVC tee connector as a salt bridge. In the DCPFC, the anode chamber was filled with organic-based wastewater, where cathode chamber was filled with diluted NaClO solution. The salt bridge was filled with 1.0 M of KCl which act as a pathway for electrons and ion transfer between anode and cathode chamber. A piece of cellulose acetate filter membrane was used to separate the solution in salt bridge, anode and cathode chamber.

Besides, the fabricated DCPFC was tested using 10 ppm methyl red dye solution to access its performance in power generation as well as degradation under different pH (pH 3, pH 4, pH 5, pH 7, pH 8), and different NaClO solution concentration (125 mL/L, 250 mL/L,

375 mL/L). The performance of DCPFC using ECD method and ultrasonicate method prepared ZnO/Zn photoanode also being investigated under different conditions. The highest power density obtained for DCPFC was under the condition of 10 ppm methyl red dye solution at pH 4 with 250 mL/L NaClO solution concentration which showed 209.83 mW/cm² while using ECD method prepared ZnO/Zn photoanode. Moreover, the DCPFC with ECD method prepared ZnO/Zn photoanode has the fastest complete methyl red dye removal rate (138 minutes) at pH 4 with 250 mL/L NaClO solution in cathode chamber. As for the volume of DCPFC, when the volume of DCPFC increased from 1 L to 2 L and 4 L, the removal rate of methyl red dye solution significantly decreased from 100% to 42.88% (4 L). It can be concluded that using ECD method prepared ZnO/Zn photoanode has significantly increased the performance of DCPFC.

The power generation and degradation efficiency of DCPFC was successfully investigated under different pH (pH 3, pH 4, pH 5, and pH 8), concentration (25%, 50%, 75%, and 100%), volume of DCPFC (1 L, 2 L, and 4 L), as well as different acids (H₂SO₄, HNO₃, HCl, H₃PO₄) added to POME solution. The optimized conditions for highest degradation efficiency and power density for DCPFC with ECD method prepared ZnO/Zn photoanode was pH 4, 25% POME solution concentration, 1 L of DCPFC, and H₂SO₄ added to POME solution. Under these conditions, the power density obtained was 236.312 mW/cm² and complete degradation of POME solution at 8th hour.

It can be concluded that the fabrication of DCPFC and ZnO/Zn photoanode prepared via ECD method greatly enhanced the power density and degradation efficiency compared to single chamber PFC. With the addition of NaClO solution in cathode chamber as oxidizing agent, the organic-based wastewater was treated in higher efficiency. Furthermore, the Cl⁻ ion provided from cathode chamber enhanced the radicals formation in anode chamber

which directly boosted the degradation rate. Besides, the ZnO/Zn photoanode prepared via ECD method used in the DCPFC significantly increased the power generation due to its larger effective surface area and smaller particle size.

5.2 Recommendations

In spite of the studies done on the factors affecting the performance of DCPFC on methyl red dye solution and POME solution, several limitations were faced during the research which halted the continuous exploration of full potential of DCPFC. First of all, the lack of instruments such as high-resolution transmission electron microscope (HRTEM), and X-ray Diffraction (XRD) for further research onto the crystalline properties, and exact chemical composition of the nano size particles form especially for ECD method prepared ZnO/Zn photoanode. Another instrument required for the studies is photoluminescence (PL) spectroscopy which was commonly applied in the study to access the optical and electronic properties of ZnO/Zn photoanode. With the access of PL spectroscopy, detailed studies on the excitation of electron from photocatalyst can be conducted using time-resolved photoluminescence (TRPL) technique. Besides the lack of instruments, the time constraint is also one of the challenges faced during the research period. As the short amount of time in research study, some of the important study such as longevity of ZnO/Zn photoanode prepared via ECD method, in-depth studies on factors affecting the degradation and power generation of DCPFC with various organic-based wastewater. The unavailability of conducting the studies was due to the long preparation and experiment period specifically longevity study on ZnO/Zn photoanode, in which the experiment period might extend from weeks to months. Not to mention, another limitation faced during the research period was

the lack of experience regarding PFC. During the study, lack of experience could lead to researcher bias where the analysis method planned might favor the expected results by the researchers.

Despite the ECD method prepared ZnO/Zn photoanode and DCPFC showed excellent effectiveness in wastewater treatment and simultaneously power generation, it is insufficient for implementation in industry scale as the daily wastewater treatment usually runs from several thousand liter to thousand tons of water. From the experiment on the volume of wastewater in DCPFC, as the capacity of DCPFC increased, the degradation rate and power generation reduced drastically. Moreover, wastewater typically has a pH value in alkaline condition. Considering the amount of wastewater treated daily, the adjustment of pH value to acidic condition is nearly impossible. Therefore, in future studies, several recommendations on DCPFC and photoanode could be applied for upscaling of PFC to achieve higher degradation rate and power generation.

To increase the total amount of wastewater treated, instead of directly increasing the volume of DCPFC, the stacked 1 L volume DCPFC could be implemented together with a reservoir. From this research, the optimum volume of DCPFC was 1 L, the stacked 1 L DCPFC utilized the full potential to achieve the highest degradation rate for organic-based wastewater in large quantities. The stacked DCPFC could be connected either in series or in parallel to increase the total power output from the system.

In order to cope with the increased volume of DCPFC, the alteration of coating method and the material used for photoanode was also considered as one of the recommended strategies. Recent years, the uprising of conducting polymer such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) made several contributions

in advancing the research on PFC. For large scale production of photoanode, the process of manufacturing could include the use of such conducting polymer as one of the base materials for increasing the performance as well as reducing cost.

Last but not least, the solution used in the DCPFC apart from the anode chamber is also one of the aspects that are worth highlighting. In order to increase the degradation rate, the salt solution in the salt bridge can be adjusted by altering the concentration of the solution or by changing the salt used. In addition, the solution in cathode chamber could replace with H_2O_2 solution or other suitable solution to further enhance the degradation of organic-based wastewater.

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APPENDICES

Appendix A: Data for COD assurance test

Appendix A1: Absorbance at 420 nm for theoretical COD concentration (200 to 1,000 mg/L)

Trials	Theoretical COD (mg/L)				
	200	400	600	800	1000
1	1.9325	1.5116	1.1242	0.6893	0.3087
2	1.953	1.5015	1.1009	0.6838	0.3091
3	1.9179	1.5245	1.1117	0.6884	0.3091
4	1.9675	1.5148	1.1185	0.6963	0.3009
5	1.9315	1.52	1.15	0.6965	0.3062
6	1.9415	1.5244	1.1054	0.695	0.302
7	1.9315	1.559	1.1092	0.703	0.3053
8	1.9483	1.5194	1.0987	0.6937	0.3054
9	1.9479	1.5062	1.1027	0.6972	0.3115
10	2.1031	1.4481	1.0453	0.635	0.316
11	1.9072	1.5409	1.108	0.6892	0.2972
12	1.8373	1.4498	1.0326	0.6121	0.3101
13	1.8903	1.4469	1.0434	0.6343	0.3123
14	1.942	1.558	1.1722	0.6782	0.3157
15	2.0821	1.6091	1.1903	0.73	0.3106

Appendix A2: Absorbance at 440 nm for theoretical COD concentration (200 to 1,000 mg/L)

Trials	Theoretical COD (mg/L)				
	200	400	600	800	1000
1	2.2001	1.7011	1.2303	0.7341	0.2888
2	2.2153	1.6894	1.2178	0.7324	0.2903
3	2.1761	1.7128	1.2286	0.7336	0.2892
4	2.231	1.7052	1.2377	0.7446	0.2814
5	2.2023	1.7127	1.2505	0.7444	0.2899
6	2.2106	1.7191	1.2265	0.7421	0.2822
7	2.2093	1.7457	1.2246	0.7469	0.2859
8	2.2023	1.7118	1.2165	0.7397	0.2863
9	2.2131	1.6945	1.2211	0.7415	0.2947
10	2.338	1.641	1.169	0.682	0.321
11	2.12	1.641	1.151	0.653	0.315
12	2.17	1.723	1.264	0.721	0.322
13	2.254	1.755	1.148	0.687	0.316
14	2.222	1.821	1.196	0.719	0.314
15	2.241	1.7011	1.184	0.667	0.314

Appendix A3: Absorbance at 600 nm for theoretical COD concentration (200 to 1,000 mg/L)

Trials	Theoretical COD (mg/L)				
	200	400	600	800	1000
1	0.085	0.1311	0.1973	0.2495	0.3074
2	0.08	0.1331	0.192	0.2543	0.3097
3	0.081	0.1302	0.1924	0.2538	0.3052
4	0.083	0.1304	0.1901	0.25	0.3039
5	0.085	0.1301	0.2004	0.2487	0.3092
6	0.087	0.1303	0.1908	0.2496	0.3049
7	0.095	0.1311	0.1924	0.2562	0.3077
8	0.094	0.1319	0.1923	0.2539	0.3078
9	0.092	0.1345	0.1948	0.2548	0.3147
10	0.097	0.136	0.197	0.256	0.319
11	0.084	0.144	0.202	0.269	0.314
12	0.084	0.142	0.209	0.266	0.322
13	0.083	0.141	0.215	0.269	0.318
14	0.091	0.149	0.198	0.258	0.315
15	0.093	0.141	0.206	0.265	0.313

Appendix A4: Absorbance at 610 nm for theoretical COD concentration (200 to 1,000 mg/L)

Trials	Theoretical COD (mg/L)				
	200	400	600	800	1000
1	0.085	0.1306	0.197	0.2494	0.3064
2	0.08	0.133	0.1915	0.2535	0.3095
3	0.081	0.1302	0.1915	0.2531	0.3048
4	0.083	0.1298	0.1895	0.2491	0.3131
5	0.085	0.1295	0.2007	0.2481	0.3082
6	0.087	0.1294	0.1896	0.2486	0.3039
7	0.095	0.1311	0.1914	0.2554	0.3066
8	0.094	0.1317	0.1909	0.2521	0.3066
9	0.092	0.1339	0.1945	0.2546	0.3148
10	0.097	0.139	0.197	0.257	0.321
11	0.084	0.142	0.201	0.261	0.317
12	0.087	0.145	0.21	0.261	0.321
13	0.081	0.143	0.215	0.27	0.317
14	0.091	0.146	0.205	0.259	0.318
15	0.093	0.148	0.207	0.265	0.315

Appendix A5: Actual COD concentration calculated at 420 nm for each theoretical COD concentration

Trials	Actual COD (mg/L)				
	200	400	600	800	1000
1	235.1173122	439.6362627	627.8772734	839.1989449	1024.135777
2	225.1561849	444.54394	639.1989449	841.8714425	1023.941413
3	242.2115785	433.3680411	633.9511315	839.6362627	1023.941413
4	218.1105095	438.081355	630.6469527	835.7975843	1027.925864
5	235.6032209	435.55463	615.3408302	835.7004026	1025.350548
6	230.7441344	433.416632	637.012356	836.4292656	1027.391365
7	235.6032209	416.6041927	635.1659031	832.5419964	1025.787866
8	227.4399556	435.8461752	640.2679439	837.0609468	1025.739275
9	227.634319	442.2601694	638.3243093	835.3602666	1022.775233
10	152.2212967	470.4914619	666.2154658	865.5837845	1020.588644
11	247.4108011	425.3991392	635.7489935	839.2475358	1029.723726
12	281.3758156	469.6654172	672.3865056	876.7110926	1023.455505
13	255.6226572	471.0745523	667.1386922	865.9239206	1022.386506
14	230.5011801	417.0901013	604.5536582	844.5925309	1020.734416
15	162.4253783	392.2601694	595.7587116	819.4224629	1023.21255

Appendix A6: Actual COD concentration calculated at 440 nm for each theoretical COD concentration

Trials	Actual COD (mg/L)				
	200	400	600	800	1000
1	209.5691798	416.2800331	611.3090307	816.8599834	1001.325601
2	203.2725766	421.1267606	616.4871582	817.5642088	1000.704225
3	219.5111848	411.4333057	612.013256	817.0671085	1001.159901
4	196.7688484	414.5816073	608.2435791	812.5103563	1004.391052
5	208.6578293	411.4747307	602.9411765	812.5932063	1000.869925
6	205.2195526	408.8235294	612.8831814	813.5459818	1004.059652
7	205.7580779	397.8044739	613.6702568	811.5575808	1002.526926
8	208.6578293	411.8475559	617.0256835	814.5401823	1002.361226
9	204.1839271	419.0140845	615.1201326	813.7945319	998.8815244
10	152.4440762	441.1764706	636.7025684	838.4424192	987.986744
11	242.7506214	441.1764706	644.1590721	850.4556752	990.4722452
12	222.038111	407.2079536	597.3487987	822.2866611	987.5724938
13	187.2410936	393.951947	645.4018227	836.3711682	990.057995
14	200.4971003	366.6114333	625.5178128	823.1151616	990.8864954
15	192.6263463	416.2800331	630.4888152	844.6561723	990.8864954

Appendix A7: Actual COD concentration calculated at 600 nm for each theoretical COD concentration

Trials	Actual COD (mg/L)				
	200	400	600	800	1000
1	203.02391	365.1195499	597.8902954	781.4345992	985.021097
2	185.443038	372.1518987	579.254571	798.3122363	993.1082982
3	188.9592124	361.954993	580.6610408	796.5541491	977.2855134
4	195.9915612	362.6582278	572.5738397	783.1926864	972.7144866
5	203.02391	361.6033755	608.790436	778.6216596	991.350211
6	210.0562588	362.3066104	575.0351617	781.7862166	976.230661
7	238.185654	365.1195499	580.6610408	804.9929677	986.0759494
8	234.6694796	367.9324895	580.3094233	796.9057665	986.4275668
9	227.6371308	377.0745429	589.0998594	800.0703235	1010.68917
10	245.2180028	382.3488045	596.835443	804.2897328	1025.80872
11	199.5077356	410.4781997	614.416315	850	1008.227848
12	199.5077356	403.4458509	639.0295359	839.4514768	1036.357243
13	195.9915612	399.9296765	660.1265823	850	1022.292546
14	224.1209564	428.0590717	600.3516174	811.3220816	1011.744023
15	231.1533052	399.9296765	628.4810127	835.9353024	1004.711674

Appendix A8: Actual COD concentration calculated at 610 nm for each theoretical COD concentration

Trials	Actual COD (mg/L)				
	200	400	600	800	1000
1	202.6371308	362.9746835	596.4486639	780.6962025	981.1181435
2	185.0562588	371.4135021	577.1097046	795.1125176	992.0182841
3	188.5724332	361.5682138	577.1097046	793.7060478	975.4922644
4	195.604782	360.161744	570.0773558	779.6413502	1004.676512
5	202.6371308	359.1068917	609.4585091	776.1251758	987.4472574
6	209.6694796	358.7552743	570.4289733	777.883263	972.3277075
7	237.7988748	364.7327707	576.7580872	801.7932489	981.8213783
8	234.2827004	366.8424754	575	790.1898734	981.8213783
9	227.2503516	374.5780591	587.6582278	798.9803094	1010.654008
10	244.8312236	392.5105485	596.4486639	807.419128	1032.45429
11	199.1209564	403.0590717	610.5133615	821.4838256	1018.389592
12	209.6694796	413.6075949	642.1589311	821.4838256	1032.45429
13	188.5724332	406.5752461	659.7398031	853.1293952	1018.389592
14	223.7341772	417.1237693	624.5780591	814.4514768	1021.905767
15	230.766526	424.1561181	631.6104079	835.5485232	1011.357243

Appendix A9: Data for APHA closed reflux, titration method of COD determination using 200 mg/L KHP calibration solution

Trials	Volume of FAS solution used (mL)		
	Before	After	Used FAS solution
1	0.1	7.1	7
2	7.1	14.4	7.3
3	14.4	21.7	7.3
4	0.1	6.9	6.8
5	6.9	13.9	7
6	14	21.1	7.1
7	0.1	7	6.9
8	7	14.3	7.3
9	14.3	21.5	7.2
10	0.2	7.4	7.2
11	7.4	14.8	7.4
12	14.8	21.6	6.8
13	0.1	7.2	7.1
14	7.2	14.5	7.3
15	14.6	21.4	6.8

Appendix B: Data for obtained voltage from DCPFC using 10 ppm methyl red dye solution

Appendix B1: Average power density every hour from DCPFC using 10 ppm methyl red dye solution at pH 4 in anode chamber with 125, 250, and 375 mL/L NaClO solution in cathode chamber

Time (hr)	Average power density (mW/cm ²)		
	125	250	375
0	104.231	105.326	131.458
1	151.801	159.806	149.831
2	219.226	209.058	190.183
3	233.703	209.831	187.246
4	285.303	N.A.	N.A.
5	277.235	N.A.	N.A.

N.A. = Not Available

Appendix B2: Average power density every hour from DCPFC using 10 ppm methyl red dye solution at pH 5 in anode chamber with 125, 250, and 375 mL/L NaClO solution in cathode chamber

Time (hr)	Average power density (mW/cm ²)		
	125	250	375
0	16.733	17.431	61.321
1	55.983	48.722	74.057
2	56.52	65.089	107.531
3	92.635	98.846	132.071
4	105.326	N.A.	N.A.

N.A. = Not Available

Appendix C: Data for obtained voltage and COD concentration from DCPFC using POME solution

Appendix C1: Average power generation every hour from DCPFC using POME solution at pH 3, 4, 5, and 8 in anode chamber with 250 mL/L NaClO solution in cathode chamber

Time (hr)	Average Power Density (mW/cm ²)			
	pH 3	pH 4	pH 5	pH 8
0	116.2629	96.99433	72.63795	15.46086
1	91.1799	117.289	87.73048	6.607333
2	121.8224	159.545	165.889	1.392238
3	130.3214	199.8614	167.9167	0.267524
4	142.6845	227.7231	204.2852	0.12981
5	195.1469	250.5224	261.6983	0.054405
6	227.6079	261.9871	195.2148	0.006786
7	205.2133	257.8748	185.7876	0.005833
8	174.8781	236.3117	164.826	0.005071

Appendix C2: Average power generation every hour from DCPFC using POME solution at 25%, 50%, 75%, and 100% POME concentration in anode chamber with 250 mL/L NaClO solution in cathode chamber

Time (hr)	Average Power Density (mW/cm ²)			
	25%	50%	75%	100%
0	96.99433	103.1319	180.27	230.9648
1	117.289	139.3498	163.0279	167.3529
2	159.545	186.6633	193.7893	138.5207
3	199.8614	228.41	167.9055	85.37952
4	227.7231	243.07	232.6062	46.81548
5	250.5224	253.9586	263.5586	32.42167
6	261.9871	279.3526	312.8031	15.30619
7	257.8748	300.0807	324.6129	7.779524
8	236.3117	324.3726	344.069	3.64881

Appendix C3: Average power generation every hour from DCPFC using POME solution at 1 L, 2 L, and 4 L volume in anode chamber with 250 mL/L NaClO solution in cathode chamber

Time (hr)	Average power density (mW/cm ²)		
	1 L	2 L	4 L
0	96.99433	18.50764	6.44294
1	117.289	13.87195	2.716119
2	159.545	78.23143	2.551655
3	199.8614	79.35119	15.55724
4	227.7231	109.3545	5.774917
5	250.5224	113.6193	9.903869
6	261.9871	126.4511	10.06337
7	257.8748	121.2764	8.282208
8	236.3117	86.21929	8.06519

Appendix C4: Average power generation every hour from DCPFC using POME solution with sulphuric acid, hydrochloric acid, nitric acid, and phosphoric acid added to POME solution in anode chamber with 250 mL/L NaClO solution in cathode chamber

Time (hr)	Average power density (mW/cm ²)			
	Sulphuric acid	Nitric acid	Hydrochloric acid	Phosphoric acid
0	96.99433	76.15295	8.240833	43.27667
1	117.289	82.1081	9.43281	40.33533
2	159.545	106.6364	9.997452	66.46195
3	199.8614	128.2126	10.82557	100.1767
4	227.7231	133.9148	8.610929	114.0712
5	250.5224	158.8452	10.47829	146.7512
6	261.9871	170.8826	9.667833	139.3881
7	257.8748	157.6498	8.629238	138.1138
8	236.3117	148.3417	7.371238	96.52867

Appendix C5: COD concentration every hour from DCPFC using POME solution at pH 3, 4, 5, and 8 in anode chamber with 250 mL/L NaClO solution in cathode chamber

Time (hr)	COD C/C ₀			
	pH 3	pH 4	pH 5	pH 8
0	1	1	1	1
1	1.115036	1.118958	2.189594	1.022554
2	1.200158	1.14806	2.152227	1.035065
3	0.870367	1.272945	2.576469	1.044219
4	0.614917	1.155647	3.728602	0.960792
5	0.575686	1.104521	4.079095	0.975969
6	0.288922	0.898184	3.0729	0.991623
7	0	0.574049	1.581218	1.020851
8	0	0	2.026447	1.017863

Appendix C6: COD concentration every hour from DCPFC using POME solution at 25%, 50%, 75%, and 100% POME concentration in anode chamber with 250 mL/L NaClO solution in cathode chamber

Time (hr)	COD C/C ₀			
	25%	50%	75%	100%
0	1	1	1	1
1	1.118958	0.80134	0.953528	0.91562
2	1.14806	0.658486	0.935012	0.784648
3	1.272945	0.772012	0.931261	0.677224
4	1.155647	0.849493	0.919486	0.719756
5	1.104521	0.889041	0.959894	0.691267
6	0.898184	0.854003	0.912715	0.639775
7	0.574049	0.733013	0.655437	0.634047
8	0	0.801274	0.967261	0.61572

Appendix C7: COD concentration every hour from DCPFC using POME solution at 1 L, 2 L, and 4 L volume in anode chamber with 250 mL/L NaClO solution in cathode chamber

Time (hr)	COD (C/C ₀)		
	1 L	2 L	4 L
0	1	1	1
1	1.118958	1.091634	0.426649
2	1.14806	0.968265	0.149016
3	1.272945	1.076361	0.163602
4	1.155647	0.980253	0.240512
5	1.104521	1.037626	0.425803
6	0.898184	1.096484	0.188672
7	0.574049	1.031874	0.179576
8	0	1.237904	0.485619

Appendix C8: COD concentration every hour from DCPFC using POME solution with sulphuric acid, hydrochloric acid, nitric acid, and phosphoric acid added to POME solution in anode chamber with 250 mL/L NaClO solution in cathode chamber

Time (hr)	COD (C/C ₀)			
	Sulphuric acid	Nitric acid	Hydrochloric acid	Phosphoric acid
0	1	1	1	1
1	1.118958	1.276782	1.078088	0.837363
2	1.14806	1.376688	1.173483	0.864439
3	1.272945	1.439425	1.263272	0.934261
4	1.155647	1.524806	1.378401	1.040059
5	1.104521	1.497035	1.41636	0.694569
6	0.898184	1.522539	1.365198	1.034981
7	0.574049	1.366838	1.445488	0.155063
8	0	1.220922	1.095304	0.305425

Appendix D: Publication

1. **Niang, A. C. K. anak**, Liu, J. C., & Tay, M. G. (2023). Electrochemical Deposition (ECD) of ZnO as the Photoanode in Dual-Chamber Photocatalytic Fuel Cell (PFC) for Methyl Red Degradation. *Advanced Materials Interfaces*, 10(12), 1–7.
<https://doi.org/10.1002/admi.202202366>