



Faculty of Resource Science and Technology

Optimization of Photocatalytic Fuel Cell (PFC) and Synthesis of Metal Complexes as Potential Photocatalysts in PFC for Synthetic Methyl Red Dye Degradation

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Optimization of Photocatalytic Fuel Cell (PFC) and Synthesis of Metal
Complexes as Potential Photocatalysts in PFC for Synthetic Methyl Red Dye
Degradation

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations 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 in candidature of any other degree.



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ABSTRACT

Photocatalytic fuel cell (PFC) is the combination of photocatalysis and fuel cell that can be used to treat wastewater and convert chemical energy to electrical energy simultaneously. Dual-chamber photocatalytic fuel cell (DCPFC) has been reported to have better performance than single-chamber photocatalytic fuel cell (SCPFC) because of the ability to prevent the electron-hole recombination in DCPFC. But there was not many side-by-side studies found in the literature to compare the performance in between SCPFC and DCPFC. This study presents a comprehensive comparison at different parameters between typical SCPFC and DCPFC for the synthetic methyl red dye degradation and power generation under different conditions. The performance of PFC influenced by the electron transfer driven by potential difference between two electrodes. SCPFC system after suffers from the fast recombination of electron-hole pairs. Besides that, the wide band gap of photocatalyst used in PFC has limited the utilization of sunlight hence has unsatisfied performance. The transition metal complexes with smaller band gap are believed to be able to improve the photocatalytic performance when applied as a photocatalyst in PFC. In the present study, a DCPFC setup was setup by separating the photoanode and cathode into two different chambers to prevent the rapid electron-hole recombination. Both types of PFC used ZnO/Zn as photoanode to treat the 10 ppm synthetic methyl red dye solution at pH 4. The DCPFC achieved a highest power generation (132.83 mW/cm^2) and 100% dye degradation, significantly outperforming than SCPFC which obtained the highest power generation (60.11 mW/cm^2) and 18.93% dye degradation. The ZnO/Zn photoanode could be reused twice in DCPFC but only once in SCPFC. This study highlights the advantages of DCPFC in its' performance and hence the design can be served as a model for the future reference. The optimized condition of DCPFC: contact time of 5-hour, and 10 ppm initial

dye concentration at pH 3 was then used to test the performance of transition metal complexes as photocatalyst and compared to ZnO photocatalyst while ZnO photocatalyst acted as the standard in this study. Although the calculated band gap of synthesized transition metal complexes was lower compared to ZnO, the power generation and dye degradation efficient of transition metal complexes were lower than that of ZnO. Under the same condition, ZnO showed highest power generation of 172.75 mW/cm^2 with 100% dye degradation while the highest power generation among transition metal complexes was only 120.96 mW/cm^2 with 73.23% dye degradation performed by tris(acetylacetonato) Cobalt(III) $[\text{Co}(\text{acac})_3]$. Low stability was deduced to be the reason of the low performance of transition metal complexes as photocatalyst.

Keywords: Dual-chamber PFC (DCPFC), dye degradation, power generation, Single-chamber PFC (SCPFC), transition metal complexes photocatalyst

Pengoptimuman Sel Fotokatalitik (PFC) dan Sintesis Kompleks Logam sebagai Pemangkin Foto Berpotensi dalam PFC untuk Degradasi Pewarna Sintetik Metil Merah

ABSTRAK

Sel fotokatalitik (PFC) adalah alat gabungan teknik fotokatalis dan sel yang dapat merawat air sisa dan menukar tenaga kimia menjadi tenaga elektrik secara serentak. Bekas dual PFC dilaporkan mempunyai prestasi yang lebih baik daripada bekas tunggal PFC kerana keupayaannya untuk mengelakkan penggabungan semula pasangan elektron-lubang dalam PFC. Namun, kurang kajian yang membandingkan prestasi bekas tunggal PFC dan bekas dual PFC secara bersebelahan dalam kajian perpustakaan. Kajian ini membentangkan perbandingan menyeluruh pada parameter yang berbeza antara bekas tunggal PFC tipikal and bekas dual PFC untuk degradasi pewarna metil merah sintetik dan penjanaan kuasa di bawah keadaan yang berbeza. Prestasi PFC dipengaruhi oleh pemindahan elektron yang didorong oleh perbezaan potensi antara dua elektrok. Sistem bekas tunggal PFC menghadapi masalah penggabungan semula pasangan elektron-lubang yang pantas. Selain itu, jurang tenaga yang lebar pada pemangkin foto yang digunakan dalam PFC telah mengehadkan kadar penggunaan cahaya matahari justeru mempunyai prestasi yang tidak memuaskan. Kompleks logam peralihan dengan jurang tenaga yang kecil dipercayai dapat meningkatkan prestasi pemangkin foto apabila digunakan sebagai pemangkin foto dalam PFC. Kompleks logam transisi dengan jurang tenaga yang kecil dipercayai boleh meningkatkan prestasi fotokatalitik apabila digunakan sebagai pemangkin foto dalam PFC. Dalam kajian ini, bekas dual PFC telah dibina dengan memisahkan fotoanod dan katod ke dalam dua bekas yang berbeza untuk mengelakkan penggabungan semula elektron-lubang yang pantas. Kedua-dua jenis PFC menggunakan ZnO/Zn sebagai fotoanod untuk merawat 10 ppm larutan pewarna metil merah sintetik pada pH 4. Bekas dual PFC mencapai penjanaan kuasa tertinggi (132.83 mW/cm^2) dan

degradasi pewarna 100%, dengan prestasi yang jauh mengatasi bekas tunggal PFC yang memperoleh penjumlahan kuasa tertinggi (60.11 mW/cm^2) dan degradasi pewarna 18.93%. Fotoanod ZnO/Zn boleh digunakan semula dua kali dalam bekas dual PFC tetapi hanya sekali dalam bekas tunggal PFC. Kajian ini menekankan kelebihan bekas dual PFC dalam prestasinya dan oleh itu reka bentuknya boleh dijadikan model untuk rujukan masa depan. Keadaan yang dioptimumkan bagi bekas dual PFC: masa reaksi 5 jam, kepekatan awal pewarna 10 ppm pada pH 3 telah kemudian digunakan untuk menguji prestasi kompleks logam transisi sebagai fotokatalis dan dibandingkan dengan fotokatalis ZnO kerana fotokatalis ZnO bertindak sebagai piawaian dalam kajian ini. Walaupun jurang tenaga kompleks logam transisi yang disintesis lebih kecil berbanding ZnO, namun penjumlahan kuasa dan kecekapan degradasi pewarna kompleks logam transisi adalah lebih rendah berbanding ZnO. Di bawah keadaan yang sama, ZnO menunjukkan penjumlahan kuasa tertinggi sebanyak 172.75 mW/cm^2 dengan degradasi pewarna 100% sementara penjumlahan kuasa tertinggi antara kompleks logam transisi hanya 120.96 mW/cm^2 dengan degradasi pewarna 73.23% yang dilakukan oleh tris(acetylacetonato) Cobalt(III) $[\text{Co}(\text{acac})_3]$. Kestabilan rendah didapati sebagai sebab prestasi rendah fotokatalis kompleks logam transisi.

Kata kunci: Bekas tunggal PFC, bekas dual PFC, kompleks logam peralihan, degradasi pewarna, penjumlahan elektrik

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LIST OF ABBREVIATIONS

•Cl	Chlorine radical
•O ₂ ⁻	Superoxide radical
•OH	Hydroxyl radical
Acac	Acetylacetone
AOPs	Advanced Oxidation Processes
Bi ₂ O ₃	Bismuth(III) oxide
BiO ₂	Bismuth(IV) oxide
BiO ₂ WO ₆	Bismuth tungstate
BOD	Biochemical oxygen demand
CaIn ₂ O ₄	Calcium indium oxide
CB	Conduction band
CDCl ₃	Deuterated chloroform
CdO	Cadmium oxide
CdS	Cadmium sulphide
CHCl ₃	Chloroform
ClO ⁻	Hyphchlorite ion
COD	Chemical oxygen demand
DCPFC	Dual-chamber photocatalytic fuel cell
DMF	Dimethylformamide
DMSO, d ₆	Deuterated dimethylsulfoxide
e ⁻	Photogenerated electron
EDTA	Ethylenediaminetetraacetic acid

Fe ₂ O ₃	Iron(III) oxide
h^+	Photogenerated hole
H ₂ O ₂	Hydrogen peroxide
HCl	Hydrogen chloride
HOCl	Hypochlorous acid
HOMO	Highest occupied molecular orbital
KBr	Potassium bromide
LUMO	Lowest unoccupied molecular orbital
MBR	Membrane biological reactor
MeOH	Methanol
MF	Microfiltration
MnO ₂	Manganese dioxide
Na ₂ CO ₃	Sodium carbonate
NaOCl	Sodium hypochlorite
Nb ₂ O ₅	Niobium pentoxide
NF	Nanofiltration
OM	Organic molecule
PFC	Photocatalytic fuel cell
Phen	1,10-phenanthroline
POME	Palm oil mild effluent
RO	Reverse osmosis
ROS	Reactive oxygen species
SA/V	Surface area to volume
SCPFC	Single-chamber photocatalytic fuel cell

$\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$	Samarium titanium sulphate oxide
TiO_2	Titanium dioxide
UF	Ultrafiltration
VB	Valance band
WO_3	Tungsten trioxide
ZnO	Zinc oxide
ZnS	Zinc sulphide
ZnWO_4	Zinc tungstate

CHAPTER 1

INTRODUCTION

1.1 Worldwide Water Pollution

Water pollution and the clean water crisis are global issues (Li *et al.*, 2024) that have significant consequences to living organisms, environmental sustainability, and socio-economic development (Wu *et al.*, 2020; Lin *et al.*, 2022). Clean and safe drinking water is basic human needs, however not everyone can have access to the clean drinking water. Contamination of water sources due to various pollutants has led to a widespread clean water crisis, affecting worldwide populations. There are about 829,000 people die each year from diarrhea caused by unsafe drinking water, poor sanitation and hygiene (Schmidt, 2019). By 2050, it is expected about 1.7 to 2.4 billion people will face clean water scarcity (UN-WWDR, 2023).

Water pollution causes the decrease of water quality in the water sources, such as rivers, oceans, and groundwater making the water source unsuitable for human use. Industrial discharges, agricultural runoff, improper waste management, and urbanization contribute to the pollution of water sources (Abdel-Shafy & Mansour, 2018; Camara *et al.*, 2019; Akhtar *et al.*, 2021). Example of contaminants include heavy metals, pesticides, fertilizers, pharmaceuticals, and plastics (Pooja *et al.*, 2020). Water pollution brings severe consequences to both ecosystems and human health. Aquatic ecosystems suffer from eutrophication, habitat destruction, and the disruption of ecological balances. Most important is water pollution leads to the spread of waterborne diseases and long-term health impacts (Hasan *et al.*, 2019).

1.2 Dye Wastewater

Dye pollution, or dye-containing wastewater pollution, is a significant environmental concern resulting from the release of dyes and textile effluents into water bodies. The textile industry, which heavily relies on dyes for coloration and printing processes, is one of the major contributors to global water pollution. According to Paraschiv *et al.* (2015), the textile industry is responsible for more than 20 % of global clean water pollution. In addition, industries such as food processing, tanning, leathers, food colorants, ink, pharmaceutical, cosmetics and printing also produce dye-containing wastewater. The improper disposal and discharge of dye and dye-containing wastewater have detrimental effects on aquatic ecosystems, water quality, and human health (Lellis *et al.*, 2019). Dyes destroy the aquatic ecosystem by reducing light penetration and hindering the photosynthesis, leading to decreased oxygen levels and disrupting ecological balance (Mehra *et al.*, 2021). Additionally, some dyes and their degradation products maybe toxic to aquatic organisms, affecting their growth, reproduction, and overall biodiversity. Furthermore, many dyes and dye intermediates are difficult to remove and persist in water bodies, causing long-term contamination (Merouani *et al.*, 2022) while some dyes contain hazardous components such as heavy metals or aromatic compounds, which can pose risks to human health.

For example, *Batik* is a traditional craft in Malaysia. *Batik* industries have contributed to the national economy by providing jobs for locals people as *Batik* is in demand by the global market (Akhir *et al.*, 2018). However, the dye wastewater pollution is growing parallel with the national economy brought by the *Batik* industry. Therefore, hard work is required to solve dye pollution, including effective treatment methods and way to reduce of environmental impact. Figure 1.1 is the common dyes used in textile

industries, namely reactive dye, disperse dye, direct dye, acid dye, basic dye, vat dye, sulphur dye and pigment dye. In this project, synthetic methyl red dye which is an example of azo dye was selected as the model dye.

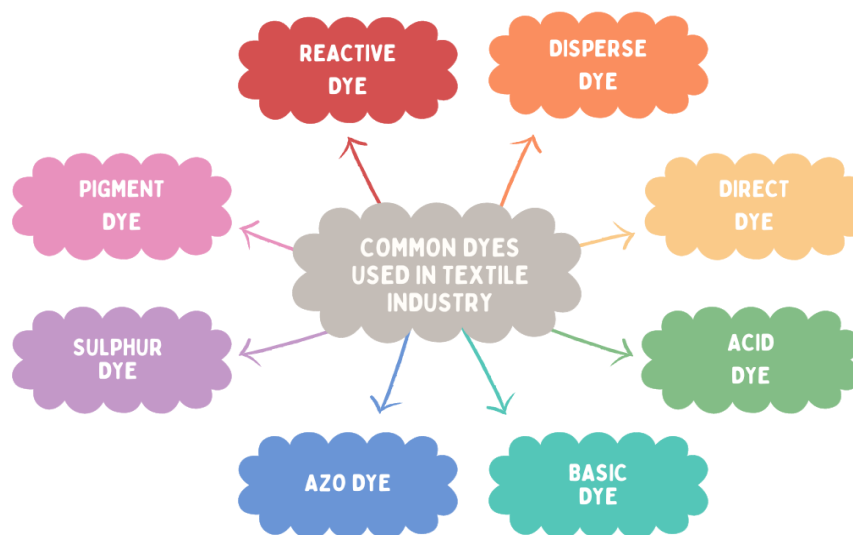


Figure 1.1: Examples of common dye used in textile industry

Azo dyes are synthetic dyes containing an azo group ($-N=N-$) and are usually bonded with aryl group. Azo dyes may contain benzene rings, naphthalene, aromatic compounds, heavy metals and may release aromatic amines, which are known to be harmful. This is why certain azo dyes, such as those capable of releasing carcinogenic aromatic amines, have been banned by the European Union. However, azo dyes remain the most commonly used dyes, accounting for more than 60 % of the total dye production. Examples of commonly used azo dyes include methyl red, methyl orange, and Congo red. Methyl red, for instance, is widely employed as a pH indicator and in textile dyeing processes. Approximately 70 % of the dyes used in fabric or textiles are azo dyes (Benkhaya *et al.*, 2020). It is also been found that around 15 – 50 % of the azo dyes are not bond to the fabric during dyeing process and are released into wastewater, leading to

environmental contamination (Lellis *et al.*, 2019). Due to their solubility in water and particle size range of 0.025 – 1.0 μm , these dyes are difficult to eliminate from water systems (Ardila-Leal *et al.*, 2021). In addition to environmental concerns, certain azo dyes pose health risks, including skin irritation, allergic reactions, respiratory issues, and potential carcinogenic effects upon prolonged exposure (Banc *et al.*, 2023; Rigali *et al.*, 2024).

1.3 Water Treatment Technologies

Water scarcity and demand for clean water sources is always a worldwide attention topic. Therefore, water treatment technologies play an important role in providing clean water for human consumption and recovering clean water back to the environment. Generally, wastewater treatment is a process to remove harmful substances to ensure safe water supply (Pakharuddin *et al.*, 2021). The water treatment technologies can be simply divided into three groups: physical treatment, chemical treatment and biological treatment.

Physical treatment refers to the use of certain tools or instruments in a treatment process. These technologies include sedimentation, filtration, separation and floatation. Physical treatment is usually the preliminary stage for wastewater treatment to purposely remove a specific size of object. For example, the first step of the conventional water treatment process is the screening or straining of large solid, floatable solids or debris in the water bodies by using a metal rake. This is to protect the downstream process or equipment from damage. Sedimentation is the settling of suspended particles by gravity, centrifuge or electrocoagulation. The settling down of suspended particles is then removed by simple filtration.

Other than that, there is also membrane filtration which involves the membrane with specific properties corresponding to the specific water quality requirements. Microfiltration (MF) can remove bacteria and larger microorganisms (typically 0.1 to 10 micron), ultrafiltration (UF) can remove viruses and macromolecules (typically 0.001 to 0.1 micron), nanofiltration (NF) can remove divalent ions and organic compounds (0.001 to 0.01 micron) and reverse-osmosis (RO) can remove dissolved ions or other dissolved contaminants (typically below 0.001 micron). In addition, RO is widely used for desalination of seawater to solve the shortage of drinking water (Dhakal *et al.*, 2022). However, membrane filtration is very costly and requires a lot of energy for maintenance. For example, membrane fouling and decay of UF membrane become the reason for the increase of total cost (Urtiaga, 2021).

The addition of chemicals in water treatment process is known as chemical treatment. Examples of chemical treatment are coagulation and flocculation, disinfection, oxidation and reduction, pH adjustment, chelation, and adsorption. Coagulation and flocculation remove particles by adding a coagulant. The commonly used coagulant is alum to form flocs. The floc is then removed through sedimentation or filtration. Disinfection is the addition of disinfectant, such as chlorine and sodium hypochlorite, to kill or deactivate pathogen bacteria in water and inhibit the growth of microorganisms in water. Chelation is the addition of chelating agent, such as EDTA, to bind metal ions, such as iron or manganese, which cause discoloration and odour issues in water. Besides that, the pH of water is maintained in a desired range by adding calcium carbonate or sodium bicarbonate to prevent corrosion in the distribution system. The pH of water sometimes is altered to meet the specific industrial processes requirements. Adsorption is applied to remove specific contaminants such as organic compounds, taste and odour compounds.

The common adsorbents used are activated carbon, ion exchange resins, zeolites, and polymer hydrogels. The application of advanced oxidation processes (AOPs) has been proven as a potential method to treat wastewater (dye, POME, blackish water) effectively (Mukherjee *et al.*, 2023). The addition of oxidants like chlorine, hydrogen peroxide and sulphate salts produces free $\bullet\text{OH}$ radicles with strong oxidizing ability to oxidize and convert contaminants into simple and less harmful molecules such as CO_2 , O_2 and H_2O .

Last but not least, there are some methods utilizing microorganisms to degrade, transform or remove the contaminants in the biological treatment. Biodegradation is the working principle of a biological treatment. Microorganisms or bacteria consume the organic matter and nutrients in wastewater and produce carbon dioxide or methane gas as by product. The biogas (i.e. methane gas) can be utilized as renewable energy and as the feedstock of grey hydrogen. Examples of these methods are activated sludge process, anaerobic digestion and constructed wetlands. Apart from that, biological treatment can be combined with physical treatment and known as biofiltration. The microorganism or bacteria is attached to a media surface forming biofilm to degrade organic matter and remove contaminants when wastewater flows through it. Membrane biological reactors (MBR) with the addition of activated carbon on reactors coupled with UF membrane chamber have enhanced the removal of organic micropollutants such as antibiotics TMP, SMX and antidepressant FLX (Alvarino *et al.*, 2018). Although biological treatment has low efficiency (Denisov *et al.*, 2016) but due to its low operating cost and environmental friendliness, it is the more widely applied treatment method in the wastewater treatment compared to the others (Roy & Saha, 2020).

1.4 Advanced Oxidation Processes (AOPs) and Photocatalysis

In recent years, Advanced Oxidation Processes (AOPs) and photocatalysis process have attracted a lot of attention due to the ability to degrade various organic pollutants. AOP is a chemical treatment method by employing strong oxidants, such as hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\bullet\text{O}_2^-$), sulphate radicals ($\bullet\text{SO}_4^-$) to initiate the degradation of organic contaminants. The targeted contaminants, when attacked by radicals, will break down into simple molecules. It has been found that AOP can efficiently remove persistent and toxic pollutants, such as pharmaceuticals, pesticides, dyes, and industrial wastewater effluents, which are hard to eliminate by conventional treatment methods (Giwa *et al.*, 2021; Babu Ponnusami *et al.*, 2023). Figure 1.2 shows the examples of AOPs, such as photocatalysis, Fenton process, ozone-based AOP, UV/ H_2O_2 , UV/ HOCl and sonolysis

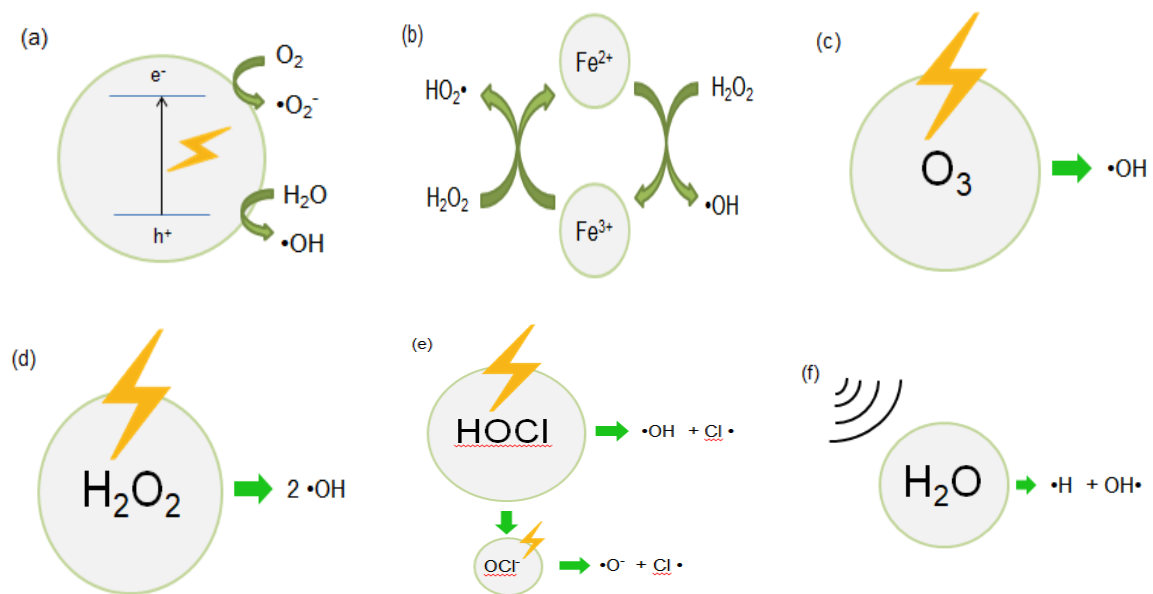


Figure 1.2: Examples of AOPs: (a) Photocatalysis; (b) Fenton process; (c) ozone based AOP; (d) UV/ H_2O_2 ; (e) UV/ HOCl ; (f) sonolysis (Saravanan *et al.*, 2022)

Photocatalysis is the use of photocatalyst to increase the rate of photoreactions. The photocatalyst, typically semiconductor materials, are capable of absorbing photons from a light source, generating electron-hole pairs, and subsequently producing reactive species, such as hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\bullet\text{O}_2^-$) and hydrogen peroxide (H_2O_2). These reactive species can react with organic pollutants, leading to the degradation into harmless byproducts. The common photocatalyst used are TiO_2 , ZnO , ZnS , CdS , WO_3 , Fe_2O_3 , Bi_2O_3 and etc. Among these photocatalyst, TiO_2 and ZnO are the most used photocatalyst as they are cheap, easy to synthesize, chemically and thermally stable, and biocompatible (Karajz & Szilágyi, 2023; Almohamadi *et al.*, 2024).

1.5 Photocatalytic Fuel Cell (PFC)

A photocatalytic fuel cell (PFC) is a tool by combining photocatalysis and fuel cell to treat wastewater and generate electricity simultaneously. In 1972, Fujishima and Honda discovered the photocatalysis phenomenon and it became the prototype of modern PFC. They found that titanium dioxide (TiO_2) electrode and platinum black electrode could split water into oxygen and hydrogen by irradiation of UV light to TiO_2 electrode (Guo *et al.*, 2019). Afterwards, scientists started to study photocatalytic processes for the enhanced production of renewable energy, H_2 gas. In 1980, it was found that a mixture of methanol-water as fuel had dramatically enhanced the photocatalytic production of H_2 (Kawai & Sakata, 1980). In 1979, Fujishima reported different types of semiconductors as photocatalyst for CO_2 reduction. This pioneering work made researchers mostly focused on using TiO_2 as a photocatalyst and photoelectrode for the improvement of photocatalytic performance but overlooked the design of PFC which could enhance the performance of PFC.

In the 1990s, the interest of researchers in the utilization of solar energy and photocatalytic reaction had increased. They also investigate materials such as TiO_2 (mostly) and ZnO for their photocatalytic properties. This has been proved by the drastically increased number of research papers in the Scopus database (Coronado *et al.*, 2013; Sordello *et al.*, 2022). It was also proposed that the field of photocatalysis entered the ‘Maturity’ period in the 1990s. The papers published between 1981-1995 provided a better understanding of the mechanism and to investigate the potential application of photocatalysis, such as water and decontamination to next generation. In 1993, Fujishima and Hashimoto proposed TiO_2 as a photocatalyst for environmental purification at ‘The 1st International conference on TiO_2 Photocatalytic Purification and Treatment for Water and Air’ (Long *et al.*, 2020). This had sparked a craze for research into the trend of photocatalytic removal of water pollutants.

The term ‘Photo Fuel Cell’ was first introduced in the mid-2000s by Kaneko and the team to describe a hybrid system that applied photocatalysis to traditional fuel cell (John *et al.*, 2022). They used nanoporous TiO_2 film photoanode and platinum foil counter electrode to decompose ammonia (ammonia used as fuel) for hydrogen and nitrogen production as well as generate photocurrent (Kaneko *et al.*, 2005). Researchers declared that PFC is a device that could utilize solar energy to drive photocatalytic reactions for electricity generation and hydrogen production. The hydrogen produced can be used for solar-driven hydrogen production, which can serve as a clean fuel for various applications, such as transportation. Starting in 2006, since PFC has the potential to play a role in wastewater treatment with energy produced simultaneously, researchers studied a lot from different aspects to improve the PFC system, including exploring new photocatalyst materials, modifying the morphology of photocatalyst, studying semiconductor

heterojunction system, enhancing light absorption, improving charge separation and transfer process etc. Therefore, 1996 to 2010 was considered to be the ‘Explosion’ of photocatalysis.

Enter 2010s, the concept of PFC had matured, therefore scalability, cost-effectiveness and practical implementation came to the fore for researchers. Continuous improvement of PFC efficiency continued focussing on light absorption and charge separation. Besides that, scientists also introduced novel materials, such as perovskite materials and other compounds for better PFC performance. Carbon-based materials are also one of the concern materials. Figure 1.3 shows that carbon nitride has attracted the interest of scientists due to its visible light activity and simplicity in preparation and modification (Melchionna & Fornasiero, 2020). Although it is proven that the wide band gap of TiO_2 limits its photocatalytic efficiency, especially under visible light, TiO_2 still remains attractive to scientists due to its excellent chemical stability, non-toxicity, and wide availability, making it effective for applications such as environmental application.

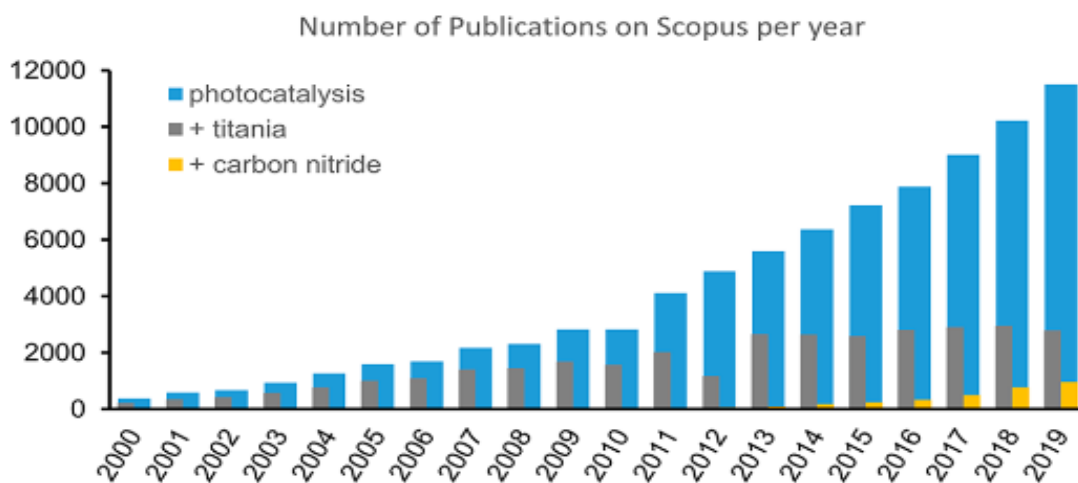


Figure 1.3: Trend in number of publication about photocatalysis (Melchionna & Fornasiero, 2020)

The future prospect of PFC will be focusing on the way to enhance the efficiency, stability, scalability of PFC for practical application, durability and reuseability of photocatalyst, cost control of PFC to make them commercially viable. The history of photocatalytic fuel cell is still evolving and on-going research will continue until a complete hybrid photocatalytic fuel cell system has been built. The brief history of PFC is presented in Figure 1.4.

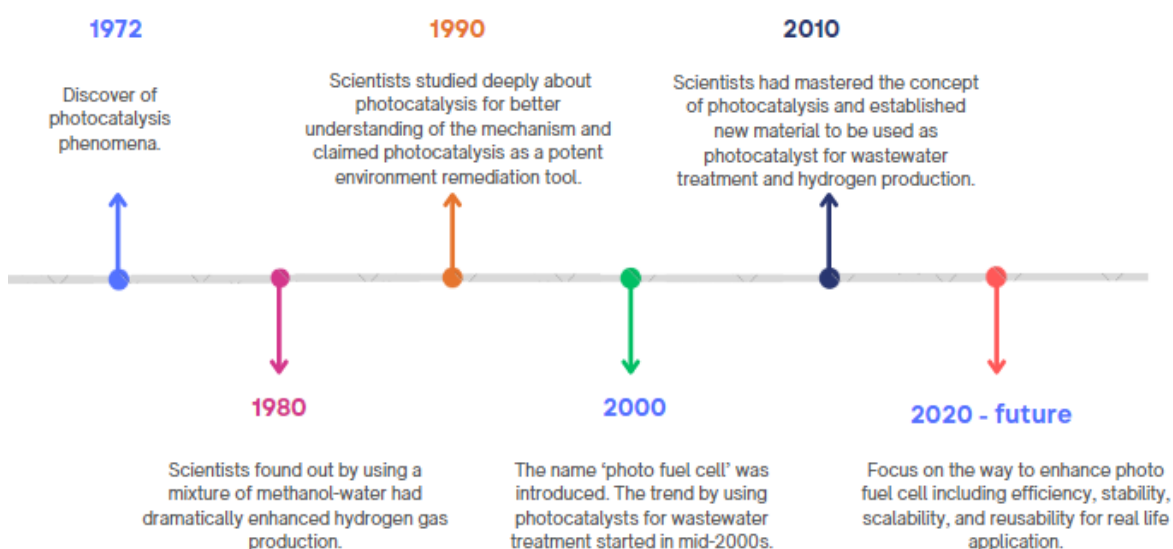


Figure 1.4: Brief history of the PFC development (Melchionna & Fornasiero, 2020)

1.6 Ligand Field Theory (LFT)

Ligand field theory (LFT) is the study of bonding, orbital arrangement, and geometry of coordination complexes. LFT can also estimate the energy difference between two molecular orbitals. Theory states that π -donor ligand has small energy difference while π -acceptor ligand has large energy difference. This energy difference is also known as band gap energy (E_g). The band gap only exists in semiconductors and insulators; conductors do not have a band gap between the valence band and conduction band, they

are overlapped. Insulator has a large band gap (normally 3 eV to 7 eV) which is impossible for electron excitation to occur, while semiconductor has a band gap lower than 3 eV which allows electron excitation. Photocatalyst is one of the examples of semiconductors.

In the field of photocatalytic fuel cell, scientists are working hard to enhance the photocatalytic activity of the fuel cell by modifying the photocatalyst. The photocatalyst will be doped with other metals or non-metals and coated on the electrode to alter the E_g and maximize the photoactivity.

Umrao *et al.* (2014) reported that TiO_2 -graphene oxide and TiO_2 -reduced graphene oxide composites successfully narrowed the band gap of TiO_2 from 3.51 eV to 2.51 eV and 3.42 eV to 2.39 eV. The TiO_2 -reduced graphene oxide composites performed the highest methylene blue photodegradation, 98.72 %, within 300 minutes while pure TiO_2 nanopowder only reached 36.84 % photodegradation in the same period. Besides that, Zhu and Zhou, (2021) modified the metal free graphite carbon nitride, g- C_3N_4 , with a band gap of 2.70 eV, doped it with nitrogen to produce nitrogen doped g- C_3N_4 , NCN. The band gap of NCN was 1.82 eV and had excellent photodegradation of phenol (70.1 %) while the g- C_3N_4 showed lower degradation of 37.6 % (Zhu & Zhou, 2021).

1.7 Significance Study and Problem Statement

The main problem occurs in PFC when generating electricity while treating wastewater is the undesirable energy output. Researchers mostly used metal oxides such as TiO_2 , ZnO , and BiO_2 as photoanode in their studies. Based on photocatalysis theory, semiconductors such as TiO_2 , ZnO , and BiO_2 can harvest the greatest effect to give high energy output due to their electronic, optical properties and their photoresponse to visible

light. However, these metal oxides suffer from significant limitations. The major issue is their wide bandgap (such as ZnO has bandgap of 3.5 eV) to limit absorption for visible light, which constitutes the majority of sunlight. Additionally, these metal oxides face rapid recombination of electron-hole pairs, leading to a substantial loss in photocatalytic efficiency. Since the studies of using metal oxide as photoanode have yielded no significant breakthroughs, researchers should explore alternative materials to be used as photoanode in order to enhance energy output performance.

The undesirable energy output in PFC arises primarily from rapid electron-hole pairs recombination and limitations in the materials used as photoanodes. Commonly used metal oxides like TiO_2 , ZnO , and BiO_2 , though effective to some extent, suffer from limited solar absorption and inefficient charge separation, resulting in low energy output. This is worsened in single compartment PFCs, where the proximity of oxidation and reduction reactions accelerates recombination. The two compartment PFC design addresses this issue by separating the reactions, thus slowing down electron-hole pairs recombination and enhancing efficiency. Additionally, the use of newly synthesized metal complexes as photocatalysts holds promise for further improving energy output. These complexes, with smaller bandgap, allowing better light absorption and improve charge separation, offering a more effective alternative to traditional metal oxides. Together, the two compartment PFC design and transition metal complexes as photocatalysts presents a novel approach to overcome the inherent drawbacks of rapid electron-hole pairs recombination and metal oxides in PFC, paving the way for more efficient PFCs.

In this study, the typical single-chamber PFC (SCPFC) was modified by which separating the photoanode and cathode into different chambers to form a dual-chamber PFC (DCPFC). The photocatalytic efficiency between SCPFC and DCPFC was compared.

The separation of photoanode and cathode in different chambers might slow down recombination of electron-hole pairs, thus enhance the efficiency of PFC. Besides, an extra oxidizing agent, sodium hypochlorite, was added to the cathode chamber of the DCPFC. The reason for adding an oxidizing agent in the cathode chamber is because it is a possible way to increase methyl red dye degradation without affecting the reaction in the reactor chamber.

Next, metal complexes of Co, Ni, Cu were synthesised to be coated on Zn plate as photoanode, employing acetylacetone (acac) and 1,10-phenanthroline (phen) as ligand. These ligands were chosen due to their strong π -donor and π -acceptor properties, which are expected to facilitate the electron excitation process and enhance photocatalytic efficiency. At the end of the research, the methyl red dye removal efficiency and maximum power output of the synthesized metal complexes were evaluated under optimal conditions of ZnO photocatalyst.

This study is significant because it explores the application of PFC for dual purposes: electricity generation and methyl red dye degradation, presenting it as an eco-friendly and sustainable wastewater treatment solution. The study compares SCPFC and DCPFC, with the dual-chamber configuration setup expected to slow down recombination and increase energy output. Furthermore, the synthesis of metal complexes of cobalt(III), nickel(II), and copper(II) as alternative photocatalysts to replace traditional metal oxide (ZnO) aims to enhance the efficiency of DCPFC. This research not only provides comprehensive information for the photocatalytic performance of SCPFC and DPFC but also offers valuable insights into the potential of metal complexes as effective photocatalysts in PFCs, contributing to the development of green technologies for wastewater treatment.

1.8 Objectives

The research was conducted with the following objectives:

- i. To compare and optimize the efficiencies in methyl red dye degradation and power generation of single-chamber PFC (SCPFC) and dual-chamber PFC (DCPFC) by using ZnO photocatalyst as standard photoanode.
- ii. To synthesize and characterize Co(III), Ni(II), and Cu(II) complexes using acac and phen ligands.
- iii. To investigate and compare the potential of Co(III), Ni(II) and Cu(II) complexes containing acac and phen ligands as photocatalysts in DCPFC under optimal experimental conditions obtained from ZnO/Zn standard photoanode.

CHAPTER 2

LITERATURE REVIEW

2.1 Photocatalytic Fuel Cell (PFC)

The concept of a PFC (Figure 2.1) revolves around the integration of a photocatalyst, typically a semiconducting material, with a fuel cell configuration. The photocatalyst absorbs photons from a light source, creating electron-hole pairs that initiate a series of redox reactions. The organic pollutants present in the wastewater serve as fuel, undergoing oxidation at the anode, while the reduction of oxygen takes place at the cathode, leading to generation of electrical energy.

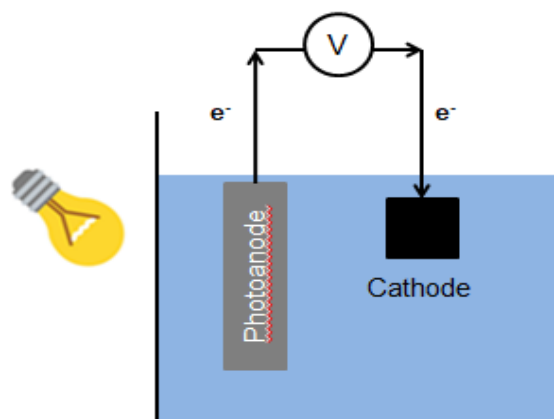


Figure 2.1: Illustration of SCPFC

In photocatalytic processes, in this case is PFC, a semiconductor material such as ZnO, absorbs light energy, excites the electron in ZnO, generating electron-hole pairs. The photogenerated electron and hole are highly reactive and can initiate chemical reactions with surrounding molecules, including pollutants.

2.2 Photocatalysts

In order to have the photocatalytic process happen, a photocatalyst is indispensable. The photocatalyst absorbs light energy and is excited to form electron-hole pairs upon illumination. A semiconductor is usually used as a photocatalyst due to the presence of a small to moderate band gap between the valence band (VB) and conduction band (CB) (Figure 2.2). With a moderate band gap, the electron can be excited when exposed to light rays hence initiate the photocatalytic reaction. Unlike semiconductors, the insulator has a huge band gap between the VB and CB and it is impossible for the electron to be excited, while the conductor has no band gap between the VB and CB as the bands are overlapped, therefore the electrons can move freely throughout the conductor material (Figure 2.2). Transition metals are used as the typical photocatalysts due to the existing vacant *d*-orbital.

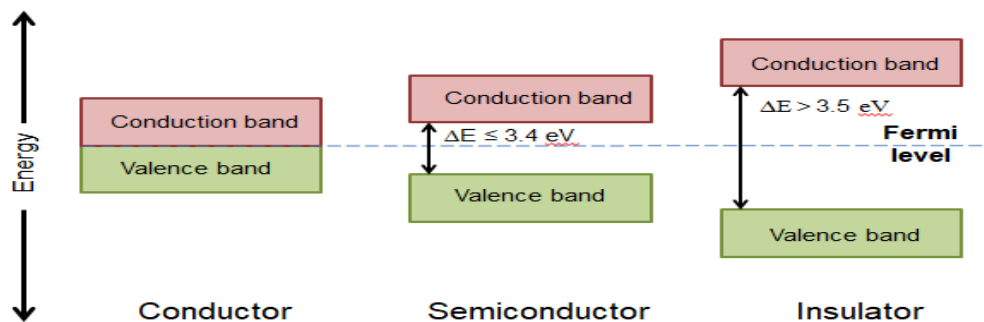


Figure 2.2: Comparison of bandgap between insulator, semiconductor and conductor (Morab *et al.*, 2023)

The Fermi level is the highest energy level that an electron can occupy at absolute zero temperature. It can be defined as the energy required to add one electron to the material. In a pure semiconductor, the Fermi level lies in the middle of the band gap. At absolute zero temperature, there are no electrons in the conduction band, but as temperature increases, some electrons are thermally excited across the band gap, creating

electrical conductivity. In doped semiconductors, the Fermi level shifts depending on the type of dopant (*p*-type or *n*-type), affecting the electrical properties of the material. The example for *p*-type or *n*-type dopants are boron and phosphorous, respectively. Boron, with three valence electrons, creates a ‘hole’, while phosphorous, with an extra electron, acts as a free carrier. In an *n*-type semiconductor, the Fermi level is near to the CB, while in a *p*-type semiconductor, it is near to the VB (Figure 2.3). The shift of Fermi level changes the energy threshold required for electron excitation. Therefore, in semiconductor devices such as LEDs and solar cells, controlling the position of the Fermi level is crucial for optimizing device performance.

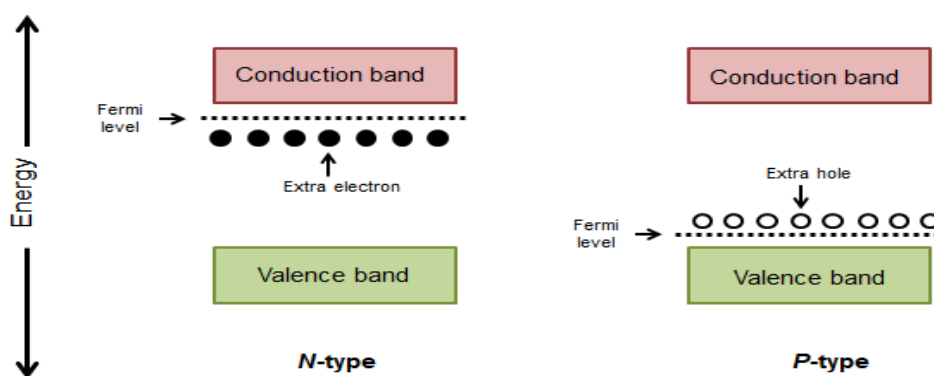


Figure 2.3: Comparison of Fermi level between *n*-type and *p*-type semiconductor (Srivastava, 2012)

Photocatalysts possess unique electronic structures that enable them to absorb photons from the incident light. This absorption prompts electronic transitions within the photocatalyst, elevates it to an excited state. Subsequent to the excitation, the photocatalyst is capable of transferring the absorbed energy to nearby reactant molecules, initiating chemical reactions that would necessitate higher activation energies. This ability to harness light energy and channel it into chemical transformations highlights the importance of photocatalysts in photocatalysis.

The photocatalyst facilitates the conversion of reactants into products without being consumed throughout the process. By lowering the energy barriers associated with specific chemical transformations, photocatalysts enable reactions to proceed at rates compatible with practical applications (Wang *et al.*, 2023b). Their ability to initiate and accelerate reaction is particularly advantageous in processes requiring mild reaction conditions, thereby minimizing energy consumption and enhancing reaction efficiency. Among the photocatalysts, ZnO, TiO₂ and Fe₂O₃ are the most widely used in PFC for wastewater purification, water splitting and power generation.

2.3 Photocatalysis Mechanism

Radicals formation (Figure 2.4) are the important factor contributing to the pollutant degradation. The photogenerated electron (e^-) and holes (h^+) react with water and oxygen molecules present in the solution, forming hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) respectively (Equations 2.1 – 2.4). The $\bullet\text{OH}$ is extremely reactive, attacking organic molecules, breaking chemical bonds and converting them into smaller, less harmful compounds like carbon dioxide and water.



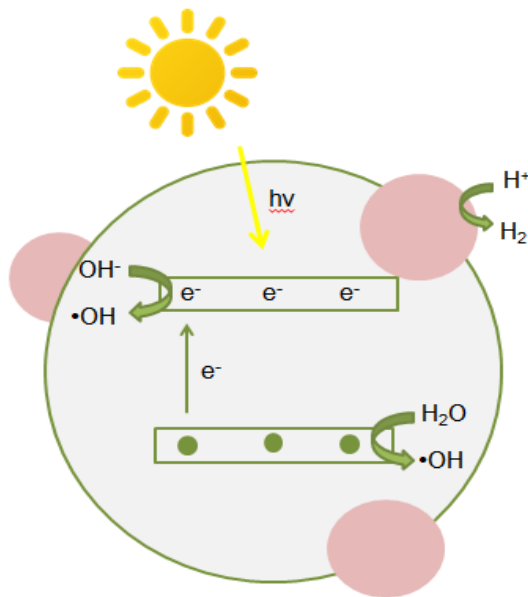
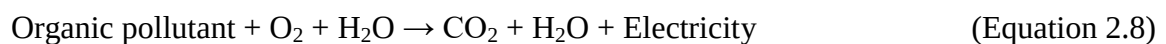


Figure 2.4: Mechanism of radical formation in a photocatalyst

Besides that, the radical reactions can also propagate in a chain reaction manner. For example, when a hydroxyl radical reacts with an organic molecule, another radical will form and react with other organic molecules (OM), creating a chain of degradation reactions (Equations 2.5 – 2.7).



Equation 2.8 shows the summarized reaction equation of the photocatalysis:

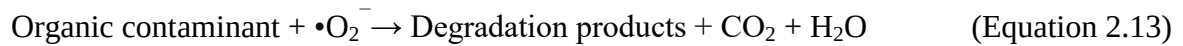
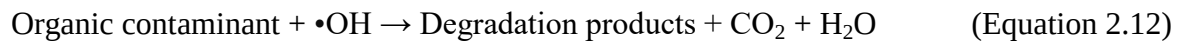


As mentioned, radicals play a vital role in degrading the contaminant and producing power. The radicals are primarily generated through photocatalytic reaction

occurring on the surface of semiconductor electrodes, typically composed of materials like TiO₂ or ZnO. When these electrodes are illuminated with light energy equal to or greater than their band gap energy, electron-hole pairs are formed. Subsequently, the charge carriers participate in redox reactions with adsorbed species, leading to the formation of radicals such as hydroxyl and superoxide radicals. The overall reaction can be represented in Equation 2.9 – 2.11:



Once generated, radicals play a crucial role in initiating the degradation of organic pollutants. Hydroxyl radicals, in particular, are highly reactive and can oxidize a wide range of organic compounds (Wang & Xu, 2012). Similarly, superoxide radicals contribute to the degradation process by participating in electron transfer reactions with organic molecules (Equation 2.12 – 2.13).



While radicals are essential for pollutant degradation, their uncontrolled generation and accumulation can lead to side reactions and decrease the efficiency of PFC (Zhao *et al.*, 2017a). Therefore, it is crucial to manage and contain radicals within the photocatalytic chamber to ensure its optimal performance.

In this project, sodium hypochlorite solution (NaOCl) was added to the cathode chamber of DCPFC as an oxidizing agent. The NaOCl served a dual purpose: it acted as an electron acceptor, facilitating the regeneration of photocatalytically active species (Parvizi *et al.*, 2021), and helped in containing and degrading excess radicals (Pellegrin *et al.*, 2013; Zou *et al.*, 2020). The reaction involving NaOCl can be represented in Equation 2.14 – 2.15:



When hypochlorite ions are exposed to UV or visible light, photons are absorbed and used as initiating energy for photochemical reactions. A homolytic cleavage of the O-Cl bond in hypochlorite then occurs to form hydroxyl radicals and chloride ions. The hydroxyl radicals react with other species to produce another molecule (Equation 2.16 – 2.21). The $\bullet\text{OH}$, $\bullet\text{Cl}$ and ClO^- then diffuse to the anode chamber and improved the rate of pollutant degradation (Kundu *et al.*, 2008; Zhu *et al.*, 2016). Besides that, ClO^- ions attract the electrons flow from the anode to the cathode, thus enhance the power generation.





The NaOCl solution was diluted with distilled water when added to cathode chamber. This means the OCl^- ions also reacted with H^+ and OH^- ions. Subsequently, HOCl undergoes a reversible reaction to generate hypochlorite ions and hydrogen ions, thereby starting the radical generation process. Besides that, the hypochlorite ions (OCl^-) react with OH^- to produce hypochlorite ions (ClO^-) along with water (Equation 2.22 – 2.23). Both OCl^- and ClO^- ions serve as sources of reactive oxygen species (ROS) through various pathways.



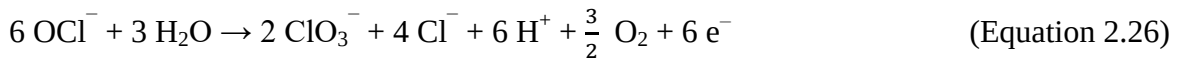
Methyl red dye, a widely used azo dye, serves as the model pollutant in this study due to its environmental significance and persistence in wastewater. Since the pH of methyl red solution was adjusted using hydrochloric acid (HCl) and sodium carbonate (Na_2CO_3), thus Cl^- ions were present in the anode chamber. The presence of excess H^+ from HCl can lower the pH of the solution and create an acidic environment. Under acidic environment, the formation of HOCl was favoured. HOCl is a precursor for ROS. The increased concentration of HOCl can enhance the radicals generation and potentially improve the efficiency of pollutant degradation. However, excess HOCl might also react with $\bullet\text{OH}$ to form water and chloride ions (Equation 2.24). This scavenging effect might reduce the concentration of $\bullet\text{OH}$ available for pollutant degradation.



Although ROS are essential for pollutant degradation in photocatalytic processes, excessive accumulation of these radicals can lead to side reactions and decrease the overall efficiency. The oxidizing ability of NaOCl makes it able to react readily with other radical species to neutralize them or convert them into less reactive forms. By effectively managing the concentration of radicals, NaOCl helped to ensure the stability and efficiency of the photocatalytic processes over prolonged operation periods. One of the key reactions involved the degradation of excess radicals as below (Equation 2.25):



Since HOCl is also an intermediate, a chain reaction based on HOCl would happen in both the anode and cathode as HOCl appeared in both chambers. As the cathode chamber was under basic conditions, the OCl^- ions reacted with OH^- and H_2O . The continuous production of hydroxyl radicals from hypochlorite ions ensures a sustained supply of reactive species for pollutant degradation, enhancing the efficiency of the photocatalytic process (Pimentel & Linden, 2024). Equation 2.26 – 2.32 show the chain reactions of HOCl to generate chlorite, chlorate, perchlorate ions (Yi *et al.*, 2019).





As the anode chamber was under acidic conditions, the ClO^- ion reacted with H^+ (Equation 2.33 – 2.36). Based on Equation 2.36, this reaction resulted in the formation of Cl^- ions, which imparted a chlorine smell to the anode chamber.



The dual functionality of PFCs offers an attractive option for decentralized energy generation and wastewater treatment in areas with limited access to clean water and electricity (Wang *et al.*, 2023c). Traditional fuel cells utilize pure fuel, such as hydrogen, while PFC utilizes a wide range of organic pollutants as fuel sources, including industrial wastewater, domestic sewage, and agricultural residues. The eco-friendly operating system makes PFC more competitive than other treatment methods (Zhang *et al.*, 2024).

Moreover, the photocatalytic process in PFCs offers additional benefits beyond electricity generation. As the organic pollutants are oxidized, their concentration in the wastewater decreases, leading to improved water quality. The photocatalyst also facilitates the breakdown of persistent organic compounds, such as pharmaceuticals and emerging contaminants, which are often resistant to conventional treatment methods (Ahmadpour *et*

al., 2024). Consequently, PFCs provide a sustainable approach to not only produce energy but also mitigate water pollution.

Although studies have examined photocatalyst efficiency using manufacturing wastewater as model pollutant, the concentration of these pollutants is often diluted and is less complex compared to the real-life wastewater. As a result, it is challenging to estimate how long a photocatalyst will last in the wastewater for effective pollution mitigation. The longevity of a photocatalyst depends on various factors, including photocatalyst material, environmental conditions, and pollutant concentrations (Koe *et al.*, 2019). Regular cleaning and regeneration may also be necessary to maintain efficiency over time.

2.4 Single-Chamber and Dual-Chamber PFC Photocatalytic Fuel Cells (PFC)

A PFC can be operated in a single- or dual-chamber setup. A typical PFC arrangement with two electrodes in one container is known as SCPFC. The components of SCPFC comprise two electrodes, which are photoanode, and cathode, organic substances, and a supporting electrolyte. As mentioned before, the commonly used photocatalysts are TiO_2 , ZnO and Fe_2O_3 . Often, to further increase the efficiency of SCPFC, researchers replaced the photoanode-cathode electrode pair with photoanode-photocathode electrode pair. Most of the previous studies were based on single-compartment cells. This is because the cost of setting up a single-compartment cell is lower than that of a two-compartment cell for commercialization (Wang *et al.*, 2014). The two-compartment cell requires a membrane or a salt bridge as a separator for two electrolytes. It is known that the smaller the pore size of the membrane, the higher the price of the membrane. Also, membranes used in treatment plants required regular replacement. Therefore, the number of journal

articles about two compartment PFCs is much lower than that of single compartment PFC (Wibowo *et al.*, 2017).

The DCPFC is a cell design that separates the photoanode and cathode into different chambers. The major drawback of SCPFC, low photodegradation and low power generation, is attributed to be the result of fast recombination of electron-hole pairs. It is suggested that clear separation of oxidation and reduction reactions in a fuel cell can prevent the fast recombination of electron-hole pairs. At first, scientists separate the anode and cathode chambers with a proton exchange membrane or glass frit. Unfortunately, the result did not show much difference compared with the SCPFC. According to John *et al.* (2022), the DCPFC is a potential design to improve the performance of PFC. Antoniadou and Lianos (2011) suggest that more power can be generated by employing two-compartment cells. Therefore, in this project, a DCPFC setup was used by separating the photoanode and cathode into different chambers and connecting them using a salt bridge. Additionally, the reports on the DCPFC on the photodegradation and power generation is very little compared to those of SCPFC .

A SCPFC was fabricated with ZnO/Zn photoanode and Pt/C cathode under sunlight irradiation. 10 mg/L methylene blue dye solution used as fuel and 85 % decolorization efficiency was reported (Lee *et al.*, 2016a).

Liu and the team (2012) selected 0.045 mmol/L tetracycline as sample pollutant for a single-chamber TiO₂-based PFC system and recorded more than 60 % tetracycline degradation efficiency (Liu *et al.*, 2012). After a few years, another team (Deng *et al.*, 2018) used Ag-TiO₂ photoanode and platinum cathode in a dual-chamber setup and recorded a 96.4 % tetracycline removal efficiency.

The Z-scheme is one of the electron excitation modes from indirect excitation (Figure 2.5). Z-scheme is known for the high separation efficiency of electron-hole pairs. It usually occurs between two different photocatalysts. When light shines, both photocatalysts are excited and generate electrons and holes. In Figure 2.5, the lower reduction potential photocatalyst I transfers the photogenerated electron to the more positive redox potential photocatalyst II. To replenish the lost electron, photocatalyst I accepts electrons from photocatalyst II. As photocatalyst II donates electrons to photocatalyst I, it is oxidized. However, it regains the electron from other sacrificial electron donors present in the environment. Due to the spatial separation of photogenerated electrons and holes between two different photocatalysts, recombination of electron hole pairs is greatly reduced. The photocatalysts with different potentials lead to a directionality of photogenerated electron transfer from one to another photocatalyst.

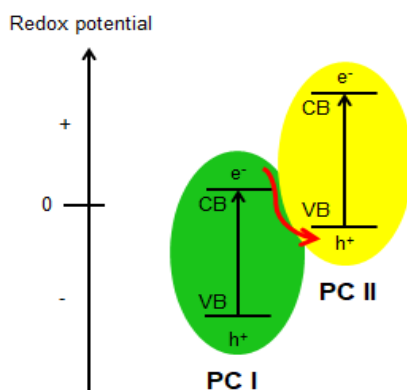


Figure 2.5: Z-scheme electron excitation mechanism

In another study by Lam and the team (2020), an anodic WO_3 -loaded on hexagonal rod-like ZnO/Zn ($\text{WO}_3/\text{ZnO}/\text{Zn}$) with the Z scheme structure was paired with a platinum electrode in a one-compartment PFC design to degrade sunset yellow dye and phenol. The COD removal of 30 mg/L sunset yellow dye and 10 mg/L phenol were 84.6 %

and 67.5 % with the power density of $0.1052 \mu\text{W}/\text{cm}^2$ and $0.0574 \mu\text{W}/\text{cm}^2$, respectively. When treating the real food industry wastewater, the COD removal was 63.6 % followed by $0.498 \mu\text{W}/\text{cm}^2$ maximum power density (Lam *et al.*, 2020).

A DCPFC setup is much more effective than a SCPFC because not only the recombination rate can be slow down, but it could also reduce some heavy metals which could not be done in SCPFC. In 2021, a research team (Lam *et al.*, 2021) reported a PFC setup with Z-scheme MoO_3 anchored-hexagonal rod-like ZnO/Zn photoanode and platinum loaded carbon cloth as the cathode achieved 89.5 % COD removal of 40 mg/L phenol in the anode chamber, 93.5 % removal efficiency of 200 mg/L Cu^{2+} in the cathode chamber and generated maximum power density of 0.007 mW cm^{-2} . By using the real plating industry wastewater collected by the team in the designated PFC system, 73.6 % of COD removal of phenol, 85.0 % of Cu^{2+} reduction and maximum power density of 0.005 mW cm^{-2} were reported, respectively.

In 2022, Sun and the team (Sun *et al.*, 2022) proposed a core-shell structured $\text{Ag}@\text{Fe}_2\text{O}_3$ nanoparticles used as the cathode materials and TiO_2 as the photoanode in a DCPFC setup. $\text{Ag}@\text{Fe}_2\text{O}_3$ nanoparticle was a composite nanoparticle of silver and iron oxide. Silver was chosen due to the relatively high catalytic activity and high surface energy thus the surface area of the $\text{Ag}@\text{Fe}_2\text{O}_3$ composite nanoparticles could be increased. They successfully decolorized 20 mg/L reactive brilliant red (X3B) dye (Figure 2.6), reduced 0.3 mM Cr(VI) to Cr(III) in the cathode chamber, and obtained the highest power density of $1.3 \mu\text{W}/\text{cm}^2$. X3B is an anionic Azo dye. Since it is a reactive dye and can react easily with fabric, X3B is commonly used in the textile industry.

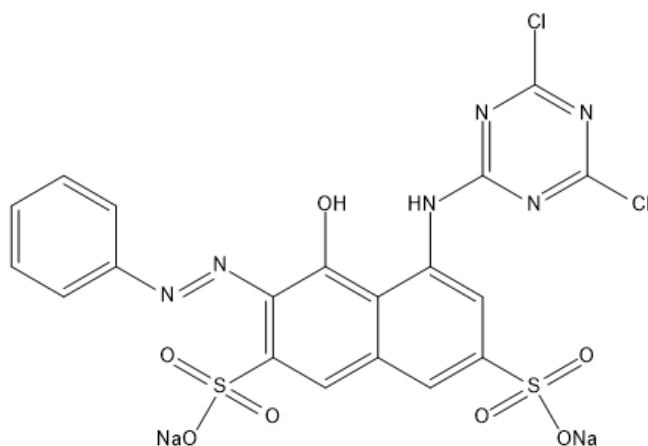


Figure 2.6: Structure of Reactive Brilliant Red (X3B) dye

In DCPFC, the electrode reaction can be separately controlled in different chambers and resulted to the high efficiency of the DCPFC setup compared to SCPFC. The oxygen reduction reaction happens at the cathode is an electron-consuming process which will negatively affect the anode performance (Sharma *et al.*, 2019). Additionally, separating the chambers has reduces the direct photogenerated carrier recombination rate. In other words, the DCPFC setup allows the optimization of conditions in each chamber, while the SCPFC setup may compromise optimal conditions for one reaction over the other. The summary of the literature reviews on the DCPFC can be found in Table 2.1 and the removal efficiency of the DCPFC were reported over 80 % in most studies.

Table 2.1: Summary of previously reported DCPFC systems

System	Fuel	Removal efficiency	Voltage output/ Power density	Limitation	References
CdS/ZnS-TiO ₂ photoanode and CuO photocathode	Methanol	N.A.	3.0 mA/cm ²	4.0 M methanol concentration	Liu <i>et al.</i> (2019b)

Table 2.1 Continued

Combination of PFC and Fenton process (TiO ₂ photoanode and Pt cathode)	X3B dye	X3B dye decolorized but removal efficiency was not mentioned	0.889 V; 0.034 mW/cm ²	pH 5.5, 50 mg/L pollutant concentration	Sun <i>et al.</i> (2019)
TiO ₂ nanotube arrays photoanode and graphite as cathode	Methylene Blue (MB) and Cr(VI)	MB decolorized and 96.8 % removal efficiency for Cr(VI)	1.06 V, 1 W/m ²	pH 6	Liu <i>et al.</i> (2019a)
TiO ₂ photoanode and Pt coated cathode	Perfluorooctanoic acid (PFOA), 4-chlorophenol (4-CP), bisphenol A (BPA), MB, and Amoxicillin (AMX)	Removal efficiency: PFOA (99 %), 4-CP (85 %), BPA (88 %), MB (98 %), AMX (93 %)	0.92 V	pH 7	Gu <i>et al.</i> (2021)
Combination of PFC and Electro-Fenton (EF)	Amaranth dye	86.2 % in PFC; 84.7 % in EF	869 mV, 1.2211 μ W/cm ²	Limitation was not mentioned	Thor <i>et al.</i> (2021)

2.5 Dye Pollution and Current Treatment

Dyes are extensively used by various industries to enhance the aesthetic appeal of products. In industries like textiles, fashion and design, dyes allow for a wide range of colours and patterns, providing visual appeal to clothing, fabrics and other consumer goods. Some companies often use specific colours or combinations to create a recognizable brand identity. This is common in sectors such as packaging, where coloured packaging helps consumers easily identify and associate with a particular brands. In the textile and fashion industry, dyes are essential for creating the diverse array of colours and patterns seen in clothing and accessories, allowing for infinite possibilities in fashion design. According to

Figure 2.7, the textile industry releases the largest proportion of dyes compared to other industries (Solayman *et al.*, 2023).

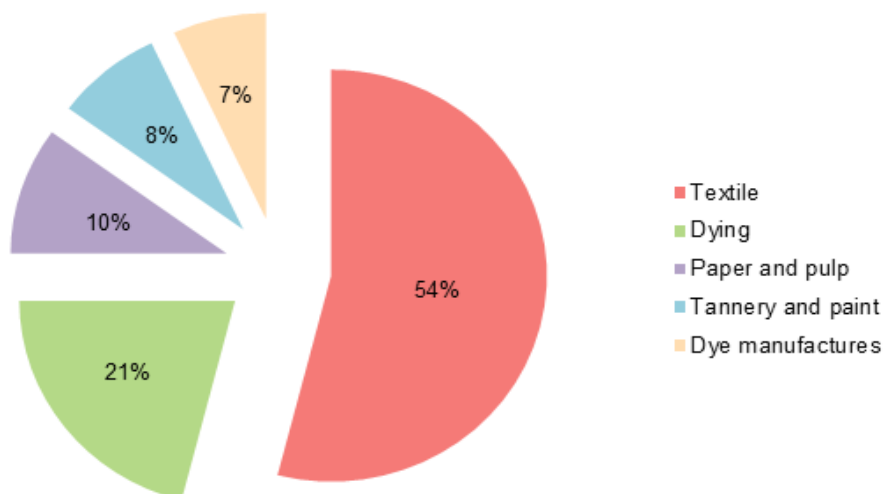


Figure 2.7: Global contribution of major industries to the release of dye wastewater into environment (Solayman *et al.*, 2023)

According to Behera *et al.* (2021), 1 kg of cloth requires a minimum of 40 L clean water used in the dyeing and printing process. The amount of water used may increase depending on the fabric, type of dye used and dyeing technique used. According to Donkadokula *et al.* (2020), 60 – 70 % of azo dyes are used by most textile industries, and 20 % of the dyes used are lost or wasted due to incomplete fixation on the fabric (Wong *et al.*, 2019). Around 15 – 20 % of the total dye is discharged into the environment during dyeing process. Highly toxic chemicals are used at the various stages in textile industries, and these chemicals are released into the environment when wastewater is discharged as effluent. Heavy metals also found in textile wastewater such as mercury, chromium, cadmium, lead, arsenic, and zinc (Al-Tohamy *et al.*, 2022). Wastewater from textile industries is a major contributor to severe water pollution. Table 2.2 summarizes the types

of chemicals involved in each stage of manufacturing process and the release of pollutant from each manufacturing stage (Solayman *et al.*, 2023).

Table 2.2: Key pollutants of textile wastewater at manufacturing process

Process	Type of chemical	Pollutant
Dyeing	Sulphate, Sulphite, Sulphuric acid, Ammonium salts, Urea, Phosphate and Hydro sulphate salts	Sulphur, Nutrients
Bleaching, Desizing, Dyeing, Finishing	Heavy metals, Reducing agents, Oxidizing agents, Quaternary ammonium salts and Biocides	Toxic compounds - dioxins, furans, formaldehyde, phenolic compound
Dyeing, Scouring	Dyes, Scoured wool impurities	Colour pigments
Scouring, Desizing, Bleaching, Mercezing, Dyeing, Neutralization	Sodium hydroxide, Mineral, Organic acids, Salicilats, Sodium chloride, Sulphate, Carbonate	Acids, Alkalis and Salts
Sizing	Starch, wax and Carboxymethyl cellulose	BOD and COD
Desizing	Fats, Waxes, Starch, Pectins and Carboxymethyl Cellulose	Sodium hydroxide and Cotton wax
Desizing, Scouring, Washing, Dyeing	Enzymes, Fats, Starch, Greases, Acetic acis, Waxes and Surfactants	Colour pigments

The huge discharge of textile wastewater has always been the main concern of scientists and new techniques for the treatment of dye wastewater are always being developed. Also, dyes are recalcitrant due to their complex structure with different chromophore groups (Ahuja *et al.*, 2021). However, an effective treatment system for

textile wastewater is non-existent. The textile wastewater is classified as an industrial wastewater and is sent to an industrial wastewater treatment plant for purification.

In the industrial wastewater treatment plants, a combination of processes and technologies is employed to neutralize or remove pollutants, ensuring the discharged water meets regulatory standards and poses minimal harm to the environment is employed (Patchaiyappan & Devipriya, 2021; Silva, 2023). Figure 2.8 shows the flow diagram of wastewater treatment processes (Xu *et al.*, 2018). As shown in Figure 2.8, the wastewater treatment starts with wastewater going through a grille to separate the small granules and suspended particles, followed by the primary treatment. Chemical coagulants are added to the wastewater to destabilize and aggregate dye particles. Flocculants are then introduced to form flocs which can be easily separated from the water through sedimentation or filtration. Various types of coagulants and flocculants are employed to speed up the process (Singh *et al.*, 2022). The common coagulant including aluminium sulphate, calcium chloride, polymer polyaluminium chloride and others.

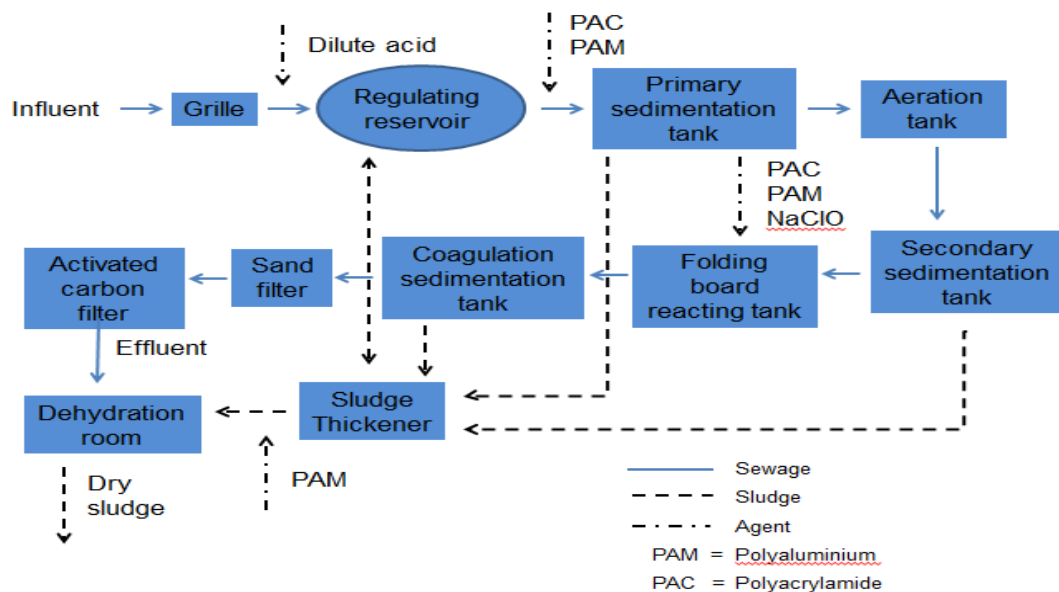


Figure 2.8: Process flow diagram of wastewater treatment (Xu *et al.*, 2018)

Activated carbon is sometimes added to the water to adsorb dye molecules from the wastewater, facilitating the pollutant removal. Other sorbents include chitosan, resin and carbon nanotubes have also been employed. The waste is then passed through a membrane to strain out the colloidal particles such as dye pollutants. A literature stated that some light weight organic dye molecules and divalent salts used for softening effect can be filtered out using nanofiltration membrane (Qiu *et al.*, 2019). A nanocomposite nanofiltration membrane modified with double sulfonated graphene and maleic anhydride modified graphene oxide was claimed to filter the textile dyes, Congo Red for 97.4% and methylene blue for 99.1 % (Xie *et al.*, 2019). Subsequently, the wastewater flows into an aerobic-anaerobic combination tank to break down the complex dye molecules. However, this method produces a large amount of sludge and requires a long reaction time (Katheresan *et al.*, 2018).

Biological treatment produces less sludge, is low-cost and environmental friendly, but it requires a long reaction time thus is less efficient (Samsami *et al.*, 2020). Physical treatments such as adsorption and membrane filtration are much more effective than biological treatment but the operating cost is higher than biological treatment due to the expensive adsorbent materials and filters that require regular replacement to ensure the treatment quality. There is also a membrane-fouling problem which may block the membrane or reduce the membrane pore size. Chemical treatment is more expensive than biological and physical treatment as large amounts of chemicals are used. Examples of chemical treatment are coagulation-flocculation, electrochemical, photolysis and oxidation.

The AOPs is classified as a chemical treatment process which can become part of a hybrid textile wastewater treatment system. Dye removal based on AOPs is the utilization of strong oxidative radicals species such as $\bullet\text{OH}$ to break down the dye molecule into

smaller and less harmful substances. There are different types of AOPs with different mechanisms, such as photochemical oxidation (UV/H₂O₂, UV/HOCl), ozone-based AOP, Fenton-based AOP, and photocatalytic oxidation (UV/TiO₂). The removal efficiency depends on the AOP type and reaction conditions (Deng & Zhao, 2015).

Since AOPs can produce highly oxidative species, enabling the break down of a wide range of organic pollutants into simple or smaller substances. It exhibits non-selective oxidation and is useful for treating complex mixture of dyes in wastewater. Beyond dyes, AOPs is able to degrade dissolved organic pollutants such as cyclic compounds, halogenated hydrocarbons, phenols (Goyal *et al.*, 2022), pesticides and even inorganic pollutants like nitrile and cyanide (Jan *et al.*, 2020). Ponnusamy *et al.* (2021) performed an ozonation catalyst pairing with MnO₂ nanosheet coated on carbon microfiber for removing Ibuprofen. With a 1 % (w/v) catalyst loading, 90 % Ibuprofen removal efficiency was achieved.

The photocatalysis process is the most recent and advanced process in wastewater treatment. It involves a photooxidation reaction using catalysts such as TiO₂, ZnO, CdO etc., to initiate the reaction (Chairungsri *et al.*, 2022). This method is suitable for treating wastewater with low biodegradability, high complexity, and high pollutant concentrations (Koe *et al.*, 2019). AOPs do not produce large amount of sludge that required additional treatment (Hutagalung *et al.*, 2020), which is often the concern of scientists. Researchers have explored various combinations among AOPs techniques with conventional physio-chemical and biological methods to develop hybrid systems for dye wastewater treatment system (Hai *et al.*, 2007). Scientists claimed that the combination of AOP techniques can enhance the overall performance of the treatment system (Mirza *et al.*, 2020). For example, a combination of electrolysis and Fenton process, which also called as hybrid electro-

Fenton process, has documented a high percentage (> 85 %) color removal and 85 – 90 % COD reduction (Su *et al.*, 2016).

2.6 Transition Metal Complexes and Their Application in Photocatalytic Degradation

Transition metal complexes play a pivotal role in photocatalysis due to their ability to absorb light and facilitate charge transfer processes, which are essential for the activation of photocatalysts and the promotion of chemical reactions. In photocatalysis, ZnO is the most studied photocatalyst besides TiO₂. Semiconductors like Fe₂O₃, Bi₂O₃, ZnWO₄, Bi₂WO₆, NaTaO₃, WO₃, Nb₂O₅, Sm₂Ti₂S₂O₅, CaIn₂O₄ showed extensive applications in water splitting and organic/inorganic compounds degradation (Devi & Kumar, 2011). The main reason for the widespread use of metal oxides as photocatalyst is due to their abundance and stability. The high abundance of metal oxide lowered the price and made it cost-effective when applied on a large scale. Apart from this, metal oxide has high chemical stability and photostability. The high stability metal oxide ensures the photocatalytic activity over time. However, the wide band gap of the metal oxides has also limited the adsorption of photons thus reducing the photocatalytic activity. Metal/transition metal oxides are the most widely used semiconductors (Adekunle *et al.*, 2020; Sanakousar *et al.*, 2022). In contrast, to the best of our knowledge, metal complexes, apart from metal oxides, are rarely used as photocatalysts in photochemical degradation reactions (Teye *et al.*, 2021).

Metal complexes are the coordination compounds formed by interaction between metal ion and ligand. The transition metals such as Fe, Cu, Co, Ni, Mn, Rh, Pt and Au have gained attention from researchers due to their unique electronic properties and catalytic

capabilities (Sangeetha *et al.*, 2019). The *d*-band electrons in transition metals contribute to their ability to absorb light, making them an effective photocatalyst under visible light irradiation (Cheng *et al.*, 2021). Besides that, transition metals have more than one oxidation state, which allows them to efficiently participate in various chemical reactions. For example, the readily interchangeable oxidation state enables the transition metal ions to take part in redox processes (Cieřla *et al.*, 2004). Metal oxides usually have a wide band gap, making them efficient at absorbing UV light, but limited absorption of visible light (Medhi *et al.*, 2020). Therefore, researchers have been exploring ways to enhance the efficiency of metal oxide photocatalyst, especially in utilizing visible light. Strategies like metal oxide doping with other elements (Chong *et al.*, 2024), creating hybrid metal oxide materials (Wang *et al.*, 2024), designing of new metal oxide nanocomposites and synthesizing transition metal complexes have been reported (Krishnan *et al.*, 2024). The current work only discusses the efficiency of transition metal complexes when they are applied in the DCPFC.

Zinatloo-Ajabshir *et al.* (2024) synthesized a novel 1-dimensional copper complex of $[\text{Cu}(\text{phen})_2(\text{OAc})]\cdot\text{PF}_6$ (Figure 2.9). Their work was inspired by excellent photocatalytic activity of Cu(II) complexes, $[\text{Cu}(\text{tba})_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ where tba = 3-[1,2,4]triazol-1-yl-benzoic acid, towards degradation of methylene blue and indole-3-acetic acid. Since copper complexes are moisture and air stable, they might be able to undergo redox reaction in solution. Besides that, the commonly used ZnO and TiO_2 photocatalyst with wide band gap can only utilize UV light, thus limiting their use in environmental remediation. The band gap of the proposed copper complex, $[\text{Cu}(\text{phen})_2(\text{OAc})]\cdot\text{PF}_6$, was calculated and testing was carried out to test the photocatalytic activity. Four different dyes, namely

malachite green, methylene blue, erythrosine, and Eriochrome Black T, were used in the photodegradation study.

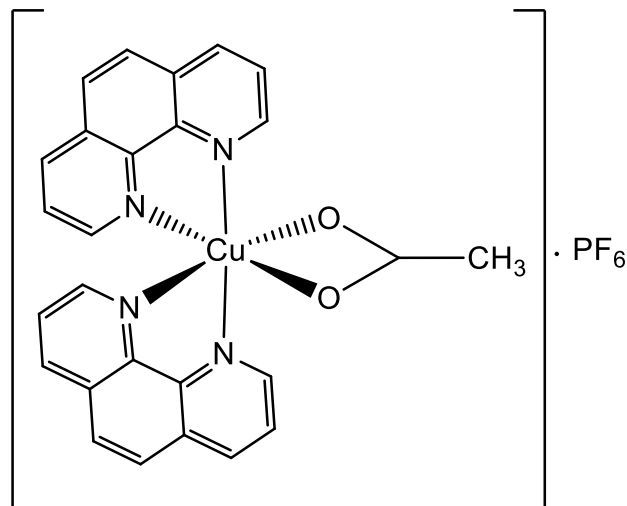


Figure 2.9: The structure of $[\text{Cu}(\text{phen})_2(\text{OAc})] \cdot \text{PF}_6$ (Zinatloo-Ajabshir *et al.* 2024)

This study reported 94.7 % malachite green , 90.1 % methylene blue , 82.4 % erythrosine and 74.3 % Eriochrome Black T degradation efficiencies under visible light. The result showed that this synthesized $[\text{Cu}(\text{phen})_2(\text{OAc})] \cdot \text{PF}_6$ was able to degrade cationic dyes more efficiently than the anionic dyes. The malachite green reached 94.7 % degradation within 120 minutes and 80 minutes in the absence and presence of H_2O_2 , respectively. This showed that an extra oxidant was needed to increase the removal efficiency of the photocatalyst. The calculated band gap of this complex was 2.88 eV and found that it could be activated under visible light and acted as a photocatalyst. The ligands (phenanthroline and acetate) used in the complex were π acceptor ligands and was expected to produce small band gap complexes.

A novel Cu complex, $[\text{Cu}(\text{3-nitrobenzoic acid})_2(\text{1-Me-im})_2]$ (Figure 2.10), (where 1-Me-im is 1-Methylimidazole) was synthesized (Jamil *et al.*, 2024). Methylene blue was

chosen to be the model pollutant in this study. Methylene blue contains a tricyclic aromatic structure with conjugated double bonds, which increases its' stability as there is few active sites on Methylene blue which can be attacked by reactive species. The Cu complex was dispersed in 40 ppm methylene blue dye solution to test the degradation efficiency. Due to changeable oxidation state, excellent thermal and electrical conductivity, and low toxicity, the authors claimed $[\text{Cu}(\text{3-nitrobenzoic acid})_2(\text{1-Me-imidazole})_2]$ was a suitable candidate to use in the control of environmental pollution and energy crisis. The switch of the oxidation state of Cu metal can release radicals and the ligand can increase the reaction surface area between the photocatalyst and pollutant.

A low Methylene blue degradation (12.3 %) was reported when only UV light irradiated but it increased to 70.13 % within 40 minutes when this copper complex was added to the methylene blue solution (Jamil *et al.*, 2024). The addition of this copper complex boosted the Methylene blue degradation and proved that this copper complex is a potent photocatalyst that can be used for dye degradation. During degradation, the copper ion in the complex undergoes a redox reaction and ROS such as hydroxyl radicals ($\bullet\text{OH}$) which are highly reactive and can attack the dye molecules. Also, the large surface of the ligand ensures the sorption of pollutant on the catalyst surface, thus enhancing the photodegradation.

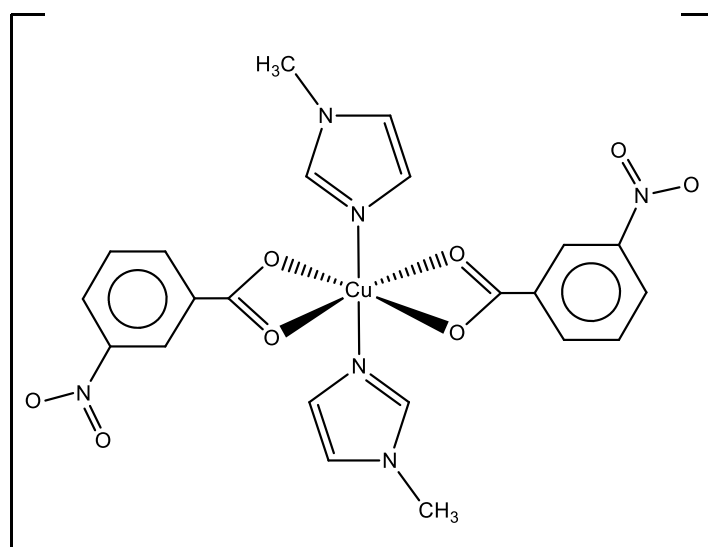


Figure 2.10: The structure of $[\text{Cu}(\text{3-nitrobenzoic acid})_2(\text{1-Me-im})_2]$ (Jamil *et al.*, 2024)

According to Sangeetha *et al.* (2019), they investigated cobalt-beta hydroxyl benzoate (Co-bhb) complex was due to the few studies on the Co-bhb photocatalytic activity. The characteristic interchange between Co^{2+} and Co^{3+} allow Co-bhb to be used for hazardous molecule detection and degradation. The ready transition between different oxidation states allows the cobalt complex to serve as a redox-active species which can easily undergo oxidation and reduction with an analyte via changes in current and potential detection. This means that the cobalt complex can catalyze the oxidation or reduction of the analyte, amplifying the signal produced. The solvothermal method was used to synthesis Co-bhb. A known concentration of methylene blue solution was used as sample pollutants for degradation testing. The Methylene blue removal was found to be about 79 % within 3 hours of UV light irradiation in the presence of 0.2 g Co-bhb powder. Besides, the lower detection limit of the cobalt complex was found to be 0.1 ppm. This approach showed potential for the cobalt complex used for electrochemical sensors and photodegradation processes.

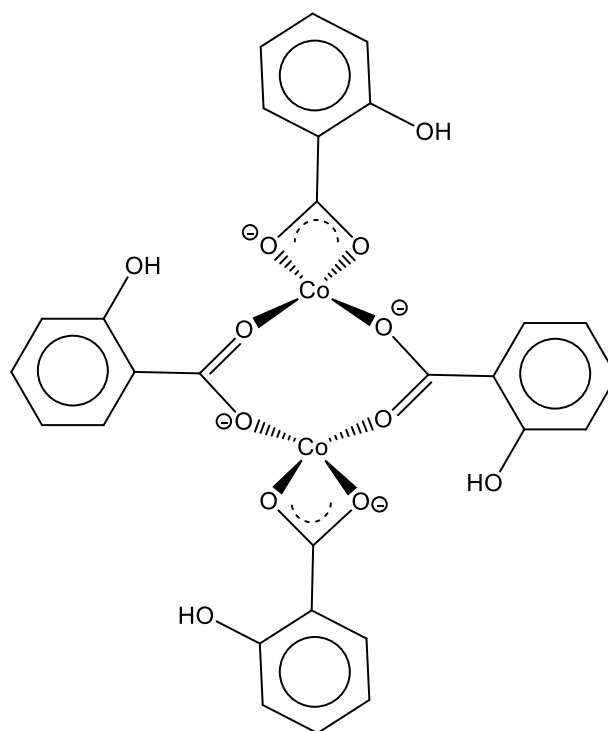
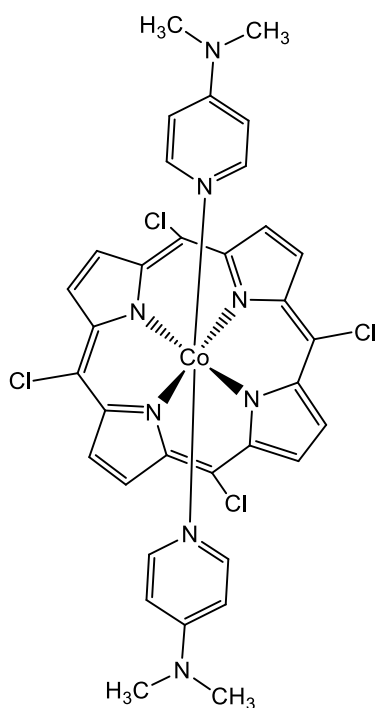


Figure 2.11: The structure of Co-bhb (Sangeetha *et al.*, 2019)

Cobalt(II) porphyrin has high sensitivity to light irradiation compared to other metal(II) porphyrins. Porphyrin has a stable structure, allowing them to maintain structural integrity under a wide range of conditions. The high stability enhances the photosensitivity of porphyrins. Two novel cobalt(II) tetraphenylporphyrin-based six-coordinate complexes: bis(4-dimethylaminopyridine)(5,10,15,20-tetrakis[4-bromophenyl]porphinato)cobalt(II) [Co(TBRPP)(DMAP)₂] (Figure 2.12.a) and bis(4-dimethylaminopyridine)(5,10,15,20-tetrakis[4-chlorophenyl]porphinato)cobalt(III) [Co(TCIPP)(DMAP)₂] (Figure 2.12.b) were synthesized (Amiri *et al.*, 2023). The photocatalytic study of the synthesized Cobalt(II) porphyrin complexes was investigated by adding it to a 20 mL of 40 ppm toluidine blue dye solution and evaluated the degradation of toluidine blue dye. The final degradation efficiency of toluidine blue dye was 84.8 % and 86.9 % for Complex 1 and Complex 2 under visible light irradiation. The removal efficiency of the complexes remained more

than 80 % for both complexes after 3 times repeated use for toluidine dye degradation. The paper concluded by claiming both cobalt complexes could become potential photocatalysts for future applications (Amiri *et al.*, 2023).

a.



b.

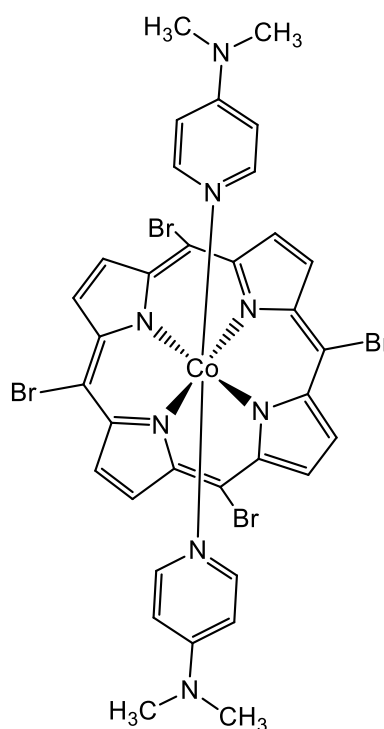


Figure 2.12: The structures of (a) [Co(TBRPP)(DMAP)₂] (Complex 1); and (b) [Co(TClPP)(DMAP)₂] (Complex 2) (Amiri *et al.*, 2023)

Many studies have declared that, besides iron, other transition metal complexes have the ability to degrade pollutants. Therefore, a comparison between metal complexes/H₂O₂ systems on phenol red dye photodegradation was conducted with Tungsten lamp irradiation. The thiocyanate complexes of iron [Fe(SCN)]²⁺, copper [Cu(SCN)]⁺, and cobalt [Co(SCN)]⁺ were synthesized (Figure 2.13). A 10 ppm phenol red dye solution was used in this experiment (Lodha *et al.*, 2008). Conclusion of the paper was iron thiocyanate complex had the excellent degradation rate compared to copper

thiocyanate and cobalt thiocyanate on the phenol red dye degradation. There was an induction period in the $[\text{Fe}(\text{SCN})]^{2+}/\text{H}_2\text{O}_2$ system which generated a large amount of radicals that could be used in the degradation process later. Nevertheless, the induction period was not observed in $[\text{Cu}(\text{SCN})]^+/\text{H}_2\text{O}_2$ and $[\text{Co}(\text{SCN})]^+/\text{H}_2\text{O}_2$ systems. However, this paper did not mention the degree of dye degradation but only the dye degradation rate, therefore the ability of the transition metal thiocyanate/ H_2O_2 system to completely decolorize phenol red dye remained unknown (Lodha *et al.*, 2008).

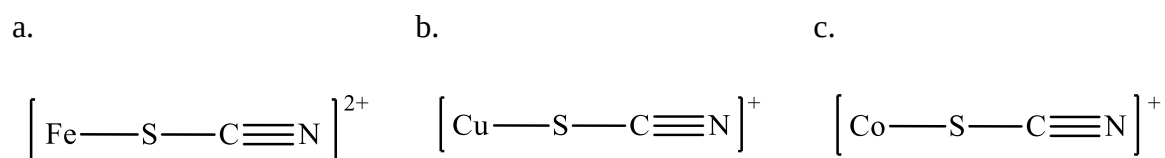


Figure 2.13: The structures of (a) $[\text{Fe}(\text{SCN})]^{2+}$; (b) $[\text{Cu}(\text{SCN})]^+$; (c) $[\text{Co}(\text{SCN})]^+$ (Lodha *et al.*, 2008)

According to Singh *et al.* (2023), coordination complexes with a large molecular structure can improve the adsorption of pollutants for purification purposes. In this study, nickel(II) picolinic acid, $[\text{Ni}(\text{2-picolate})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ was synthesized through hydrothermal method. Various types of dye (crystal violet, methylene blue, methyl violet, safranine O, neutral red, rose bengal, rhodamine B, rhodamine 6G, fluorescein, Eriochrome Black T, congo red, and methyl orange) were used as model dye pollutants for the photocatalytic activity testing of the nickel(II) picolinic acid complex. At the same time, the detection limit of the complex was also examined. 0.16mmol of $[\text{Ni}(\text{2-picolate})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ was added to 40 mL of 10 ppm dye solution for the photocatalytic activity testing. The dye degradation varied widely. Crystal violet showed the highest degradation (94.19 %) among the tested dyes, but rhodamine 6G showed only 8.7 % degradation. The crystal violet, methylene blue, methyl violet, neutral red and safranine O

showed better degradation, >82 %, whilst the rest had <50 % degradation. It was found out that the Ni(II) complex can efficiently degrade cationic dyes as methylene blue, methyl violet, safranin O and crystal violet were cationic dyes while neutral red was a neutral dye. Only five mostly degraded dyes were tested for detection limit and the detection limit was found to be 0.58 ppm (crystal violet), 0.77 ppm (methylene blue), 1.05 ppm (methyl violet), 1.25 ppm (neutral red), and 1.75 ppm (safranin O), respectively.

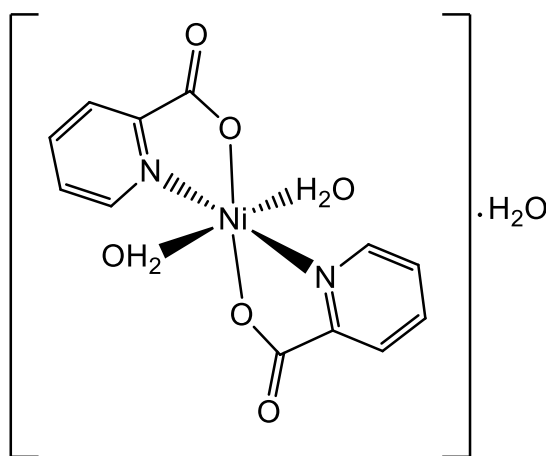


Figure 2.14: The structure of $[\text{Ni}(\text{2-picolinate})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (Singh *et al.*, 2023)

Based on the literature discussed, it can be concluded that copper, cobalt and nickel complexes have the potential to be used as photocatalysts in PFC. In this project, acetylacetone and 1,10-phenanthroline (Figure 2.15) were selected as ligands to react with these three transition metals to form transition metal complexes. Acetylacetone is pi-donor ligand while 1,10-phenanthroline is pi-acceptor ligand. The synthesized transition metal complexes were used as photocatalysts in the DCPFC and compared with ZnO as the model metal oxide photocatalyst for synthetic dye degradation.

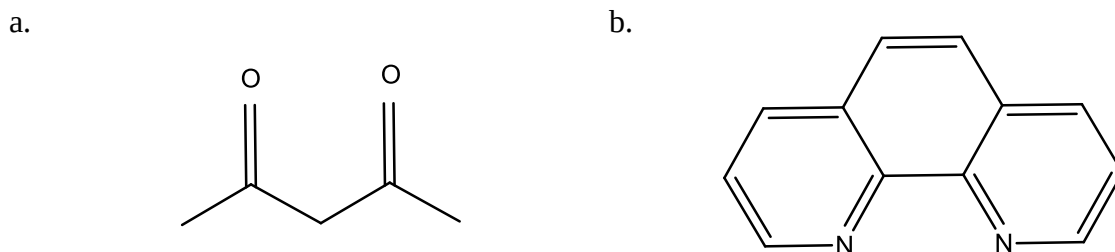


Figure 2.15: Chemical structures of (a) acac; and (b) phen ligands

Acetylacetone (acac), also known as pentane-2,4-dione, is a β -diketone with chemical formula $C_5H_8O_2$. It is an oxygen-based bidentate ligand. It consists of two carbonyl groups ($C=O$) separated by a methylene group ($-CH_2-$) which makes it an interesting ligand for forming coordination complexes with metal ions. Acetylacetone has proven to be a potent photo-activator (Zhang *et al.*, 2021). Metal acetylacetonate complexes are widely studied and they are claimed to be potential photocatalysts (Almeida *et al.*, 2020). The carbonyl groups in acetylacetone provide a strong binding site for metal ions, leading to the formation of stable complexes. Also, the lone pairs from oxygen atoms in acetylacetone allow for efficient electron transfer between ligand and metal ion. The low-energy electron transfer between metal and ligand can enhance the photocatalytic activity (Zeng & Zhang, 2021). Besides that, the conjugated system in acetylacetone allows for π - π^* transition, which can be exploited in the light absorption.

In a work of Zhang and the group (2021), the UV/Acetylacetone AOP system was designed for aromatic pollutant degradation and compared with the UV/ H_2O_2 system (Zhang *et al.*, 2021). A 0.5 mM acetylacetone was added to a solution containing sample dye as pollutant and the solution was placed under UV irradiation. It was observed that acetylacetone had better photocatalytic activity than H_2O_2 . This was because of the π - π^*

transition of the enol structure was more effective for photon absorption than H_2O_2 . However, the UV/AA system showed functional group selectivity towards -OH substituted azo dye compared to ortho- SO_3^- substituted azo dye, which reduced the efficiency of the system in the dye degradation.

1,10-phenanthroline (phen) is a bidentate nitrogen-containing ligand with the chemical formula $\text{C}_{12}\text{H}_8\text{N}_2$. It consists of a planar aromatic system containing two nitrogen atoms at position 1 and 10, which serve as binding sites for coordination with metal ions. It has high planarity due to its large conjugated area (Liu *et al.*, 2021) and the conjugated system of alternating single and double bonds within the aromatic ring (Li *et al.*, 2019c). The continuous ring of π electrons in the aromatic system of 1,10-phenanthroline allow the π -stacking reaction to occur between 1,10-phenanthroline and the aromatic components of dye molecules. The π -stacking interaction can increase the effective absorption area (Huang *et al.*, 2023) for both metal 1,10-phenanthroline complex and dye molecules to initiate the photocatalysis. 1,10-phenanthroline, with good planarity and a high conjugation degree, make it a promising electron acceptor to trap and stabilize the received electron (Liu *et al.*, 2022b).

Band gap is one of the key factors to determine the efficiency of the photocatalytic activity of a photocatalyst. Theory states that the smaller the band gap, the easier the electron excitation, the higher the photocatalytic activity. Acac with π donor properties and phen with π acceptor properties were chosen as ligands to bind with the selected metals (Co, Ni, Cu) to form different metal complexes. The band gap of the complexes was calculated to know the effects of π donor and π acceptor in a complex.

2.7 Coating Method

Photoanode is the most important component in a PFC system. It determines the degradation and power generation of a PFC. Therefore, it is important to develop a method to maximize the performance of photoanode in PFC. It is reported that the performance of photoanode influenced by their surface area and morphology (Li *et al.*, 2019a). Photocatalysis is a process where the catalyst will be fixed on the substrate and activated by sunlight to initiate chemical reaction. The fixation of catalyst on a substrate is called ‘immobilization’ (Morshed, 2021). The photocatalytic activity of the catalyst highly depends on the immobilization method and substrate material. Stability, recyclability, and ease of recovery of the photocatalyst are determined by the immobilization method or coating method (Sorathiya *et al.*, 2016). This means that coating method influences the photoanodes efficiency by attaching/forming different sizes and shapes of catalyst on photoanode.

The coating method for photoelectrode involves applying a thin layer or specific film material onto the substrate surface to become photoanode or photocathode (Antonio Abarca *et al.*, 2023). This process aims to modify the surface characteristics of photocatalyst to enhance photocatalytic activity (Park *et al.*, 2013; Faraldos & Bahamonde, 2018; Guo *et al.*, 2020). Various coating methods have been developed and each method has its unique advantages and considerations (Butt, 2022). Table 2.3 summarises how the researchers used different coating methods based on the specific requirements of photocatalytic application and desired modification to the surface characteristics of photocatalyst.

Table 2.3: Description of coating method principles and their advantages

Method	Principle	Advantages	Reference
Spin coating	Applying a liquid coating material onto the substrate surface and spread it by spinning	Provides uniform coating on flat surface, widely used in laboratory setting	Zakria <i>et al.</i> (2021)
Dip coating	Immersing the substrate in a solution containing the coating material and withdrawing it at a controlled rate	Simple and cost effective, forms a uniform coating on complex geometries	Tang & Yan (2017)
Spray pyrolysis	Atomized solution containing coating material is sprayed onto the heated substrate surface, leading to film formation	Scalable and adaptable to large surfaces, good for industrial application	Fotovvati <i>et al.</i> (2019)
Chemical bath deposition	Coating material is precipitated onto the substrate surface from a chemical bath	Simple and cost effective, applicable to large area coating	Budida & Srinivasan (2023)
Electrophoretic deposition	Charged particles in a suspension migrate towards the substrate under the influence of electric field. The particles deposited onto substrate surface, forming a coating	Uniform coating with control thickness, can coat both conductive and non-conductive substrates	Visai <i>et al.</i> (2011)
Electrochemical anodization	Oxidation of substrate in electrolyte to form metal oxide layer	Tailorable pore size and structure, increase surface area and improve corrosion resistance	Visai <i>et al.</i> (2011)
Ultrasonication	High frequency ultrasound waves is applied to a liquid containing coating material, creating cavitation bubbles, lead to the formation and fine particle or stable dispersion onto the substrate surface	Effective for producing nanoparticles or dispersing materials, enhance coating uniformity	Teh <i>et al.</i> (2017)
Doctor blade	A blade is used to spread coating material evenly over a flat substrate surface	Simple and cost effective, provides precise control over coating thickness, suitable for large scale production	Frederichi <i>et al.</i> (2021)
Powder spray	A process applying a dry powder coating material onto a substrate using spray gun	Uniform coating thickness, can be applied to wide range substrate, well-suit for large scale production	Frederichi <i>et al.</i> (2021)

Table 2.3: Continued

Magnetron sputtering	High-energy ions from plasma are used to dislodge atoms from a target materials and deposited on substrate surface	High deposition rate, excellent adhesion, suitable for metallic coating	Zakria <i>et al.</i> (2021)
Atomic layer deposition	Layer-by-layer deposition of atomic layer using sequential surface reaction, resulting in precise and conformal coating	Atomic-level control over thickness, uniform and controlled deposition	Zakria <i>et al.</i> (2021)
Aerosol-assisted chemical vapour deposition	A precursor is aerosolized and carried to the substrate surface where a chemical reaction takes place, resulting in deposition of a thin film	Uniform and conformal coating, suitable for large scale production, allow deposition of complex composition	Sabzi <i>et al.</i> (2023)

The most common applied photocatalyst coating method can be classified into two groups: solution-based method and gas-based method (Figure 2.16). Solution-based methods include spin coating, dip coating, spray pyrolysis, chemical bath deposition, electrophoretic deposition, electrochemical anodization, ultrasonication and doctor blade. Powder spray coating, magnetron sputtering, atomic layer deposition and aerosol-assisted chemical vapour deposition are classified as the gas-phase methods.

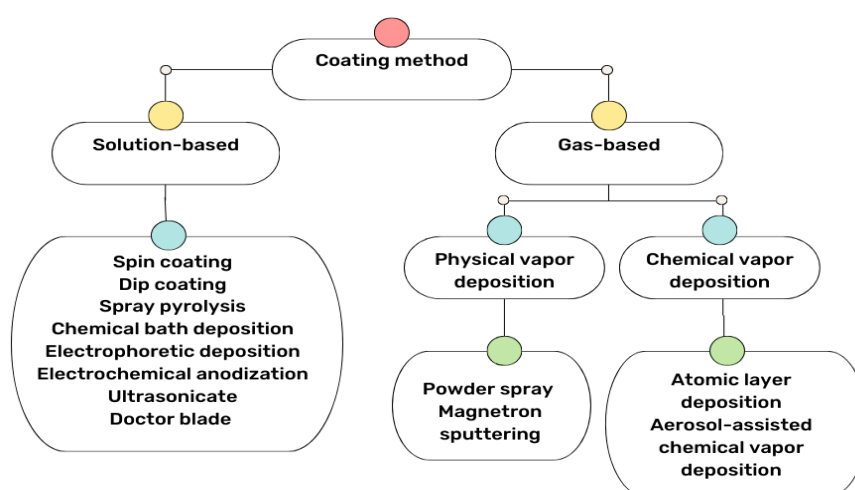


Figure 2.16: Classification of photocatalyst coating methods (Pitchaimuthu *et al.*, 2022)

Each coating method results in different particle sizes and shapes. Generally, smaller particle sizes result in larger surface areas, providing more active sites for photocatalytic reactions to occur. Nanoscale photocatalysts have gained significant attention due to their enhanced surface area, improved light absorption, and increased catalytic activity (Liu *et al.*, 2015; Rajaiatha *et al.*, 2022). Chan *et al.* (2014) and Li *et al.* (2020a) stated that particle size and surface area-to-volume ratio are inversely related; as particle size decreases, the surface-area-to-volume increases, leading to an exponential increase in reaction rate. This relationship is advantageous for photocatalysis as it facilitates a higher density of active sites available for the interaction with targeted molecules. According to Shih and Lin, (2012)'s work, the degradation rate of Reactive Black 5 dye increased when the particle size of TiO₂ nanopowder used was less than 500 nm. When TiO₂ nanopowder with particle size larger than 500 nm was used in the photocatalytic system, the degradation rate of Reactive Black 5 decreased. In conclusion, the photocatalyst coating method is crucial to determine the efficiency of photocatalytic system. The choice of coating method determines the uniformity and stability of the photocatalyst layer on the substrate. Simultaneously, the particle size directly affects the reaction surface, with smaller particles offering a larger surface area and, consequently, more active sites for catalysis.

The design of PFC aims to treat wastewater while generating electricity, with efficiency dependent on the selection of photocatalysts, photoanodes, oxidizing agents, and coating methods. While traditional metal oxides like TiO₂ are commonly used, their large band gap limits light absorption. To enhance photocatalytic activity, researchers are exploring metal complexes that reduce this band gap. The choice of oxidizing agent is also critical, as it affects the generation of reactive radicals that improve pollutant degradation

efficiency. Additionally, innovative photocatalyst coating methods are being developed to maximize light absorption, enhance charge separation, and improve the stability of the photoanode, thereby significantly boosting overall PFC performance.

The literature review highlights the importance of the energy gap in determining the effectiveness of photocatalysts for pollutant degradation. Traditional metal oxides like TiO_2 , ZnO possess a large band gap, limiting their ability to absorb visible light and effectively catalyze reactions. Recent studies indicate the metal complexes with reduced energy gaps can enhance photocatalytic activity by improving light absorption and charge separation. This advancement allows for more efficient degradation of pollutants under visible light, paving the way for more effective photocatalytic applications.

CHAPTER 3

METHODOLOGY

3.1 Materials and Reagents

All materials and chemicals used were purchased from Bendosen R&M, J.T. Baker and Merck. Zinc oxide (ZnO, M.W. = 81.37 g/mol) with a purity of 99.92 %, purchased from Bendosen, was directly used as photocatalyst by coating the photoanode surface using the ultrasonic coating, dip coating, or spray coating methods without further purification.

Ethanol was purified by refluxing 900 mL of ethanol with iodine (1.50 g) and magnesium turning (3.50 g) until the mixture turned colorless. The purified ethanol was then collected through distillation. All solvents used in the synthesis were of analytical grade, while other reagents were used without further purification. The synthesized metal complexes were coated on zinc plates to be used as a photoanode via the ultrasonication method, dip coating method, or spray coating method.

3.2 Instrumentation Used for the Characterizations of Photocatalyst and Photoanode Used

The infrared spectra were recorded using a Thermo Scientific/Nicolet iS10 Fourier Transform Infrared spectrophotometer with KBr disc used for solid samples. Meanwhile, UV-Vis spectra were recorded in ethanol and CHCl₃ solution using a Agilent Carry 60 UV-Vis spectrophotometer with 1 cm quartz cuvette in the range of 200 – 800 nm. The

absorption data was interpreted and used in Tauc plot graph to estimate the band gap energy of the synthesized transition metal complexes. The ^1H and ^{13}C NMR spectra were recorded on a JEOL NMR-ECA 500 MHz spectrophotometer, with chemical shift were reported relative to TMS and were referenced via residual proton NMR resonance of the appropriate deuterated solvent (DMSO- d_6 : δH 2.50 ppm) (CDCl_3 : δC 77.5 ppm) (CDCl_3 : δH 7.26 ppm). The elemental analysis was done by using a ThermoFisher Scientific Flashsmart CHN elemental analyser. The morphology of fabricated photoanodes was observed under scanning electron microscopy (SEM) (JEOL, Japan, Model: JSM-IT500HR) at 10 kV accelerating voltage.

The zinc plate was dried using Protech Lab Dryer, BS-100 while the FOCUS, 18 W/6500 K, 220 – 240 V light bulb was used throughout the experiment. A Elmasonic Easy 30H Elma Schmidbauer GmbH ultrasonicator was used to prepare the ultrasonic-coated ZnO/Zn photoanode. The pH of the analyte were recorded on a Eutech 700 pH meter. The resistance and current produced from PFC system were measured using Shanghai Domao ZX21d resistor and XEOLE XL830L multimeter.

3.3 Preparation of Methyl Red Dye Solution

The stock solution of 1,000 ppm methyl red dye solution was prepared by dissolving 0.10 g of methyl red powder in 100 mL of distilled water. A 10 % v/v of HCl solution was added to the solution to ensure the methyl red powder was totally dissolved, the solution was then top up to 100 mL calibration mark with distilled water. To prepare 10 ppm methyl red solution, 10 mL of stock solution was taken out and added with 990 mL of distilled water.

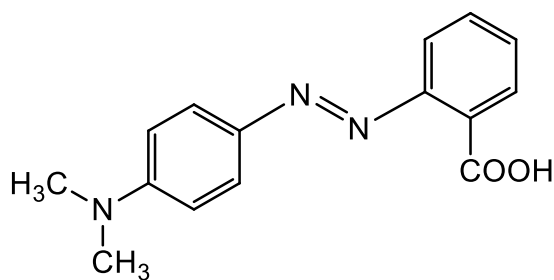


Figure 3.1: Chemical structure of methyl red dye

3.4 Preparation of Photoanode

3.4.1 Pre-treatment of Zinc Plate

A zinc plate (99.999 % purity) with the thickness of 0.38 mm was cut into dimensions of 6.0 cm (L) $\times$ 2.0 cm (W). The cut zinc plate was then polished with P400 grid sandpaper to achieve even surface and remove oil stains on the zinc plate. The zinc plate was then dipped into 10 % v/v hydrochloric acid (HCl) for 3 seconds and rinsed with distilled water to remove any residual HCl. Lastly, the zinc plate was dried in the oven at 120 °C for 2 hours. The reason of HCl treatment was to remove surface impurities and aid in the formation of a rough surface to have better adhesion, ensuring high-quality coating.

3.4.2 Preparation of Photoanode Using ZnO, ZnO/Zn and Metal Complexes, Metal Complex/Zn

Three different photocatalyst coating methods were employed in the fabrication of photoanode in this project, namely dip coating, spray coating and ultrasonic coating. The coating method significantly influenced key properties of the photocatalyst, such as film thickness, surface morphology and adhesion. By experimenting various techniques, the most efficient and cost-effective coating method could be determined.

3.4.2.1 Ultrasonic method

The immobilized ZnO/Zn and metal complex/Zn photoanode was made based on methods described in Lee *et al.*, (2017); Moksin *et al.*, (2021) with minor modifications. A processed zinc plate was immersed and sonicated in a ZnO suspension (1.00 g of ZnO powder in 100 mL distilled water) and metal complex suspension (1.00 g of synthesized metal complex powder in 100 mL distilled water) for 1 hour in a beaker respectively. The zinc plate was then dried in an oven for 24 hours at 120 °C.

3.4.2.2 Sol-Dip coating method

The agar solution was prepared by mixing 1.00 g of antibacterial agar powder with 80 mL hot distilled water. The solution was stirred for 20 minutes until all agar powder dissolved completely. The ZnO and metal complex suspensions were prepared by adding 1.00 g ZnO powder and 1.00 g of metal complex powder to 20 mL distilled water separately. These suspensions were added separately to the agar solution and mixed thoroughly. The processed zinc plate was dipped into the ZnO-agar solution and metal complex-agar solution for 3 seconds, took out dried with hair drier respectively. The dipping-drying procedure was repeated 8 – 10 times until a desired coating thickness was achieved. The zinc plate was then dried in the oven at 60 °C for 1 hour.

3.4.2.3 Spray coating method

The spray coating method was adopted according to Li *et al.* (2020b) with some modification. The processed zinc plate was immersed in polyurethane waterproof coating for 5 seconds then taken out and the excess coating was shaken off. After that, 1.00 g ZnO powder and metal complex powders were evenly sprayed onto the zinc plate using a

powder spraying bottle. The coated zinc plate was then left to air dry for 1 hour. Lastly, the dried zinc plate was rinsed with distilled water to remove the poorly attached ZnO and metal complexes powder.

3.5 PFC Operation on Methyl Red Dye Solution

3.5.1 PFC Setup

A SCPFC was fabricated with ZnO/Zn as the photoanode and a graphite plate (5.0 cm $\times$ 4.0 cm $\times$ 0.3 cm) as the cathode, as shown in Figure 3.2. The cell was filled with 800 mL of 10 ppm methyl red solution and potassium chloride (2.0 g) was added as the supporting electrolyte. The pH of SCPFC was kept at initial pH (c.a. pH 4) and a fluorescent bulb (approximately 1050 lux) was used as the light source. The cell was aerated with an air pump at room temperature throughout the experiment.

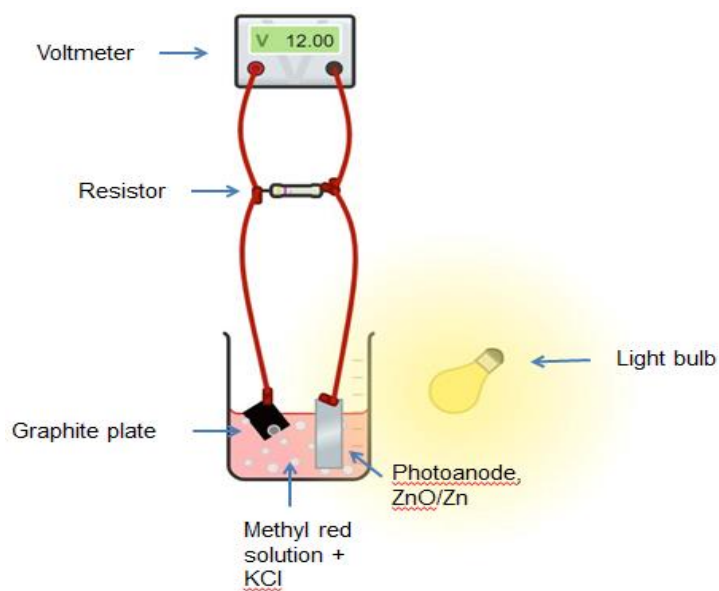


Figure 3.2: SCPFC setup

A DCPFC system was constructed by connecting two chambers with a salt bridge (Figure 3.3). The photoanode used was ZnO/Zn, and the cathode was a graphite plate (5.0 cm $\times$ 4.0 cm $\times$ 0.3 cm). The photoanode was placed in a reactor chamber filled with 800 mL of 10 ppm methyl red solution, while the graphite plate was placed in a cathode chamber filled with diluted NaOCl solution. It is worth to note that NaOCl solution was not added in SCPFC because the organic pollutant can be degraded directly by OCl^- ion due to its' strong oxidizing ability. This can affect the efficiency of the SCPFC by preventing electron movement across the circuit and subsequently producing no voltage. A 1.0 mol potassium chloride solution was used as the salt bridge. The pH of the DCPFC was maintained at the initial pH (c.a. pH 4) and a fluorescent bulb (approximately 1050 lux) was used as the light source. The cathode was aerated with an air pump at room temperature during the experiment.

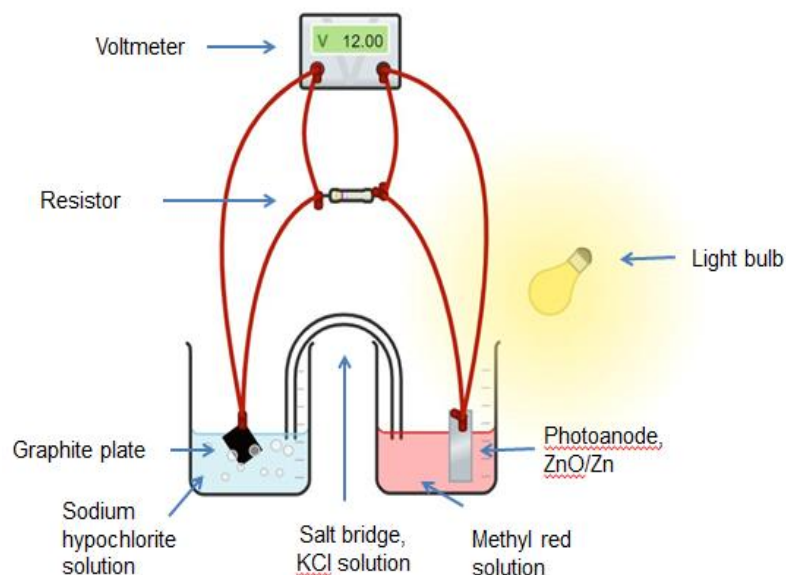


Figure 3.3: DCPFC setup

The initial and final pH was recorded using a pH meter. Both PFC systems were connected to an external resistor and a multimeter to measure the current across varying

resistance from 1 to 1,000,000 Ω . The data obtained was used to calculate the maximum power density ($P_{\max}$) generated by the system.

The power density ($P_{\max}$) generated was calculated based on Equation 3.1:

$$P_{\max} = J_{sc} V_{oc} \quad (\text{Equation 3.1})$$

where

$P_{\max}$ = Power density,

J_{sc} = current density,

V_{oc} = voltage output.

The current of the dual-chamber PFC was calculated based on Equation 3.2:

$$I = \frac{V}{R} \quad (\text{Equation 3.2})$$

where

V = voltage (V),

I = current (A),

R = resistance (Ω).

The current density (J_{sc}) was calculated by dividing the calculated current by the surface area of ZnO/Zn photoanode (12 cm²).

The dye removal efficiency was calculated using Equation 3.3:

$$\text{Removal efficiency (\%)} = \frac{\text{Initial dye concentration} - \text{Final dye concentration}}{\text{Initial dye concentration}} \times 100\% \quad (\text{Equation 3.3})$$

3.5.2 Optimization of PFC

3.5.2.1 Retention Time

The performance of both SCPFC and DCPFC setups was monitored over 5 hours to determine the optimal contact hour for the synthetic methyl red dye degradation. The 10 ppm, pH 4 synthetic methyl red dye solution was prepared and used in the experiment. The optimal retention time was determined by the sample with the highest synthetic methyl red dye removal efficiency (%). The voltage reading was taken hourly. The dye degradation efficiency (%) determination was carried out using UV-Vis spectroscopy. The absorbance at wavelength 525 nm was determined and recorded. Each experiment was carried out in triplicates to increase accuracy and precision of the results.

3.5.2.2 Initial Dye Concentration

Synthetic methyl red dye solutions at pH 4 of different concentrations (5 ppm, 10 ppm and 20 ppm) were prepared. The setup was placed under fluorescent bulb irradiation of approximately 1050 lux for 5 hours. In the 5-hour experiment, the voltage reading was taken hourly, and the dye degradation efficiency was also determined. The experiment was repeated three times with newly coated ZnO/Zn photoanodes to obtain a more accurate result. The chosen of initial concentration of 5 ppm, 10 ppm and 20 ppm was based on literatures' result for assessing photocatalytic efficiency without overwhelming the system or causing saturation to ensure a relevant result (Khanmohammadi *et al.*, 2024).

3.5.2.3 pH

In this experiment, the 10 ppm methyl red dye solutions with various pH (pH 3, pH 4, pH 5) were prepared. The concentrated hydrochloric acid (10 % v/v) and sodium carbonate solution (10 % w/v) were used to adjust the pH value of the prepared dye solution and the pH value was monitored with a pH meter. The setup was placed under fluorescent bulb irradiation of approximately 1050 lux for 5 hours. The voltage reading was taken hourly and the dye degradation efficiency was determined. The experiment was repeated at least three times to ensure the reproducibility and reliability of the result. The selection of pH values 3, 4, 5 was based on the literatures' results especially on the influence of acidic and alkaline condition on dye degradation (Li *et al.*, 2019b).

3.5.2.4 Reusability of Photoanode

After establishing the optimal conditions of the PFC, the used ultrasonic-prepared ZnO/Zn photoanode was reused for four consecutive treatment cycles under these conditions. The used photoanode was rinsed with distilled water and then dried in the oven at 100 °C for 4 hours before being used in the subsequent cycles. The voltage reading was taken hourly.

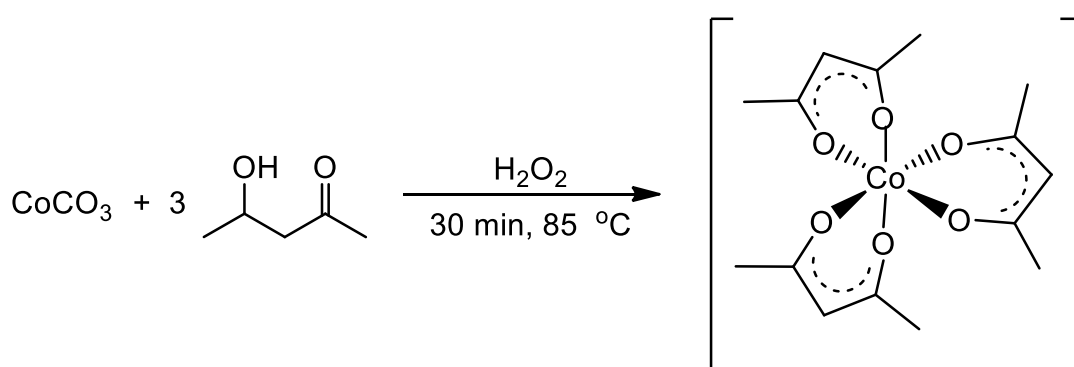
3.5.3 Application of Metal Complex/Zn as Photoanode in PFC

The synthesized metal complexes were coated on the processed zinc plate using different methods. The efficiency of the metal complex/Zn photoanode used in the DCPFC

under optimal conditions of ZnO/Zn was compared through the methyl red dye removal efficiency and power generation. The experiment period for metal complex/Zn was 5 hours. The data recording method was same as mentioned in Section 3.5.2.

3.6 Preparation of Co, Ni and Cu Complexes with Selected Ligands

3.6.1 Preparation of tris(acetylacetonato) cobalt(III), [Co(acac)₃]

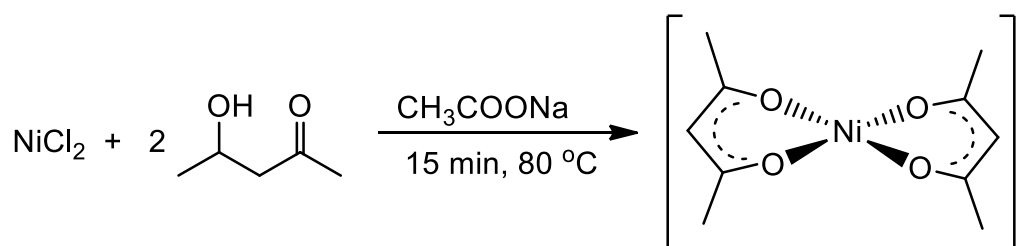


Scheme 3.1: Reaction scheme of [Co(acac)₃]

The synthesis of [Co(acac)₃] was done based on the method reported by Amason *et al.* (2021). Acetylacetone (10 mL, 0.1 mole) was poured into a round bottom flask containing cobalt(II) carbonate (1.20 g, 0.01 mole). The mixture was stirred and heated in a water bath at 85 °C for 30 minutes. A 15 mL H₂O₂ was added dropwise into the mixture until effervescence stopped. The flask was then chilled in an ice-salt bath for product precipitation. The dark green product was vacuum filtered and washed with cold ethanol to remove any unreacted material or impurities. To further purify the product, it was dried at 110 °C for 30 minutes to ensure complete removal of solvent and moisture. Yield: 2.89 g, 81 %. Anal. Calcd for [Co(C₅H₈O₂)₃]: C, 50.57; H, 5.94; Found: C, 50.23; H, 5.75. ¹H NMR (CDCl₃, 500 MHz, 7.25 ppm): δ1.65, 2.17 (s, 6H, -CH₃), 5.51 (s, 1H, Ar-H). ¹³C

NMR (CDCl₃, 126 MHz, 77.5 ppm): δ 189.6, (s, 6C, C=O), 97.2 (s, 3C, methine carbon), 26.1 (s, 6C, -CH₃). IR (KBr, cm⁻¹): ν (C-H) 2997, 2922, ν (C=O) 1574, ν (C=C) 1519, δ (C-H) 1381, ν (C-O) 1278, ν (C-C) 1017, δ (C-H) 936, δ_{out} (C-H) 768, ν (Co-O) 635, 466. UV-Vis (CHCl₃)(λ_{max} /nm): 260 (π - π^* transition), 595 (d - d transition).

3.6.2 Preparation of bis(acetylacetonato) nickel(II), [Ni(acac)₂]

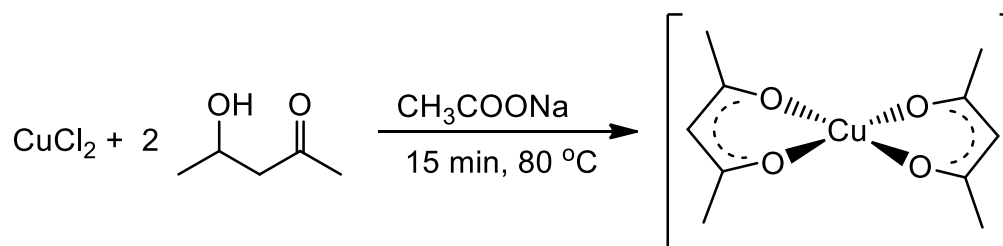


Scheme 3.2: Reaction scheme of [Ni(acac)₂]

The synthetic method was adapted from previous literature reported by Eleruja *et al.* (2007). Nickel(II) chloride hexahydrate (2.377 g, 0.01 mole) was dissolved in 10 mL distilled water. Acetylacetone (1.96 mL, 0.02 mole) in methanol (4 mL) was then added dropwise to the stirring nickel(II) chloride solution. Sodium acetate (2.70 g, 0.03 mole) was dissolved in 6 mL distilled water and slowly added to the resulting mixture. The mixture was continuously stirred and heated on hot plate at 80 °C for 15 minutes, cooled to room temperature and placed in ice bath for precipitation. The green solid was filtered, washed with cold distilled water to remove soluble impurities. The crude product was further purified by drying in oven at 100 °C for 2 hours to ensure the removal of moisture and any remaining solvents. Yield: 1.522 g, 59 %. Anal. Calcd for [Ni(C₅H₈O₂)₂]: C, 46.75; H, 6.27; Found: C, 46.98; H, 6.11. ¹H NMR (CDCl₃, 500 MHz, 7.25 ppm): δ 2.03 (s, 6H, -CH₃), 5.49 (s, 1H, Ar-H). IR (KBr, cm⁻¹): ν (C-H) 2994, 2920, ν (C=O) 1610, ν (C=C) 1519, ν (C-O)

1258, $\nu(\text{C-C})$ 1020, $\delta(\text{C-H})$ 928, $\delta_{\text{out}}(\text{C-H})$ 764, $\nu(\text{Ni-O})$ 580, 421. UV-Vis (DMF) ($\lambda_{\text{max}}/\text{nm}$): 295 ($\pi\text{-}\pi^*$ transition), 650 ($d\text{-}d$ transition).

3.6.3 Preparation of bis(acetylacetonato) copper(II), $[\text{Cu}(\text{acac})_2]$

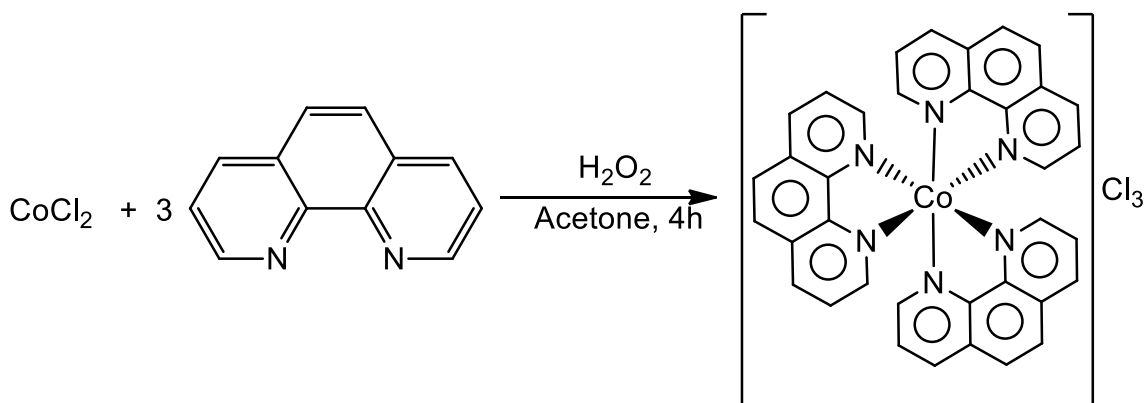


Scheme 3.3: Reaction scheme of $[\text{Cu}(\text{acac})_2]$

The complex of $[\text{Cu}(\text{acac})_2]$ was prepared according to the method described in the literature (Moeller *et al.*, 1957). Copper(II) chloride dihydrate (1.705 g, 0.01 mole) and sodium acetate (2.70 g, 0.03 mole) was dissolved with 25 mL and 6 mL distilled water respectively. Acetylacetone (1.96 mL, 0.02 mole) in methanol (4 mL) was added dropwise to the rapid stirring of copper(II) chloride solution. Sodium acetate solution was then added gradually to the resultant mixture. The mixture was continuously stirred and heated at 80 °C for 15 minutes and then let it cool to room temperature. The solution was then cooled in an ice bath for precipitation and was vacuum filtered. The precipitate was washed with cold distilled water to remove residual salts or unreacted species. To purify the product, it was dried in oven at 110 °C for 2 hours. The dry blue powder was dissolved into 100 mL methanol and heated at 60 °C. The solution was left overnight for recrystallization. The blue $[\text{Cu}(\text{acac})_2]$ precipitate was filtered and air dried. Yield: 1.638 g, 63 %. Anal. Calcd for $[\text{Cu}(\text{C}_5\text{H}_8\text{O}_2)_2]$: C, 45.89; H, 5.39; Found: C, 45.49; H, 5.18. IR (KBr, cm^{-1}): $\nu(\text{C-H})$ 2922, $\nu(\text{C=O})$ 1583, $\nu(\text{C=C})$ 1532, $\delta(\text{C-H})$ 1415, $\nu(\text{C-O})$ 1274, $\nu(\text{C-C})$

1019, $\delta(\text{C-H})$ 937, $\delta_{\text{out}}(\text{C-H})$ 782, $\nu(\text{Cu-O})$ 652, 613, 454. UV-Vis (CHCl_3) ($\lambda_{\text{max}}/\text{nm}$): 290 (π - π^* transition), 650 (d - d transition).

3.6.4 Preparation of tris(1,10-phenanthroline)cobalt(III) trichloride, $[\text{Co}(\text{phen})_3]\text{Cl}_3$

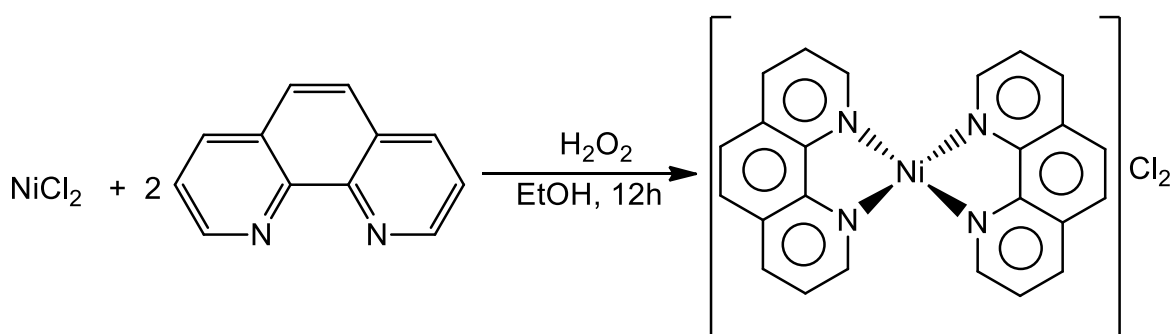


Scheme 3.4: Reaction scheme $[\text{Co}(\text{phen})_3]\text{Cl}_3$

The synthesis of $[\text{Co}(\text{phen})_3]\text{Cl}_3$ was done according to the procedure reported by Arun Kumar *et al.* (2011) with some modification. Cobalt(II) chloride hexahydrate (0.238 g, 0.001 mole) was dissolved in 150 mL of acetone and stirred for 30 minutes to get homogeneous solution. Next, 1,10-phenanthroline (0.54 g, 0.003 mole) was dissolved in 100 mL of acetone. The 1,10-phenanthroline-acetone solution was added dropwise into the heated and vigorously stirred of cobalt(II) chloride-acetone solution. About 2 mL of 35% hydrogen peroxide solution was added slowly and allowed to react for two hours. A dark red coloured solution was formed and the reaction mixture was allowed to settle for two hours. The dark red coloured product was filtered using vacuum filtration, washed thoroughly with excess acetone to remove unreacted materials, and subsequently dried in an oven at 60 °C for 2 hours to ensure the removal of solvent. Yield: 1.173 g, 83%. Anal.

Calcd for $[\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)_3]\text{Cl}_3$: C, 61.26; H, 3.43; N, 11.91; Found: C, 61.03; H, 3.34; N, 11.59. ^1H NMR (DMSO-d_6 , 500 MHz, 2.50 ppm): δ 8.40 (d, 1 H, Ar-H), 8.56 (m, 1 H, Ar-H), 8.82 (d, 1 H, Ar-H), 9.30 (d, 1 H, Ar-H). IR (KBr, cm^{-1}): $\nu(\text{C-H})$ 3044, 2992, $\nu(\text{C=N})$ 1622, $\nu(\text{C=C}_{\text{Aromatic}})$ 1579, 1512, $\delta(\text{C-H}_{\text{Aromatic}})$ 1425, $\delta(\text{CH})$ 1142, $\delta(\text{C-N})$ 1102, $\delta_{\text{out}}(\text{C-H}_{\text{Aromatic}})$ 848, $\delta_{\text{out}}(\text{CH})$ 726, $\nu(\text{Co-N})$ 639, 420. UV-Vis (MeOH) ($\lambda_{\text{max}}/\text{nm}$): 270 ($\pi\text{-}\pi^*$ transition), 480 ($d\text{-}d$ transition).

3.6.5 Preparation of bis(1,10-phenanthroline)nickel(II) dichloride, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$

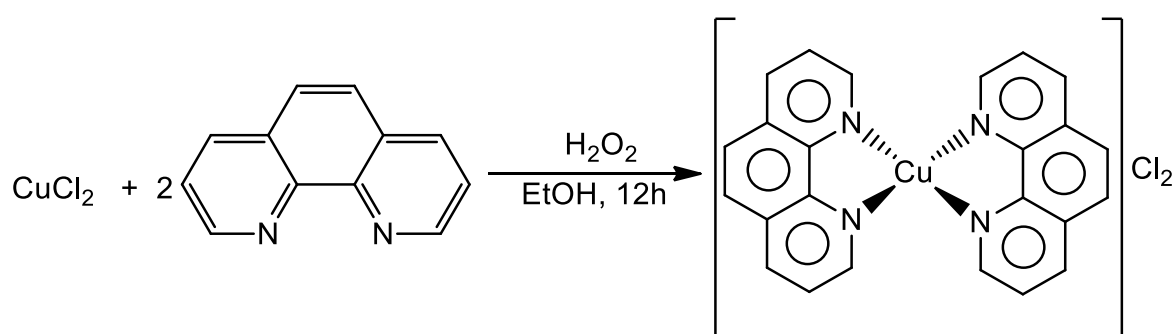


Scheme 3.5: Reaction scheme of $[\text{Ni}(\text{phen})_2]\text{Cl}_2$

The synthesis of $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ was based on the method reported by Corey *et al.* (1965). Nickel(II) chloride hexahydrate (0.238 g, 0.001 mole) and 1,10-phenanthroline (0.36 g, 0.002 mole) were dissolved in 200 mL and 150 mL ethanol respectively. The ethanolic 1,10-phenanthroline solution was added dropwise to the heated ethanolic nickel(II) chloride solution with vigorous stirring. The solution was stirred for 12 hours and was allowed to stand a few hours for precipitation. The pale blue coloured product was collected by vacuum filtration, washed with cold ethanol to eliminate any impurities or excess ligands, and then dried in oven at 80 °C for 2 hours to obtain a pure solid. Yield:

0.321 g, 66 %. Anal. Calcd for $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{Cl}_2$: C, 58.83; H, 3.29; N, 11.43; Found: C, 58.23; H, 3.08; N, 11.09. IR (KBr, cm^{-1}): $\nu(\text{C-H})$ 3045, $\nu(\text{C=N})$ 1624, $\nu(\text{C=C}_{\text{Aromatic}})$ 1583, 1514, $\delta(\text{C-H}_{\text{Aromatic}})$ 1424, $\delta(\text{C-H})$ 1142, $\delta(\text{C-N})$ 1103, $\delta_{\text{out}}(\text{C-H}_{\text{Aromatic}})$ 850, $\delta_{\text{out}}(\text{C-H})$ 726, $\nu(\text{Ni-N})$ 642, 423. UV-Vis (MeOH)($\lambda_{\text{max}}/\text{nm}$): 270 (π - π^* transition), 585 (d - d transition).

3.6.6 Preparation of bis(1,10-phenanthroline)copper(II) dichloride, $[\text{Cu}(\text{phen})_2]\text{Cl}_2$



Scheme 3.6: Reaction scheme of $[\text{Cu}(\text{phen})_2]\text{Cl}_2$

The synthesis of $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ was done by adapting the method reported by Corey *et al.* (1965). A solution of 1,10-phenanthroline (0.36 g, 0.002 mole) in 150 mL of ethanol was added to a 200 mL ethanolic solution of copper(II) chloride dihydrate (0.171 g, 0.001 mole) under continuous stirring. The reaction solution was heated and stirred for 12 hours and was allowed to stand for a few hours for precipitation. The resulting green precipitate was collected through vacuum filtration, thoroughly washed with cold ethanol to remove any residual unreacted material, and dried in oven at 80 °C for 2 hours for purification. Yield: 0.346 g, 70 %. Anal. Calcd for $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{Cl}_2$: C, 58.25; H, 3.26; N, 11.32; Found: C, 58.20; H, 3.36; N, 11.22. IR (KBr, cm^{-1}): $\nu(\text{C-H})$ 3044, $\nu(\text{C=N})$ 1626, $\nu(\text{C=C}_{\text{Aromatic}})$ 1584, 1515, $\delta(\text{C-H}_{\text{Aromatic}})$ 1424, $\delta(\text{C-H})$ 1146, $\delta(\text{C-N})$ 1107, $\delta_{\text{out}}(\text{C-H}_{\text{Aromatic}})$

854, $\delta_{\text{out}}(\text{C-H})$ 722, $\nu(\text{Cu-N})$ 644, 430. UV-Vis (MeOH)($\lambda_{\text{max}}/\text{nm}$): 270 (π - π^* transition), 680 (d - d transition).

3.7 Bandgap Determination of Transition Metal Complex

The bandgap energy of the synthesized complexes was determined through Tauc plot using the data obtained from UV-visible spectroscopy. The Tauc plot equation was:

$$(\alpha h\nu)^\gamma = A(h\nu - E_g) \quad (\text{Equation 3.4})$$

where,

α = absorption coefficient

h = Plank's constant, 6.626×10^{-34} Js

ν = photon's frequency

A = proportionality constant

E_g = bandgap energy

γ = nature of electronic transition

The Tauc plot appeared as:

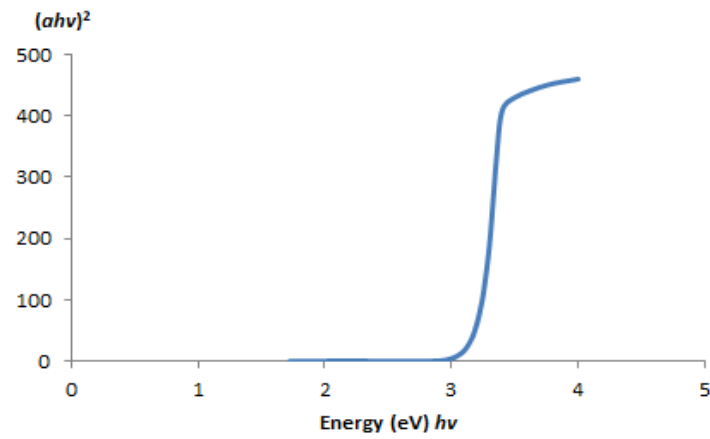


Figure 3.4: Tauc plot

When compared the Tauc plot equation to a linear equation,

$$(\alpha h\nu)^\gamma = A(h\nu - E_g)$$

$$y = m(x) \tag{Equation 3.5}$$

$$0 = A(h\nu - E_g)$$

Thus,

$$h\nu = E_g \tag{Equation 3.6}$$

The extrapolation of the linear region of the plot in the Tauc plot graph to the x-axis determines the bandgap energy.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Comparison between SCPFC and DCPFC

From Literature Review in Chapter 2, we know that there is another setup that may boost the efficiency of PFC which is DCPFC setup. To prove the statement, an experiment was conducted to compare between SCPFC and DCPFC. A SCPFC is the setup by putting photoanode and cathode into the same chamber containing organic pollutant as fuel while DCPFC is setup by separating photoanode and cathode into two different chambers. The efficiency of SCPFC and DCPFC with ZnO/Zn photoanode was assessed in this study. The influencing factors such as contact time, initial dye concentration, solution pH and the reusability of photoanode investigated.

4.1.1 Contact Time of PFC Setup

The optimal contact time for SCPFC and DCPFC was studied by using 10 ppm synthetic methyl red dye solution at pH 4 and a fluorescent bulb was used as the irradiation source. The power density of DCPFC reached its peak at 132.83 mW/cm^2 whereas the SCPFC only achieved 60.11 mW/cm^2 (Figure 4.1a). This can be attributed to the dual-chamber configuration, which improves charge separation and reduces electron-hole recombination. This allows for better utilization of photogenerated electrons, enhancing power output. The stronger photocatalytic activity of the DCPFC is directly linked to its ability to achieve 100 % methyl red dye degradation within 5 hours, whereas the SCPFC

showed only 18.93% degradation at the same time, with no further improvement in the 5th hour (Figure 4.1b). This highlights the significant efficiency gap between the two systems.

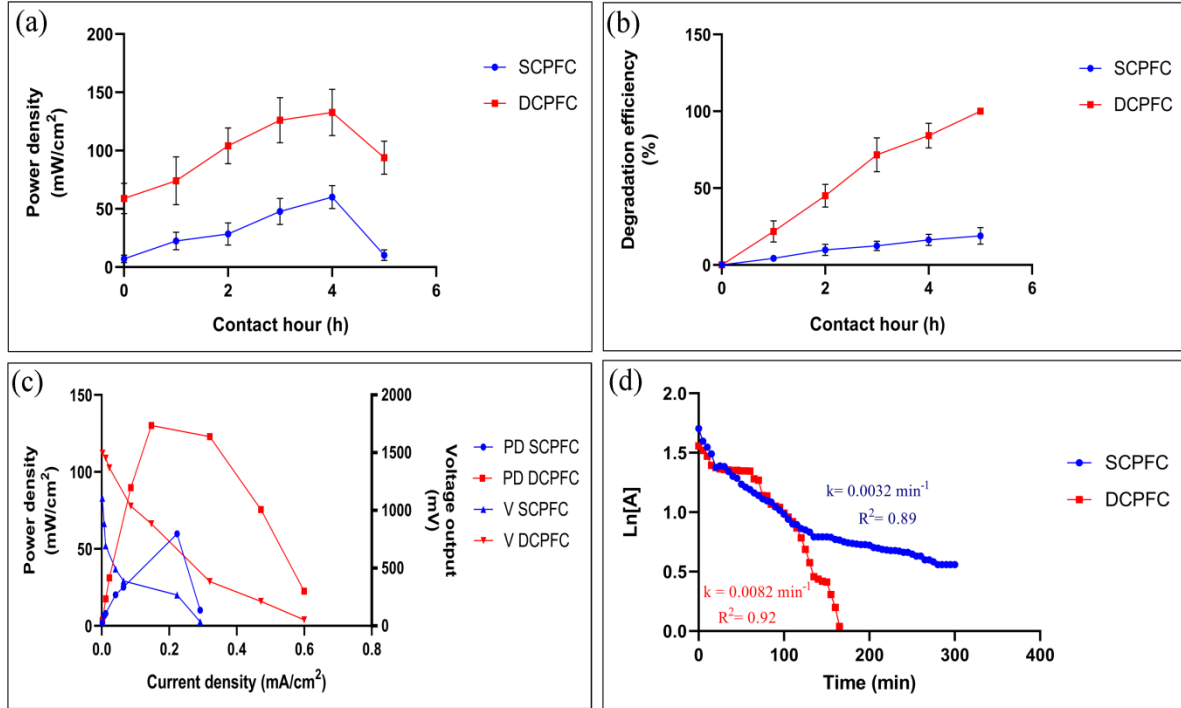


Figure 4.1: PFC performance evaluation of SCPFC and DCPFC: (a) Power density curve illustrating the maximum power output at every hour; (b) methyl red dye degradation efficiency, showing the percentage of dye degraded over time; (c) polarization curves comparing power density and voltage versus current density, demonstrating the energy conversion efficiency of the systems; (d) rate of reaction for the methyl red dye degradation process, illustrating the reaction speed.

The polarization curves display voltage and power density versus current density, further illustrate these differences (Figure 4.1c). The DCPFC demonstrates higher voltage and performs better at increased current densities but it has higher internal resistance (283.45 mΩ) compared to the SCPFC (221.13 mΩ) (Table 4.1). This was due to the presence of the salt bridge, making the ions harder to transfer between two chambers (Sfaelou & Lianos, 2016) and increased ionic resistance to the system. In contrast, the shorter distance between the photoanode and cathode in the SCPFC enhances the mass

transport of reactants and reduces diffusion limitation, resulting in low internal resistance. Despite the higher internal resistance, the DCPFC still achieves superior power output and more effective dye degradation, likely due to improved charge separation and reduced recombination. Conversely, the lower power generation and photocatalytic efficiency of the SCPFC are primarily limited by less effective charge transfer and photocatalyst performance.

Table 4.1: Comparison of internal resistance and highest power density at pH 4 between SCPFC and DCPFC

	SCPFC	DCPFC
Rate of Reaction, min^{-1}	0.0032	0.0082
Internal resistance, $\text{m}\Omega$	221.13	283.45
Electromotive force, V	803.01	1410.50
Highest power density, mW/cm^2	60.11	132.83

Although SCPFC has a low internal resistance than DCPFC, DCPFC demonstrated a higher electromotive force (1410.50 V) compared to in SCPFC (803.01 V). Electromotive force is a measure of the potential difference between the anode and cathode. The high electromotive force indicates a high driving force for the strong electrochemical reaction between two electrodes, promoting efficient methyl red dye degradation. According to Ohm's law, $P = IV$, electromotive force is directly proportional to power. Therefore, the DCPFC generates more power than SCPFC. Furthermore, the reaction rate of DCPFC ($k = 0.0082 \text{ min}^{-1}$) was faster than that of SCPFC ($k = 0.0032 \text{ min}^{-1}$). The degradation graph of methyl red solution similar to the degradation graph of malachite green reported by Khan *et al.* (2019). Therefore, it is agreed that the kinetic rate of methyl

red degradation (Figure 4.1d) obtained was pseudo-first order kinetic model (Equation 4.1). Additionally, the reaction rate graph highlights the kinetic differences between the two systems. The rapid degradation of the dye in the DCPFC within the first 4 hours suggests a significantly higher rate constant compared to the SCPFC. This indicates that the DCPFC can maintain faster reaction rates, while the SCPFC's catalytic capacity is limited, leading to slower degradation. The combination of these factors demonstrates the DCPFC's superior performance in both power generation and photocatalytic dye degradation.

$$\ln[A] = -kt + \ln[A_0] \quad (\text{Equation 4.1})$$

where,

[A] = final concentration of methyl red dye solution

k = rate reaction

t = time (min)

[A₀] = initial concentration of methyl red dye solution

On the other hand, the diffusion of •OCl radicals from the cathode chamber to the anode chamber through the salt bridge facilitated the complete degradation of methyl red dye in DCPFC and simultaneously enhanced power generation. The complete methyl red dye degradation in DCPFC was attributed to the addition of diluted NaOCl solution in cathode, leading to the production •OCl radicals (Equation 4.2 – Equation 4.3). The added NaOCl oxidant not only acts as an electron trap to prevent the recombination of electron-hole pairs but also contributes to the dye degradation as the amount of reactive radicals has been elevated when the amount of oxidant increases (Antonopoulou & Konstantinou, 2014).



To complete the redox reaction, OCl^- ions at the cathode attract electrons from anode, thereby enhancing power generation. Since the NaOCl solution was diluted with distilled water, OCl^- ion reacts with H^+ ion and OH^- ion in the solution. Subsequently, HOCl undergoes a reversible reaction to generate hypochlorite ions and hydrogen ions (Equation 4.4).



The $\bullet\text{OCl}$ and ClO^- ion then diffused to the anode chamber. Since the pH of methyl red solution was adjusted using hydrochloric acid (HCl) solution, the Cl^- ions were present in the anode chamber. The presence of excess H^+ from HCl lowered the pH of the solution, creating an acidic environment which is favourable for HOCl formation (Equation 4.5 – Equation 4.6).



Increasing the amount of oxidant provides more potential reaction sites for electron transfer, thereby improving the performance of DCPFC. During dye degradation, the efficient transfer of electrons to cathode also results in higher power generation in DCPFC compared to SCPFC (Vasseghian *et al.*, 2020).

4.1.2 Effect of Initial Dye Concentration on PFC Setup

The concentration of organic matters can greatly affect the performance of a PFC. Although higher concentrations of organic matter typically result in higher power generation (mW) but extremely high concentrations can hinder the process. This is because excessive amounts of dye may limit the penetration of light to the photoanode surface and lowering power output. In this study, different initial dye concentrations (5 ppm, 10 ppm, 20 ppm) were prepared to study their effect on both PFC setups. The pH of solution was fixed at 4 for 5 hours. The results are as shown in Figure 4.2.

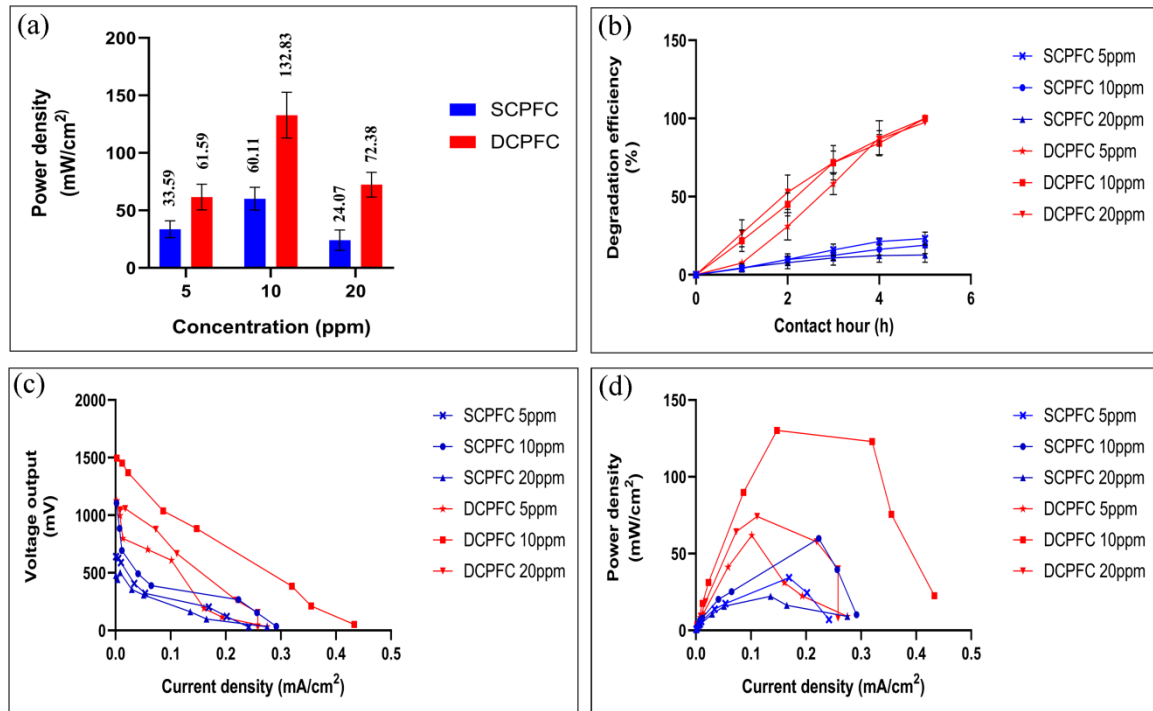


Figure 4.2: PFC performance evaluation of SCPFC and DCPFC: (a) Power density curve illustrating the maximum power output with different methyl red dye concentration; (b) methyl red dye degradation efficiency with different methyl red dye degradation; (c, d) polarization curves of methyl red solution with different concentrations, providing a comparative view for the performance of PFC system.

Figure 4.2(a-b) illustrates the highest power density and dye degradation efficiency of both PFC setups at different dye concentrations. Among all initial dye concentration, DCPFC has the highest power density of 132.83 mW/cm^2 compared to SCPFC (60.11 mW/cm^2) at 10 ppm. Meanwhile, Figure 4.2b highlights that DCPFC achieved 100% dye degradation efficiency for two different concentrations (5 ppm, 10 ppm), while 20 ppm showed 97.53 % dye degradation. Conversely, the degradation efficiency for SCPFC was only 23.24 %, 18.93 % and 12.66 %, respectively, as a function of decreasing dye concentration.

This significant difference in performance between the DCPFC and SCPFC can be attributed to the enhanced separation of electron-hole pairs in the DCPFC (Chen *et al.*, 2024). The efficient electron-hole separation becomes particularly important because it ensures the generation of sufficient reactive species (such as $\bullet\text{OH}$) that are responsible for the degradation of contaminants (in this case is methyl red dye). Since DCPFCs can maintain a higher population of these active species, they exhibit better photocatalytic performance even in environments with higher pollutant concentrations. On the other hand, SCPFC suffer from quicker recombination due to the proximity of the photoanode and cathode, limiting their ability to handle such pollutant loads (Liu *et al.*, 2022a).

Based on the graphs (Figure 4.2c-d), both PFC setups performed optimally at 10 ppm methyl red dye concentration where SCPFC recorded $P_{\text{max}} = 60.11 \text{ mW/cm}^2$, $J_{\text{sc}} = 0.22 \text{ mA/cm}^2$ and $V_{\text{oc}} = 273 \text{ mV}$ while DCPFC recorded $P_{\text{max}} = 132.83 \text{ mW/cm}^2$, $J_{\text{sc}} = 0.15 \text{ mA/cm}^2$ and $V_{\text{oc}} = 902 \text{ mV}$. The higher voltage in DCPFC indicates a greater potential difference between the electrodes, enhancing the driving force for electron transfer despite the lower J_{sc} compared to SCPFC (Figure 4.2c). This trend in the polarization curves correlates with the observed methyl red dye degradation efficiency, as the DCPFC

achieves 100 % dye degradation across all tested concentrations. Figure 4.2d show that the DCPFC at 10 ppm dye concentration exhibits the largest power density curve while the SCPFC at 20 ppm shows the smallest curve. This larger power density curve of the DCPFC suggests that it has a more efficient charge separation and transport mechanism compared to the SCPFC. The DCPFC may facilitate better electron flow and reduces recombination of charge carriers, leading to higher power output. Additionally, power generation decreased when the initial dye concentration was increased to 20 ppm or decreased to 5 ppm for both PFC setups. Figure 4.2a shows at the 20 ppm, the SCPFC and DCPFC had $P_{\max}$ of 24.07 mW/cm² and 72.38 mW/cm² respectively whereas at 5 ppm, the SCPFC and DCPFC had $P_{\max}$ of 33.59.38 mW/cm² and 61.59 mW/cm², respectively.

The $P_{\max}$ decreased with the decreasing initial dye concentration. This is due to the low dye concentration, fewer dye molecules, the chances of effective collision with radicals are also lowered. Thus, lesser molecules would be degraded at the photoanode. As a result, there are fewer electrons available for the power generation (Equation 4.7).



According to Lee *et al.* (2017), higher organic compound concentrations can cause more molecules to be adsorbed on the ZnO photocatalyst surface, resulting in the decline of power generation. The overcrowding of ZnO surface with organic molecules reduces the chance for the hydroxyl groups (H₂O and OH⁻) to react with the h^+_{VB} on the photocatalyst for radicals production (Gnanaprakasam *et al.*, 2015). Consequently, the number of electron produced decreases and fewer electrons flow towards the cathode, prompting the drop of power generation. Besides, the colour of solution becomes darker along with the increase in dye concentration, reducing the photocatalysis of ZnO as the dark colour of the

dye solution limits the penetration of light to reach the photocatalyst's surface. This slows down the radical formation process (Abdel-Monem, 2016). Although both PFC setups being limited at 20 ppm dye concentration, the DCPFC showed superior performance with $P_{\max} = 72.38 \text{ mW/cm}^2$ and 97.53 % degradation, compared to SCPFC with $P_{\max} = 24.07 \text{ mW/cm}^2$ and 12.66 % degradation. It is suggested that the presence of NaOCl in DCPFC ensured the formation of radicals and guaranteed the degradation process. Therefore, more electrons transferred to the cathode for power generation. For the 20 ppm methyl red dye concentration, DCPFC took longer time (>5 hours) to complete the degradation process indicating that the optimal initial dye concentration for this study was 10 ppm.

Similar observations were recorded with other dyes when higher dye concentration is used. A study on azo dye Reactive Green 19 electricity generation and degradation reported a decline in electricity generation and dye degradation when the initial concentration of Reactive Green 19 dye increased from 10 mg/L to 20 and 30 mg/L. The complete decolorization of 20 and 30 mg/L Reactive Green 19 was achieved after 5 hours and 8 hours respectively, while the 10 mg/L Reactive Green 19 was completely decolorized after 2 hours (Lee *et al.*, 2016b). Besides that, a similar trend (degradation decreased while initial dye concentration increased) in the degradation of the textile dye Basic Yellow 28 was observed and reported by Djokić *et al.* (2012). In summary, a longer time is needed for complete decolorization when a higher dye concentration is used.

4.1.3 Effect of pH on PFC Setup

Solution pH plays a vital role in the photocatalytic efficiency. Since PFC is derived from the same principle of photocatalyst, the effect of pH on SCPFC and DCPFC was

conducted at various pH values (pH 3, pH 4, pH 5). In fact, increasing the concentrations of the H^+ and OH^- ion in the solution can negatively affect both dye removal efficiency and power generation due to their reaction with ZnO. Thus, the experiment was conducted between pH 3, pH 4, and pH 5 as the photocatalyst performs better under acidic condition than basic condition (Daneshvar *et al.*, 2003; Dao *et al.*, 2023).

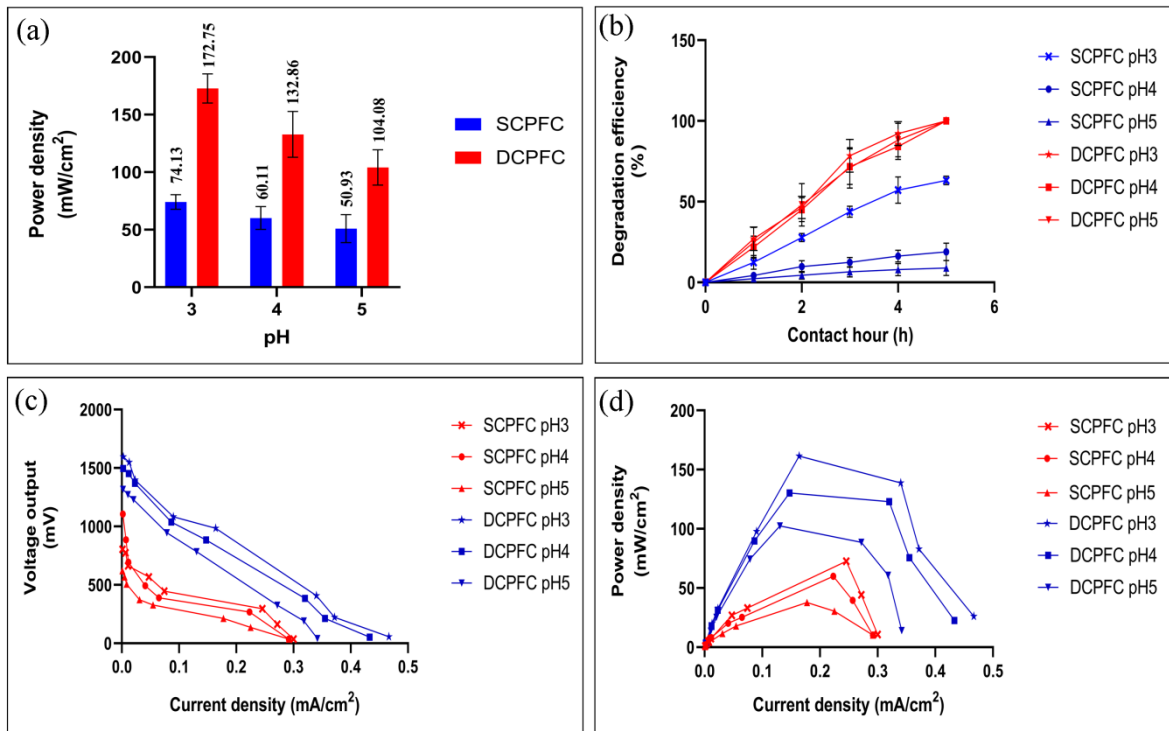


Figure 4.3: PFC performance evaluation of SCPFC and DCPFC: (a) Power density curve illustrating the maximum power output in different solution pH; (b) methyl red dye degradation efficiency in different solution pH; (c, d) polarization curves of methyl red solution degradation at different pH levels highlight changes in power output and current density, which can be attributed to variations in photocatalytic activity and electron transfer processes influenced by the pH values.

The highest power density for SCPFC and DCPFC were observed at pH 3 (74.13 mW/cm^2 ; 172.75 mW/cm^2) respectively (Figure 4.3a). Figure 4.3b shows the 100 % dye degradation efficiency of DCPFC from pH 3 to 5 while the highest dye degradation

efficiency on SCPFC was only 63.21 % at pH 3. The lowest dye degradation efficiency of 8.89 % was at pH 5 in SCPFC.

From Figure 4.3a, the power generation of both SCPFC and DCPFC increased with the decreasing pH from pH 5 to pH 3. At lower pH, the high concentration of H^+ ion in the dye solution increased the mass transfer of electrons in the PFC. According to Jang *et al.* (2017), the high power density from SCPFC and DCPFC at pH 3 was due to the high concentration of H^+ ion in the solution as hydrogen is widely known as an effective charge carrier. Thus, in acidic conditions, the power generation of both SCPFC and DCPFC increases. However, the further increases of H^+ ion concentration in the solution may cause ZnO to dissociate (Equation 4.8) (Ong *et al.*, 2020). When the pH of the solution increased, the OH^- ion in the solution reacts with Zn^{2+} ion from the photoanode forming $[Zn(OH)_4]^{2-}$ (Equation 4.9), hence reducing the overall efficiency of SCPFC and DCPFC.



Both SCPFC and DCPFC exhibit a decline graph in Figure 4.3c. This is characteristic of electrochemical systems where increasing voltage leads to a higher internal resistance or a reduction in the efficiency of charge transfer processes. The DCPFC at pH 3, pH 4, and pH 5 demonstrate steeper slopes compared to SCPFC at the same pH levels, indicating more efficient electron transfer. The graph in Figure 4.3d further supports this observation, with DCPFC at pH 3 showing the largest power density curve, corresponding to the highest power output. In contrast, SCPFC at pH 5 has the smallest curve, reflecting reduced power generation efficiency. The enhanced power

density of DCPFC across the pH range suggests the better charge separation and transport mechanisms, especially at lower pH levels, where the high concentration of H^+ ions improves the electron flow. However, at very low pH, the dissociation of ZnO (Equation 4.8) could become a limiting factor, eventually decreasing the system's efficiency due to the formation of $[Zn(OH)_4]^{2-}$ (Equation 4.9) at higher pH levels.

Li and team (2013) set up a PFC with BiOCl/Ti photoanode and Pt cathode and reported a decrease of current density (from 0.0116 mA/cm^2 to 0.0087 mA/cm^2) and dye removal efficiency with increasing pH (from pH 2 to pH 8) (Li *et al.*, 2013). Similarly, Thor and colleagues (2020) found that the dual-cell hybrid system consisting of PFC and EF (electro-Fenton) process showed the largest power density ($2.221 \text{ } \mu\text{W/cm}^2$) and highest decolorization at pH 3. The power density and decolorization showed a decreasing trend when the pH was increased. In a separate study the degradation of methyl orange using TiO_2 nanotube photoanode showed a current density output of $1.57 \text{ } \mu\text{A/cm}^2$ and 97.34 % degradation efficiency at pH 1.5 but the current density and degradation efficiency reduced to $0.83 \text{ } \mu\text{A/cm}^2$ and 49.61 % when pH increased to 3 (Zhao *et al.*, 2017b). However, when the pH dropped to 1.0, the current density output decreased to $1.06 \text{ } \mu\text{A/cm}^2$ and the degradation efficiency decreased to 80.54 %. This observation indicate that excessive H^+ ion and OH^- ion in the solution could lower the degradation efficiency of PFC.

The colour change of methyl red dye solution was observed in SCPFC. The colour change started at the 2nd hour of the experimental period at pH 4. The colour change from red to yellow indicated a pH change of the solution during photocatalysis reaction. Figure 4.4 shows that methyl red dye is present in yellow colour as an azo analogue ($-N=N-$) in alkaline solution. But the structure changes to hydrazone analogue ($-C=N-$) which is red in

colour if the solution is acidic (Khadka & Bhattarai, 2020). Nevertheless, no colour change was observed in DCPFC during the study, indicating different degradation process in the anode chamber of DCPFC compared to SCPFC. This is an advantage of DCPFC where the dye degradation process in DCPFC is not be affected by solution pH change in the system.

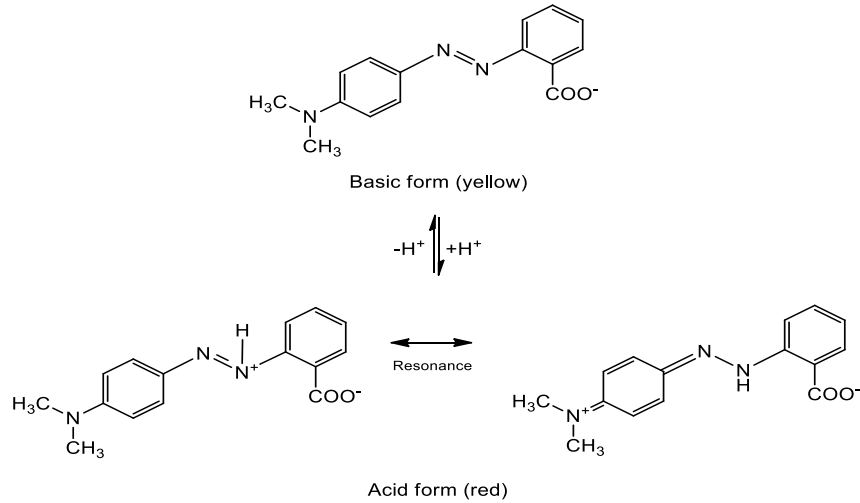


Figure 4.4: Chemical structure change of methyl red dye under pH different conditions

The colour change from red to yellow of methyl red dye in SCPFC indicated the change of solution pH. When the system is aerated, electrons are captured at the cathode by oxygen, oxygen reduction reaction was bias (Equation 4.10 – Equation 4.12). The aeration in SCPFC promoted the formation $\bullet\text{OH}$ radicals and OH^- ion (Equation 4.13 – Equation 4.13) (He *et al.*, 2022). However, when the amount of OH^- ions produced exceeds the h^+_{VB} , the unreacted OH^- ions could cause the pH in the reaction chamber increase.





In addition to $\bullet\text{O}_2^-$ radicals, $\bullet\text{OH}$ radicals and H_2O_2 are formed as shown in Equation 4.10 – Equation 4.12. However, the excessive $\bullet\text{O}_2^-$ radicals and $\bullet\text{OH}$ radicals can recombine (Equation 4.13) before degrading dye molecules, reducing overall dye degradation efficiency. At the same time, the formation of OH^- in Equation 4.11 and Equation 4.12 could increase the solution pH in SCPFC. Li *et al.* (2018) states that $\bullet\text{OH}$ in high pH condition cause low degradation efficiency. This statement was supported by decreasing trend of power density and degradation efficiency when the pH increased from pH 3 to 5 in SCPFC. In contrast, the negligible pH effect on DCPFC was likely due to the aeration occurring in the cathode chamber (Table 4.2). Although both OH^- and OCl^- were formed in DCPFC, the oxidising power of $\bullet\text{OCl}$ is stronger than the $\bullet\text{OH}$ (Khalik *et al.*, 2016). As such, $\bullet\text{OCl}$ was selected in the photodegradation process.

Parvizi *et al.* (2021) compared degradation efficiency of Acid Blue 113 (AB113) dye under the absence and presence of NaOCl solution. Their results showed that the PFC system with NaOCl had higher efficiency than that without NaOCl. The presence of OCl^- ion has led to the production of reactive radical ($\bullet\text{OCl}$), hence the removal efficiency of AB113 rose to 92 % when 0.2 mM concentration of NaOCl solution was added compared to the system without NaOCl solution, which only reported 45 % AB113 removal efficiency. Additionally, the challenging nitrogen degradation was confirmed to be completely eliminated using $\bullet\text{Cl}/\bullet\text{OCl}$ radicals in photocatalysis fuel cell setup due to high N_2 selectivity (Jiang *et al.*, 2023). The strong oxidizing ability of $\bullet\text{ClO}$ radical with strong

oxidizing ability is suitable for organic waste degradation. Table 4.2 shows the pH changes in the SCPFC setups before and after photocatalysis, which were not observed in DCPFC, where the pH remained unchanged throughout the experiment.

Table 4.2: The initial and final solution pH for SCPFC and DCPFC

SCPFC		DCPFC	
Initial pH	Final pH	Initial pH	Final pH
3.01	5.30	3.05	3.10
4.08	6.93	4.11	4.18
5.11	7.80	5.14	5.20

In the SCPFC, significant changes in pH were observed after the photocatalytic process. The rises of pH values were observed for pH 3, pH 4 and pH 5. This pH increase could be attributed to the close proximity of the photoanode and cathode, where the oxidation and reduction reactions occur in the same compartment. This proximity accelerates proton (H^+) consumption during reduction at the cathode, which removes protons from the solution and increases the pH (Equation 4.14). Additionally, accumulation of hydroxide ions (OH^-) due to the reduction of oxygen in the cathode can further elevate the pH in the solution (Equation 4.11 – Equation 4.12).



On the other hand, the pH changes in DCPFC were minimal, with only slight variations in the final pH values (initial pH 3.05 to final pH 3.10). This stability can be attributed to the separation of the photoanode and cathode in different chambers in DCPFC. The separation slows down the recombination of electron-hole pairs and maintains a balanced environment in each chamber, preventing drastic shifts in pH. The isolated

environments for oxidation (in anode chamber) (Equation 4.15) and reduction (in cathode chamber) allow the reactions to occur without directly influencing each other thus keeping the pH stable throughout the experiment. Although H^+ ions are produced at the anode chamber, they are later utilized in radical formation, minimizing their impact on the overall pH.



This variation highlights the benefit of DCPFC in maintaining a more controlled and stable reaction environment, which can lead to better efficiency photocatalytic processes.

4.1.4 Surface Morphology

The morphology of prepared ZnO/Zn photoanode was observed using SEM (JEOL; JSM-6390) at 10 kV accelerating voltage and magnification ranging from 10,000x to 30,000x. Figure 4.5a shows the surface morphology of freshly prepared ZnO/Zn photoanode by ultrasonic method at 30,000x magnification. The rod-like structures of ZnO were observed in Figure 4.5a, which is same as the literature reported by Tymoszuik and Wojnarowicz (2020). Figure 4.5b and Figure 4.5c show the irregular branching and porous of ZnO (at 30,000x magnification) after being used in SCPFC and DCPFC respectively. The rod-like of ZnO was gone and become fibrous net shape after being used in SCPFC and DCPFC. According to Moksin *et al.* (2021), ZnO could react with H^+ to produce water and soluble Zn^{2+} , resulting in the dissociation of ZnO from the photoanode surface.

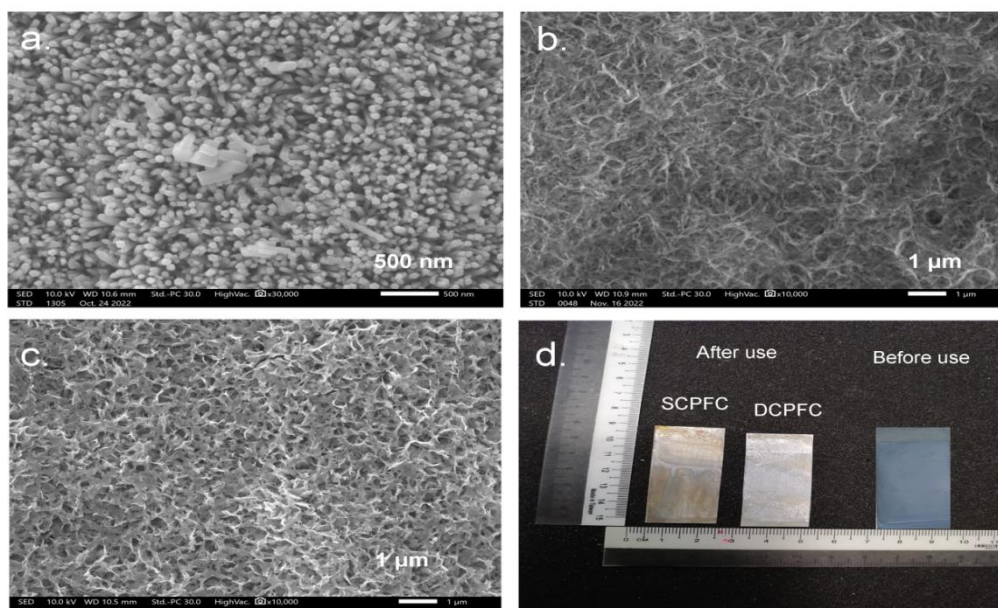


Figure 4.5: SEM images of ZnO coating on Zn substrate:
 (a) freshly prepared ultrasonic photoanode; (b) via SCPFC; (c) via DCPFC;
 (d) photoanode after photocatalysis of SCPFC (left); DCPFC (right)

From Figure 4.5d, the used ZnO photoanode in SCPFC showed severe dissociation compared to in DCPFC. This is because not all ZnO was tightly attached on the Zn substrate and the vibration produced from aeration in the SCPFC caused the detachment of ZnO from the Zn substrate that eventually affect the PFC performance. The loss of photocatalyst in SCPFC decreased the surface area to volume (SA/V) ratio leading to the low dye degradation efficiency and power generation (Niang *et al.*, 2023). Meanwhile, the photoanode in DCPFC was still intact and not affected by the air-bubbling in the cathode as they were placed in two different chambers.

4.1.5 Reusability of Photoanode

Reusability test was performed on the same ultrasonic-prepared ZnO/Zn photoanode for five consecutive cycles in SCPFC and DCPFC, respectively. Figure 4.6

shows the power density loss and maximum dye degradation efficiency for SCPFC and DCPFC for five successive runs. As illustrated in Figure 4.6(a-b), the ZnO/Zn photoanode could only be used for one time in SCPFC but the same ZnO/Zn photoanode could be reused twice, albeit with the reduced power generation ability.

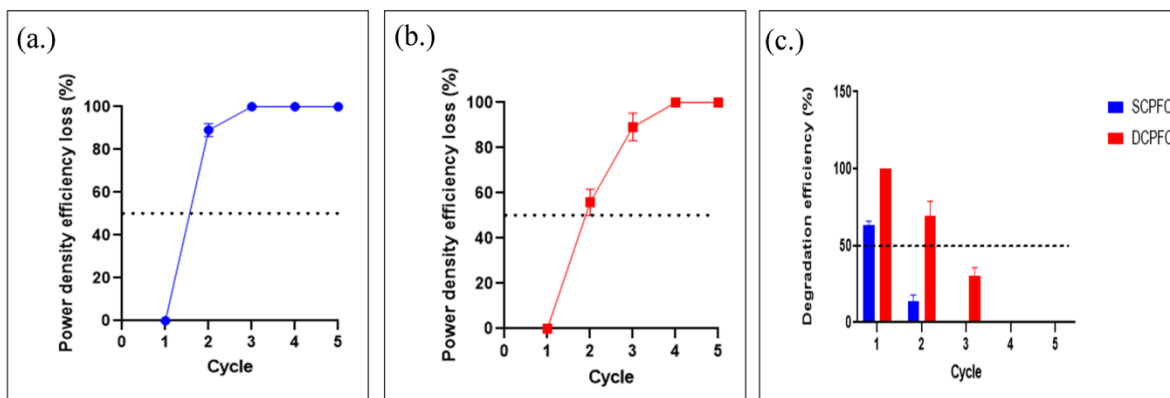


Figure 4.6: PFC performance evaluation of SCPFC and DCPFC: (a) Power density efficiency loss in SCPFC; (b) power density efficiency loss in DCPFC; (c) methyl red dye removal efficiency for 5 consecutive cycles

The power density efficiency loss in SCPFC and DCPFC after two consecutive photocatalytic cycles was 89.15 % and 55.85 %, respectively. Although the power density efficiency loss in DCPFC was more than 50 % but its dye degradation efficiency was relatively high (69.45 %) when compared to the degradation efficiency of SCPFC (13.88 %). The power density obtained from SCPFC and DCPFC for the second use of ZnO/Zn was 8.04 mW/cm² and 76.27 mW/cm², respectively. The decreased of power generation and dye degradation efficiency might be due to the dissociated (Figure 4.5b-c) ZnO over time based on Equation 4.7 – 4.8. Severe dissociation of ZnO/Zn photoanode after single use in SCPFC and DCPFC presents a significant challenge in maintaining its reusability. As comparing the Figure 4.5b and Figure 4.5c, the degree of ZnO dissociation

from the Zn plate is more obvious, this has resulted SCPFC has the lower removal efficiency and electricity generation than DCPFC in the second cycle of reuse.

Based on our findings comparing between SCPFC and DCPFC, it was found that the DCPFC could achieve a maximum 100 % dye removal efficiency with power density of 172.75 mW/cm^2 at 10 ppm initial dye concentration within 5 hours of operation at pH 3. However, the SCPFC only showed power density of 74.13 mW/cm^2 and 63.21 % dye removal efficiency at pH 3. The results prove that dual-chamber configuration had successfully elevated the performance of the PFC in methyl red dye removal by raised the power generation 133.04 % compared to single-chamber configuration. The optimal conditions were then used to assess the performance of synthesized transition metal complexes/Zn photoanode in dye removal.

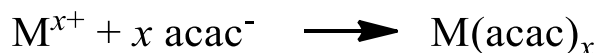
4.2. Synthesis and Characterization of Transition Metal Complexes,

[TM(acac)_n]&[TM(phen)_n]Cl_n, where n = 2, 3

Transition metal has undeniable impact on photocatalytic reaction. In this project, three transition metals (cobalt, nickel and copper) and two ligands (acetylacetone, acac and 1,10-phenanthroline, phen) were chosen to form transition metal complexes. Acac acted as pi-donor while phen acted as pi-acceptor. The synthesized transition metal complexes were [Co(acac)₃], [Ni(acac)₂], [Cu(acac)₂], [Co(phen)₃]Cl₃, [Ni(phen)₂]Cl₂ and [Cu(phen)₂]Cl₂. The potential of these complexes as photocatalyst was explored by applying the transition metal complexes on a Zn plate as the photoanode in DCPFC. The efficiency of these complexes used as photocatalyst for methyl red dye degradation are discussed.

4.2.1 Synthesis and Characterization of [TM(acac)_n], where n = 2, 3

The synthesis of [Co(acac)₃], [Ni(acac)₂], and [Cu(acac)₂] followed well-established methods and resulted in successful formation of the desired metal acetylacetonate complexes. The general reaction for these syntheses can be represented as:



Scheme 4.1: General synthetic scheme of acac-ligand based complexes

where M represents the metal ion (Co³⁺, Ni²⁺, Cu²⁺), acac is the acetylacetonate ligand and x is the number of ligand depending to the metal center. The [Co(acac)₃] was synthesized by reacting cobalt carbonate and acac in the presence of hydrogen peroxide (Amason *et al.*, 2021) where hydrogen peroxide was added to oxidize the cobalt (II) to cobalt (III) in the complex. While the synthesis routes for [Ni(acac)₂] and [Cu(acac)₂] involved reacting the nickel(II) chloride and copper(II) chloride, respectively, with acetylacetone, followed by the addition of sodium acetate (Moeller *et al.*, 1957; Eleruja *et al.*, 2007). The role of sodium acetate was to deprotonate the acac, forming acac[−] anion before it reacted with the nickel or copper ions.

In all three cases, the syntheses were successful. The techniques used across the procedures included heating, stirring, precipitation by cooling, and purification through filtration followed by air-drying or oven-drying. The products were greenish-black for [Co(acac)₃], emerald green for [Ni(acac)₂], and blue for [Cu(acac)₂]. The yield for the products were 81 % for [Co(acac)₃], 59 % for [Ni(acac)₂], and 63 % for [Cu(acac)₂].

4.2.1.1 Spectroscopic Characterization of [TM(acac)_n], (n = 2, 3)

Solubility tests for all three [TM(acac)_x] complexes were carried out (Table 4.3) using 12 common different solvents. These complexes were more soluble in polar solvents like acetonitrile, acetone, chloroform and dimethylformamide compared to the non-polar solvents like diethyl ether, hexane and toluene. Each complex exhibited a unique solubility profile which can be attributed to differences in their molecular structures and metal-ligand interactions. Notably, [Co(acac)₃] showed broader solubility across various solvents compared to [Ni(acac)₂] and [Cu(acac)₂].

The solubility test for the synthesized acac ligand-based complexes in various solvents is essential for several reasons. First, the solubility behavior of metal complexes provides insights into their potential applications, especially in catalysis, material science, and pharmaceuticals, where solvent compatibility is crucial. Conducting solubility tests in different solvents also aids in practical applications, such as determining suitable solvents for purification, crystallization, or UV-Vis analysis. This data is fundamental in deciding which solvents are most effective for processing or further studies of the metal complexes.

Table 4.3: Solubility test of [Co(acac)₃], [Ni(acac)₂] and [Cu(acac)₂]

Solvents	[Co(acac) ₃]	[Ni(acac) ₂]	[Cu(acac) ₂]
Hexane	Insoluble	Insoluble	Insoluble
Toluene	Soluble	Insoluble	Insoluble
Diethyl ether	Insoluble	Insoluble	Insoluble
Dichloromethane	Soluble	Slightly soluble	Slightly soluble
Chloroform	Soluble	Soluble	Soluble
Acetone	Insoluble	Insoluble	Slightly soluble
Acetonitrile	Soluble	Soluble	Slightly soluble
Ethanol	Slightly soluble	Slightly soluble	Slightly soluble
Methanol	Soluble	Soluble	Soluble
Dimethylformamide	Slightly soluble	Soluble	Slightly soluble
Dimethylsulfoxide	Slightly soluble	Insoluble	Insoluble
Water	Insoluble	Insoluble	Insoluble

Figure 4.7 compares the FTIR spectra of free acac and [Co(acac)₃], [Ni(acac)₂] and [Cu(acac)₂]. The significant peaks in acac spectrum included ν CH peak at 2925 cm⁻¹, ν C=O peak at 1727 cm⁻¹, ν C=C peak at 1604 cm⁻¹ while these significant peak were shifted in the spectra of the complexes, indicating coordination between acac ligand and central metals (Co, Ni, Cu). Whilst, the wavenumber of -CH stretching showed no significant differences between acac ligand and metal complexes suggesting that -CH was not involved in the coordination between ligand and metal.

The C=O peak shifted to lower wavenumber (1574 cm⁻¹ for [Co(acac)₃], 1610 cm⁻¹ for [Ni(acac)₂] and 1583 cm⁻¹ for [Cu(acac)₂]) compared to the C=O stretching at 1727 cm⁻¹ in free acac ligand (Hashem & Refat, 2006; Jian *et al.*, 2014). This shift suggested a decrease of C=O bond strength, indicating coordination of carbonyl oxygen to the metal centre which weaken the C=O bond due to partial electron transferred from the oxygen to the metal, leading to a decrease in the stretching frequency. Among the three complexes, [Co(acac)₃] showed the most significant shift toward lower wavelength because Co is the more electropositive metal compared to Ni and Cu, thus it's pi-back bonding electron to the acac ligand is the strongest and weakened the C=O bond in acac.

Likewise, the C=C peak also shifted to lower wavenumber in the complexes. The new C=C peaks for [Co(acac)₃], [Ni(acac)₂] and [Cu(acac)₂] shifted to 1519 cm⁻¹, 1517 cm⁻¹ and 1532 cm⁻¹, respectively (Diaz-Acosta *et al.*, 2003; Seyedkatouli *et al.*, 2018). This shift can be attributed to the influence of the metal centre on the π electron density of the C=C bond, resulting to the decrease of bond strength hence obtained a decreased stretching frequency.

Furthermore, the degree of C=O and C=C peak shift could be arranged from high to low as follows: [Co(acac)₃], [Cu(acac)₂], [Ni(acac)₂]. The degree of peak shift might be influenced by electron density of metal ion. The Co(III) ion with a charge of +3 has a higher positive charge density compared to Cu(II) and Ni(II) ions with +2 charge. The higher positive charge leads to stronger electrostatic interaction between carbonyl oxygen and metal ion, forming stronger coordination bond and resulting to a relatively larger peak shift compared to [Cu(acac)₂] and [Ni(acac)₂].

Apart from the shifted peak wavenumber, new peaks were also observed in these complexes spectra. The new peaks were observed to be of medium-strong and medium intensity at 466 cm⁻¹, 421 cm⁻¹ and 454 cm⁻¹, indicating indicated the newly-formed Co-O, Ni-O bond and Cu-O in the [Co(acac)₃], [Ni(acac)₂] and [Cu(acac)₂] complexes, confirming the successful synthesis of the complexes. Table 4.4 compares the assigned wavenumber of [Co(acac)₃], [Ni(acac)₂] and [Cu(acac)₂] with some previously reported literature.

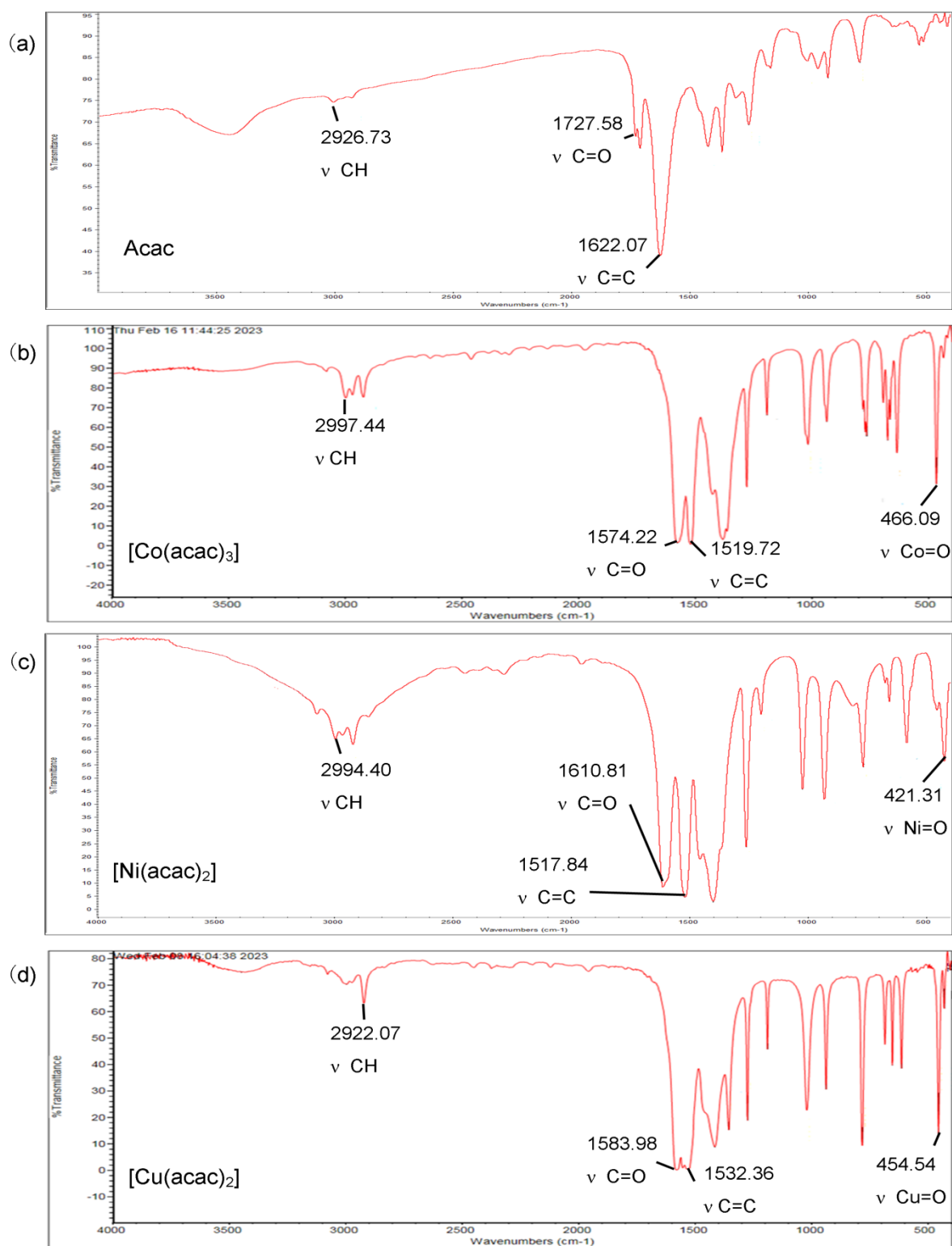


Figure 4.7: FTIR spectra of (a) free acac; (b) [Co(acac)₃]; (c) [Ni(acac)₂]; and (d) [Cu(acac)₂]

The FTIR result were compared with reported literature and showed no significant differences (Table 4.4). This became the strong evidence for the formation of [TM(acac)_n] (n = 2, 3) complexes.

Table 4.4: Assigned wavenumber (cm⁻¹) of [Co(acac)₃], [Ni(acac)₂] and [Cu(acac)₂]

		Assignment			
		$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{C-H})$	$\nu(\text{M-O})$
[Co(acac) ₃]	This work	1574	1519	2922	466
	(Diaz-Acosta <i>et al.</i> , 2003)	1568	1520	2950	466
	(Hashem & Refat, 2006)	1571	1514	3007	471
	(Kadhiravan & Sivajiganesan, 2015)	1591	-	-	652
	(Amason <i>et al.</i> , 2021)	1566	1516	-	-
[Ni(acac) ₂]	This work	1610	1517	2994, 2920	421
	(Babich <i>et al.</i> , 1997)	1520	1596	-	-
	(Nour <i>et al.</i> , 2003)	1515	1592	-	666, 450
	(Rafiqi & Majid, 2016)	1580	-	2954	683
	(Bani-Fwaz <i>et al.</i> , 2021)	1580	-	-	425
[Cu(acac) ₂]	This work	1583	1532	2922	454
	(Raissi <i>et al.</i> , 2005)	1578	1534	2958, 2925	455
	(Jian <i>et al.</i> , 2014)	1575	1531	2920	451
	(Vakili <i>et al.</i> , 2014)	1578	1554	2970	455
	(Seyedkatouli <i>et al.</i> , 2018)	1578	1554, 1532	2856	448

Figure 4.8 shows the NMR spectra of acac, [Co(acac)₃] and [Ni(acac)₂]. The NMR solvent used for the free acac ligand, was DMSO, [Co(acac)₃] and [Ni(acac)₂] were dissolved in CDCl₃, respectively. The chemical shift of 1.99 ppm and 2.1 ppm suggested a hydrogen atom was in a shielded environment, likely a methyl group. In acac, there are three methyl groups, so the peak at 1.99 ppm could correspond to the methyl group (CH₃) in the enol form of free acac. The peak observed at 2.1 ppm was slightly deshielded

compared to 1.99 ppm and could be assigned to the methyl group (CH_3) in keto form of acac. At 5.65 ppm, the hydrogen atom was relatively deshielded suggested it corresponded to the enol proton (OH-C=C-C=O) which between C-OH and C=O groups. Lastly, the 3.65 ppm chemical shift was attributed to the methylene between two carbonyl groups (C=O) in the keto form.

Upon deprotonation, acetylacetonate anion (acac^-) is formed and stabilized by resonance, contributing to the structure where both oxygen atoms are double-bonded to carbon atom (C=O). When acac^- coordinates with metal ion, two coordinate covalent bonds are formed with the metal ion through donating the lone pairs from its' two oxygen atoms and forming a stable coordination bond. The coordination from metal ion provide extra stabilization without disrupting the resonance structure (Rufanov *et al.*, 2024), allowing the ligand to maintain a structure where the negative charge is effectively spread out, resembling to the keto-like structure (Lozada-Garcia, 2012).

In the $[\text{Co}(\text{acac})_3]$ spectrum, the signal at 2.17 ppm was assigned to CH_3 groups while the signal at 5.51 ppm was assigned to aryl-H in $[\text{Co}(\text{acac})_3]$. The $[\text{Ni}(\text{acac})_2]$ complex, which contains the diamagnetic Ni^{2+} ion, exhibited a sharper and more defined peaks in the proton NMR spectrum. The d^8 low spin electron configuration of Ni^{2+} indicate the absence of unpaired electrons in $[\text{Ni}(\text{acac})_2]$. Peaks at 2.03 ppm and 5.49 ppm were attributed to methyl group ($-\text{CH}_3$) and methine group ($-\text{CH}$) of acac. The peak at 2.26 ppm may arise from slight variations in the coordination environment of the acac ligands. It is possible that interactions between the acac ligands and the nickel center causing small deviations from the expected peak positions. On the other hand, the peak at 0.96 ppm might be due to trace amounts of water, which is consistent with the water peak in CDCl_3 , usually around 1.5 ppm in proton NMR spectra.

The square planar $[\text{Cu}(\text{acac})_2]$ with d^9 electron configuration of Cu^{2+} could not be analysed by NMR spectroscopy analysis. The paramagnetic nature cause rapid relaxation of nuclei and broaden the NMR signals due to interactions between unpaired electrons and the nuclei.

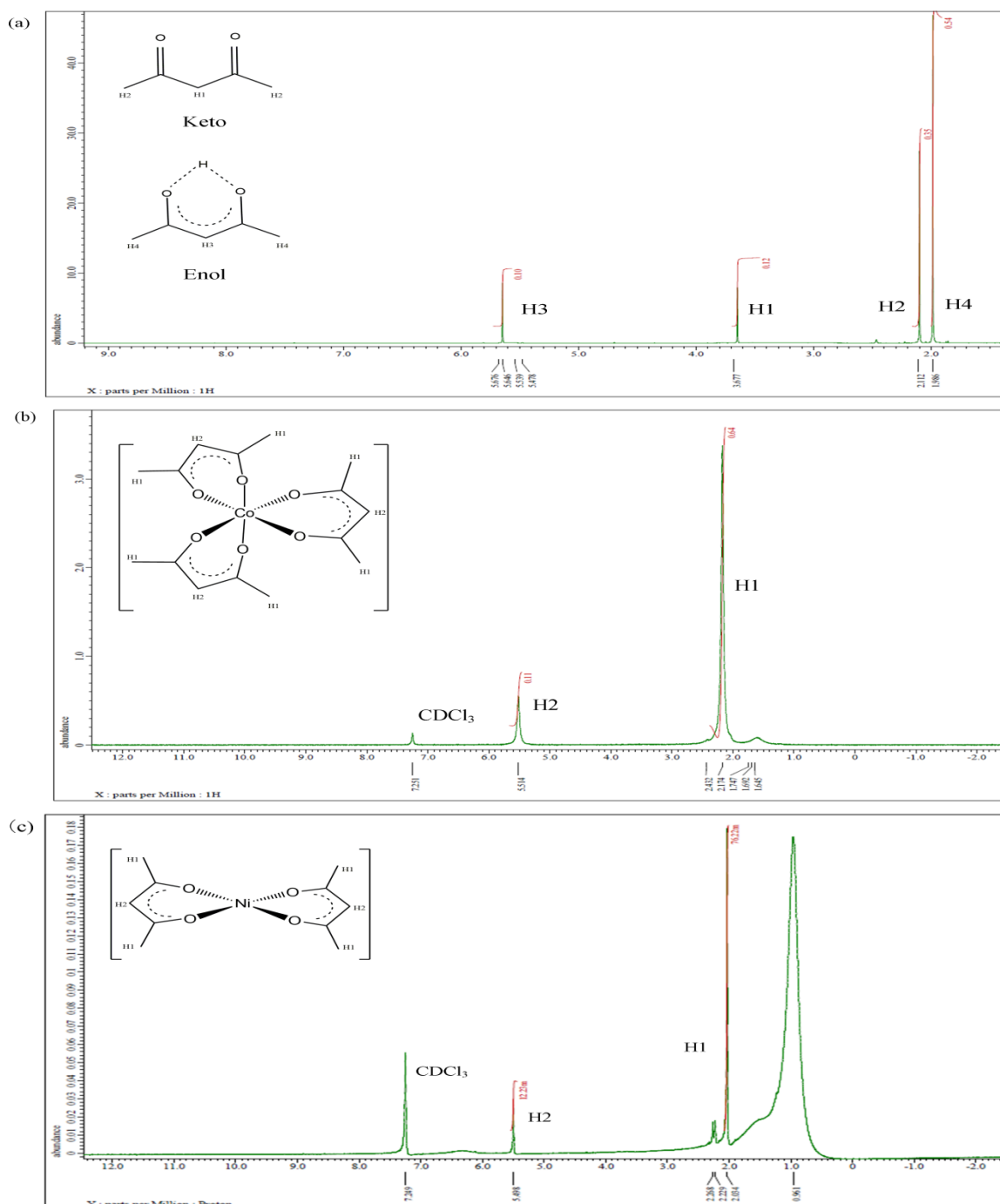


Figure 4.8: ^1H NMR spectra of (a) free acac; (b) $[\text{Co}(\text{acac})_3]$; and (c) $[\text{Ni}(\text{acac})_2]$

Figure 4.9 is the ^{13}C NMR spectral of the free acac ligand and $[\text{Co}(\text{acac})_3]$. There were 7 signals shown at the ^{13}C NMR spectrum of free acac (Figure 4.9a). The most downfield signals observed at 201.85 ppm and 190.91 ppm corresponded to carbonyl carbon in keto form and enol form, respectively. The chemical shift at 201 ppm indicated a highly deshielded carbonyl carbon which is consistent with the keto form where the carbonyl group is strongly electron-withdrawing. The most upfield chemical shifts at 30.16 ppm and 24.32 ppm corresponded to the least shielded methyl carbon with 30.16 ppm representing the methyl carbon in keto form and 24.32 ppm representing the methyl carbon in enol form. Whilst, the signals at 100.00 ppm and 57.80 ppm were attributed to the carbon in $\text{C}=\text{C}-\text{OH}$ group in enol form and the methine carbon in keto form, which is deshielded due to the electron-withdrawing effect of the adjacent carbonyl groups. This assignments reflected the coexistence of both keto and enol tautomers of acac in solution.

In the spectrum of $[\text{Co}(\text{acac})_3]$ (Figure 4.9b), 4 peaks were shown: 189.57 ppm, 97.15 ppm, 77.08 ppm and 26.12 ppm. The peak at 189.6 ppm corresponded to the carbonyl carbon ($\text{C}=\text{O}$), reflecting the deshielded nature of this carbon. The peak at 97.1 ppm was assigned to the methine carbon (CH), which was also deshielded but to a lesser extent than the carbonyl group as it located between two carbonyl groups. Lastly, the peak at 26.1 ppm ascribed to the methyl carbon (CH_3) of the acac ligand.

Unfortunately, the carbon NMR spectrum of $[\text{Ni}(\text{acac})_2]$ showed no significant signal other than the residual signal of NMR solvent, CDCl_3 although the analysis was run overnight. Low sample amount might be responsible for this condition. NMR spectroscopy is an important tool for molecular study between a metal and ligand but it has low sensitivity and sometimes limits the detection of signal (Webb, 2012; Dudek *et al.*, 2021).

Due to the low sensitivity of NMR analysis and the insufficient sample amount, no peaks was observable on the spectrum, making it difficult or impossible to distinguish and interpret the signals from the compound (Lohr *et al.*, 2004).

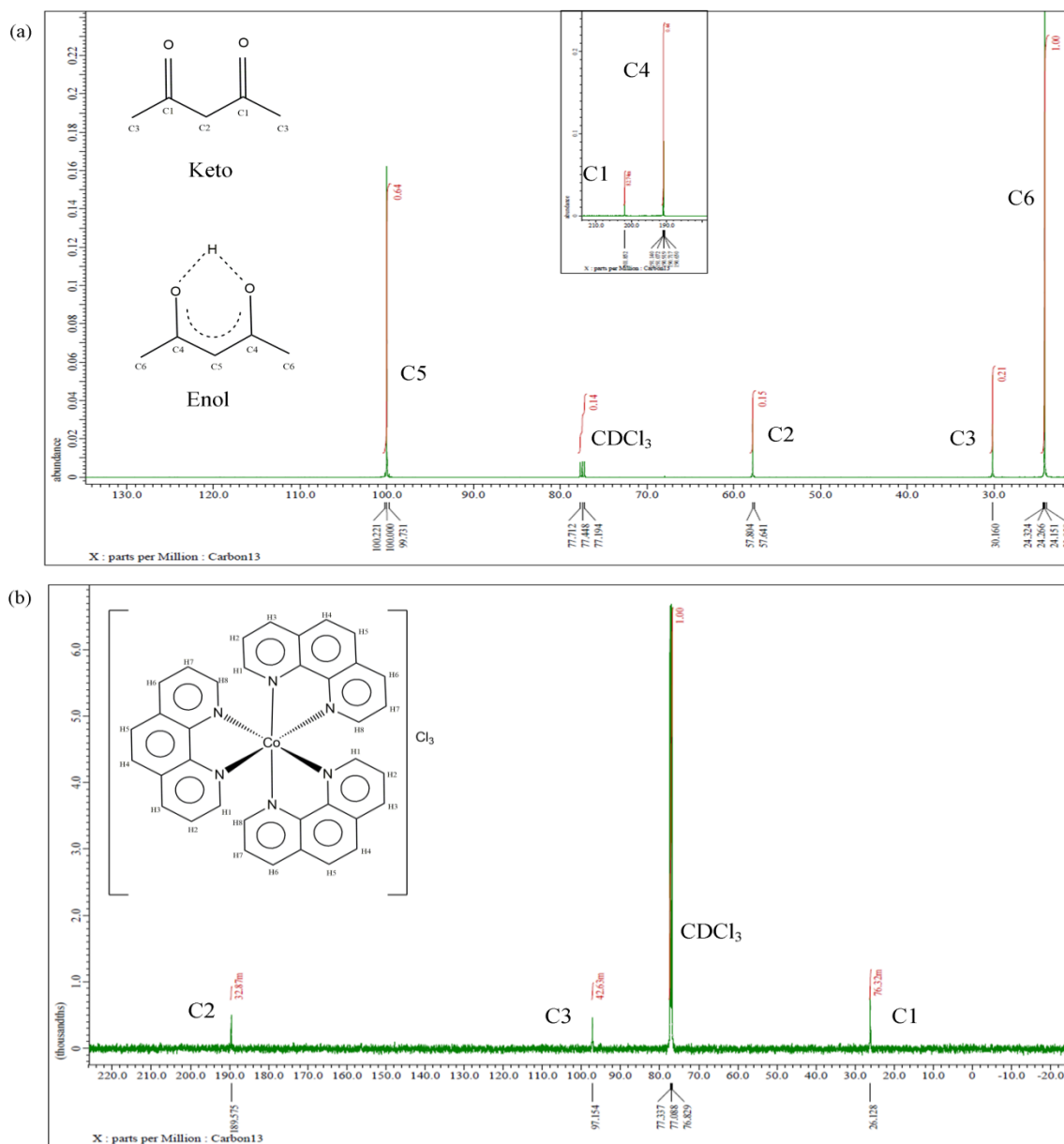


Figure 4.9: ^{13}C NMR spectra of (a) free acac; and (b) $[\text{Co}(\text{acac})_3]$

The UV-Vis spectra of free acac ligand and $[\text{Co}(\text{acac})_3]$, $[\text{Ni}(\text{acac})_2]$ and $[\text{Cu}(\text{acac})_2]$ are shown in the Figure 4.10. The single peak at 275 nm from acac compound (Figure 4.10a) was assigned to $\pi - \pi^*$ electronic transition of the carbonyl group (Yoda *et al.*, 2017).

The blue shift of the $\pi - \pi^*$ transition was observed in $[\text{Co}(\text{acac})_3]$. The $\pi - \pi^*$ transition assigned peak in acac ligand shifted to 260 nm from 275 nm in $[\text{Co}(\text{acac})_3]$ complex (Kadhiravan & Sivajiganesan, 2015; Zhong *et al.*, 2022). The possible reason for the blue shift of UV peak was the polar solvent (dichloromethane) which might have stabilized the electronic state and leading to change in the energy level of electronic transition. The UV peak at 595 nm was assigned to the $d-d$ transition in $[\text{Co}(\text{acac})_3]$ (Amason *et al.*, 2021).

Two peaks, 295 nm and 650 nm were depicted in the UV-Vis spectrum of $[\text{Ni}(\text{acac})_2]$ (Figure 4.10c). The peak assigned to $\pi - \pi^*$ transition in carbonyl group had shifted from 275 nm to 295 nm. The shift suggested an interaction within ligand and metal ion. The peak observed at 650 nm is attributed to the $d-d$ electronic transition in $[\text{Ni}(\text{acac})_2]$. Lewis *et al.* (1993) assigned peaks at 298 nm and 644 nm to $\pi - \pi^*$ transition and $d-d$ transition of the complex in his work, respectively. Additionally, Rafiqi & Majid (2016) also assigned a peak at 642 nm to $d-d$ electronic transition in $[\text{Ni}(\text{acac})_2]$.

For the $[\text{Cu}(\text{acac})_2]$ (Figure 4.10d), two prominent absorption bands were observed at 290 nm and 650 nm. These bands correspond to the electronic transitions characteristic of $[\text{Cu}(\text{acac})_2]$. As reported in studies by Sridaeng *et al.* (2015) and Seyedkatouli *et al.* (2018), the absorption bands at 291 nm and 292 nm are associated with $\pi-\pi^*$ transitions of the acetylacetonate ligand, while the band around 657 nm corresponds to a $d-d$ transition, indicated the copper center's coordination environment. These assignments align well with the expected electronic behavior of $[\text{Cu}(\text{acac})_2]$, reinforcing the successful synthesis and coordination of the acac ligands to the copper ion.

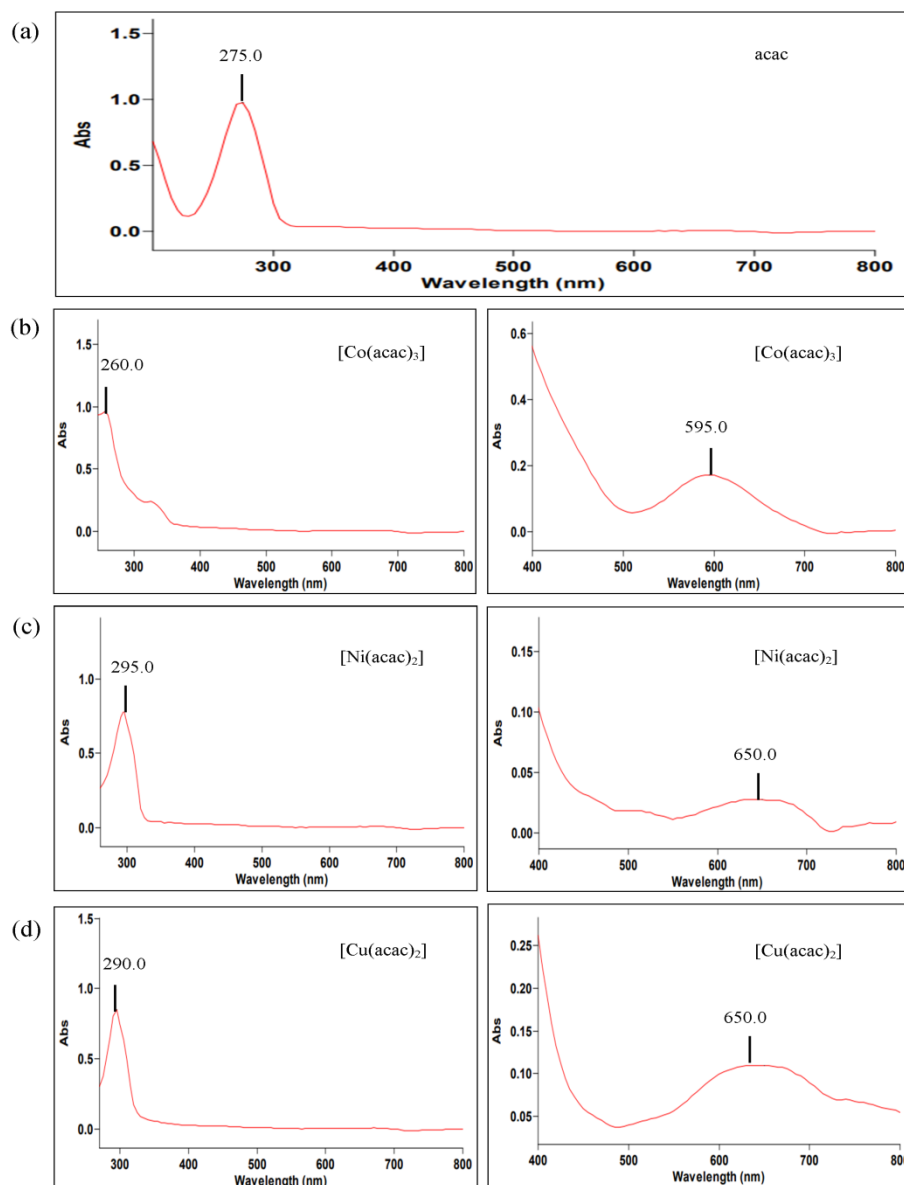


Figure 4.10: UV-Vis spectra of (a) free acac; (b) $[\text{Co}(\text{acac})_3]$; (c) $[\text{Ni}(\text{acac})_2]$; and (d) $[\text{Cu}(\text{acac})_2]$. The UV-Vis spectra highlight electronic transitions for each complex, reflecting their distinct coordination geometries. $[\text{Co}(\text{acac})_3]$ exhibits $d-d$ transitions typical of octahedral $\text{Co}(\text{III})$, while $[\text{Ni}(\text{acac})_2]$ and $[\text{Cu}(\text{acac})_2]$ show transitions characteristic of square planar geometries. The variation in absorption band corresponds to differences in electronic structure and metal-ligand interactions.

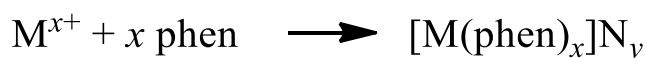
Other than that, the CHN result of the acac-based metal complexes showed the little difference ($<0.4\%$) with the theoretical values in each complex (Table 4.5). Hence, the CHN results supported the ratio of ligand acac to metal in each complex as postulated in Schemes 3.1 – 3.3 in Chapter 3.

Table 4.5: CHN analysis of [Co(acac)₃], [Ni(acac)₂] and [Cu(acac)₂]

	Carbon		Hydrogen	
	Theoretical (%)	Found (%)	Theoretical (%)	Found (%)
[Co(acac) ₃]	50.57	50.23	5.94	5.75
[Ni(acac) ₂]	46.75	46.98	6.27	6.11
[Cu(acac) ₂]	45.99	45.49	5.39	5.18

4.2.2 Synthesis and Characterization of [TM(phen)_n]Cl_n, where n = 2, 3

The synthesis of [Co(phen)₃]Cl₃, [Ni(phen)₂]Cl₂, and [Cu(phen)₂]Cl₂ followed well-established methods and resulted in successful formation of the desired metal acetylacetonate complexes. The general reaction for these syntheses can be represented as:



Scheme 4.2: General synthetic scheme of phen-ligand based complexes

where M represents the metal ion (Co³⁺, Ni²⁺, Cu²⁺), phen is the 1,10-phenanthroline ligand, N is the counterion (in this case is Cl⁻ ion), x is the stoichiometry of ligand depending on the metal center, and y is the corresponding charge balance. The [Co(phen)₃]Cl₃ was synthesized by reacting cobalt chloride and phen in acetone, in the presence of hydrogen peroxide where hydrogen peroxide served as an oxidizing agent to oxidize the cobalt (II) to cobalt (III) in the complex. Additionally, hydrogen peroxide could maintain the integrity of the ligand environment by providing a controlled oxidation process, ensuring the formation of stable Co(III)-phen coordination complex. While the synthesis routes for [Ni(phen)₂]Cl₂ and [Cu(phen)₂]Cl₂ involved reacting the nickel(II) chloride and copper(II) chloride, respectively, with phen in ethanol. (Corey *et al.*, 1965).

The synthesis of the metal complexes was successfully carried out using crystallization and purification techniques. The long reaction time (12 hours) was employed to ensure an even distribution of reagents for the homogeneity of crystal growth and allow complete coordination. Adequate stirring was crucial to avoid inconsistent crystallization, which could lead to the formation of impure crystals. The resulting products and its yield were dark red for $[\text{Co}(\text{phen})_3]\text{Cl}_3$ (83 %), light blue for $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ (66 %), and green for $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ (70 %).

4.2.2.1 Spectroscopic Characterization of $[\text{TM}(\text{phen})_x]\text{Cl}_x$, where $n = 2, 3$

Table 4.6 shows the solubility test for $[\text{Co}(\text{phen})_3]\text{Cl}_3$, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ complexes. All three complexes showed solubility in polar protic solvent such as methanol and ethanol, as well as polar aprotic solvents like acetonitrile and dimethylsulfoxide. This is because the complexes are present in ionic form and the presence of -NH bond in the complexes to give polar or partially polar characteristics.

Table 4.6: Solubility test of $[\text{Co}(\text{phen})_3]\text{Cl}_3$, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$

Solvents	$[\text{Co}(\text{phen})_3]\text{Cl}_3$	$[\text{Ni}(\text{phen})_2]\text{Cl}_2$	$[\text{Cu}(\text{phen})_2]\text{Cl}_2$
Hexane	Insoluble	Insoluble	Insoluble
Toluene	Insoluble	Insoluble	Insoluble
Diethyl ether	Insoluble	Insoluble	Insoluble
Dichloromethane	Insoluble	Insoluble	Insoluble
Acetone	Insoluble	Insoluble	Insoluble
Acetonitrile	Slightly soluble	Slightly soluble	Soluble
Chloroform	Insoluble	Insoluble	Insoluble
Ethanol	Slightly soluble	Slightly soluble	Slightly soluble
Methanol	Soluble	Soluble	Soluble
Dimethylformamide	Insoluble	Insoluble	Insoluble
Dimethylsulfoxide	Slightly soluble	Slightly soluble	Slightly soluble
Water	Insoluble	Insoluble	Insoluble

Figure 4.11 is the FTIR spectral of free phen ligand and $[\text{Co}(\text{phen})_3]\text{Cl}_3$, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ complexes. The spectrum of phen showed 4 significant peaks at 3410 cm^{-1} , 1639 cm^{-1} , 1586 cm^{-1} and 736 cm^{-1} . The peak at 3410 cm^{-1} was assigned to the stretching of OH group, while those at 1639 cm^{-1} and 1586 cm^{-1} were assigned to C=N and C=C stretching vibrations, respectively, and 736 cm^{-1} was associated with the out-plane bending vibration peak of C-H bond. The appeared OH peak in the spectra was attributed to moisture in the air had reacted with phen (Wang *et al.*, 2015).

In the free phen ligand, the C=N stretching vibration occurred at 1639 cm^{-1} . Upon complexation, the C=N stretching vibration shifted to a lower wavenumbers at 1622 cm^{-1} in $[\text{Co}(\text{phen})_3]\text{Cl}_3$, 1624 cm^{-1} in $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ and 1626 cm^{-1} in $[\text{Cu}(\text{phen})_2]\text{Cl}_2$. The shift indicated the coordination bond formed between the nitrogen atom and the metal centre. The coordination transferred the electron density from C=N to the metal ion and weakened the C=N bond hence has decreased the stretching frequency. Among the three complexes, $[\text{Co}(\text{phen})_3]\text{Cl}_3$ exhibited the most significant shift. The Co(III) ion is at higher oxidation state and exhibits a stronger ligand field compared to Ni(II) and Cu(II) ion, resulting in a more significant back-donation of electron density from the metal to the anti-bonding orbitals of C=N bond. The bond is thus weakened and shifted to lower frequency.

Similarly, the vibration frequency of C=C bond also decreased after complexation. The C=C bond at 1586 cm^{-1} in free phen ligand was shifted to 1579 cm^{-1} in $[\text{Co}(\text{phen})_3]\text{Cl}_3$ (Sharma *et al.*, 2010), 1582 cm^{-1} in $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ (Alramadhan *et al.*, 2023) and 1585 cm^{-1} in $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ (Crispini *et al.*, 2018). This indicates that complexation affects the π electron density in the aromatic system, weakening the bond strength and lowering down the stretching frequency.

[Co(phen)₃]Cl₃ showed largest shift in both C=N and C=C vibration frequencies compared to [Cu(phen)₂]Cl₂ and [Ni(phen)₂]Cl₂, suggesting a stronger bonding between cobalt and phen ligand compared to copper and nickel metal centre. The cobalt ion in [Co(phen)₃]Cl₃ exists with a formal charge of +3 was coordinated by six nitrogen atoms around it while Cu²⁺ and Ni²⁺ ions only coordinated by four nitrogen atoms. A greater electron transfer between Co³⁺ ion and nitrogen atom compared to Cu²⁺ and Ni²⁺ ions and led to stronger metal-ligand interaction thus a more significant shift in peak frequencies.

Also, the new peaks appeared in the spectra of the complexes suggested to the complete complexation between phen ligand and the metal ions. The new peaks observed at 420 cm⁻¹, 425 cm⁻¹ and 430 cm⁻¹ which were assigned to newly formed Co-N (Singh *et al.*, 2008), Ni-N (Çolak *et al.*, 2010) and Cu-N (Wang *et al.*, 2015) bonds. To validate the accuracy of peak assignments in this work, a few data was collected from other works for comparison.

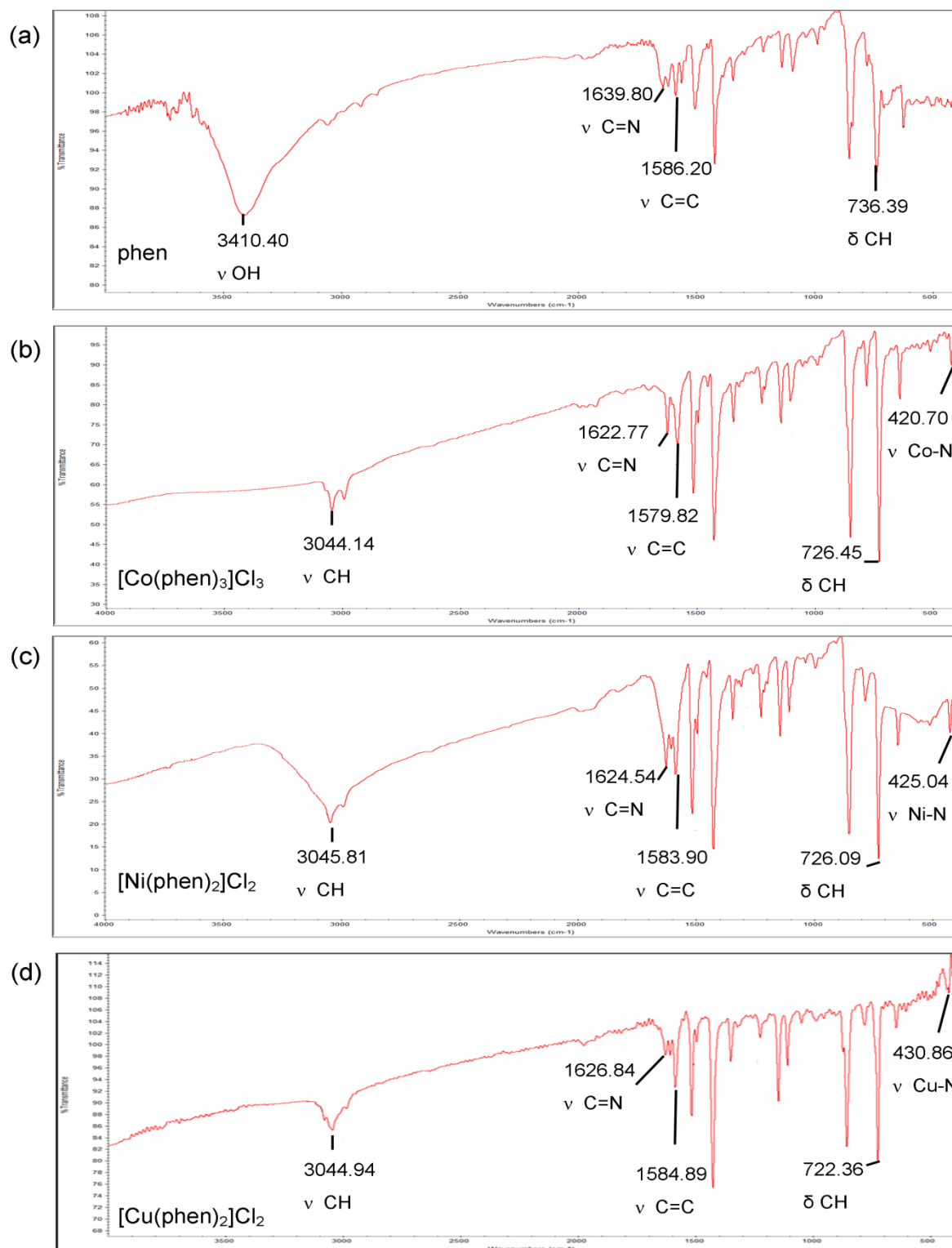


Figure 4.11: FTIR spectra of (a) free phen; (b) [Co(phen)₃]Cl₃; (c) [Ni(phen)₂]Cl₂; (d) [Cu(phen)₂]Cl₂

A cross comparison of the wavenumbers of proposed the $[\text{Co}(\text{phen})_3]\text{Cl}_3$, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$, and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ is presented in Table 4.7. The wavenumbers observed in FTIR spectra were in good agreement with reported values in the literatures.

Table 4.7: Comparison of major peak wavenumber (cm^{-1}) of $[\text{Co}(\text{phen})_3]\text{Cl}_3$, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$, and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ with literature

		Assignment			
		$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\delta(\text{C}-\text{H}, \text{phen})$	$\nu(\text{M}-\text{N})$
$[\text{Co}(\text{phen})_3]\text{Cl}_3$	This work	1622	1579	726	420
	(Singh <i>et al.</i> , 2008)	1621	1574	726	456
	(Sharma <i>et al.</i> , 2008)	1626	1581	713	464
	(Sharma <i>et al.</i> , 2009)	1636	1589	709	466
	(Sharma <i>et al.</i> , 2010)	1634	1582	-	-
$[\text{Ni}(\text{acac})_2]\text{Cl}_2$	This work	1624	1582	726	425
	(Çolak <i>et al.</i> , 2010)	-	1582	-	444
	(Abdou, 2022)	1626	-	-	450
	(Alramadhan <i>et al.</i> , 2023)	1629	1589	726	-
	(Hamdani <i>et al.</i> , 2023)	1631	-	724	-
$[\text{Cu}(\text{acac})_2]\text{Cl}_2$	This work	1626	1585	736	430
	(Feng <i>et al.</i> , 2005)	1624	1587	-	-
	(Thebo <i>et al.</i> , 2011)	-	-	-	438
	(Wang <i>et al.</i> , 2015)	1626	1587	719	435
	(Crispini <i>et al.</i> , 2018)	1627	1585	721	-

The ^1H NMR spectrum of free phen ligand and $[\text{Co}(\text{phen})_3]\text{Cl}_3$ is shown in Figure 4.12, with $\text{DMSO}-d_6$ used as NMR solvent. In the spectrum of phen ligand (Figure 4.12a), 4 sharp peaks are observed at 9.06 ppm, 8.45 ppm, 7.95 ppm and 7.73 ppm. The multiplet at 9.06 ppm was belonged to H1 and H8. Nitrogen atom with high electronegativity was next to these protons caused them to have the most deshielded effect on it thus shifted to downfield. Meanwhile, the multiplet at 8.45 ppm assigned to H3 and H6 which para to nitrogen atom and experienced more deshielding effect from conjugated system compared to H2 and H7. Hence, the multiplet appeared at 7.73 ppm attributed to H2 and H7. While

the singlet at 7.945 ppm assigned to H4, H5 as they were located in the central ring and less affected by other protons so appearing upfield compared to other protons.

In Figure 4.12b, the four significant broad peaks shown in the spectra of $[\text{Co}(\text{phen})_3]\text{Cl}_3$ were 8.41 ppm, 8.56 ppm, 8.82 ppm, and 9.31 ppm. These signals were all downfield shifted and broadened compared to free phen ligand suggested complexation between phen ligand and Co^{3+} ion. The most downfield peak observed at 9.31 ppm was belonged to H1, H8 which were most affected by nearby nitrogen atoms. The moderately deshielded H3, H6 contributed to peak at 8.82 ppm. The multiplet at 8.56 ppm corresponded to H2, H7 which were surrounded by H1, H3 and H6, H8. Since H4, H5 were the most further from nitrogen atom, therefore they were least deshielded and showed peak at relatively upfield, 8.41 ppm.

For the $[\text{Ni}(\text{phen})_2]\text{Cl}_2$, no detectable signal was shown despite running an overnight analysis. This might be due to the solubility issue as the phen ligand-based complexes were slightly soluble in DMSO. In the case of $[\text{Co}(\text{phen})_3]\text{Cl}_3$, the observed signals were broadened and of low intensity, likely due to solvent interactions, such as hydrogen bonding, or rapid proton exchange at higher temperatures. At elevated temperatures, protons are more energetically active, leading to rapid exchange between different environments and broadened NMR signals. By lowering the temperature during NMR analysis, the molecular motion and proton exchange could be slowed down to give sharp peaks.

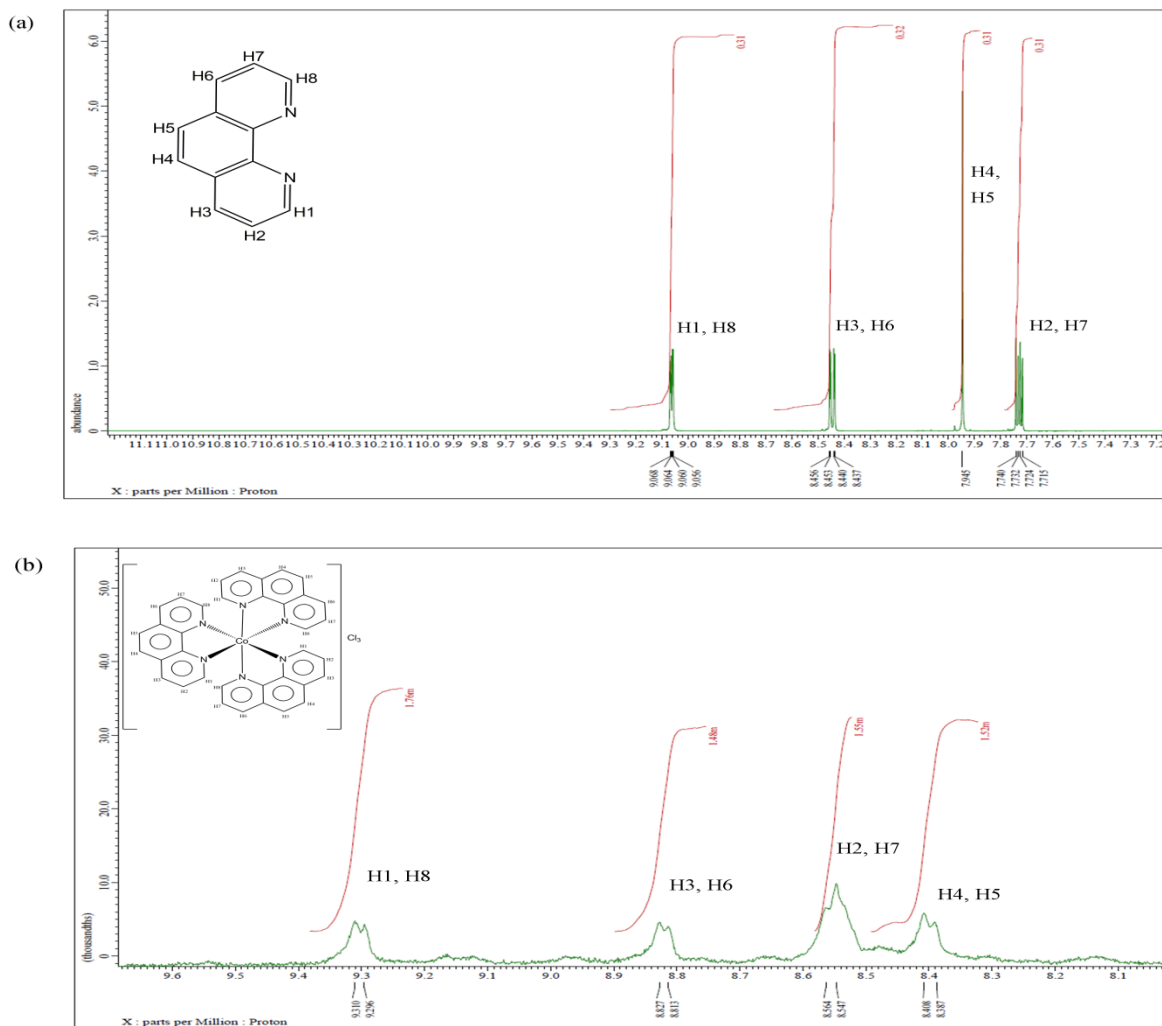


Figure 4.12: ^1H NMR spectra of (a) free phen; and (b) $[\text{Co}(\text{phen})_3]\text{Cl}_3$

The ^{13}C NMR spectrum of free phen is shown in Figure 4.13. Excluding the residual peak of DMSO (40.0 ppm), 6 significant peaks were observed, revealing 6 carbon environments existed in phen ligand. These signals appeared at 123.83 ppm, 127.21 ppm, 128.98 ppm, 136.72 ppm, 146.09 ppm, 150.48 ppm. C1, C10, and C11, C12 were all deshielded by nitrogen atoms but C11 and C12 were significantly deshielded as both C11 and C12 located between two nitrogen atoms, hence signal at 150.48 ppm and 146.09 ppm attributed to C11, C12 and C1, C10 respectively. The most upfield signal, at 123.83 ppm, assigned to C5, C6 as these two carbon experienced the least deshielded effect from

nitrogen atoms. C4 and C7 were tertiary carbon while C2, C9 and C3, C8 were secondary carbon, the tertiary carbon is more deshielded by secondary carbon, thus peak at 136.71 ppm corresponded to C4, C7. Note that the meta carbon relative to nitrogen will be less deshielded, therefore, peak at 127.21 ppm and 128.98 ppm assigned to C2, C9 and C3, C8 respectively.

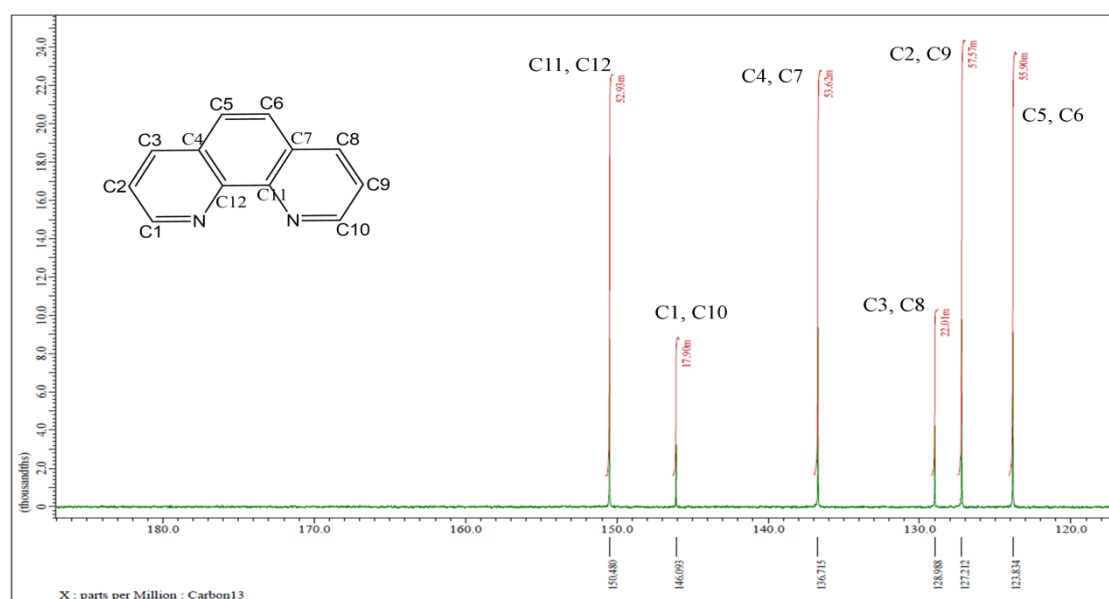


Figure 4.13: ^{13}C NMR spectrum of free phen

The ^{13}C NMR spectra for $[\text{Co}(\text{phen})_3]\text{Cl}_3$ and $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ could not be obtained although the NMR experiment had been extended overnight, which might be attributed to the the extremely low solubility of $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ in DMSO-d_6 solvent and low sample amount of $[\text{Co}(\text{phen})_3]\text{Cl}_3$ used in NMR analysis.

Figure 4.14 illustrates the UV-Vis spectra of free phen ligand and $[\text{Co}(\text{phen})_3]\text{Cl}_3$, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$, and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ complexes. In Figure 4.12a, a peak attributed to π - π^* transition of the aromatic $\text{C}=\text{C}$ bond appeared at 260 nm (Hamdani *et al.*, 2023). This peak was observed to shift to 270 nm in all complexes (Figure 4.14b-d) $[\text{Co}(\text{phen})_3]\text{Cl}_3$ (Louise

et al., 2019), and $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ (Srinivasulu *et al.*, 2022). The bathochromic shift of the characteristic peak of phen ligand in $[\text{Co}(\text{phen})_3]\text{Cl}_3$, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ evidenced the coordination between the metal ions and phen ligands.

Moreover, new peaks corresponding to *d-d* electronic transition were observed in the UV spectra of $[\text{Co}(\text{phen})_3]\text{Cl}_3$ (480 nm) (Riordan *et al.*, 2005); $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ (585 nm) (Srinivasulu *et al.*, 2022) and of $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ (680 nm). These peaks are the characteristics peaks of electronic transition within the metal complexes that further confirm their formation.

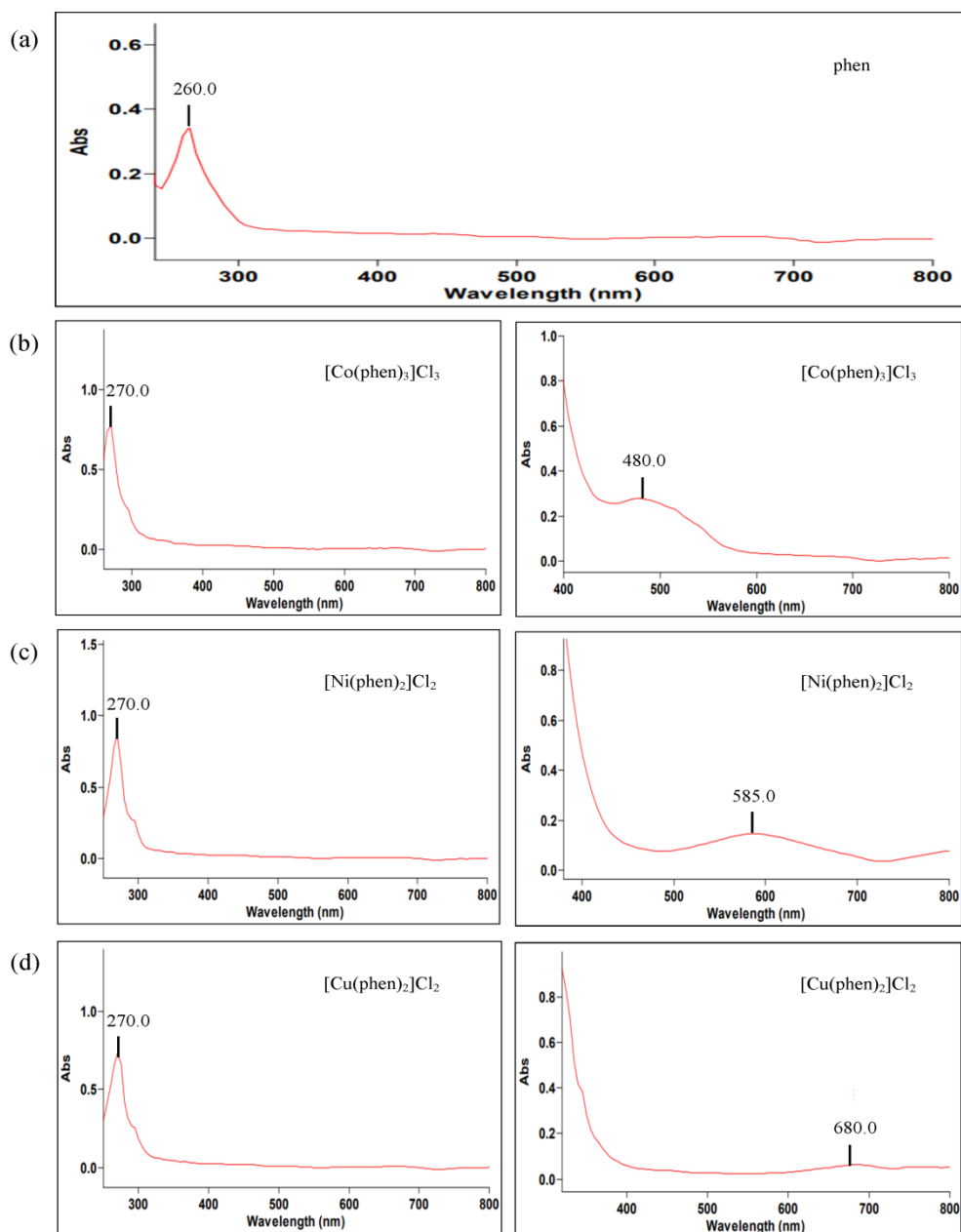


Figure 4.14: UV-Vis spectra of (a) free phen; (b) $[\text{Co}(\text{phen})_3]\text{Cl}_3$; (c) $[\text{Ni}(\text{phen})_2]\text{Cl}_2$; and (d) $[\text{Cu}(\text{phen})_2]\text{Cl}_2$. The spectra illustrate the electronic transitions characteristic of each complex, reflecting their distinct coordination environments and metal-ligand interactions. The observed absorption features indicate differences in the ligand field strength of the complexes.

Table 4.8 is the elemental analysis results of the formation metal complexes containing phen ligand. The data showed that the differences of carbon and hydrogen percentages between theoretical values and experimental results were less than 0.4 %. Thus

the elemental analysis results agreed to the postulated structure of phen ligand-based complexes.

Table 4.8: CHN analysis of [Co(phen)₃]Cl₃, [Ni(phen)₂]Cl₂, and [Cu(phen)₂]Cl₂

	Carbon		Hydrogen		Nitrogen	
	Theoretical	Found	Theoretical	Found	Theoretical	Found
	(%)	(%)	(%)	(%)	(%)	(%)
[Co(phen) ₃]Cl ₃	61.26	61.03	3.43	3.34	11.91	11.59
[Ni(phen) ₂]Cl ₂	58.83	58.43	3.29	3.08	11.43	11.09
[Cu(phen) ₂]Cl ₂	58.25	58.20	3.26	3.36	11.32	11.22

4.3 Application of Transition Metal Complexes in DCPFC

The transition metal complexes/Zn photoanode was fabricated and used in DCPFC to examine the photodegradation ability of the synthesized complexes on methyl red dye degradation and power generation. Electricity generation and dye removal efficiency were the criteria to assess the efficiency of transition metal complexes as a photoanode in DCPFC system in comparison to the standard ZnO/Zn photoanode.

Since the aim of this project was to compare the efficiency of the DCPFC system with different photocatalysts on the methyl red dye removal and power generation, the experimental conditions were based on the optimal conditions of DCPFC with ZnO/Zn as the photoanode because ZnO acted as standard photocatalyst.

Figure 4.15a show the highest power density generated by the transition metal complex photocatalysts. Notably, the acac ligand-based complexes performed better than the phen ligand-based complexes, with the acac ligand-based complexes showing three

times greater power density than the phen ligand-based complexes. However, all complex photocatalysts demonstrated lower power generation compared to ZnO photocatalyst. Similarly, the dye degradation efficiency by the acac ligand-based complexes was higher than that of phen ligand-based complexes but still lower than ZnO (Figure 4.15b).

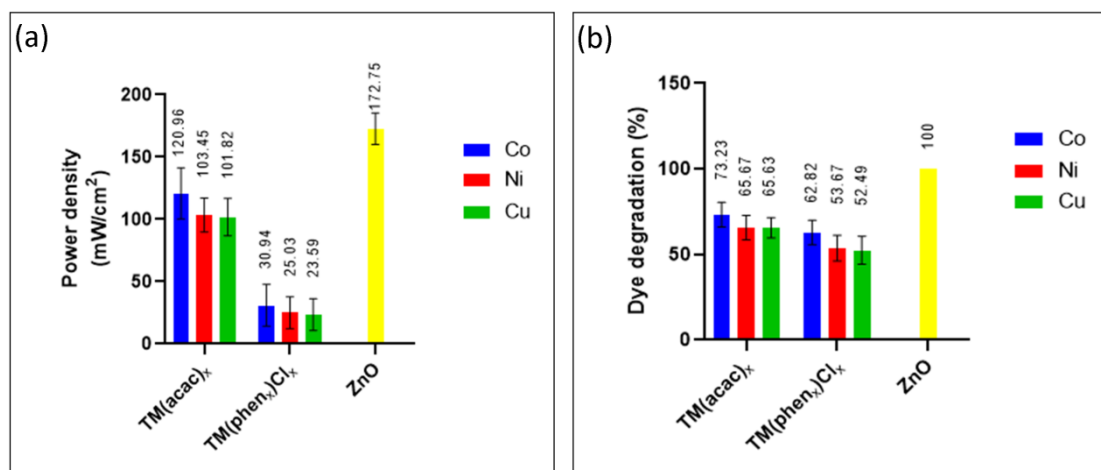


Figure 4.15: Comparison: (a) the highest power density of the synthesized metal complex photoanode with ZnO photoanode; (b) the highest dye degradation of the synthesized metal complex photoanode with ZnO photoanode

From Figure 4.15a, the power generation of the complexes are arranged from the highest to the lowest: [Co(acac)₃] (120.96 mW/cm²) > [Ni(acac)₂] (103.45 mW/cm²) > [Cu(acac)₂] (101.82 mW/cm²) > [Co(phen)₃]Cl₃ (30.94 mW/cm²) > [Ni(phen)₂]Cl₂ (25.03 mW/cm²) > [Cu(phen)₂]Cl₂ (23.59 mW/cm²). A similar decreasing trend in the dye degradation performance was observed for the complexes, with [Co(acac)₃] photocatalyst showing highest dye degradation efficiency (73.23 %) and [Cu(phen)₂]Cl₂ showed lowest dye degradation efficiency (52.49%). As a whole, acac ligand-based complexes and phen ligand-based complexes demonstrated similar dye degradation efficiency but large differences in the power generation. The highest power generation from the acac ligand-based complexes was 3× of those phen ligand-based complexes.

There are two types of ligand: weak field ligand and strong field ligand. The weak field ligand produces small splitting of *d*-orbitals (Reiher *et al.*, 2001; Jackson & Miliordos, 2020), facilitating efficient electron transfer while strong field ligand produces large splitting of *d*-orbitals (Griffith & Orgel, 1935; Zhang *et al.*, 2020), hindering electron excitation. Acac ligand, being a weak field ligand and π -donor, contributes to the formation of a smaller bandgap for acac ligand-based complex compared to phen ligand. It forms a relatively weak bond with the metal central. With a weak ligand field, there is a higher electron density around the central metal. The electrons in *d*-orbitals are more delocalized, and the metal-ligand bonds are not that strong (Kraka & Freindorf, 2020), hence a high energy, less stable molecule is anticipated. Also, the higher population of the delocalized electrons in the metal's *d*-orbitals led to better electronic conductivity (Chen *et al.*, 2023).

On the contrary, phen is a strong field ligand and π -acceptor ligand, causing lower electron density around the metal central and forms a relatively strong bond with the metal to have a relatively more stable molecule (Reinholdt *et al.*, 2015). However, a stable molecule requires a lot of energy (eg. UV range photon) for its' electron excitation. So, the electron excitation for complexes with π -acceptor ligand is more difficult than the complexes with π -donor ligand (May & Dempsey, 2024). Figure 4.16 shows the estimated bandgap of the synthesized complexes using the Tauc plot method. All these complexes showed smaller bandgaps compared to standard photocatalyst ZnO (3.5 eV), with the acac ligand-based complexes exhibiting smaller bandgaps compared to phen ligand-based complexes. The estimated bandgaps arrange from the lowest to the highest: [Ni(acac)₂] (2.83 eV) < [Co(acac)₃] (2.9 eV) < [Cu(acac)₂] (2.94 eV) < [Ni(phen)₂]Cl₂ (3.2 eV) < [Co(phen)₃]Cl₃ (3.25 eV) < [Cu(phen)₂]Cl₂ (3.4 eV).

The bandgap of a metal complex is the energy difference of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) (Kateris *et al.*, 2023). Beside ligand, there are other factors which can influence the bandgap such as oxidation state of metal centre (Wang *et al.*, 2023a). Transition metal complexes often exhibit *d-d* transition. The oxidation state of metal centre can influence the coordination environment and the nature of metal-ligand interaction. A higher oxidation state of the metal centre usually means more positive charge on the metal which can attract electron more strongly. The energy separation of *d*-orbitals increases along with the increases of oxidation state. The splitting become bigger hence the bandgap become wider (Singh *et al.*, 2017).

Among the complexes studied, [Cu(phen)₂]Cl₂ has the largest bandgap (3.4 eV), yet it shows a relatively low-energy *d-d* transition absorption band at 680 nm. While this might seem contradictory, it could be due to the *d-d* transition referring to the splitting of *d*-orbitals within the *d*-orbital, which is different from the overall HOMO – LUMO gap. The *d-d* transition reflects intra-orbital electron transitions, and the energy required for such transitions is lower compared to the energy required for an electron to jump from the HOMO to the LUMO.

Furthermore, across period 3, atomic size decreases and effective nuclear charge increases. This results in stronger attraction between the valence electrons and the nucleus, contributing to higher energy requirements for electron excitation from the VB to the CB (Renuka *et al.*, 2017; Mukherjee *et al.*, 2020). The increasing charge density of the metal center in Cu²⁺ complexes leads to tight metal-ligand interactions, explaining the larger

bandgap. However, because the $d-d$ transition occurs within the d -orbitals, it is less energy-intensive compared to the HOMO – LUMO transition.

Thus, the bandgap is determined by multiple factors such as atomic size, charge density, and oxidation state, while the $d-d$ transition reflects specific electronic transitions within the d -orbitals and therefore does not directly correlate with the bandgap.

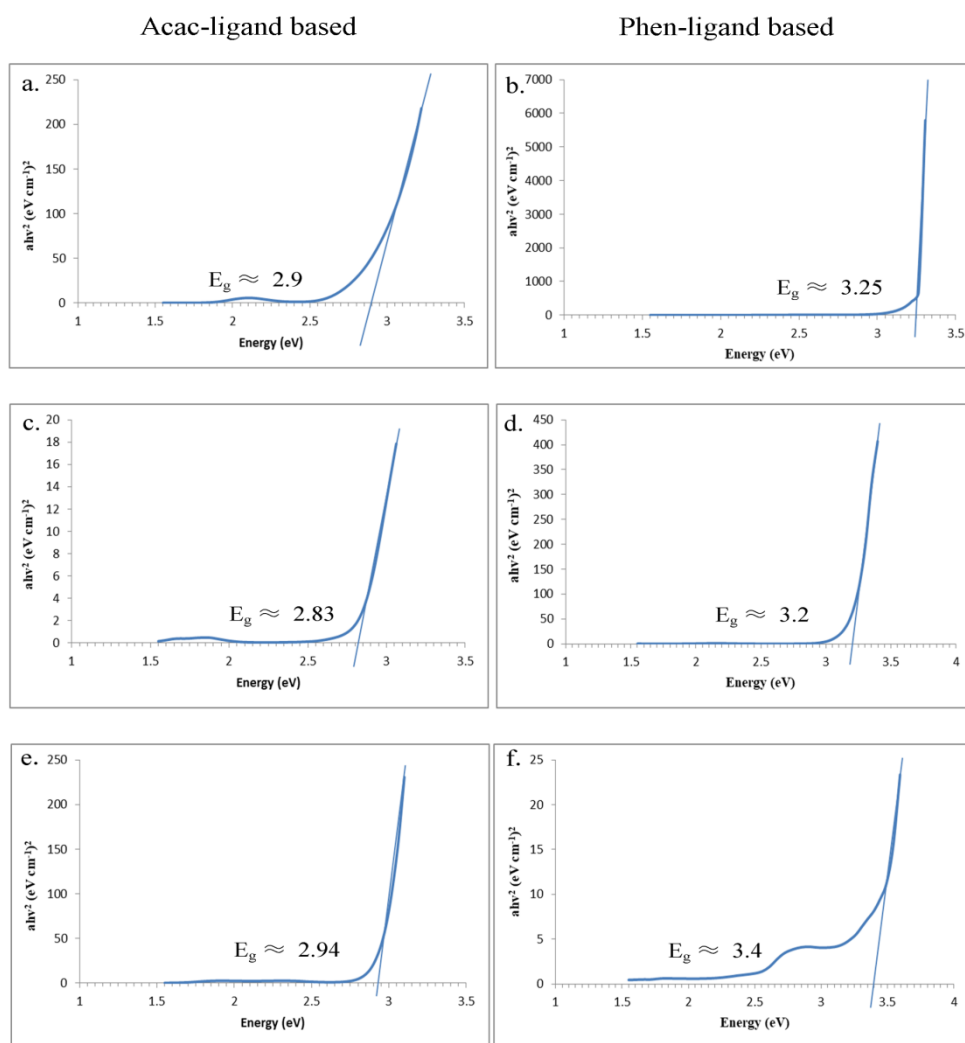


Figure 4.16: The estimated bandgap of synthesized complexes: (a) $[\text{Co}(\text{acac})_3]$; (b) $[\text{Co}(\text{phen})_3]\text{Cl}_3$; (c) $[\text{Ni}(\text{acac})_2]$; (d) $[\text{Ni}(\text{phen})_2]\text{Cl}_2$; (e) $[\text{Cu}(\text{acac})_2]$; (f) $[\text{Cu}(\text{phen})_2]\text{Cl}_2$

PFC is famous due to its ability to produce electricity during water purification processes (Sfaelou & Lianos, 2016; Vasseghian *et al.*, 2020). To degrade organic

pollutants, the band gap of the semiconductor should be high enough to absorb high energy photons required to create active radicals species (Lianos, 2011). The estimated bandgaps of the synthesized complexes ranging between 1.5 – 3.5 eV, suggests that they are within the ideal range for efficient photocatalytic activity. This range is optimal for generating radicals required for pollutant degradation, as these bandgaps allow sufficient absorption of visible light to drive photocatalytic processes (Tahir *et al.*, 2021).

Regrettably, lower power generation ($23.59 \text{ mW/cm}^2 - 120.96 \text{ mW/cm}^2$) and dye degradation efficiency (52.49 % – 73.23 %) of these complexes were recorded compared to standard ZnO (172.75 mW/cm^2 ; 100 %). Based on the findings from literature, metal complexes were expected to have outstanding performance on power generation and dye degradation when applied in DCPFC system because of the smaller energy band gap compared to ZnO which means lower energy photon is needed for the electron excitation. Nonetheless, the *n*-type character and high electron mobility in ZnO had ensured its' photocatalytic activity (Gautam *et al.*, 2020). According to Danish *et al.* (2021) and Hassaan *et al.* (2023), high chemical and physical stability are one of the main reasons for the extensive use of metal oxides (TiO_2 , ZnO, SnO_2 , CeO_2 , V_2O_5 , Cr_2O_3) as photocatalyst. This is because oxide has anti-corrosion properties thus can withstand harsh environment. Also, Han *et al.* (2016) stated that metal complexes usually degrade rapidly into free transition metal ion, leading to poor stability of the molecular catalyst. This could likely be the main reason for the high power generation and dye degradation of ZnO photocatalyst compared to the metal complexes photocatalyst.

A supporting data of the chemically unstable of transition metal complex is shown in Figure 4.17. The degradation efficiency and power generation of transition metal

complexes photocatalyst decreased drastically compared to the ZnO photocatalyst when the photoanodes were reused in the first-cycle of photocatalysis. The degradation of the ultrasonic-prepared reused ZnO/Zn was still rather high at 69 % while the rest of the ultrasonic-prepared transition metal complexes photoanode were lower than 20 % dye degradation efficiency. This strongly proved that ZnO is chemically more stable than the transition metal complexes (Singh *et al.*, 2020). The Zn^{2+} ions are relatively small and have a full d^{10} electron configuration, minimizing its reactivity compared to the often incomplete d -orbitals of many transition metals, leading to higher chemical inertness. Many transition metal complexes exhibit lower stability due to their higher tendency to undergo ligand exchange reactions, redox changes, or decomposition in aqueous environments, with factors such as ligand type, ionic radius, and oxidation states affecting their stability. The residual ZnO on photoanode ensured the degradation efficiency with the recycled ZnO/Zn photoanode.

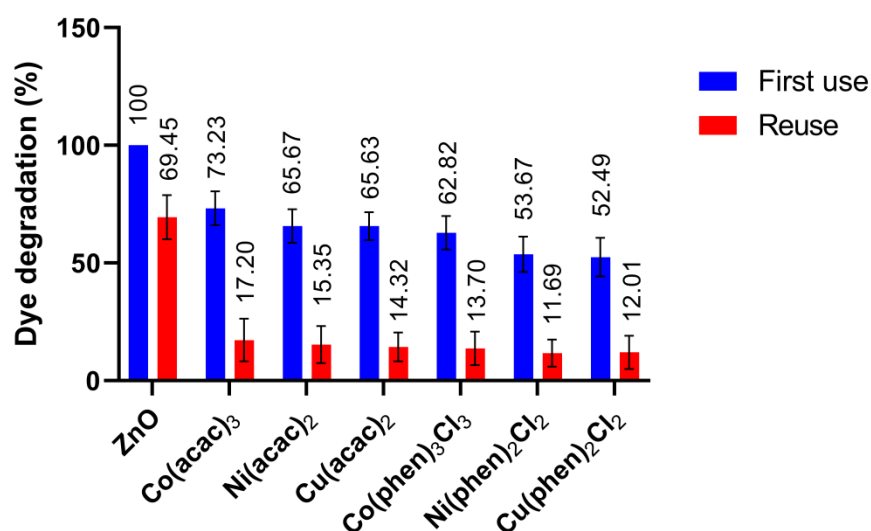


Figure 4.17: Reusability test of ultrasonic-prepared photoanodes on methyl red dye degradation efficiency (%)

It was well-known that the primary oxidizing species in PFC system are holes, which can directly oxidize contaminants or adsorbed water to produce $\bullet\text{OH}$ radicals (Guo *et al.*, 2011; Gligorovski *et al.*, 2015). When a photocatalyst is chemically unstable in the pollutants containing medium, the number of electrons/holes pairs reduces and limits the pollutant degradation process.



Based on the Equation 4.16 – 4.17, there is a direct relationship between electron excitation and power generation of a photocatalyst. When an organic compound is degraded at the anode chamber, electrons are released as byproduct and transmitted to the cathode through an external circuit (Vasseghian *et al.*, 2020; Mishra *et al.*, 2021). This explains the higher power generation of ZnO photocatalyst than the acac ligand-based and phen ligand-based photocatalysts as ZnO can withstand better in harsh environment and ensure the electrons excitation.

4.3.1 Effects of Coating Method on PFC Performance

The coating method can affect the efficiency of photocatalytic reactions by producing coating containing different particle sizes (Chang & Robinson, 1990), morphologies (Salleh *et al.*, 2022) and thickness (Barth *et al.*, 2013) on the substrate. Generally, the surface area to volume ratio (S/V ratio) increases with the decrease of particle size. Larger surface area provides more active sites for radical formation and photodegradation reactions (Cheng *et al.*, 2014) hence enhances photocatalytic efficiency.

In this project, the synthesized complexes were immobilized on Zn plate as photocatalysts using three different coating methods, namely dip coating, spray coating and ultrasonic coating method. The transition metal complexes/Zn photocatalyst with different coating methods were then applied in DCPFC. Figure 4.18 presents the power density of photocatalyst with different coating method.

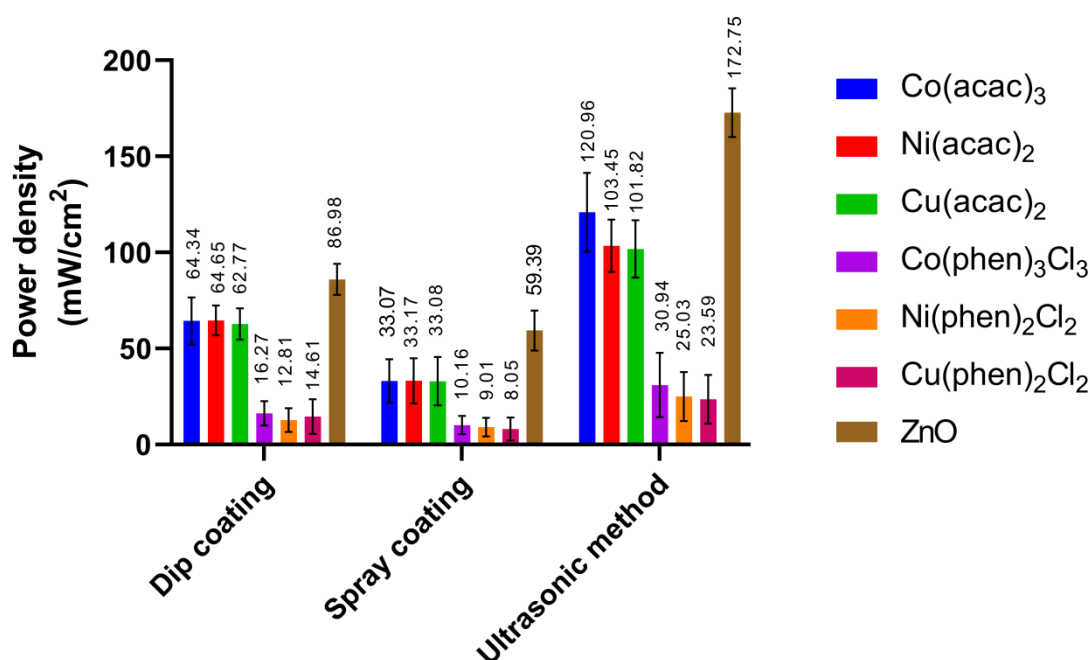


Figure 4.18: Power generation (mW/cm²) of photocatalysts with different coating method

From the graph (Figure 4.18), ultrasonic method showed a superb efficiency while spray coating was the least efficient coating method. The efficiency of coating method arranged from highest to lowest was ultrasonic coating, dip coating, spray coating.

Photocatalytic chemical reactions are initiated on the surface of photocatalyst to produce photo-generated electrons and holes on the surface. Therefore, the surface properties of the photocatalyst dominates the efficiency of electron-hole pairs generation (Yu *et al.*, 2000). Coating method is one of the ways to control the surface properties of

photocatalyst. Uniformity, thickness of coated photocatalyst, as well as adhesion and stability play crucial roles in determining the efficiency of photocatalytic reaction. A uniform coating not only increases the surface area to provide more active sites but also ensures the entire surface is exposed to light, maximizing photon absorption for the reaction. Meanwhile, the thickness of photocatalyst layer can affect the light penetration and electron diffusion, thereby influencing the reaction rates. According to Ghemid *et al.* (2021) and Ibrahim *et al.* (2022), the photocatalytic efficiency of photocatalyst is linearly proportional to the thickness of the coated photocatalyst because it can affect the generation and transportation of charge carriers. Besides that, the adhesion of photocatalyst determines the durability of photocatalyst on the substrate. The strong adhesion between photocatalyst and substrate is favoured to ensure the lifespan of the photocatalyst on the photoanode and better photocatalytic performance can be achieved. Poor adhesion between photocatalyst and substrate can lead to delamination of photocatalyst over time, reducing its effectiveness. Proper adhesion guarantees the continuous light exposure to the photocatalyst and enhancing overall performance. The SEM images of ZnO and the acac ligand-based photocatalysts are shown in Figure 4.19. Figure 4.20 demonstrates SEM images of phen ligand-based photocatalysts prepared using different coating methods.

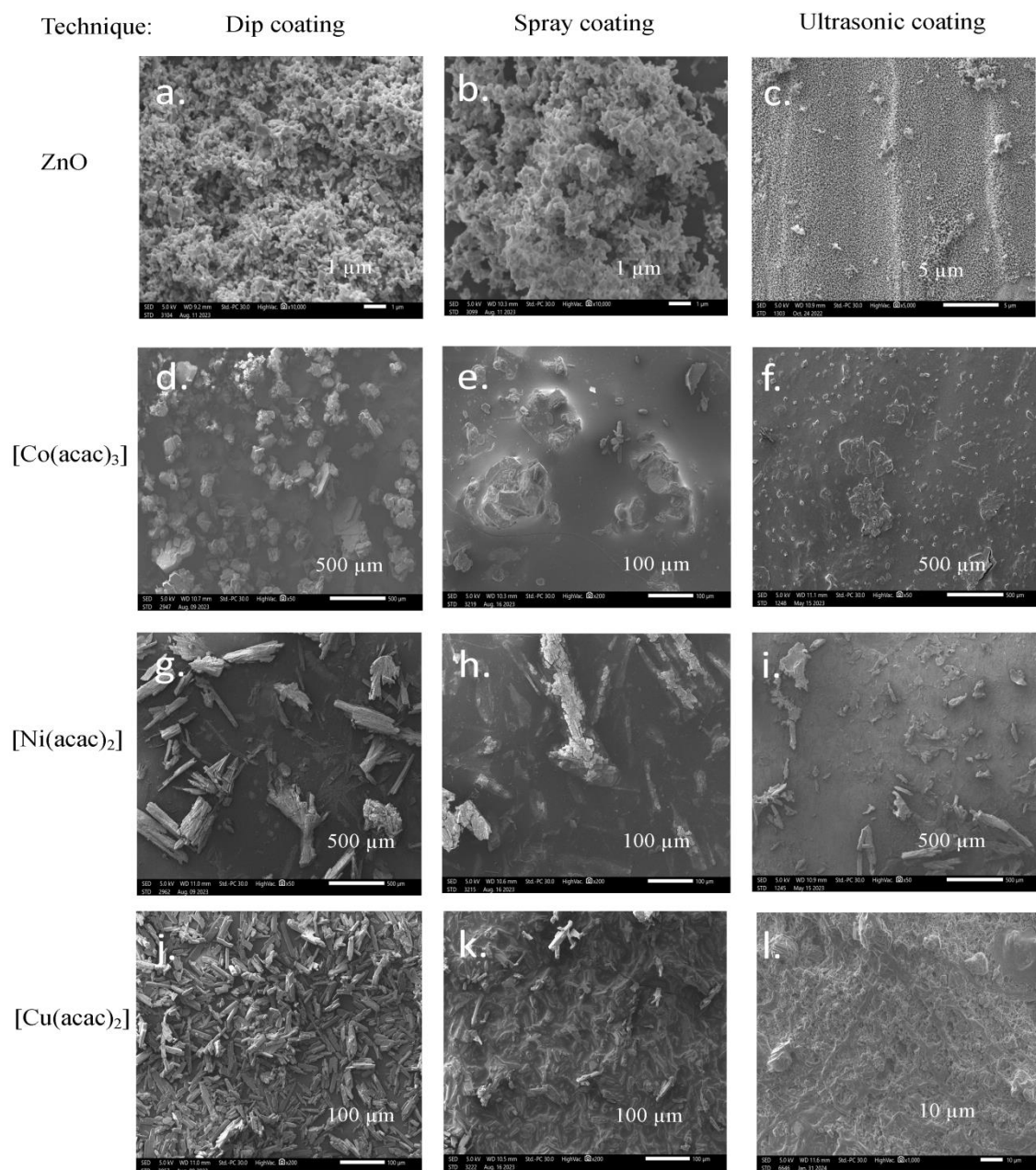


Figure 4.19: SEM images of acac ligand-based complexes as photocatalysts with different coating methods under different magnification.

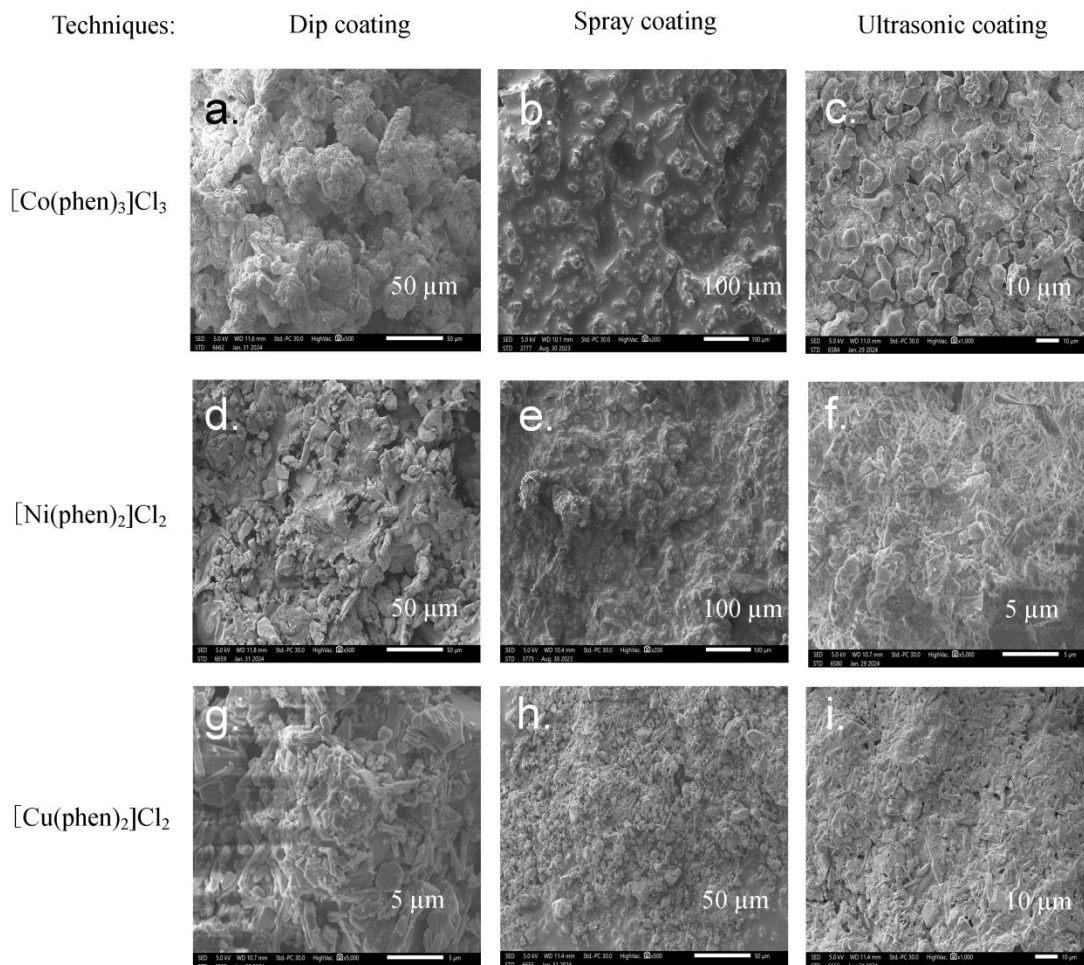


Figure 4.20: SEM images of phen ligand-based complexes as photocatalysts prepared via different coating methods under different magnification.

Overall, the particle size of ZnO (Figure 4.19a-c) was smallest (1 – 5 μm) compared to others. The smaller particle size usually indicate higher surface area to volume ratio compared to larger particles (Rose *et al.*, 2022; Princy *et al.*, 2023). The increased surface area provides more active sites for photocatalytic reaction to occur, leading to higher catalytic activity. The larger particles with fewer active sites tend to suffer from limited light adsorption and activation of reactant molecules. Moreover, smaller particles might exhibit shorter charge carrier diffusion lengths and faster charge separation rates (Wheeler *et al.*, 2012; Vithanage *et al.*, 2013). The shorter diffusion length ensure the charge carriers could reach the surface quickly, enhancing the kinetics of

surface-mediated reactions. This efficient charge carrier transport to the particle surface facilitated rapid redox reactions, enhancing photocatalytic activity. According to Kajitvichyanukul and Pongpom (2005), the photocatalytic efficiency decreases with the increase of photocatalyst size. In their work, TiO_2 thin film was prepared on soda lime glass using acetylacetone as TiO_2 stabilizer to improve the quality of the film. They reported that larger nanoparticle size of TiO_2 decrease the photocatalytic activity of TiO_2 nanoparticles.

The acac ligand-based complexes are discussed due to their slightly higher efficiency than phen ligand-based complexes in terms of power generation (Figure 4.18). In dip coating, this process resulted in relatively large particles for $[\text{Co}(\text{acac})_3]$ and $[\text{Ni}(\text{acac})_2]$ (500 μm), while $[\text{Cu}(\text{acac})_2]$ produced smaller particles (100 μm). The dip coating method often leads to larger particle sizes due to slower solvent evaporation, which can promote particle aggregation and decrease the overall surface area. Surprisingly, despite the relatively large particle size of $[\text{Co}(\text{acac})_3]$ and $[\text{Ni}(\text{acac})_2]$ (500 μm) produced under ultrasonic method, their photocatalytic performance still showed better results compared to those dip coating and spray coating acac ligand-based complexes photocatalysts (Figure 4.18). This could be due to the uniform distribution of particles, which contributes to a consistent surface morphology and facilitates better charge transport. Conversely, spray coating produces smaller particles (100 μm) for all acac ligand-based complexes, as fast solvent evaporation effectively prevents aggregation and ensures effective surface area for light absorption. However, dip coating acac ligand-based complexes photocatalysts showed the least photocatalytic efficiency. This could be attributed to the less uniform or uneven particle distribution compared to ultrasonic method. The inconsistency in particle morphology can negatively impact charge transfer rates, and

consequently, photocatalytic activity. This illustrates the importance of selecting an appropriate coating method to optimize the photocatalyst used for photocatalytic applications.

Among the three coating methods, ultrasonic method (Figures 4.19 c, f, i, l) (Figures 4.20 c, f, j) gave the most uniform photoanode coating. Ultrasonication creates cavitation force (Tudela *et al.*, 2015) that disperses the photocatalyst particles uniformly (Chen *et al.*, 2022) and forms relatively strong adhesive bond with the substrate (Heidarian *et al.*, 2010; Lu, 2010). The neat and even coating ensures the photocatalyst can absorb sunlight better. It has been found that ultrasonic method can minimize formation of agglomerates which could reduce the effective surface area for photocatalytic reaction (Pellegrino *et al.*, 2017). The size of agglomerate formed in dip coating and powder spray coating was larger than that of ultrasonic coating method. Besides that, the thin coating allows more light to reach the active sites within the material, potentially increasing photocatalytic activity. To the contrary, a thick layer not only limits the light penetration but also impede the diffusion rate of reactants to the active site and resulted a decrease of efficiency (Chen *et al.*, 2000; Kumari *et al.*, 2021; Heredia Deba *et al.*, 2023). In other words, thin coating smooths the charge carrier diffusion to the surface hence minimizing recombination losses.

Sol-gel dip coating method involves immersion of substrate into a sol-gel solution containing the photocatalyst, followed by drying and annealing to form the coating. The slightly lower photocatalytic performance of the coated dip coating photocatalyst could be ascribed to the potential issues with coating uniformity and thickness. The slow solvent evaporation allows more time for particles aggregation during the film formation process. Viscosity, dip and withdraw speed, and drying condition are the uncertainties to affect the

coating quality (Strobel *et al.*, 2011; Motealleh *et al.*, 2016; Tang & Yan, 2017). Unsuitable condition can result to uneven coating and low porosity structure (Pontin *et al.*, 2005; Alias *et al.*, 2018). Non-uniform coating distribution and low porosity has limited the accessibility of photocatalysts' active site, hence reducing overall efficiency. Inappropriate drying temperature also can cause film to crack and reduced the film porosity (Chen *et al.*, 2017). The film with reduced porosity makes it difficult for pollutant to diffuse to the active sites of the photocatalyst. In another words, the porosity determined the availability of surface area for interaction with pollutants.

The spray coating method with polyurethane as the adhesive agent showed the lowest photocatalytic activity among the three coating methods. Spray coating process disperses the photocatalyst particles in a carrier fluid before being deposited onto the substrate surface. In this case, the adhesive properties of polyurethane might not provide sufficient bonding strength, leading to the detachment of photocatalyst particles and decreased the stability during photocatalytic reaction. From Figures 4.19 (b, e, h, k) and Figures 4.20 (b, e, h), it was observed that photocatalyst particles was covered by a smooth layer, possibly polyurethane. This might hinder the active sites and reduced the exposure of photocatalyst to pollutants or water to form radicals thus lower down the PFC performance. The polyurethane layer with unevenly sprayed photocatalyst on the substrate might create areas of low photocatalytic activity.

As a whole, the particle size of acac ligand-based complexes (10 – 500 μm) is larger than that of phen ligand-based complexes (5 – 100 μm) (Figure 4.19 – Figure 4.20). This difference could result from the molecular structures of the ligands. Although both acac and phen are bidentate ligands, phen, with its bulkier structure compared to acac, imposes steric hindrance and prevent aggregation, leading to smaller particle size

compared to acac ligand-based complexes during deposition. The observed particle sizes correlate with the photocatalytic efficiency, as smaller particle size photocatalysts (ZnO) is more efficient than larger particle size photocatalysts in photocatalysis, with smaller particles offer more active sites, thereby improving overall performance.

To summarize, the variation of photocatalytic activity among different coating methods can be attributed to differences in coating uniformity, coating thickness, adhesion strength, particles dispersion, surface area and accessibility of active sites. Ultrasonic coating yielded the highest activity due to its ability to produce uniform coatings with strong adhesion, while dip coating method suffered from uniformity problem and lastly spray coating method utilizing polyurethane having challenges in achieving uniform coverage and maintaining strong adhesion for photocatalyst particles.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The objectives of this study were all achieved. The PFC was successfully upgraded from a single-chamber configuration to a dual-chamber configuration, enhancing the photocatalytic activity. The separation of the photoanode and cathode in DCPFC not only slowed down the recombination of electron-hole pairs but also maximized the reactions for radical formation in the respective chambers without compromising one for the other. Both ZnO/Zn SCPFC system and ZnO/Zn DCPFC system were fabricated. It was concluded the DCPFC was more efficient than SCPFC. The DCPFC successfully generated a maximum power density of 132.83 mW/cm^2 and completely degraded 10 ppm synthetic methyl red dye, outperforming the SCPFC with the maximum power density of 60.11 mW/cm^2 and dye degradation efficiency of 18.93 %. This higher power density of DCPFC was due to its' high electromotive force (1410.50 V) compared to SCPFC (803.01 V).

The operational conditions study of DCPFC was determined for optimal power degradation and dye generation. The optimal conditions for DCPFC were 5 hours contact time, 10 ppm initial methyl red dye concentration and pH 3 dye solution. The highest power density of 172.75 mW/cm^2 was obtained at pH 3 dye solution. The better photocatalytic performance of the DCPFC at pH 3 dye solution was due to the high concentration of H^+ ions which facilitated charge transfer and improved photocatalytic performance. This emphasizes the importance of pH control in optimizing the DCPFC for

both power generation and dye degradation. The optimal conditions then used to assess the photocatalytic activity of the synthesized metal complexes.

The complexes $[\text{Co}(\text{acac})_3]$, $[\text{Ni}(\text{acac})_2]$, $[\text{Cu}(\text{acac})_2]$, $[\text{Co}(\text{phen})_3]\text{Cl}_3$, $[\text{Ni}(\text{phen})_2]\text{Cl}_2$, and $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ were successfully synthesized and used as photocatalysts in the DCPFC under the optimized conditions. The phen ligand-based complexes generally showed lower power generation and dye degradation than the acac ligand-based complexes. The calculated bandgaps of all the synthesized complexes were lower than that of ZnO (3.5 eV): $[\text{Ni}(\text{acac})_2]$ (2.83 eV) < $[\text{Co}(\text{acac})_3]$ (2.9 eV) < $[\text{Cu}(\text{acac})_2]$ (2.94 eV) < $[\text{Ni}(\text{phen})_2]\text{Cl}_2$ (3.2 eV) < $[\text{Co}(\text{phen})_2]\text{Cl}_2$ (3.25 eV) < $[\text{Cu}(\text{phen})_2]\text{Cl}_2$ (3.4 eV). The smaller bandgaps of acac ligand-based complexes compared to phen ligand-based complexes was attributed to the π -donor nature of acac ligand, which facilitates electron delocalization and reduces the energy required for electron excitation. Despite the smaller bandgaps of the acac ligand-based and phen ligand-based complexes compared to ZnO, the acac ligand-based photocatalyst and phen ligand-based photocatalyst were found to be less efficient than ZnO photocatalyst in terms of power generation and dye degradation. The $[\text{Co}(\text{acac})_3]$ is a potential photocatalyst candidate but does not outperform ZnO as it generated a lower power density of 120.96 mW/cm². The low chemical stability of acac ligand-based and phen ligand-based complexes as photocatalysts was the main reason for the low photocatalytic performance even they had smaller bandgaps compared to ZnO photocatalyst.

Last but not least, ultrasonic coating method was the most effective coating method compared to dip coating and spray coating method based on the highest power density generated by the ultrasonic ZnO/Zn PFC system. SEM images showed that the ultrasonication method produced the more uniform and even coating of the photocatalyst.

The even distribution of the photocatalyst not only improved surface coverage but also enhanced charge separation efficiency, contributing to better photocatalytic performance. In contrast, dip and spray coating methods often resulted in uneven particle distribution, leading to higher recombination rates of electron-hole pairs, which hindered their performance. It can be concluded that the ligand influences the bandgap of metal complexes and the coating method for photocatalyst can affect the efficiency of PFC system.

5.2 Recommendations

This study focused on evaluating the efficiency of PFC with different setups and the possibility of utilizing transition metal complexes as photocatalyst, for dye degradation. There are many missing points in this project. A few recommendations are given to improve the future DCPFC study.

The first part of this project was the comparison between SCPFC and DCPFC on the power generation and pollutant degradation. A new DCPFC without salt bridge can be set up to reduce the internal resistance and potentially increase power generation. Additionally, a new membrane material could be developed to enhance the exchange between anode and cathode.

Next, different types of oxidizing agent can be used in future DCPFC study. To the best of our knowledge, the study of the effect of using different oxidants in PFC setup is only carried out in SCPFC. Future DCPFC study could include different types of oxidizing agents such as hydrogen peroxide, potassium permanganate, potassium persulphate,

potassium dichromate and peroxymonosulphuric acid to evaluate their impact on power generation and pollutant degradation.

Based on literature, transition metal complexes easily degrade under harsh environment. Therefore, transition metal oxides are recommended as photocatalyst candidate than transition metal complexes as the metal oxide has anti-corrosion properties. However, it is possible to optimize transition metal complexes to improve their stability. This could be done through the encapsulation of complexes with protective layers, such as silica or polymer coating, to shield them from degradation while maintaining their catalytic activity.

Additionally, different coating methods for photocatalysts need to be explored to improve their stability and enhance their efficiency as photocatalyst in DCPFC. While ultrasonic coating was effective for ZnO/Zn systems in this study, alternative methods such as electrochemical deposition or chemical vapor deposition (CVD) could provide more uniform and stable coatings. Each of these methods offers advantages in terms of producing uniform, stable coatings that could better withstand prolonged use in DCPFC.

Last but not least, further optimization of operating conditions, including pH, temperature, and light intensity, could lead to improved photocatalytic performance. Testing metal complexes under a variety of conditions will help determine the most favorable environment for maximum pollutant degradation and energy generation. By focusing on these areas, future studies could significantly improve the performance of DCPFC and enhance the potential of transition metal complexes as photocatalysts in PFC.

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APPENDICES

Appendix A: Journal Publications

1. Niang, A. C. K., 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, 1-7.

<https://doi.org/10.1002/admi.202202366>

Appendix B: NMEA data

Appendix B1: Power density from SCPFC and DCPFC using ZnO photocatalyst with ultrasonic method and 10 ppm methyl red dye solution at pH 4 as model pollutant.

Contact time (h)	Power density (mW/cm ²)		Degradation efficiency (%)	
	SCPFC	DCPFC	SCPFC	DCPFC
0h	7.10	58.91	0	0
1h	22.48	74.07	4.30	21.83
2h	28.36	104.00	9.87	45.05
3h	44.75	126.13	12.49	71.65
4h	60.11	132.83	16.36	84.23
5h	10.30	93.90	18.93	100

Appendix B2: Power density from SCPFC and DCPFC using ZnO photocatalyst with ultrasonic method and different concentration (5 ppm, 10 ppm, 20 ppm) methyl red dye solution at pH 4 as model pollutant.

Concentration (ppm)	Power density (mW/cm ²)		Degradation efficiency (%)	
	SCPFC	DCPFC	SCPFC	DCPFC
5	33.59	61.59	23.24	100
10	60.11	132.83	18.93	100
20	24.07	72.38	12.66	97.53

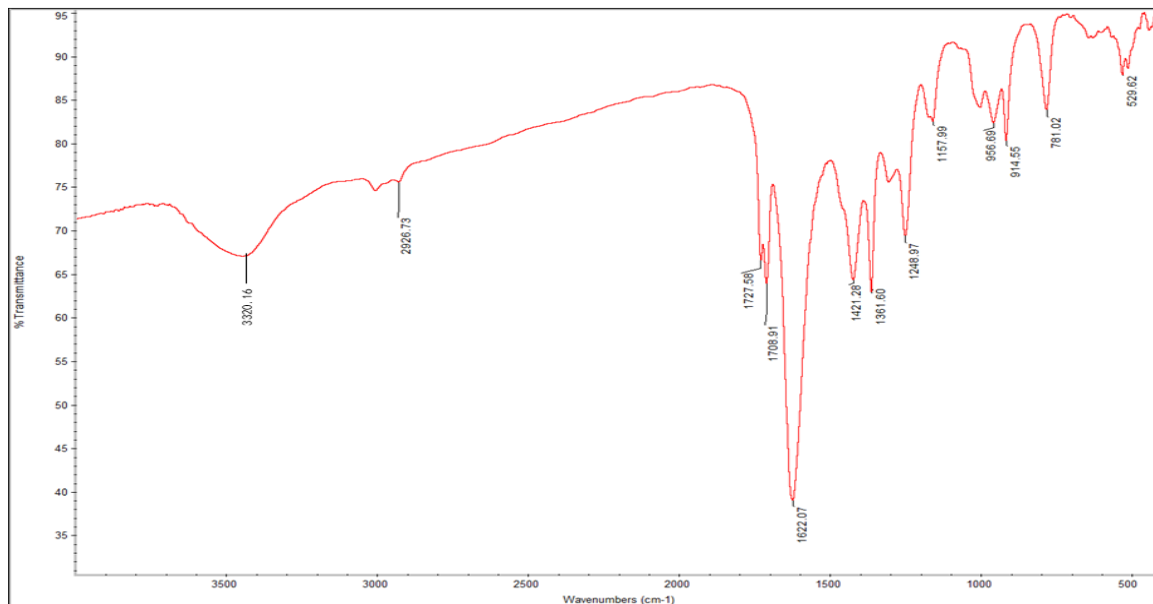
Appendix B3: Power density from SCPFC and DCPFC using ZnO photocatalyst with ultrasonic method and 10 ppm methyl red dye solution at different pH (pH 3, pH4, pH 5) as model pollutant.

pH	Power density (mW/cm ²)		Degradation efficiency (%)	
	SCPFC	DCPFC	SCPFC	DCPFC
3	74.13	172.75	63.21	100
4	60.11	132.86	18.93	100
5	50.93	104.08	8.89	100

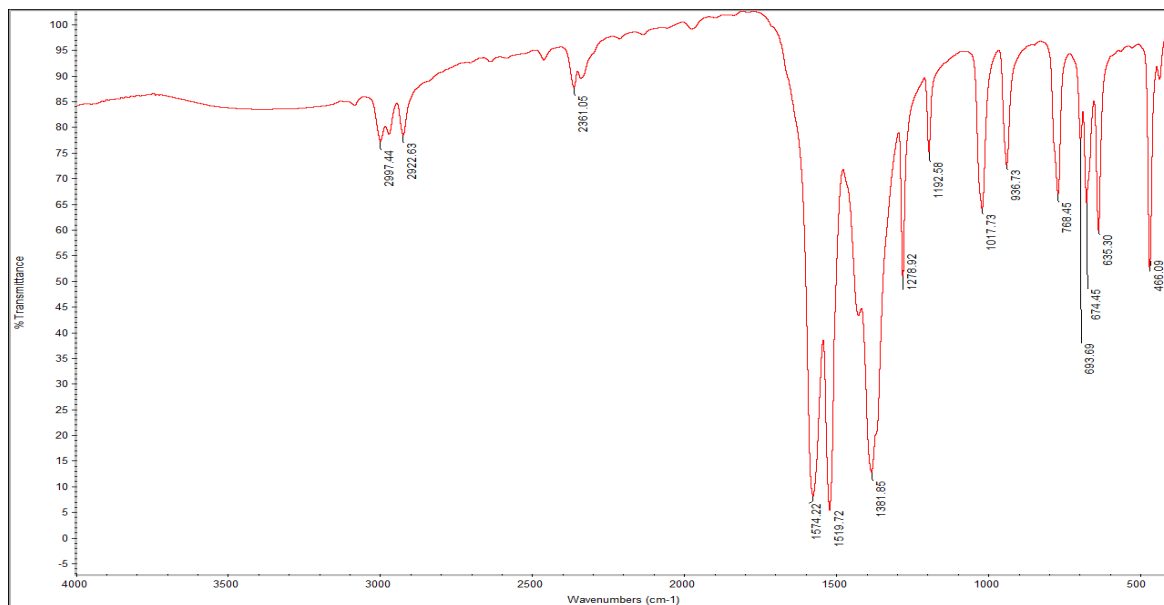
Appendix B4: Reusability test for SCPFC and DCPFC using ZnO photocatalyst with ultrasonic method and 10 ppm methyl red dye solution at pH 3 as model pollutant.

Cycle	Power density efficiency loss (%)		Degradation efficiency (%)	
	SCPFC	DCPFC	SCPFC	DCPFC
1	0	0	663.21	100
2	69.15	55.85	13.88	69.45
3	100	89.18	0	30.17
4	100	100	0	0
5	100	100	0	0

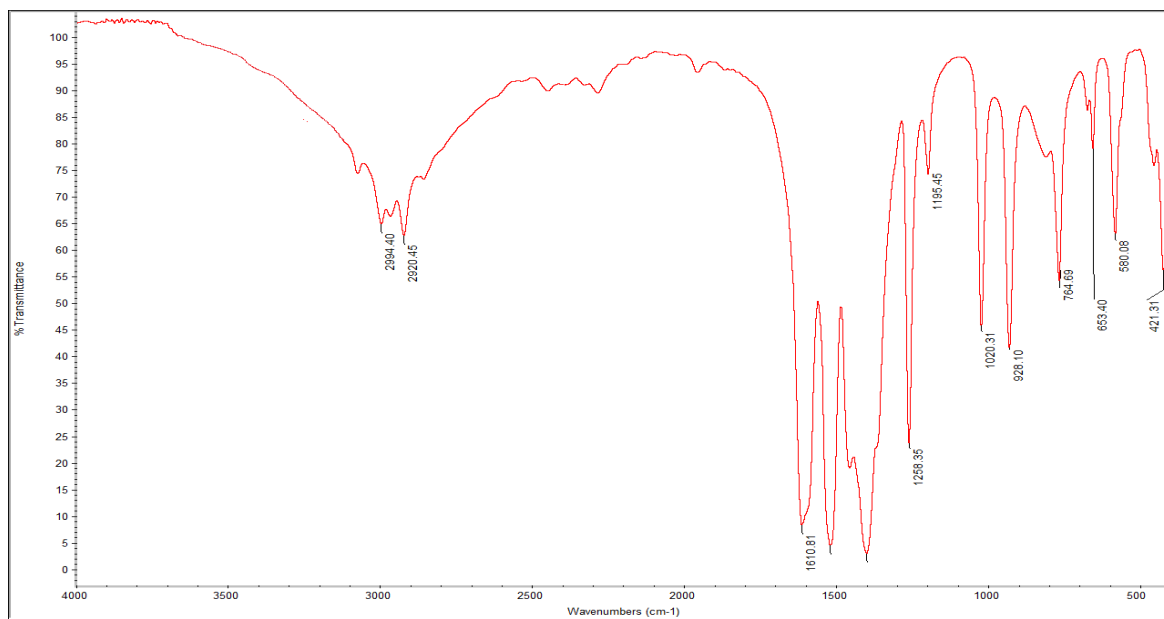
Appendix B5: IR spectrum of acac



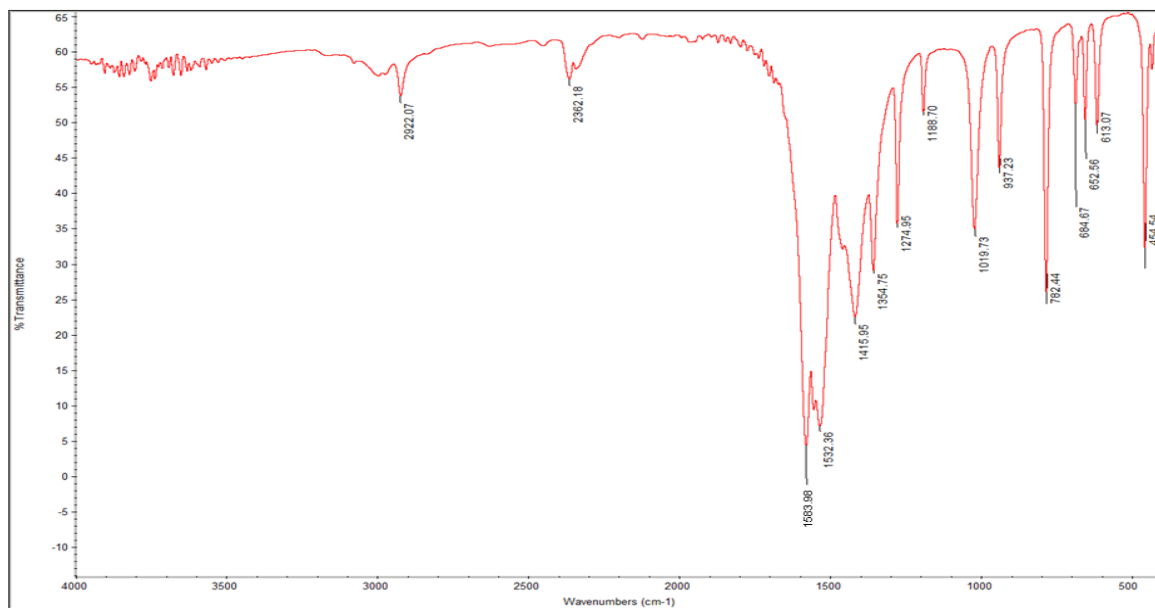
Appendix B6: IR spectrum of [Co(acac)₃]



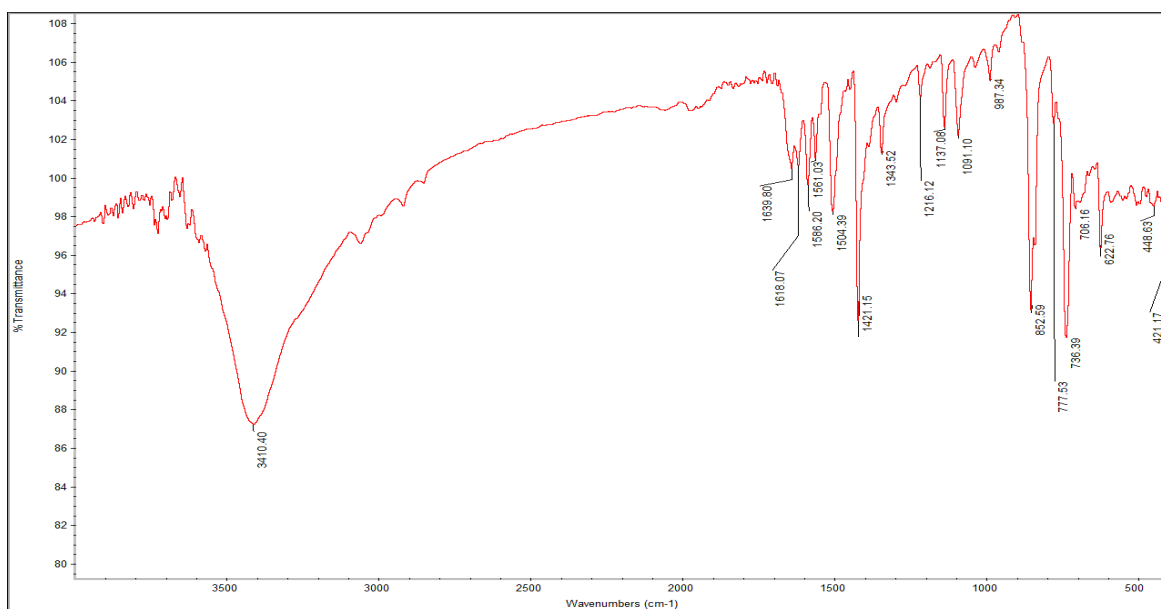
Appendix B7: IR spectrum of [Ni(acac)₂]



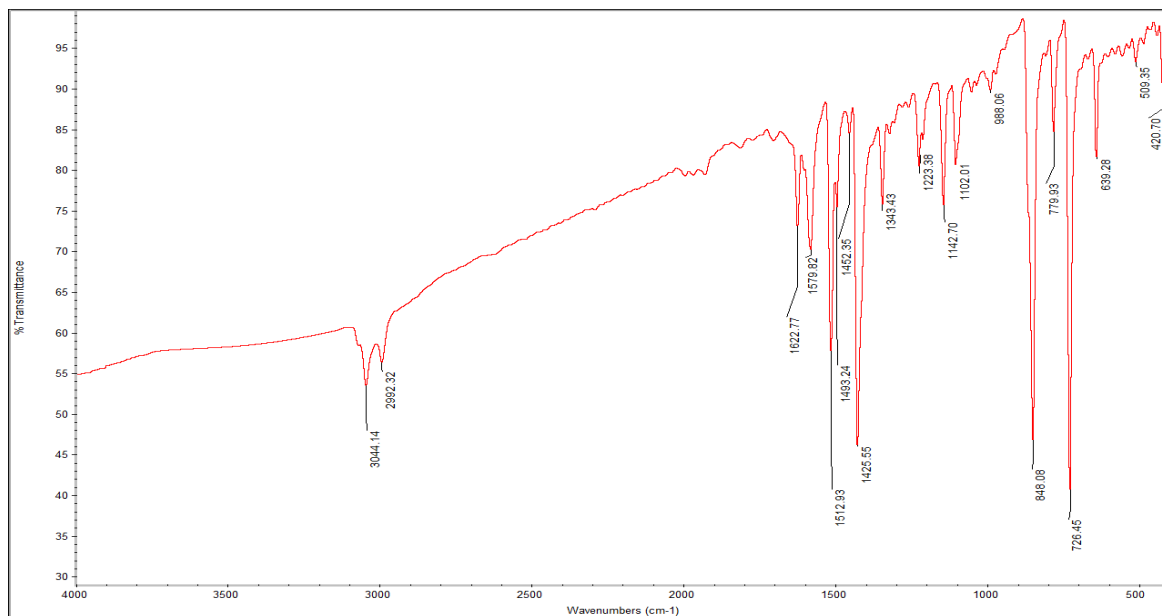
Appendix B8: IR spectrum of [Cu(acac)₂]



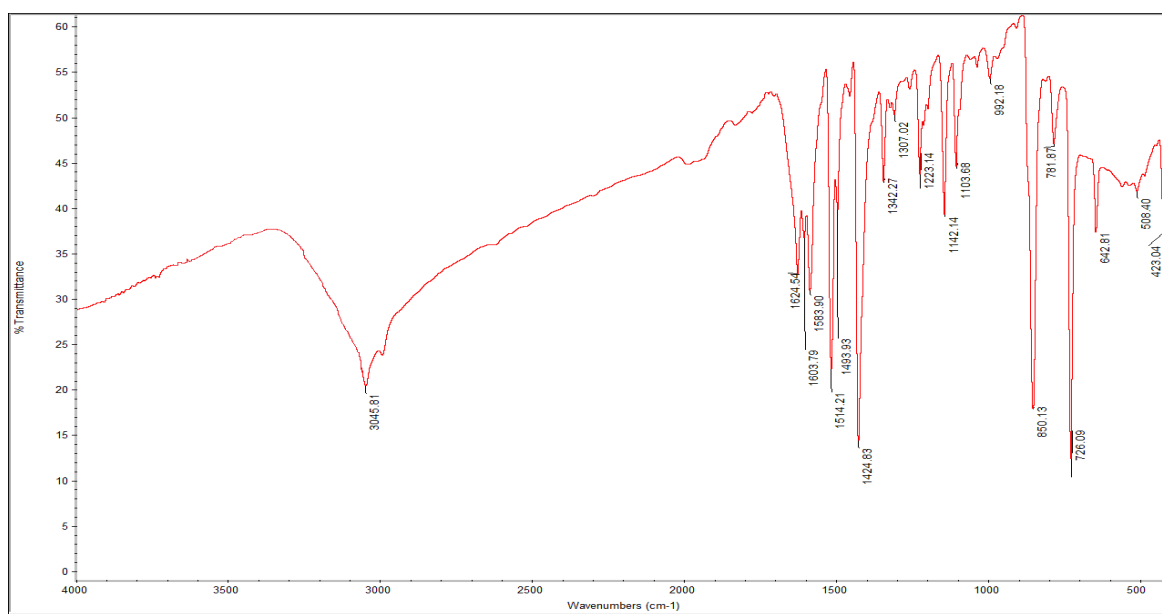
Appendix B9: IR spectrum of phen



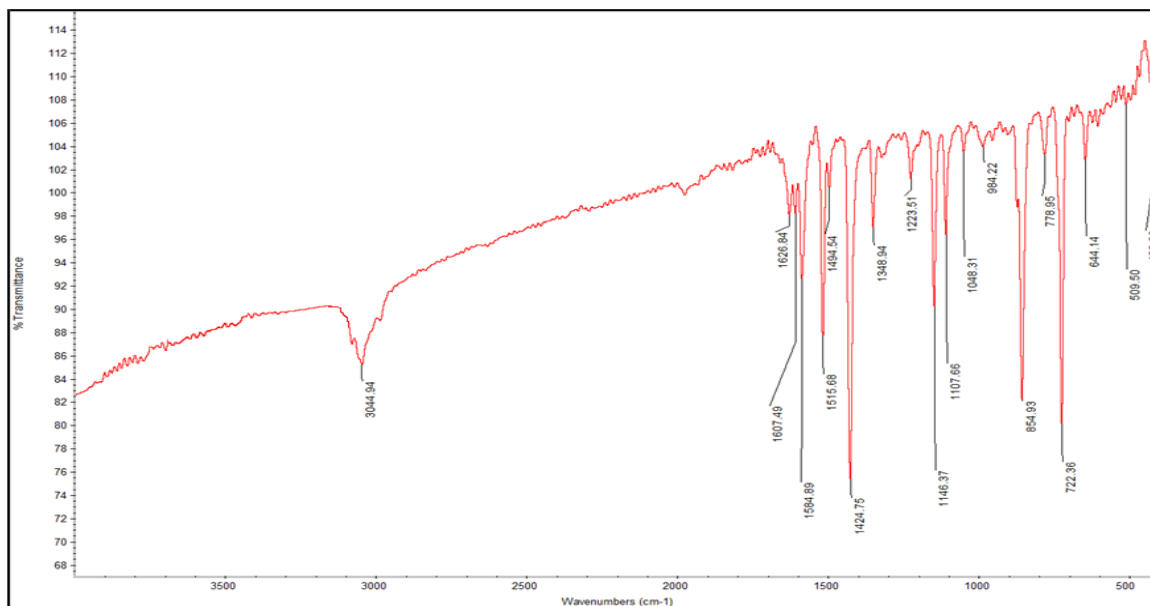
Appendix B10: IR spectrum of $[\text{Co}(\text{phen})_3]\text{Cl}_3$



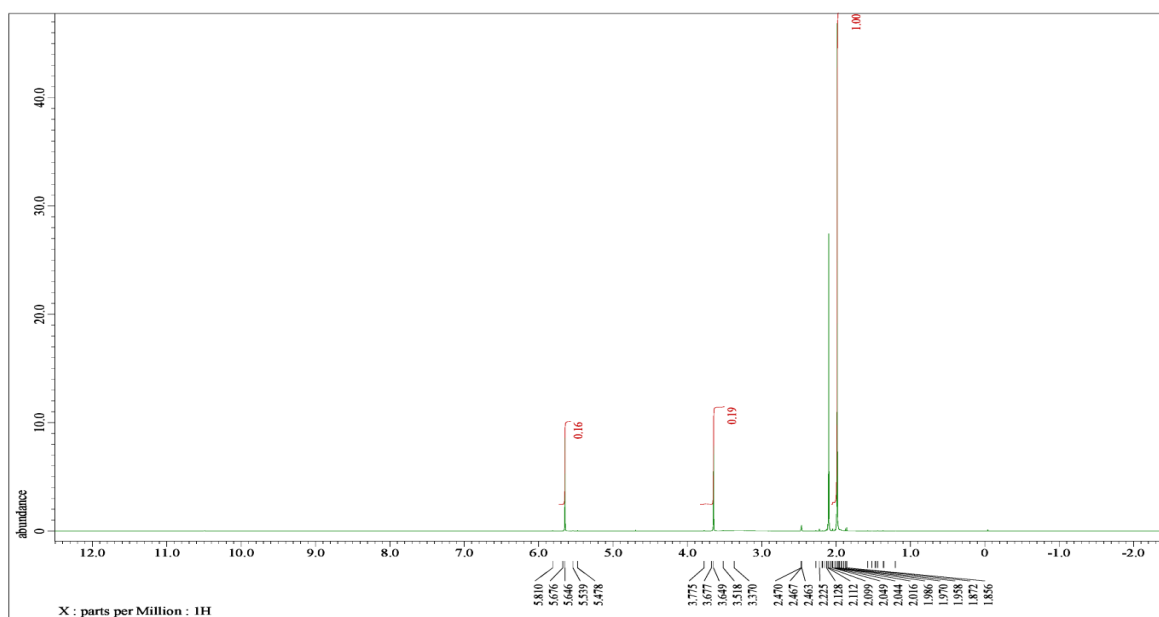
Appendix B11: IR spectrum of $[\text{Ni}(\text{phen})_2]\text{Cl}_2$



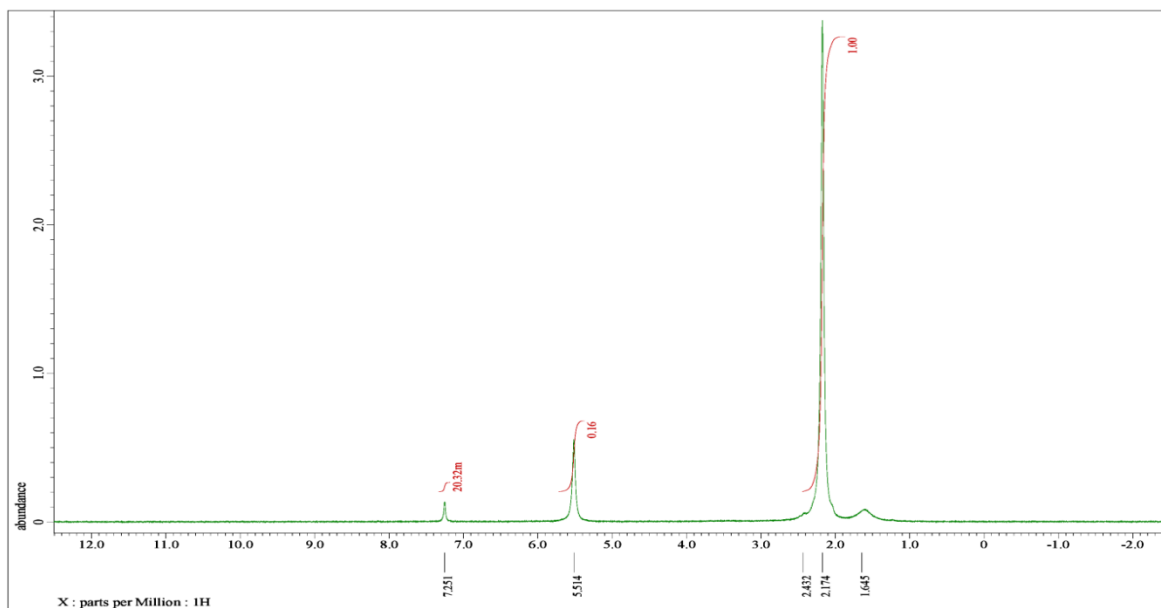
Appendix B12: IR spectrum of $[\text{Cu}(\text{phen})_2]\text{Cl}_2$



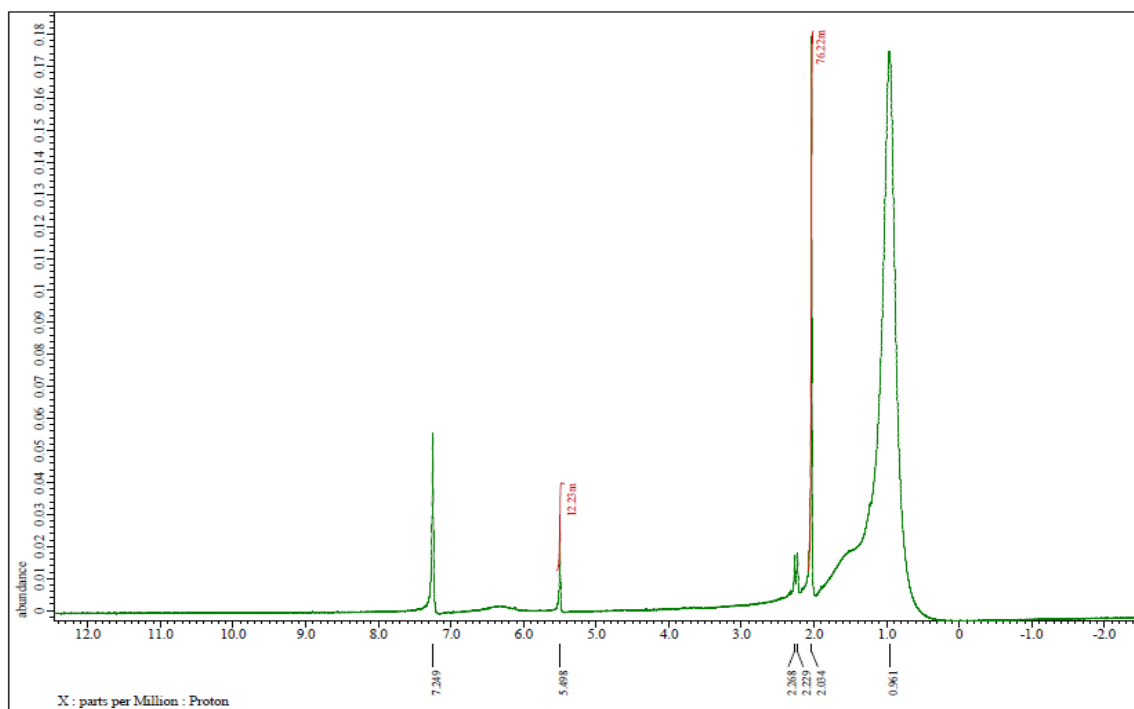
Appendix B13: ^1H NMR spectrum of acac



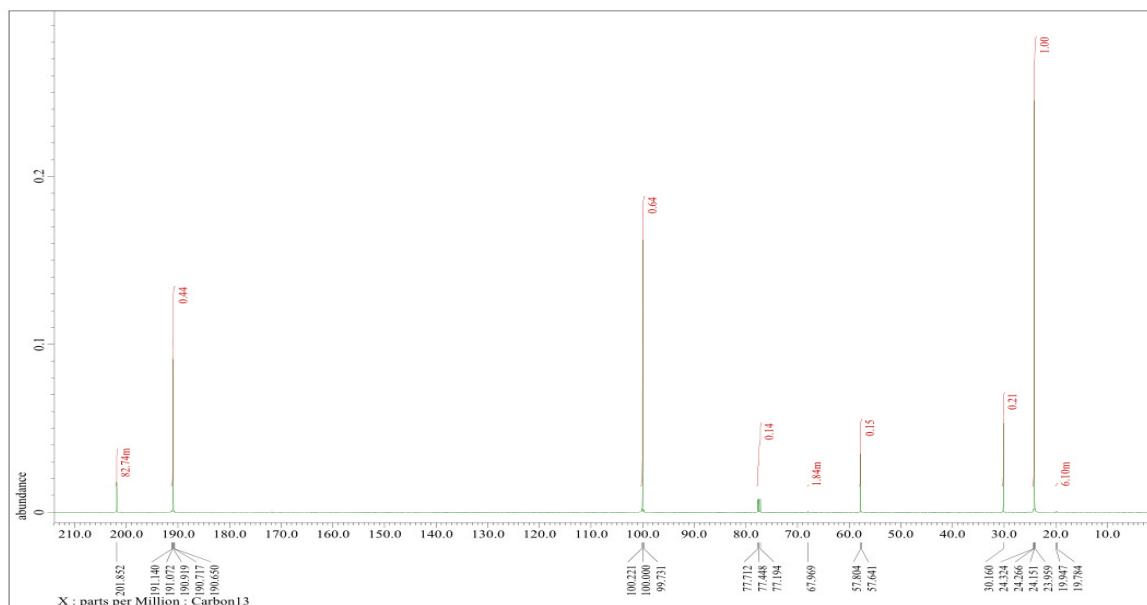
Appendix B14: ^1H NMR spectrum of $[\text{Co}(\text{acac})_3]$



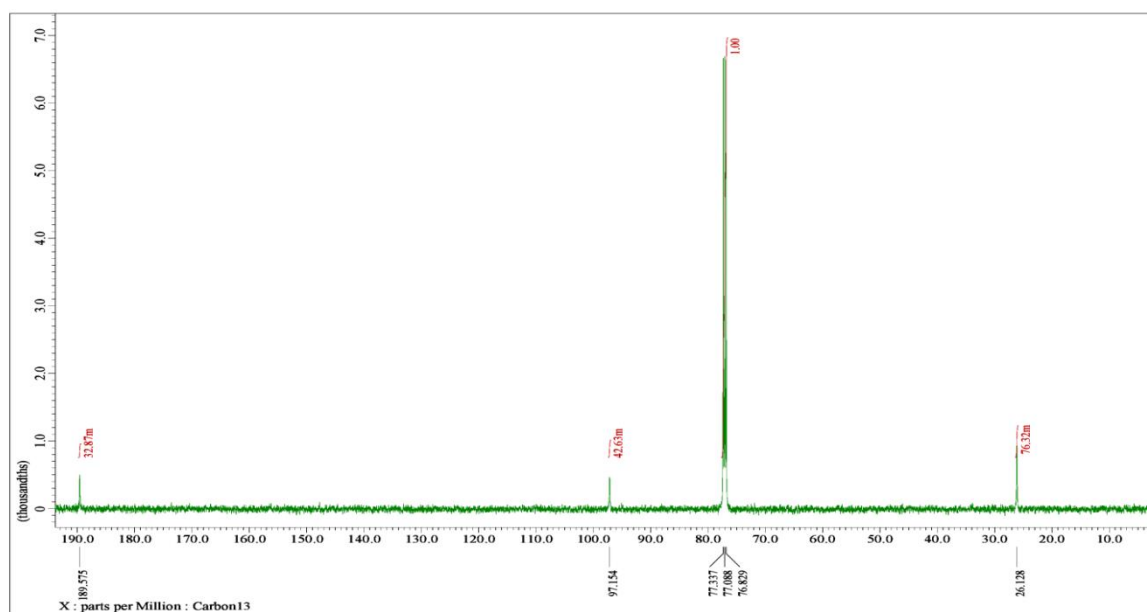
Appendix B15: ^1H NMR spectrum of $[\text{Ni}(\text{acac})_2]$



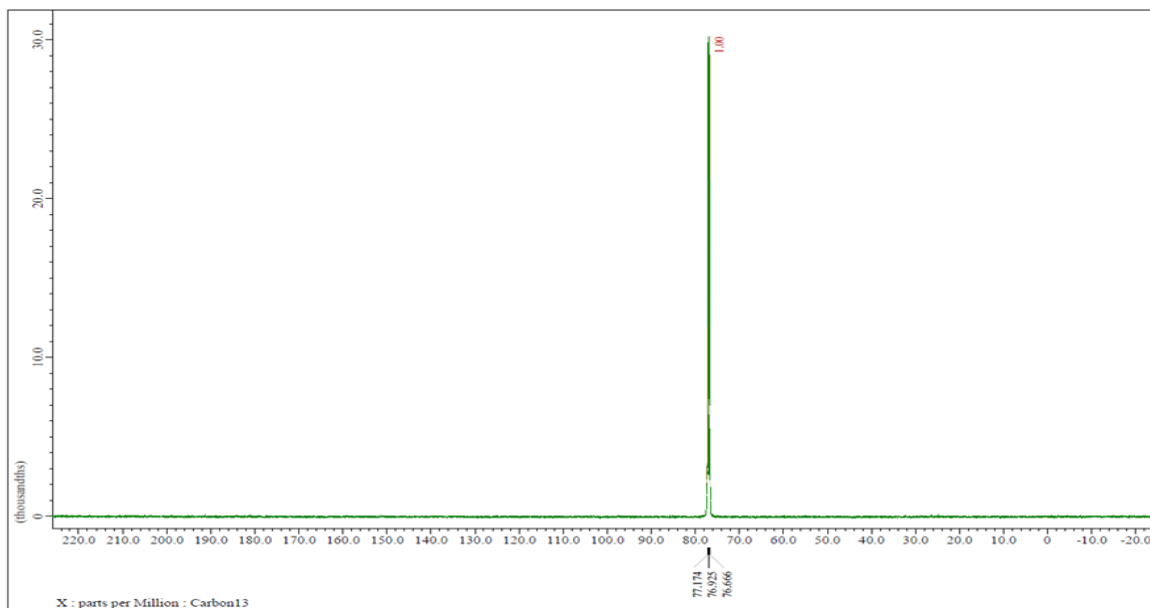
Appendix B16: ^{13}C NMR spectrum of acac



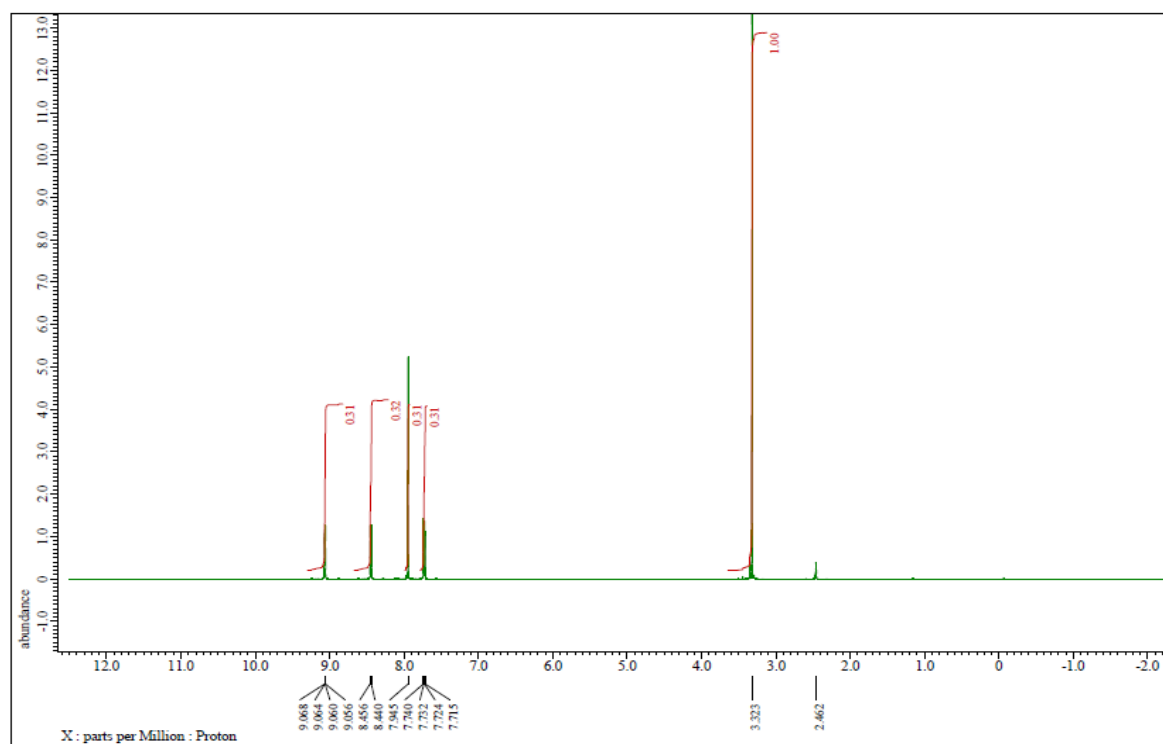
Appendix B17: ^{13}C NMR spectrum of $[\text{Co}(\text{acac})_3]$



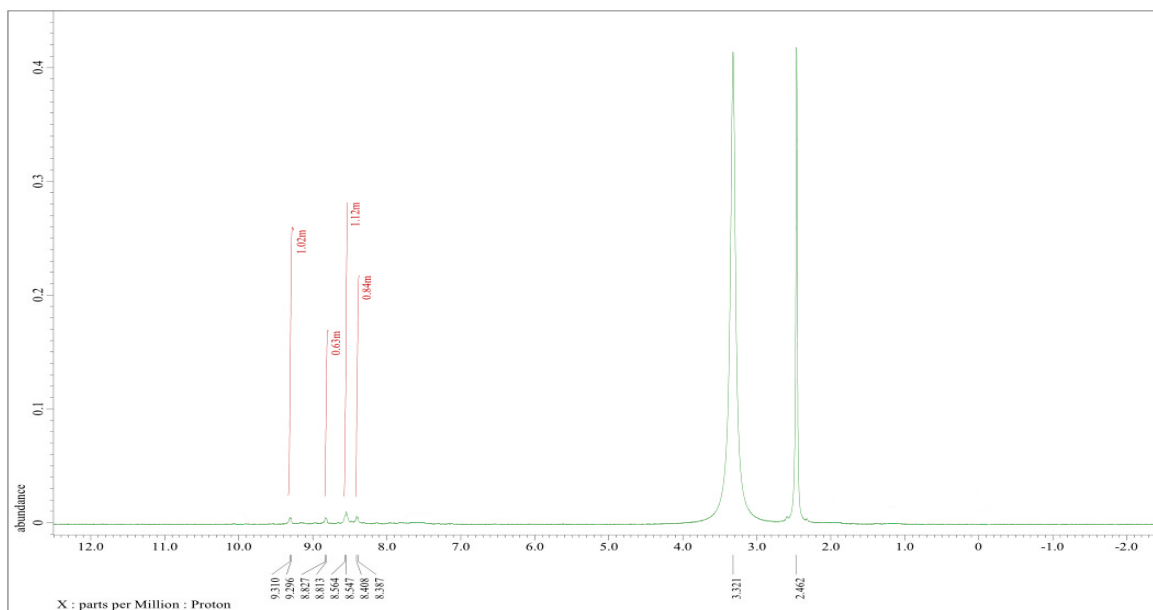
Appendix B18: ^{13}C NMR spectrum of $[\text{Ni}(\text{acac})_2]$



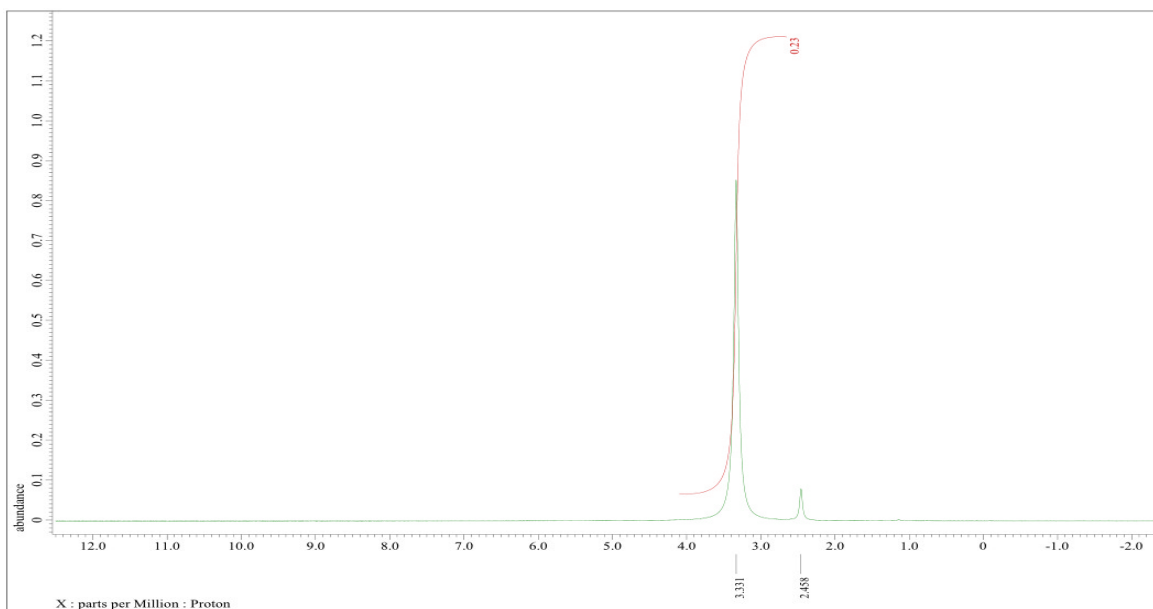
Appendix B19: ^1H NMR spectrum of phen



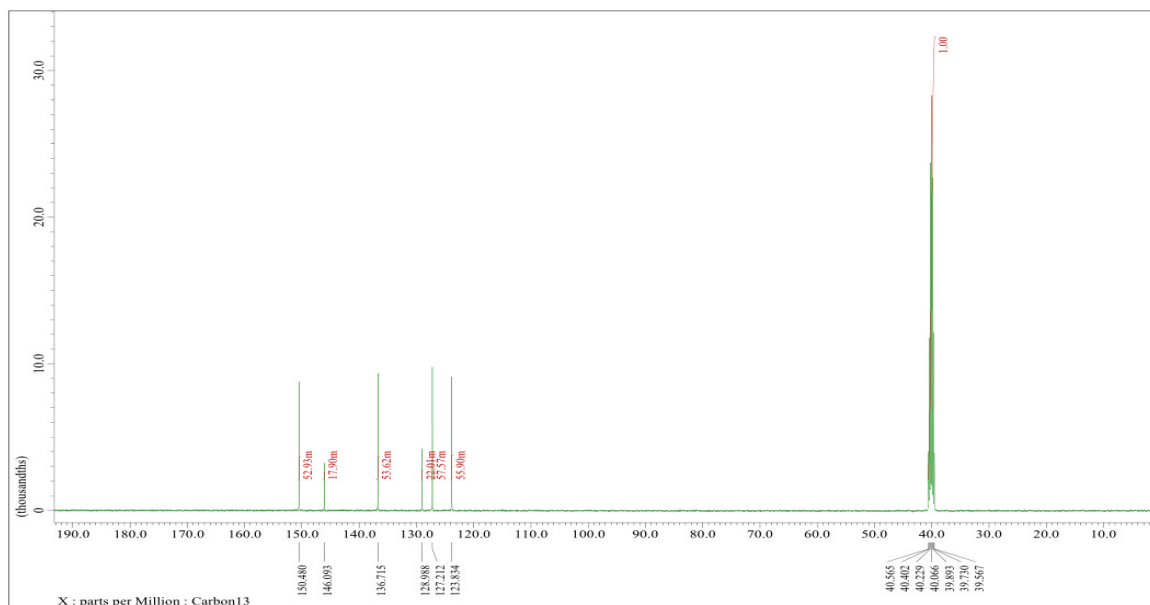
Appendix B20: ^1H NMR spectrum of $[\text{Co}(\text{phen})_3]\text{Cl}_3$



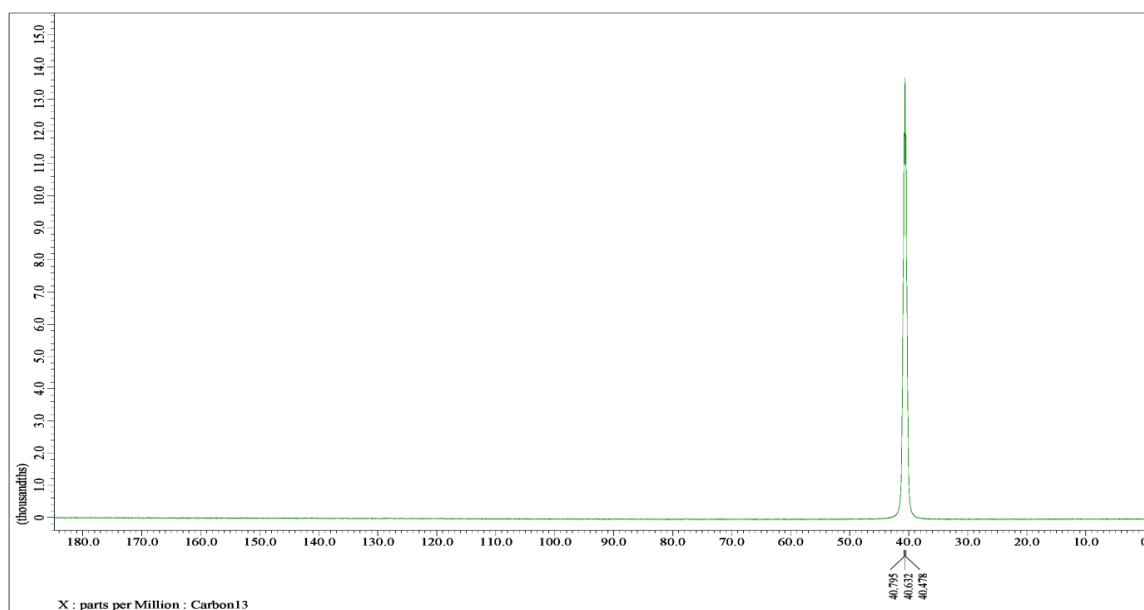
Appendix B21: ^1H NMR spectrum of $[\text{Ni}(\text{phen})_2]\text{Cl}_2$



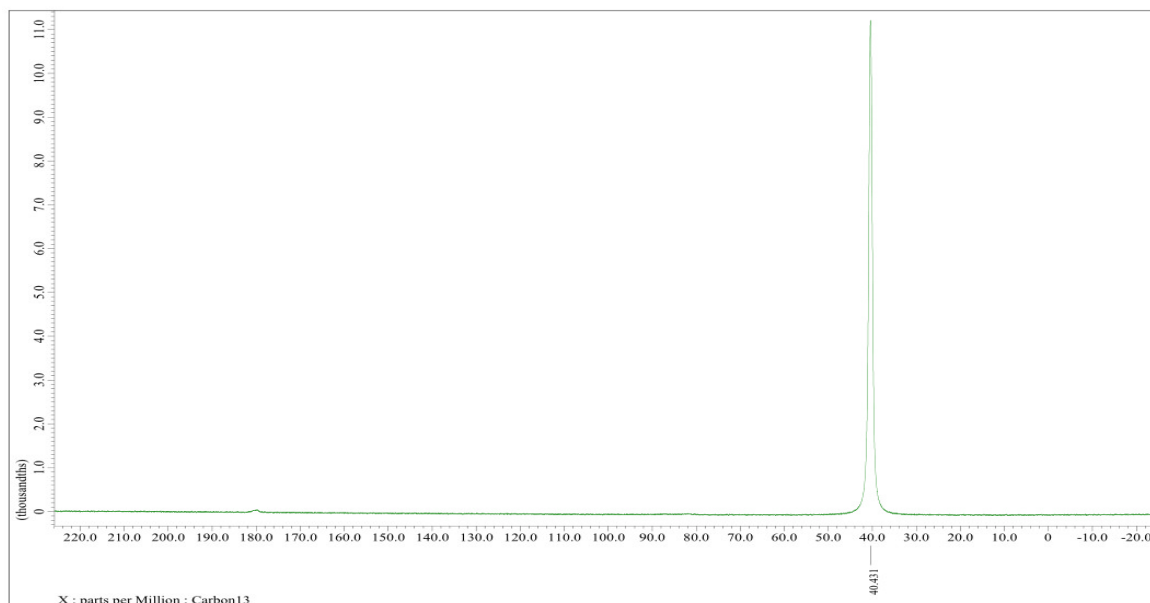
Appendix B22: ^{13}C NMR spectrum of phen



Appendix B23: ^{13}C NMR spectrum of $[\text{Co}(\text{phen})_3]\text{Cl}_3$



Appendix B24: ^{13}C NMR spectrum of $[\text{Ni}(\text{phen})_2]\text{Cl}_2$



Appendix B25: Power density of different photocatalysts with ultrasonic method and 10 ppm methyl red dye solution at pH 3 as model pollutant.

Photocatalysts	Power density (mW/cm^2)	Degradation efficiency (%)
ZnO	172.75	100
$[\text{Co}(\text{acac})_3]$	120.96	73.23
$[\text{Ni}(\text{acac})_2]$	103.45	65.67
$[\text{Cu}(\text{acac})_2]$	101.82	65.63
$[\text{Co}(\text{phen})_3]\text{Cl}_3$	30.94	62.82
$[\text{Ni}(\text{phen})_2]\text{Cl}_2$	25.03	53.67
$[\text{Cu}(\text{phen})_2]\text{Cl}_2$	23.59	52.49

Appendix B26: Reusability test of different photocatalysts with ultrasonic method and 10 ppm methyl red dye solution at pH 3 as model pollutant.

Photocatalyst	Degradation efficiency (%)	
	First use	Second use
ZnO	100	69.45
[Co(acac) ₃]	73.23	17.20
[Ni(acac) ₂]	65.67	15.35
[Cu(acac) ₂]	65.63	14.32
[Co(phen) ₃]Cl ₃	62.82	13.70
[Ni(phen) ₂]Cl ₂	53.67	11.69
[Cu(phen) ₂]Cl ₂	52.49	12.01

Appendix B26: Power density from DCPFC using different photocatalyst with different coating methods (dip, spray, ultrasonic) and 10 ppm methyl red dye solution at pH 3 as model pollutant.

Photocatalyst	Power density (mW/cm ²)		
	Dip coating	Spray coating	Ultrasonic coating
ZnO	86.98	59.39	172.75
[Co(acac) ₃]	64.34	33.07	120.96
[Ni(acac) ₂]	64.65	33.17	103.45
[Cu(acac) ₂]	62.77	33.08	101.82
[Co(phen) ₃]Cl ₃	16.27	10.16	30.94
[Ni(phen) ₂]Cl ₂	12.81	9.01	25.03
[Cu(phen) ₂]Cl ₂	14.61	8.05	23.59