Performance Evaluation of Photocatalytic Fuel Cell for Simultaneous Electricity Generation and Dyes Degradation

by

LEE SIN LI
(1440411532)

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TABLE OF CONTENTS

PAGE

DECLARATION OF THESIS **i**

ACKNOWLEDGMENT **ii**

TABLE OF CONTENTS **iii**

LIST OF TABLES **vi**

LIST OF FIGURES **vii**

LIST OF ABBREVIATIONS **ix**

ABSTRAK **x**

ABSTRACT **xi**

CHAPTER 1 : INTRODUCTION **1**

1.1 Introduction 1

1.2 Problem statement 4

1.3 Research objectives 6

1.4 Scope of study 7

CHAPTER 2 : LITERATURE REVIEW **8**

2.1 Treatment methods for organic wastewater 8

2.2 Advanced oxidation processes (AOPs) 9

2.3 Photocatalysis 12

- 2.3.1 Homogeneous photocatalysis 13
- 2.3.2 Heterogeneous photocatalysis 14

2.4 Photoelectrocatalysis (PEC) 15

2.5 Photocatalytic fuel cell (PFC) 16

2.6 Working principle of photocatalytic fuel cell 17

2.7 Design of photocatalytic fuel cell 18

2.8 Photoanode 21

2.9 Fabrication methods of photoanodes 22

  2.9.1 Anodizing method 24

  2.9.2 Immobilization method 28

2.10 Cathode 31

2.11 Supporting electrolytes 32

2.12 Electricity evaluation on photocatalytic fuel cell 33

2.13 Degradable compounds by photocatalytic fuel cell 34

  2.13.1 Fuel 34

  2.13.2 Dye 38

  2.13.3 Reactive Green 19 40

  2.13.4 Methylene Blue 41

  2.13.5 Acid Orange 7 42

2.14 Summary 43

CHAPTER 3 : PUBLISHED PAPERS 44

3.1 Introduction 44

3.2 Synopsis 46

3.3 Enhanced electricity generation and degradation of the azo dye Reactive Green 19 in a photocatalytic fuel cell using ZnO/Zn as the photoanode 54

3.4 A highly efficient immobilized ZnO/Zn photoanode for degradation of azo dye Reactive Green 19 in a photocatalytic fuel cell 66

3.5 Comparative Study of Photocatalytic Fuel Cell for Degradation of Methylene Blue under Sunlight and Ultra-Violet Light Irradiation 78

3.6 Role of dissolved oxygen on the degradation mechanism of Reactive Green 19 and electricity generation in photocatalytic fuel cell 88

3.7 Exploring the Relationship between Molecular Structure of Dyes and Light Sources for Photodegradation and Electricity Generation in Photocatalytic Fuel Cell 97

CHAPTER 4 : UNPUBLISHED RESEARCH WORK 116

4.1 Introduction 116

4.2 Degradation mechanism of Reactive Green 19 in photocatalytic fuel cell 116

CHAPTER 5 : CONCLUSION 120

5.1 Conclusion 120

5.2 Recommendation for Future Work 123

REFERENCES 124

APPENDIX A 137

LIST OF TABLES

NO. **PAGE**

Table 2.1: Power output of PFC using different fuels based on TiO_2 photoanode (1cm × 1cm) and Pt/Pt black cathode (1cm × 1cm) under O_2 in 0.1 M Na_2SO_4 with a 500 W Xe lamp irradiation (Kaneko et al., 2006) 36

Table 2.2: Electricity generation by PFC in different fuels (Liu et al., 2011) 37

Table 2.3: Characteristics and structures of Methylene Blue and its reduced and oxidized forms (Mills & Wang, 1999) 42

Table 4.1: Intermediates of RG 19 identified by GC-MS analysis 118

LIST OF FIGURES

NO. **PAGE**

Figure 2.1: Biological treatment methods on organic pollutants 9

Figure 2.2: Treatment methods including conventional techniques and advanced oxidation processes for the degradation of organic pollutants 11

Figure 2.3: The working principle of photocatalytic degradation process 13

Figure 2.4: The working principle of photoelectrocatalytic process based on TiO_2 photoanode and the reactions involved (Garcia-Segura & Brillas, 2017) 15

Figure 2.5: Experimental set-up of solar photoelectrocatalysis treating 100 mL of Acid Orange 7 solution (Garcia-Segura et al., 2013) 16

Figure 2.6: Typical double chamber photocatalytic fuel cell separated by silica frit (Antoniadou & Lianos, 2010) 17

Figure 2.7: Schematic diagram of a single chamber PFC based on nanocrystalline titania (n-TiO_2) deposited on a fluorine-doped tin oxide electrode (FTO) photoanode and Pt wire or sheet photocathode 18

Figure 2.8: (a) Schematic of the PFC with solar responsive photoanode and air-breathing cathode, (b) Images of the PFC photoanode and air-breathing cathode (L. Li et al., 2015) 19

Figure 2.9: (a) Schematic of the PFC with visible-light responsive photoanode and air-breathing cathode, (b) working principle of the PFC (Liao et al., 2015) 20

Figure 2.10: PFC based on TiO_2 nanorod coated FTO glass photoanode (H. Zhang et al., 2016) 20

Figure 2.11: Four CdS/STNA-based PFC systems in series to light a LED indicative lamp under visible light (AM1.5) irradiation (Yanbiao Liu, Li, Zhou, Chen, et al., 2011) 21

Figure 2.12: The cross sectional image of sol–gel titania with two layer film deposited on FTO electrode (Antoniadou & Lianos, 2010) 22

Figure 2.13: The cross sectional image of the combination of sol–gel titania with one layer of P25 titania deposited on FTO electrode (Antoniadou & Lianos, 2010) 22

Figure 2.14: Morphology of TiO_2 nanotube arrays at various anodizing voltages (a) 20 V, (b) 40 V, (c) 50 V, (d) 60 V for 3 h (Sun et al., 2011) 25

Figure 2.15: Example of electrochemical cell used to produce TiO_2 films by anodization of Ti sheet (Grimes & Mor, 2009) 26

Figure 2.16: The morphologies of ZnO nanostructures obtained with different electrolytes: (a) H_3PO_4; (b) HNO_3; (c) HCl; (d) $H_2C_2O_4$; (e) NaOH; (f) $KHCO_3$ (Ramirez-Canon et al., 2013) 27

Figure 2.17: The (a) cross sectional; (b) Top view SEM images of nanoporous WO_3/W photoanode (L. Xia et al., 2016) 28

Figure 2.18: SEM images of TiO_2 nanoparticles deposited on glass plates: (a) first coat, (b) second coat, and (c) third coat (Khataee et al., 2009) 29

Figure 2.19: SEM micrographs of immobilized ZnO on glass plates prepared with different catalyst dosages: (a) 2, (b) 4, and (c) 10 g L^{-1} (M. A. Behnajady et al., 2009) 30

Figure 2.20: Cross-sectional SEM image of a composite $Cu_2O/SnO_2/RuO_2$ photocathode 32

Figure 2.21: Dye classification flow chart 39

Figure 2.22: Molecular structure of Reactive Green 19 40

Figure 2.23: Molecular structure of Acid Orange 7 42

Figure 3.1: Flow chart of the published research works 45

Figure 4.1: Proposed degradation pathway of RG 19 treated by PFC 119

LIST OF ABBREVIATIONS

AOP	Advanced oxidation process
CB	Conduction band
CdS	Cadmium sulfide
CO_2	Carbon dioxide
CuO	Copper (II) oxide
EAOP	Electrochemical advanced oxidation process
EDX	Energy-dispersive X-ray
FSP	Flame spray pyrolysis
FTO	Fluorine-doped tin oxide
GC-MS	Gas chromatography mass spectrometry
HF	Hydrogen fluoride
H_2SO_4	Sulphuric acid
ITO	Indium tin oxide
KNO_3	Potassium nitrate
KOH	Potassium hydroxide
$LiClO_4$	Lithium perchlorate
NaOH	Sodium hydroxide
Na_2SO_4	Sodium sulfate
PEC	Photoelectrocatalysis
PET	Polyethylene terephthalate
Pt/C	Platinum loaded carbon
RG 19	Reactive green 19
ROS	Reactive oxygen species
SEM	Scanning electron microscope
TCO	Transparent conductive oxide
TiO_2	Titanium dioxide
TNA	Titanium dioxide nanotube array
UV	Ultraviolet
VB	Valence band
WO_3	Tungsten trioxide
XRD	X-ray diffraction
ZnO	Zinc oxide

Penilaian Prestasi Bahan Api Fotopemangkin Untuk Penjanaan Tenaga Elektrik Dan Degradasi Pewarna Secara Serentak

ABSTRAK

Sel bahan api fotopemangkin (PFC), sel bahan api yang mampu menghasilkan elektrik dari sebatian organik apabila disinari oleh cahaya, terbukti menjadi salah satu alternatif yang paling menjanjikan dalam pemulihan tenaga daripada air buangan organik. Walau bagaimanapun, banyak kajian telah dilaporkan terhadap PFC skala kecil berdasarkan photoanode TiO_2. Ruang tunggal PFC yang terdiri daripada zink oksida (ZnO) fotoanod dan kertas karbon yang dimuatkan platinum sebagai katod dibina dengan menggunakan pewarna diazo Reactive Green 19 (RG 19) sebagai bahan pencemar organik. ZnO fotoanod difabrikasi melalui kaedah penganodan dan immobilisasi. Kecekapan fotoanod, contohnya, penganodan plat Zn dengan ZnO (ZnO/Zn), immobilisasi kerajang Zn dengan ZnO (ZnO/Zn) dan immobilisasi plat karbon dengan ZnO (ZnO/C) telah disiasat. Selain itu, kajian parameter asas dan operasi terhadap faktor-faktor yang mengawal kecekapan PFC seperti kesan fotolisis, litar lengkap dan litar tertutup, jenis elektrolit sokongan, kepekatan awal pewarna, pH, sumber cahaya dan kepekatan oksigen terlarut telah dinilai. Berbanding dengan fotolisis sahaja, kecekapan penyingkiran warna RG 19 meningkat apabila ZnO fotoanod dikaji dalam sistem PFC. PFC berdasarkan penganodan plat Zn dengan ZnO fotoanod menunjukkan kecekapan penyingkiran warna sebanyak 73% daripada 10 mg L^{-1} RG 19 selepas 8 jam di bawah penyinaran UV, manakala PFC yang menggunakan immobilisasi kerajang Zn dengan ZnO sebagai fotoanod mencapai penyingkiran warna yang lengkap selepas 7 jam. Peningkatan kepekatan awal RG 19 dari 10 hingga 30 mg L^{-1} telah mengakibatkan pengurangan ketumpatan arus (J_{sc}) dan ketumpatan kuasa maksimum (P_{max}) dalam PFC yang berdasarkan penganodan plat Zn dengan ZnO fotoanod dengan penambahan elektrolit sokongan. Sementara itu, J_{sc} dan P_{max} bagi PFC berdasarkan immobilisasi kerajang Zn dengan ZnO fotoanode meningkat dengan peningkatan kepekatan pewarna awal dari 5 hingga 30 mg L^{-1} dan menurun pada 40 mg L^{-1}. Penjanaan elektrik dan kecekapan degradasi disiasat dengan penambahan natrium klorida (NaCl), natrium sulfat (Na_2SO_4) dan magnesium sulfat ($MgSO_4$) sebagai elektrolit sokongan dalam PFC berdasarkan penganodan plat ZnO/Zn fotoanod. Keputusan menunjukkan bahawa penambahan Na_2SO_4 sebagai elektrolit sokongan menghasilkan J_{sc} tertinggi iaitu 2.64 mA cm^{-2} dan P_{max} 1.27 mW cm^{-2}. Walau bagaimanapun, dari segi degradasi, penambahan NaCl sebagai elektrolit sokongan mencapai degradasi pewarna tertinggi. Bagi sistem PFC yang berdasarkan immobilisasi kerajang ZnO/Zn fotoanod, penyingkiran warna lengkap hampir dicapai dalam 8 jam apabila 30 mg L^{-1} RG 19 dirawat dalam PFC tanpa penambahan sebarang elektrolit sokongan. Selain itu, kelayakan PFC untuk merawat Acid Orange 7 (AO7) dan Methylene Blue (MB) dengan menggunakan immobilisasi kerajang ZnO/Zn fotoanod juga disiasat. Kesan kepekatan oksigen terlarut (DO) terhadap prestasi PFC berdasarkan immobilisasi plat karbon dengan ZnO/C fotoanod dari segi kecekapan degradasi dan penjanaan elektrik telah pun disiasat. Penyingkiran warna lengkap RG 19 telah dicapai pada penghujung 8 jam apabila kadar kelajuan udara pada PFC ditetapkan pada 200 mL min^{-1}. Kewujudan oksigen terlarut mampu mempertahankan pemisahan pasangan elektron-lubang dalam ZnO dan meningkatkan kecekapan degradasi dan penjanaan elektrik PFC. Kesimpulannya, keputusan amat membuktikan bahawa PFC dapat menghasilkan tenaga elektrik untuk jangka masa yang panjang melalui penggunaan cahaya dan sisa organik sebagai bahan api.

Performance Evaluation of Photocatalytic Fuel Cell for Simultaneous Electricity Generation and Dyes Degradation

ABSTRACT

Photocatalytic fuel cell (PFC), a fuel cell which is capable to produce electricity from organic compounds when irradiated by light, proves to be one of the most promising alternative in energy recovery from organic wastewater. However, numerous studies have been reported on small scale PFC based on the TiO_2 photoanode. A single-chambered PFC which comprised of a zinc oxide (ZnO) photoanode and a platinum loaded carbon cathode was constructed using diazo dye Reactive Green 19 (RG 19) as organic pollutant. Zinc oxide (ZnO) photoanode was fabricated by using anodizing and immobilization method. Efficiency of the photoanodes, for example, the anodized ZnO loaded Zn plate (ZnO/Zn), immobilized ZnO loaded Zn foil (ZnO/Zn) and immobilized ZnO loaded carbon plate (ZnO/C), were investigated. Besides, the fundamental and operating parameter study on the factors governing the performance of PFC such as the effect of photolysis, open and closed circuit, different types of supporting electrolytes, initial dye concentration, pH, light source and dissolved oxygen concentration were evaluated. As compared to photolysis alone, the color removal efficiency of RG 19 was enhanced when ZnO photoanode was employed in the PFC system. The PFC based on anodized ZnO/Zn photoanode showed color removal efficiency with 73 % in 10 mg L^{-1} of RG 19 after UV irradiation for 8 h, whereas the PFC system using immobilized ZnO/Zn as photoanode yielded complete color removal after 7 h. The increase of initial RG 19 concentration from 10 to 30 mg L^{-1} had resulted in a reduction of short-circuit current (J_{sc}) and maximum power density (P_{max}) of PFC based on anodized ZnO/Zn photoanode with the presence of supporting electrolytes. Meanwhile, the J_{sc} and P_{max} of PFC based on immobilized ZnO/Zn photoanode increased with increasing initial dye concentration from 5 to 30 mg L^{-1} and dropped at 40 mg L^{-1}. Electricity generation and degradation efficiency were investigated in the presence of sodium chloride (NaCl), sodium sulfate (Na_2SO_4) and magnesium sulfate ($MgSO_4$), respectively, as supporting electrolyte in PFC based on anodized ZnO/Zn photoanode. Results revealed that the addition of Na_2SO_4 as supporting electrolyte yielded the highest J_{sc} of 2.64 mA cm^{-2} and P_{max} of 1.27 mW cm^{-2}. However, in terms of photocatalytic degradation, the presence of NaCl as supporting electrolyte led to the highest dye degradation efficiency. For PFC system based on immobilized ZnO/Zn as photoanode, almost complete decolorization could be achieved in 8 h when 30 mg L^{-1} of RG19 was treated in a PFC without any supporting electrolyte. Besides, the feasibility of PFC in treating Acid Orange 7 (AO7) and Methylene Blue (MB) using immobilized ZnO/Zn photoanode was investigated too. The effect of dissolved oxygen (DO) concentration on the performance of PFC based on immobilized ZnO/C photoanode in terms of degradation efficiency and electricity generation was investigated. Complete decolorization of RG 19 was accomplished at the end of 8 h when the air flow rate of the PFC was fixed at 200 mL min^{-1}. The presence of dissolved oxygen could efficiently retain the electron-hole pair separation of ZnO and enhanced the degradation efficiency and electricity generation of PFC. In conclusion, the results strongly proved that PFC was able to produce electricity for a long period of time through utilizing light and organic waste as fuel.

CHAPTER 1: INTRODUCTION

1.1 Introduction

Physical treatment methods such as adsorption (Martin, Artola, Balaguer, & Rigola, 2003; Nasuha, Hameed, & Din, 2010; Rauf, Qadri, Ashraf, & Al-Mansoori, 2009), ion flotation (Shakir, Elkafrawy, Ghoneimy, Elrab Beheir, & Refaat, 2010), coagulation (Ahmad & Puasa, 2007; Riera-Torres, Gutiérrez-Bouzán, & Crespi, 2010) and sedimentation (Zodi, Potier, Lapicque, & Leclerc, 2010) were found useful and versatile to remove the color of dyes. However, these methods can cause secondary pollution where further treatments are needed. Although conventional biological processes were employed to degrade the dye effluents, it was found that these technologies were ineffective for synthetic dyes due to the recalcitrant nature of the dyes (Z. Y. Wang, Ye, & Zhang, 2011).

Energy recovery from wastewater treatment has become the present day interest of researchers worldwide. Researchers found that organic compounds in wastewater can be recovered and converted to potential energy such as electricity. Photocatalytic fuel cell (PFC) has been gaining attention in the research field recently due to its ability to treat organic wastewater and generate electricity simultaneously. The idea was developed after the employment of photoelectrochemical (PEC) water splitting by Fujishima and Honda in 1972 using a metal oxide semiconductor photoelectrode to produce hydrogen (Fujishima & Honda, 1972). PFC is an integration of photocatalysis and fuel cell technologies which consumes organic compounds and produces electricity by using the light photon energy. A number of scientific publications about PFC based on titanium dioxide (TiO_2) nanoparticulate film photoanode were reported by the researchers over the past few years (Antoniadou, Kondarides, Labou, Neophytides, & Lianos, 2010; Hu et al., 2015; Kaneko et al., 2006; J. Li, Li, Chen, Bai, & Zhou, 2013; K. Li et al., 2014).

Basically, a PFC comprises of a photoanode loaded with semiconductor photocatalyst, a cathode and liquid electrolyte. In fact, the working principle of the PFC was described and proposed (Antoniadou & Lianos, 2010; Chen et al., 2014; Yuanyuan Liu, Liu, & Yang, 2016). Upon illumination, the electrons are excited across the band gap from valence band (VB) into the conduction band (CB) due to the photon energy equal or greater than the band gap of the photocatalyst, leaving positive holes (h_{VB}^{+}) at the valence band as shown in Equation 1.1. Based on Equation 1.2 and 1.3, the positive holes then react with water molecules or hydroxide ions (OH^{-}) to produce hydroxyl radicals ($\cdot OH$). The organic compounds (e.g. R) are then oxidized either directly by the photogenerated holes (Equation 1.4) or indirectly by $\cdot OH$ (Equation 1.5), which subsequently leads towards the degradation of organic compounds. Meanwhile, the electrons either migrate to cathode via external circuit and react with hydrogen ions (H^{+}) that are produced during the photooxidation for the formation of water (Equation 1.6), or the electrons reduce oxygen molecules (O_2) to form superoxide radical anions ($^{\bullet}O_2^{-}$) (Equation 1.7). These highly oxidant species ($\cdot OH$ and $^{\bullet}O_2^{-}$) are responsible for the photocatalytic degradation of organic pollutants i.e. dyes, especially in the destruction of aromatic compounds to form volatile low molecular weight compounds.

$$ZnO + hv \rightarrow h_{VB}^{+} + e_{CB}^{-} \qquad 1.1$$

$$h_{VB}^{+} + H_2O \rightarrow \cdot OH + H^{+} \qquad 1.2$$

$$h_{VB}^{+} + OH^{-}_{(ads)} \rightarrow \cdot OH \qquad 1.3$$

$$h_{VB}^{+} + \mathrm{R} \rightarrow \mathrm{R}^{\bullet +} \qquad 1.4$$

$$\cdot\mathrm{OH} + \mathrm{R} \rightarrow \mathrm{R}^{\bullet} \qquad 1.5$$

$$4\mathrm{H}^{+} + \mathrm{O}_2 + 4e^{-} \rightarrow 2\mathrm{H}_2\mathrm{O} \qquad 1.6$$

$$e_{\mathrm{CB}}^{-} + \mathrm{O}_2 \rightarrow {}^{\bullet}\mathrm{O}_2^{-} \qquad 1.7$$

TiO_2 is a well-known photocatalyst that has been broadly studied for photocatalytic water splitting (T. Bak, Nowotny, Rekas, & Sorrell, 2002; Mohapatra, Misra, Mahajan, & Raja, 2007; Ni, Leung, Leung, & Sumathy, 2007; H. Park, Bak, Ahn, Choi, & Hoffmannn, 2012), wastewater treatment (An et al., 2010; Fujishima, Rao, & Tryk, 2000; X. Z. Li & Li, 2001; Ryu & Choi, 2008; Silva, Nouli, Xekoukoulotakis, & Mantzavinos, 2007) and electricity generation in dye-sensitized solar cell (Z.-S. Wang & Zhou, 2009). TiO_2 nanotube array (TNA) photoanode has also been studied by several researchers due to its high performance in PFC (Li et al., 2013; Liu et al., 2011a, 2011b, 2009b). The well aligned TNA photoanode fabricated via anodizing process in hydrofluoric (HF) electrolytes and forms a natural Schottky-type contact between TiO_2 and Ti substrate which provides a unidirectional channel to ease the transport of photogenerated electrons. Besides that, there is a handful of publications on PFC which comprised of TiO_2 photoanode that can be fabricated by other methods (Antoniadou et al., 2010; Kaneko et al., 2006). The deposited photocatalyst on the anode provides a broad choice of organic pollutants to be degraded by PFC, such as methanol (Hu et al., 2015; Xia et al., 2016), ethanol (Antoniadou & Lianos, 2010; Sfaelou, Sygellou, Dracopoulos, Travlos, & Lianos, 2014), glucose (L. Li et al., 2015; Ying et al., 2016), tetracycline (Xia et al., 2016), triethanol amine (Hu et al., 2015), heavy metal ion (D. Wang et al., 2017) and dye (Chen et al., 2014; Yang et al., 2014; Sui et al., 2015; Tantis et al., 2015).

In this research, the application of zinc oxide (ZnO) photoanode in the PFC system was evaluated by using anodizing and immobilization method. Besides, Zn plate, Zn foil and carbon plate were used as the substrates for the photoanode. Some fundamental studies were also carried out in order to understand the mechanisms involved in the PFC. Reactive green 19 (RG 19) was chosen as the target organic pollutant in this research due to the increasing use of this dye in the textile industry over the past few years (Hsueh et al., 2014; Das and Mishra, 2017). The degradation efficiency and electricity generation of RG 19 treated by PFC were evaluated. In addition, the effect of operating parameter such as different types of supporting electrolytes, initial dye concentration, pH, light source and dissolved oxygen concentration on the degradation efficiency and electricity generation were investigated. In addition, the degradation mechanism and pathway of RG 19 treated in PFC are proposed.

1.2 Problem statement

TiO_2 nanoparticles were found to aggregate and scatter the incident light where post-treatment recovery is required, leading towards large-scale application economically impractical (Mahlambi, Ngila, & Mamba, 2015). Hence, immobilization of photocatalyst on solid support is capable to solve the post-treatment problems and enable the reuse of the photocatalyst. With the assistance of photocatalytic process, organic compounds can be oxidized and mineralized when treated in PFC.

Different types of semiconductors such as TiO_2 (Kaneko et al., 2006; J. Li et al., 2013), cadmium sulfide (CdS) (Liu, Li, Zhou, Chen, et al., 2011; Wu et al., 2015), tungsten trioxide (WO_3) (Chen et al., 2012, 2014), bismuth vanadate ($BiVO_4$) (García-

Pérez, Sepúlveda-Guzmán, Martínez- de la Cruz, & Peral, 2012; S. Wang, Chen, Yun, Hu, & Wang, 2017) and hematite-Fe_2O_3 (B. R. Kim et al., 2013; Kment et al., 2017) have been investigated as photoanodes in PFC. Although TiO_2 has good charge transport properties, it can only absorb in the UV region (Tantis et al., 2015). Besides that, metal sulfide quantum dots (QDs) such as CdS and CdSe which act as sensitizers for titania faced difficulties in hydroxyl radicals production, thereby reducing their effectiveness in degradation of organic compounds (Sfaelou et al., 2014). It was found that the WO_3 photoanode is less stable when compared to TiO_2 and it only favored in acidic electrolytes (Hilliard et al., 2017). $BiVO_4$ photoanode, on the other hand, has low charge mobility and extensive electron-hole recombination behavior (Y. Park, McDonald, & Choi, 2013) while hematite ($\propto$-Fe_2O_3) photoanode exhibits low conductivity and fast recombination of charge carries (A. Bak, Choi, & Park, 2011). According to a recent literature, mesoporous nanocrystalline anatase titania remains the best option as the photoanode in PFC (Lianos, 2017). ZnO is considered as an alternative to TiO_2 due to its similar band gap (3.37 eV) and high excitation binding energy of 60 mV (J. B. Xia & Zhang, 2006). Besides, the electron mobility of ZnO (200 $cm^2\ V^{-1}\ s^{-1}$) is higher as compared to TiO_2 (30 $cm^2\ V^{-1}\ s^{-1}$) (Quintana, Edvinsson, Hagfeldt, & Boschloo, 2007). However, little work has been reported on the application of ZnO as a functional photoanode in PFC.

Besides, the selection of suitable supporting electrolyte is an important concern in PFC as the presence of supporting electrolyte could reduce the internal resistance of PFC reactor. Sodium sulfate (Na_2SO_4) is the most commonly used electrolyte in PFC (Iyatani et al., 2012; Liu, Li, Zhou, Li, et al., 2011; B. Wang, Zhang, Lu, Xuan, & Leung, 2014). However, there is lack of study on the effect of other supporting electrolytes such as sodium chloride and magnesium sulfate on the performance of PFC. Thus, the investigation on the effect of supporting electrolyte on the performance of PFC are essential. The treatment of organic compounds by PFC in larger volume is required as most of the organic compound solutions in PFC studies were conducted in small scale. The reaction solutions that were usually employed are approximately 10 mL to 150 mL (Antoniadou & Lianos, 2010; Chen et al., 2014; Yanbiao Liu et al., 2009, 2012). Since PFC is a potential alternative wastewater treatment, the effect of dye need to be further investigated because different types of dyes have different degradation behaviors in photodegradation process which in turn will affect the performance of the PFC. Besides, the effect of light source is an important parameter in the initiation of photocatalytic process in PFC. Thus, the effect of light source is worthy to explore as the study on the effect of light source on the PFC performance is limited. Last but not least, the evaluation combined with the fundamental understanding on the degradation mechanism and pathway of RG 19 in PFC are essential to impart constructive information in the development of an effective and novel PFC.

1.3 Research objectives

i. To fabricate and characterize the photoanodes by using different methods for application in photocatalytic fuel cell.
ii. To evaluate the operating parameter that affect the efficiency of the photocatalytic fuel cell for simultaneous wastewater treatment and electricity generation.
iii. To investigate the degradation pathway of azo dye Reactive Green 19 treated in photocatalytic fuel cell.

1.4 Scope of study

The scope of study covers the four main objectives of this research. The research begins with the fabrication of ZnO photoanode and development of single chamber PFC. The anodized ZnO loaded Zn plate, immobilized ZnO loaded Zn foil and immobilized ZnO loaded carbon plate were fabricated. PFC based on self-fabricated ZnO as photoanode and platinum loaded carbon (Pt/C) as cathode was constructed in order to evaluate the feasibility of PFC for simultaneous wastewater treatment and electricity generation. The fabricated ZnO photoanode was then characterized by using scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray spectrometry (EDX), respectively. Concentrations of the dyes were measured by using UV-Vis spectrometer.

In the aspect of PFC, the fundamental and operating parameter study on the factors governing the performance of PFC were investigated. For instance, the effect of photolysis, open and closed circuit, different types of supporting electrolytes, initial dye concentration, pH, light source, dissolved oxygen concentration and effect of different types of dyes were evaluated. Last but not least, the degradation mechanism of the target pollutants, RG 19, treated by the PFC was proposed and analyzed with gas chromatography mass spectrometry (GC-MS) to identify the intermediates generated in PFC.

CHAPTER 2: LITERATURE REVIEW

2.1 Treatment methods for organic wastewater

Organic contaminants occupy the major role in wastewater pollution. There are various types of organic wastewater pollutants, such as polychlorinated biphenyl (PCBs), pesticides, herbicides, polycyclic aromatic hydrocarbons (PAHs), phenols, aliphatic, heterocyclic compounds, industrial and agricultural contaminants production (C. Zheng, Zhao, Zhou, Fu, & Li, 2013). The organic wastewater compounds can be treated by biological, chemical oxidation, adsorption and other technologies, such as solvent extraction, incineration, photocatalysis and ultrasonic. Biodegradation is a process to degrade and convert the organic contaminants into harmless by using microorganisms, fungi, green plants and their enzymes. Biological treatment can degrade organic compounds aerobically, anaerobically or the combination of aerobic and anaerobic (Scott & Ollis, 1995) as depicted in Figure 2.1.

Some of the organic wastewater pollutants was found refractory to the microorganisms and less effective to be degraded biologically where chemical oxidation was introduced to treat and transform these organic compounds into smaller and less harmful molecules by using chemical oxidant such as H_2O_2, O_3, ClO_2, K_2MnO_4, and K_2FeO_4 and etc. However, oxidizing agents such as ozone and hydrogen peroxide exhibit lower degradation rate. Thus, advanced oxidation processes (AOPs) have emerged as a promising technology to treat refractory organic pollutants with the production of high reactivity of hydroxyl radicals (C. Zheng et al., 2013).

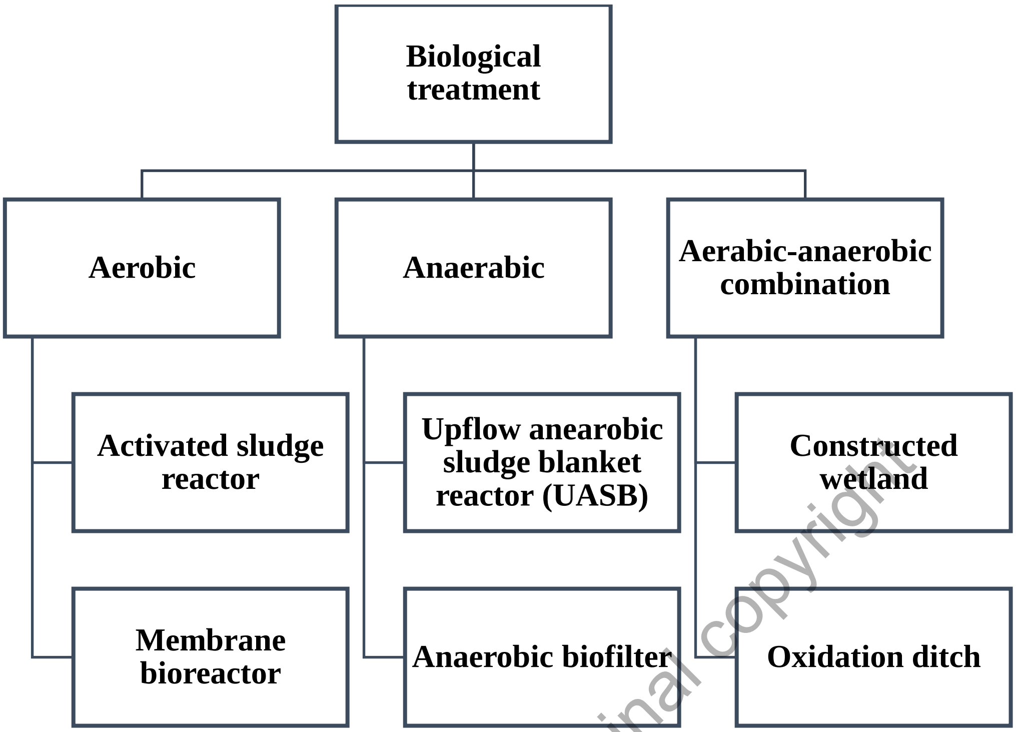

Figure 2.1: Biological treatment methods on organic pollutants

2.2 Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) have emerged as alternative or complementary wastewater treatment method for the conversion of organic pollutants into harmless products (Lewandowski & Ollis, 2003). The high oxidation potential of AOPs rely particularly on in situ production of hydroxyl radicals (·OH) (Soutsas et al., 2010) which bring about a nearly complete mineralization of the pollutants to yield final products of CO_2 and H_2O (Sadik, Nashed, & El-Demerdash, 2007). Hydroxyl radicals are produced with the use of one or more oxidants such as ozone (O_3), hydrogen peroxide (H_2O_2), energy sources (ultrasounds, UV light, solar light) and catalysts (metal oxides, electrodes, iron ions) (Suri et al., 1993).

AOPs are found effective in degrading recalcitrant intermediates as compared to the conventional treatment techniques. Figure 2.2 depicts the treatment methods of organic pollutant under conventional techniques and AOPs. The common examples of AOPs that have been employed in wastewater treatment are ozonation (O_3), ozonation combined with hydrogen peroxide (O_3/H_2O_2) and UV irradiation (O_3/UV) or both (O_3/H_2O_2/UV), ozonation combined with catalysts (O_3/catalysts), UV light coupled with hydrogen peroxide (UV/H_2O_2), Fenton (Fe^{2+}/H_2O_2) and photo-Fenton processes (Fe^{2+}/H_2O_2/UV), photocatalysis and ultrasonic cavitation process (Bethi, Sonawane, Bhanvase, & Gumfekar, 2016).

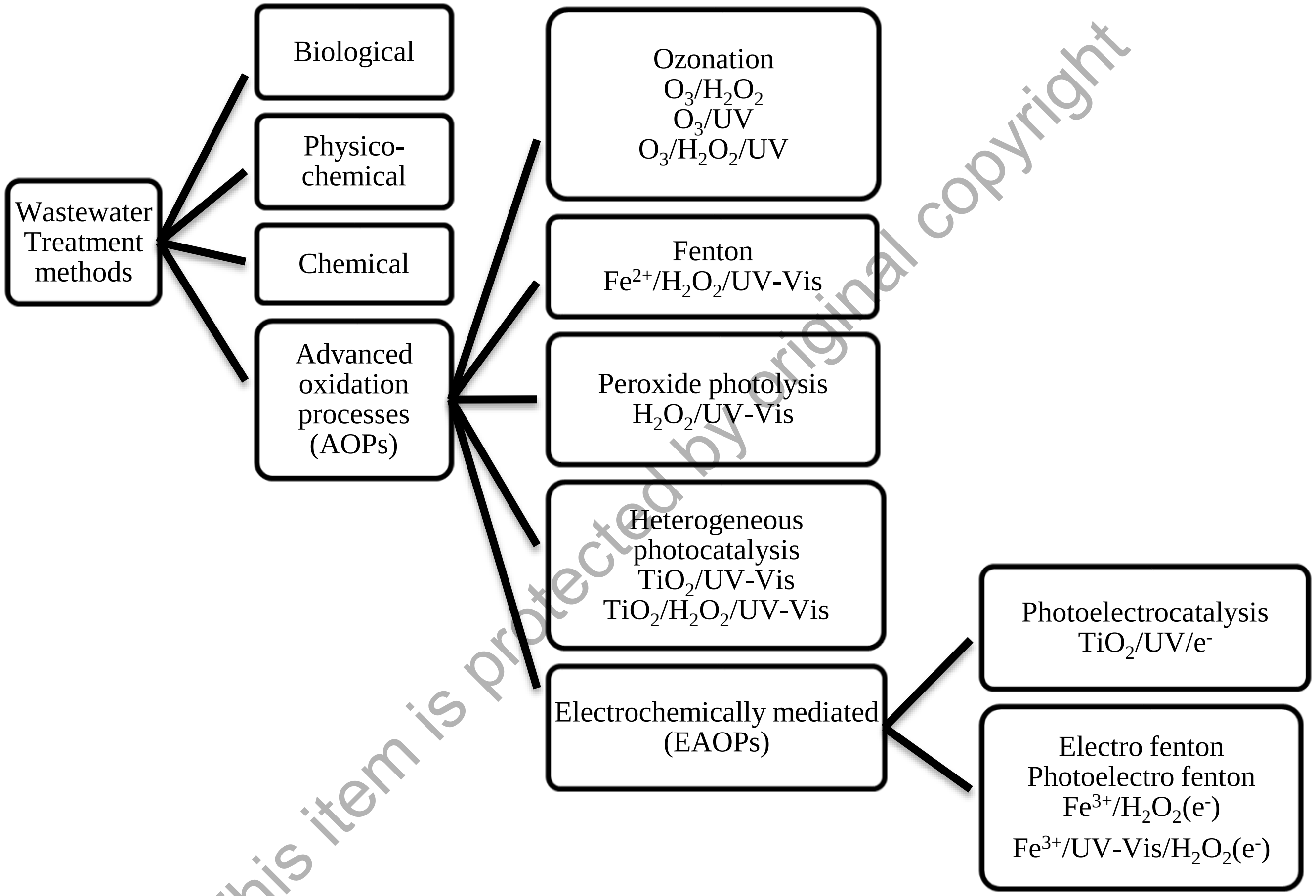

Figure 2.2: Treatment methods including conventional techniques and advanced oxidation processes for the degradation of organic pollutants

2.3 Photocatalysis

A catalyst increases the rate of reaction without undergoing change in itself in the chemical reaction. Photocatalysis is defined as the acceleration of a reaction in the presence of photocatalyst. Photocatalytic process can lead to a total mineralization of organic compound to carbon dioxide, water and mineral acids which use atmospheric oxygen as the oxidant and carried out under ambient conditions (Rauf, Meetani, & Hisaindee, 2011).

Photocatalytic process occurs when the energy of the photon is equal or higher than the band gap of the photocatalyst. Band gap refers to the energy difference between the valence band (VB) and conduction band (CB) (Beydoun, Amal, Low, & McEvoy, 1999). Photocatalyst can generate electron-hole pairs with free electrons (e^-) produced in the empty CB leaving positive holes in the VB (Hoffmann, Martin, Choi, & Bahnemann, 1995). The photoexcited electrons from CB diffuse out to the surface of photocatalyst and initiate a series of chemical reactions as shown in Figure 2.3. The photoexcited electrons at CB are usually scavenged by oxygen molecule and produce superoxide anion radicals ($^\bullet O_2^-$) in aerobic environment (S. Zheng, Jiang, Cai, Dionysiou, & O'Shea, 2014). Meanwhile, powerful oxidants (e.g. $\cdot OH$) are produced and initiate oxidative process at the surface of the photocatalyst when reacts with adsorbed H_2O or OH^- (Jiang, Joens, Dionysiou, & O'Shea, 2013). There are two types of photocatalytic reactions: homogeneous photocatalysis and heterogeneous photocatalysis.