OIL PALM KERNEL SHELL-DERIVED GRAPHENE DERIVATIVE ANODE ELECTRODES: CHARACTERIZATIONS AND APPLICATION IN MICROBIAL FUEL CELL

IDRIS MUSTAPHA OMENESA

UNIVERSITI SAINS MALAYSIA

2024

OIL PALM KERNEL SHELL-DERIVED GRAPHENE DERIVATIVE ANODE ELECTRODES: CHARACTERIZATIONS AND APPLICATION IN MICROBIAL FUEL CELL

by

IDRIS MUSTAPHA OMENESA

Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

September 2024

DECLARATION BY AUTHOR

This thesis is entirely my original work, with no material previously published or reported by another individual except as cited. My thesis content is the outcome of work I completed throughout my PhD research project and does not include a substantial part of work submitted elsewhere for the award of a degree or diploma in any university or other tertiary institution. Furthermore, a significant part of this thesis work has previously been published in reputable journals by myself and my supervisors. On the last page of the thesis, there is a list of publications originating from my PhD work.

Regards,

Mustapha Omenesa Idris	**Prof. Dr. Mohamad Nasir Mohamad Ibrahim**
PhD Scholar	Main Supervisor

ACKNOWLEDGEMENT

First and foremost, I would like to express gratitude to Allah (SWT) for providing me with the strength to pursue the PhD programme. The most profound appreciation goes to my main supervisor, Prof. Dr. Mohamad Nasir Mohamad Ibrahim, who never got tired of my recurred consultations along the research's progress. His patience, support, and suggestions were vital to the success of my research. I must acknowledge my field supervisor, Dr. Asim Ali Yaqoob, for his advice and dedication to this work. I am grateful to my co-supervisor, Dr. Nur Asshifa Md Noh, whose facilities I used for the electro-microbiological analysis. I would also like to recognise the Material Technology Research Group (MaTRec) and the School of Chemical Sciences, USM for providing sufficient and favourable environment for seamless research operations. I am grateful to TETFund Nigeria for the sponsorship, through Kogi State University Anyigba.

Finally, I would like to express my profound appreciation to my beloved parents, Mr. and Mrs. Idris Omenesa, as well as all of my siblings. I specially thank my mentor, Prof. Abdulrahman Ochi Suberu, who has been an inspiration to me since my early education career. Thank you, my dear son and daughter, Abdulbasit Mustapha and Rahamatullah Mustapha, for your tremendous endurance and understanding throughout my PhD adventure. Ashraf Bello, who, despite his relatively young age, has shown me a great deal of affection as his father. To my beloved wife and very motivating partner, Khadijah Abdulkareem, I appreciate all of your efforts. I must not forget to remember my late wife, Zainab Audu, who encouraged me in my early career. You were a great wife and mother. May Allah make you one of the most elevated persons in Jannah.

TABLE OF CONTENTS

ACKNOWLEDGEMENT ..... **ii**

TABLE OF CONTENTS ..... **iii**

LIST OF TABLES ..... **vii**

LIST OF FIGURES ..... **viii**

LIST OF ABBREVIATIONS ..... **xii**

LIST OF SYMBOLS ..... **xiv**

ABSTRAK ..... **xv**

ABSTRACT ..... **xvii**

CHAPTER 1 INTRODUCTION **1**

1.1 Research Background 1

1.2 Problem Statement 5

1.3 Research Objectives 8

1.4 Scope of study 8

1.5 Organization of Thesis 10

CHAPTER 2 LITERATURE REVIEW **11**

2.1 Introduction 11

2.2 Advances in Electrodes for MFC Application 14

2.2.1 Significance of Anode Electrodes in MFC 15

2.2.2 Metal Oxides Decorated Anode Electrodes 16

2.3 Biowaste Materials as Anode Electrodes 17

2.4 Biowaste Derived Graphene Derivative-Based Composite Anodes 28

2.5 Anode-Microbial Interaction in MFC 30

2.6 Future Prospect of Anode Electrodes in MFC Application 32

2.7 Application of MFC in Wastewater Treatment 34

2.7.1 Organic Pollutant Degradation Through MFC 34

2.7.2 Mechanism of Organic Pollutant Degradation in MFC 35

2.7.3 Microbes-Organic Pollutant Interaction 40

2.8 Factors Affecting Biodegradation of Organic Pollutants 42

2.8.1 Physicochemical Factors 43

2.8.2 Biological Factors 45

2.9 Influence of Organic Pollutant Degradation on the Power Output Generation of MFC 46

2.10 Comparative Degradation of Other Toxic Pollutants and Organic Pollutants 52

2.11 Challenges and Prospect of Organic Pollutant Degradation in MFC 55

2.12 Concluding Remarks of Literature Survey 56

CHAPTER 3 EXPERIMENTAL DETAILS 57

3.1 Reagents and Chemicals 57

3.2 Preparation of Palm Kernel Shell (PKS) Biochar 57

3.3 Material Synthesis for Anode Fabrications 58

3.3.1 Synthesis of PKS-GO and PKS-rGO 58

3.3.2 Synthesis of PKS-rGO/TiO_2 and PKS-rGO/ZnO 59

3.4 Characterizations of the Anode Materials 59

3.5 Fabrication of the Anode Electrodes 61

3.6 Preparation of Rotten Sweet Potato (RSP) Juice Organic Substrate 62

3.7 MFC Operations and Configuration 63

3.8 Experiment 1: Application of PKS-GO Anode in the MFC 64

3.8.1 Experiment 1.1: PKS-GO Anode for Formaldehyde (FA) Biodegradation with Energy Generation 65

3.8.2 Experiment 1.2: PKS-GO Anode for Naphthalene Biodegradation with Energy Generation 65

3.9 Experiment 2: Application of PKS-rGO Anode in the MFC 66

3.9.1 Experiment 2.1: PKS-rGO Anode for FA Biodegradation with Energy Generation 66

3.9.2 Experiment 2.2: PKS-rGO Anode for Naphthalene Biodegradation with Energy Generation 67

3.10 Experiment 3: Application of PKS-rGO/TiO_2 Anode in the MFC 67

3.10.1 Experiment 3.1: PKS-rGO/TiO_2 Anode for FA Biodegradation with Energy Generation 67

3.10.2 Experiment 3.2: PKS-rGO/TiO_2 Anode for Naphthalene Biodegradation with Energy Generation 68

3.11 Experiment 4: Application of PKS-rGO/ZnO Anode in the MFC 69

3.11.1 Experiment 4.1: PKS-rGO/ZnO Anode for FA Biodegradation with Energy Generation 69

3.11.2 Experiment 4.2: PKS-rGO/ZnO Anode for Naphthalene Biodegradation with Energy Generation 69

3.12 Experiment 5: Application of Commercial Graphite (CGr) Anode in the MFC 70

3.12.1 Experiment 5.1: Commercial Graphite (CGr) Anode for FA Biodegradation with Energy Generation 70

3.12.2 Experiment 5.2: Commercial Graphite (CGr) Anode for Naphthalene Biodegradation with Energy Generation 71

3.13 Electrochemical Equations and Analysis 71

3.14 Biodegradation Efficiency 73

3.15 Microbiological Characterization 74

CHAPTER 4 RESULTS AND DISCUSSION 76

4.1 Characterization of Materials 76

4.1.1 FTIR, XRD, Raman and TGA Studies 76

4.1.2 BET and XPS Studies 80

4.1.3 SEM, TEM, EDX and AFM Studies 84

4.2 Performance Evaluation of PKS-GO and PKS-rGO Anodes Involving Biodegradation of Formaldehyde (FA) 91

4.3 Performance Evaluation of PKS-GO and PKS-rGO Anodes Involving Biodegradation of Naphthalene 110

4.4 Performance Evaluation of PKS-rGO/TiO_2 and PKS-rGO/ZnO Anodes Involving Biodegradation of Formaldehyde (FA) 128

4.5 Performance Evaluation of PKS-rGO/TiO_2 and PKS-rGO/ZnO Anodes Involving Biodegradation of Naphthalene 142

4.6 Performance Evaluation of Commercial Graphite Anode Involving Biodegradation of Formaldehyde (FA) and Naphthalene 153

4.7 Comparative Discussion of PKS-GO, PKS-rGO, PKS-rGO/TiO_2, PKS-rGO/ZnO and CGr Anode Performances 159

CHAPTER 5 CONCLUSION AND FUTURE RECOMMENDATION 164

5.1 Conclusion 164

5.2 Future Recommendations 167

REFERENCES 169

LIST OF PUBLICATIONS

LIST OF TABLES

Page

Table 2.1 Summary of recently used biowaste materials for anode electrodes fabrication in MFC. 21

Table 2.2 Some synthesis methods for biowaste-derived materials in various energy applications.....26

Table 2.3 List of microbes utilized in MFC with their energy output. 51

Table 2.4 The comparative power performance of some pollutant degradations..... 54

Table 3.1 The physiochemical properties of the wastewater for Experiments 1.1 and 2.1.....65

Table 3.2 The physiochemical properties of the wastewater for Experiments 1.2 and 2.2.....66

Table 3.3 The physiochemical properties of the wastewater for Experiments 3.1 and 4.1.....68

Table 3.4 The physiochemical properties of the wastewater for Experiments 3.2 and 4.2.....68

Table 3.5: The physiochemical properties of the wastewater for Experiment 5.1..... 70

Table 3.6 The physiochemical properties of the wastewater for Experiment 5.2..... 71

Table 4.1 Comparison of the BET data from the present study.....82

Table 4.2 Energy generation performance of some anode materials compared to the current material under study.....101

Table 4.3 Cp Values of the Elecrodes at Various MFC Operational Intervals.....116

LIST OF FIGURES

Page

Figure 2.1 Schematic presentation of a typical double chamber MFC with the components. 13

Figure 2.2 SEM image of biomass carbon derivative materials. (a) bamboo charcoal tube surface (b) orange peels biochar (c) cauliflower leaves biochar (d) almond shell carbon (Reprinted from reference [62, 75, 76] with permission of copyright from Elsevier). 19

Figure 2.3 Samples of biomass that have been recently used for anode fabrication in MFC (a, b) king mushroom, FE-SEM micrographs of carbonized king mushroom (c, d) wild mushroom, FE-SEM micrographs of carbonized wild mushroom and (e, f) corn stem, FE-SEM micrographs of carbonized corn stem. (Adapted from Reference [63, 77] with permission of copyright from Elsevier) 20

Figure 2.4 Schematic presentation of bacterial-anode interaction in MFC system (Reproduced from reference [134] with copyright permission from Springer Nature). 32

Figure 2.5 The MFC system mechanism in the degradation of hydrocarbon contaminants (modified from Reference [4] with permission from MDPI) 36

Figure 2.6 Microbes and organic pollutant interaction in the anode chamber of MFC along with the methods of electron transfer (Modified from Reference [162]) 42

Figure 2.7 Factors affecting organic pollutants biodegradation 43

Figure 2.8 Microbial metabolism and electron generation in xylene degradation though MFC (Reprinted from Reference [191] with permission from Elsevier) 47

Figure 3.1 (A) The sample fabricated anode electrodes (B) The fabrication scheme of the anode electrodes 62

Figure 3.2 (A) MFC operational mechanism system (B) Schematic representation of the single chamber MFC model used in the present work (C) The actual set-up of the single chamber MFC 64

Figure 4.1 (A) FTIR spectra, (B) X-ray diffraction pattern of the materials 78

Figure 4.2 (A) Raman spectra, (B) TGA curve of the materials 80

Figure 4.3 Nitrogen adsorption-desorption isotherms of the materials with pore size distribution (inserted) 81

Figure 4.4 The C 1s XPS spectra of the anode materials 83

Figure 4.5 The O 1s XPS spectra of the anode materials 84

Figure 4.6 SEM images: (A) PKS-GO (B) PKS-rGO (C) PKS-rGO/TiO_2 (D) PKS-rGO/ZnO. TEM images: (E) PKS-GO, (F) PKS-RGO (G) PKS-rGO/TiO_2 (H) PKS-rGO/ZnO 87

Figure 4.7 The EDX spectra of PKS-GO, PKS-rGO, PKS-rGO/TiO_2 and PKS-rGO/ZnO materials 89

Figure 4.8 AFM image of PKS-GO, PKS-rGO, PKS-rGO/TiO_2 and PKS-rGO/ZnO materials 91

Figure 4.9 SEM image of electrode biofilm study after 70 days of MFC operation: (A) PKS-GO anode, (B) Commercial graphite cathode Versus PKS-GO anode, (C) PKS-rGO anode, (D) Commercial graphite cathode Versus PKS-rGO anode 94

Figure 4.10 Cyclic voltammetry curves of PKS-rGO and PKS-GO anodes MFC system at different days of operation 96

Figure 4.11 Nyquist plots (EIS) spectra of the PKS-GO and the PKS-rGO anodes at different MFC operational days 97

Figure 4.12 (A) Conductivity of anodic wastewater Vs period of MFC operation, (B) Relationship between voltage (mV) Vs PKS-GO anode wastewater at every 10 days operational intervals, (C) Relationship between voltage (mV) Vs PKS-rGO anode wastewater at every 10 days operational intervals 100

Figure 4.13 Schematic presentation of the biodegradation pathway and microbial electron transfer in the FA containing MFC 103

Figure 4.14 The UV-visible spectra of FA collected from the MFC system at various intervals, with calibration of treated FA samples inserted: (A) PKS-GO anode containing MFC, (B) PKS-rGO anode containing MFC 105

Figure 4.15 SEM image of electrode biofilm study after 70 days of MFC operation: (A) PKS-GO anode, (B) Commercial graphite cathode Versus PKS-GO anode, (C) PKS-rGO anode, (D) Commercial graphite cathode Versus PKS-rGO anode. 107

Figure 4.16 EDX spectra of anode electrodes after 70 days of MFC operation: (A) PKS-GO anode, (B) PKS-rGO anode 108

Figure 4.17 Phylogenetic tree showing positions of prominent anodic bacterial species: (A) PKS-GO anode biofilm, (B) PKS-rGO anode biofilm 109

Figure 4.18 (A) Daily voltage output trend of the MFC operations (B) Polarization curve of PKS-GO anode MFC operation with 100 Ω–7 kΩ range of external resistance(C) Polarization curve of PKS-rGO anode MFC operation with 100 Ω–7 kΩ range of external resistance. 113

Figure 4.19 Cyclic voltammogram of PKS-GO and PKS-rGO anodes at different MFC operational days 115

Figure 4.20 EIS Nyquist plots of the anodes at various MFC operational days 117

Figure 4.21 (A) Anodic wastewater conductivity at different intervals; Voltage and conductivity relationship (B) PKS-GO MFC system (C) PKS-rGO MFC system..... 120

Figure 4.22 Naphthalene biodegradation pathway and electron transportation in the present study 122

Figure 4.23 The UV-visible spectra of naphthalene collected from MFC reactor with calibrated naphthalene treated samples (inserted): (A) PKS-GO anode MFC system (B) PKS-rGO anode MFC system 123

Figure 4.24 SEM image of anodes and cathode at the end of the MFC operation (A) The PKS-GO anode (B) The graphite cathode in the PKS-GO anode system (C) The PKS-rGO anode (D) The graphite cathode in the PKS-rGO anode system 125

Figure 4.25 The EDX spectra of used anodes (A) PKS-GO (B) PKS-rGO 126

Figure 4.26 Phylogenetic analysis of microbial isolate from the MFC, showing the dominant phylogenetic positions: (A) PKS-GO anode biofilm, (B) PKS-rGO anode biofilm..... 128

Figure 4.27 (A) Voltage output behaviour of the materials and polarization pattern of (B) PKS-rGO/TiO_2, (C) PKS-rGO/ZnO..... 131

Figure 4.28 Cyclic voltammetry curves of the materials on several days 133

Figure 4.29 EIS Nyquist plot of the anode materials on the 10th and 70th days 134

Figure 4.30 Plot of UV-visible spectra of FA biodegradation along with the calibration of treated FA (inserted): (A) PKS-rGO/TiO_2 anode system (B) PKS-rGO/ZnO anode system 138

Figure 4.31 SEM images of the used electrodes (A, C) PKS-rGO/TiO_2 anode Vs commercial graphite cathode, (C, D) PKS-rGO/ZnO anode Vs commercial graphite cathode 140

Figure 4.32 Phylogenetic tree trend of the isolated microbial species PKS-rGO/TiO_2 and PKS-rGO/ZnO biofilm 142

Figure 4.33 (A) Daily voltage pattern and polarization curves of (B) PKS-rGO/TiO_2, (C) PKS-rGO/ZnO anodes 144

Figure 4.34 (A-B) Cyclic voltammogram of the anodes on operational interval of days, and (C) Nyquist plots (EIS) of the anode materials..... 146

Figure 4.35 The UV-visible spectra of naphthalene and biodegradation efficiency (inserted): (A) PKS-rGO/TiO_2 and (B) PKS-rGO/ZnO anodes..... 149

Figure 4.36 SEM images of the electrodes after MFC operation (A, C) PKS-rGO/TiO_2 anode Vs graphite cathode, (B, D) PKS-rGO/ZnO anode Vs graphite cathode 151

Figure 4.37 Phylogenetic tree positions of dominant isolated microbial species PKS- rGO/TiO_2 and PKS-rGO/ZnO biofilm 153

Figure 4.38 (A) Voltage distribution trend of CGr-FA and CGr-Naphthalene anodes, (B) Polarization curve of CGr-FA anode versus graphite cathode, (C) Polarization curve of CGr-Naphthalene anode versus graphite cathode..... 155

Figure 4.39 (A-B) Cyclic voltammetry curves of the CGr anode systems on several days of operation, (C-D) EIS Nyquist plot of the CGr anode systems 157

Figure 4.40 The UV-visible spectra of (A) FA collected from the MFC system at various intervals, with calibration of treated FA samples inserted (B) Naphthalene collected from the MFC system at various intervals, with calibration of treated Naphthalene samples inserted..... 159

Figure 4.41 Comparative energy generation profile of all anodes: (A-B) During FA biodegradation, (C-D) During naphthalene biodegradation. 162

Figure 4.42 Comparative biodegradation efficiency profile of all anodes: (A) FA biodegradation, (B) Naphthalene biodegradation..... 163

LIST OF ABBREVIATIONS

3D	Three dimensional
A	Cross-sectional area
AAS	Atomic adsorption spectroscopy
AFM	Atomic force microscopy
Ag	Silver
AgCl	Silver chloride
BE%	Biodegradation efficiency
BET	Brunauer-Emmett-Teller
CD	Current density
CGr	Commercial graphite
CNTs	Carbon nanotubes
Cp	Specific capacitance
CV	Cyclic voltammetry
DNA	Deoxyribonucleic acid
EDX	Energy disperse X-ray
EET	Extracellular electron transfer
EIS	Electrochemical impendence spectroscopy
FA	Formaldehyde
FTIR	Fourier Transform Infrared
GAC	Granular activated carbon
GO	Graphene oxide
Gr	Graphite
MFC	Microbial fuel cell
nm	Nanometer
NPs	Nanoparticles
PANI	Polyaniline
PCR	Polymerase chain reaction

PD	Power density
PEM	Proton exchange membrane
PKS	Palm kernel shell
r	internal resistance
R	External resistance
rGO	Reduced graphene oxide
rGO/TiO_2	Reduce graphene oxide/Titanium oxide composite
rGO/ZnO	Reduced graphene oxide/Zinc oxide composite
RSP	Rotten sweet potato
SEM	Scanning electron microscope
SS	Stainless steel
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
UV	UV-VIS
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

Ω	Resistance
%	Percentage
°C	Degree Celsius
µL	Microliter
A/M^2	Ampere per square metre
cm	Centimetre
cm^{-1}	Per centimeter
CO_2	Carbon dioxide
e^-	Electron
Emf	Electromotive force
mg	Milligram
F/g	Specific capacitance
L	Litre
H^+	Proton
I	Current
kHz	Kilohertz
mA	Milliampere
mA/m^2	Milliampere per square meter
mHZ	Millihertz
mV	Millivolt
mW/cm^2	Milliwatts per centimetre square
mW/m^2	Millwatts per metre square
ppm	Parts per million

ELEKTROD ANOD GRAFIN TERBITAN DARIPADA TEMPURUNG KELAPA SAWIT: PENCIRIAN DAN APLIKASI DALAM SEL BAHAN BAKAR MIKROB

ABSTRAK

Sel bahan bakar mikrob (MFC) telah menarik minat ramai dalam bidang bioelektrokimia sebagai teknik yang menghasilkan elektrik dan pada masa yang sama menyingkirkan bahan pencemar daripada air buangan. Walau bagaimanapun, kebolehannya untuk mengangkut elektron merupakan halangan utama dalam membangunkan teknik ini ke tahap skala industri. Bahan anod telah diserlahkan sebagai komponen kritikal MFC yang perlu dipertingkatkan untuk menangani isu kadar pengangkutan elektron yang rendah. Dalam kajian ini, sisa cengkerang kelapa sawit (PKS) telah berjaya digunakan untuk membuat elektrod anod untuk aplikasi MFC. Oksida grafena (GO) dan oksida grafena terkurang (rGO) telah disintesis daripada sisa PKS dan masing-masing dilabelkan sebagai PKS-GO dan PKS-rGO. Kemudian, PKS-rGO telah digabungkan dengan ZnO dan TiO_2 untuk menghasilkan bahan komposit masing-masing sebagai PKS-rGO/ZnO dan PKS-rGO/TiO_2. Beberapa teknik pencirian telah digunakan untuk mengesahkan kejayaan sintesis bahan untuk penghasilan anod. Anod ini kemudiannya telah diuji dalam MFC untuk menentukan prestasi penjanaan kuasa bersama potensi biodegradasi formaldehid (FA) dan naftalena. Anod grafit komersial (CGr) telah digunakan dalam MFC yang berfungsi sebagai rujukan untuk membanding prestasi anod yang direka. Anod komposit PKS-rGO/ZnO menunjukkan potensi prestasi tertinggi dalam kajian ini. Anod PKS-rGO/ZnO menyampaikan ketumpatan kuasa maksimum (PD) keseluruhan sebanyak

45.49 mW/m^2 dan ketumpatan arus maksimum (CD) sebanyak 114.0 mA/m^2. Manakala, anod CGr mampu menawarkan PD maksimum 8.73 mW/m^2 dan CD maksimum 50.75 mA/m^2. Hal ini menunjukkan bahawa anod PKS-rGO/ZnO mempunyai PD yang 5.21 kali lebih tinggi daripada anod CGr. Tambahan pula, CD anod PKS-rGO/ZnO adalah 2.25 kali lebih tinggi daripada anod CGr. Anod terbitan PKS lain juga berprestasi lebih baik daripada anod CGr. Begitu juga, anod terbitan PKS mengatasi anod CGr dari segi kecekapan biodegradasi, dengan PKS-rGO/ZnO menawarkan kecekapan tertinggi. Kecekapan biodegradasi maksimum ialah 94.30% bagi naftalena dan 93.0% bagi FA. Manakala kecekapan biodegradasi yang diperoleh dengan anod CGr ialah 70% bagi naftalena dan 75% bagi FA. Tambahan pula, kajian ini menunjukkan bahawa pengubahsuaian lanjut bahan PKS-rGO dengan oksida logam (TiO_2 dan ZnO) adalah pendekatan berkesan untuk meningkatkan prestasi bahan anod. Secara keseluruhannya, anod PKS-rGO/ZnO mengatasi setiap anod lain yang dinilai dalam kajian ini, baik dari segi output kuasa dan degradasi bahan pencemar.

OIL PALM KERNEL SHELL-DERIVED GRAPHENE DERIVATIVE ANODE ELECTRODES: CHARACTERIZATIONS AND APPLICATION IN MICROBIAL FUEL CELL

ABSTRACT

Microbial fuel cell (MFC) has attracted much interest in the bioelectrochemical field as a technique that produces electricity and at the same time removes pollutants from wastewater. However, their abilities to transport electrons is a major barrier in developing the technique to an industrial scale level. The anode material has been highlighted as a critical component of the MFC that needs to be enhanced to address the low electron transportation rate issue. In this study, palm kernel shell (PKS) waste was successfully employed to fabricate the anode electrodes for MFC applications. PKS waste was utilised to synthesise graphene oxide (GO), and reduced graphene oxide (rGO) was prepared from the synthesised GO, which are referred to as PKS-GO and PKS-rGO, respectively. Later, the PKS-rGO was combined with ZnO and TiO_2 to generate the composite materials of PKS-rGO/ZnO and PKS-rGO/TiO_2, respectively. Several characterization techniques have been used to confirm the successful synthesis of materials for anode production. These fabricated anodes were then evaluated in an MFC to determine power generation performance along with formaldehyde (FA) and naphthalene biodegradation potential. A commercial graphite anode (CGr) has been used in the MFC that serves as a reference to compare the performance of the fabricated anodes. The PKS-rGO/ZnO composite anode showed the highest performance potential in this study. The PKS-rGO/ZnO anode delivered an overall maximum power density (PD) of 45.49 mW/m^2 and a maximum current density (CD)

of 114.0 mA/m^2. Meanwhile, the CGr anode was able to offer a maximum PD of 8.73 mW/m^2 and a maximum CD of 50.75 mA/m^2. This implies that the PKS-rGO/ZnO anode has a PD that is 5.21 times higher than the CGr anode. Furthermore, the CD of the PKS-rGO/ZnO anode was 2.25 times higher than that of the CGr anode. Other PKS-derived anodes also performed better than the CGr anode. Similarly, the PKS-derived anodes surpassed the CGr anode in terms of biodegradation efficiency, with PKS-rGO/ZnO offering the highest efficiency. The maximum biodegradation efficiency was 94.30% for naphthalene and 93.0% for FA. While the biodegradation efficiency obtained with CGr anode is 70% for naphthalene and 75% for FA. Furthermore, this work demonstrated that the further modification of the PKS-rGO material with metal oxides (TiO_2 and ZnO) is an effective approach that enhanced the anode material's performance. Overall, the PKS-rGO/ZnO anode outperforms each of the other anodes evaluated in this study, both in terms of power output and pollutant degradation.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The world expanding industrialisation has resulted in a sharp increase in energy consumption. Sustained access to some energy sources, such as petroleum–based fuels, has contributed significantly to environmental pollution, resulting in adverse human health issues and negative impacts on terrestrial ecosystems. Some of the consequences of the unintentional release of petroleum hydrocarbons into the environment include air pollution, which may contribute to global climate change causing major setbacks in sustainable development [1-3]. Therefore, the necessity to look for an alternative source of energy that can be found in every country in the world has geopolitical, economic, and environmental benefits. Microbial fuel cell (MFC) represents a viable alternative with promising technology to counter the above-mentioned challenges. In MFC, bio-energy is generated from organic matter through the metabolic activities of microbes such as bacteria and can simultaneously decontaminate toxic pollutants in the system [4]. The fundamental introduction to MFC in terms of components and mechanisms has been extensively defined in previous works [5]. Despite all of the advancements in MFC, the power output performance is still very low for commercial application [6]. Efforts are being made to improve the performance of MFC while lowering their set-up and operating costs. According to a review of the literature, the transfer of electrons from anode to cathode is critical in improving MFC performance [7]. Electron transportation is hampered as a result of the utilization of a poor material as an anode. For example, metal-based anode electrodes can transfer electrons more effectively, but after a while, they create

corrosion, which inhibits microbial growth and activity. Similarly, other common carbon materials such as graphite, carbon rods, and so on, have failed to transport the electrons, despite the fact that carbon, with the exception of carbon nanotubes (CNTS), is not hazardous to microbial species. According to recent research, carbon derivatives can be a beneficial strategy to address such a problem [8, 9]. Yaqoob et al. [10] comprehensively researched the graphene oxide-based anode in MFC and achieved considerable good results with no hazards. Commercial graphene is not an ideal solution due to economic feasibility. As a result, Yaqoob et al. [10] proposed that the biomass-derived graphene derivatives material can fulfil the economic feasibility criteria. Graphene-derived biomass materials for anode fabrication are currently receiving careful attention from researchers in MFC because of the material's requisite property stipulations, which can contribute massively to the high-performance process rate of an MFC [11]. Graphene derivatives are the purest grade carbon-based compounds that may be produced from bio-waste [12, 13]. Biomass has recently received a lot of attention due to its sustainability and ability to be transformed into functional carbon-based materials. The precise composition of biomass materials varies depending on the biomass resources used. However, they are mostly made up of lignin, hemicellulose, and cellulose. Certainly, a variety of process conditions, such as feedstock type, temperature, residence time, heating rate, and pressure, would influence the properties of the resulting biomass-based carbonaceous materials; different combinations would lead to a variety of characteristics, such as surface area, surface functional groups, porosity, and so on. As a result, a better understanding of such combinations is required for various applications of biomass-based carbonaceous materials. Raw biomass, on the other hand, is typically composed of organic substances such as saccharides, vitamins, and fatty acids. Many organic substances

will be decomposed into H_2O and CO_2 during the thermal carbonization process, eventually escaping through pores [14]. To achieve high-quality biomass-based carbonaceous materials, researchers have worked to optimize the pore structure, modify the surface property, and adjust the degree of graphitization during the preparation process.

Previous research indicates that when graphene derivatives such as graphene oxide (GO) or reduced graphene oxide (rGO) were prepared from bio-waste material, the process produced relatively poor quality when compared to commercial graphene derivatives [15]. The material conductivity may be changed owing to quality assurance. Therefore, several studies show that the utilization of metal oxide as a modifier with graphene derivatives can bring a significant breakthrough in MFC as an anode. Recently, Yaqoob et al. [10] conducted a brief study on GO-metal oxide composite-based anode for MFC. Up to date, the utilization of metl oxides such as zinc oxide, titanium oxide, and others as modifiers with rGO has been shown to be a beneficial step toward improving energy performance. According to a review of the literature, metal oxide nanomaterials are a promising emerging modifier due to their high thermo-chemical stability, good elasticity, biocompatibility, good tensile strength, large surface, high loading capability, excellent penetrability, best electro-catalytic activity, and ability to support remarkable electron-transfer [16-18]. Furthermore, metal oxides are typically thought to be anti-bacterial. To avoid this problem, a conductive polymer such as polysulfone must be used as a binder during the synthesis of the rGO-metal oxide composite anodes [19]. The conductive polymer used acts as a barrier between bacterial species and the rGO-metal oxide nanocomposite composition [20]. Polysulfone is the most important material for successfully transporting electrons to the rGO-metal oxide nanocomposite anode for further

transport to the cathode. These features provide a suitable approach for wastewater treatment and energy generation enhancement with increasing the electron transfer rate in electrochemical reactions [21]. However, challenges abound in achieving this on an industrial or commercial scale. The production costs of graphene-derived anodes and their sustainability for industrial MFC application have not been adequately harnessed. Fabricating anodes through biomass waste has provided a promising alternative for cost-effectiveness. Insight on the synthesis routes and modification can provide wider knowledge on its large-scale application for MFC. Furthermore, MFC technique has made good progress in removing toxic metals from wastewater [10]. Recently, however, researchers have begun to apply MFC technology to the degradation of organic pollutants [22]. Only few studies were studied utilizing MFC for the degradation of organic pollutants.

In this study, we evaluated biowaste-derived rGO and their metal oxide composites for fabricating the anode electrode based on the latest literature directions and our previous knowledge. Furthermore, Malaysia is one of the world's largest palm oil producers, the large amount of palm kernel shell (PKS) disposed as waste during the palm oil mill process has created additional challenges for the country in terms of waste management costs and other environmental concerns [23]. Therefore, palm oil biowaste, particularly PKS waste, is readily available for scientific research in Malaysia. Hence, we proposed using PKS waste to synthesize the GO and rGO (PKS-GO and PKS-rGO) and then to prepare its metal oxide composites (PKS-rGO/ZnO and PKS-rGO/TiO_2). Additionally, the study considered the MFC's secondary application in terms of pollutant removal. Since not much emphasis has been placed on MFC for organic pollutant removal from wastewater. Consequently, in this study, formaldehyde (FA) and naphthalene supplemented wastewaters were used as the organic pollutant to

be biodegraded in the MFC system. FA as an organic pollutant occurs naturally in the environment and is a by-product of many natural processes, particularly biomass combustion. FA is moderately toxic to aquatic organisms and inhibits reproduction in both animals and humans. Naphthalene is polycyclic aromatic hydrocarbon (PAHs) and its contamination in wastewater has received increased attention in recent years. They are hydrophobic, with high boiling and melting points, low water solubility, and electrochemical stability. As a result, they can occur and accumulate in soils or water for long periods of time. Mainly, PKS-GO, PKS-rGO, PKS-rGO/ZnO, and PKS-rGO/TiO_2 composites are synthesized, characterized, and examined as the anode in an MFC to generate electricity during FA and naphthalene supplemented wastewater treatment. The goal is to improve extracellular electron transport within microbial species and anodes. The anolyte solution is the supplemented wastewater, with rotten sweet potato (RSP) juice serving as the organic substrate. Various characterization tools were used to study the properties of the anode materials and composites. Furthermore, comparative study carried out indicates the enormous potential of such rGO, and its metal oxide composites as anode electrodes in improving the overall performance of bio-electrochemical systems such as the MFC.

1.2 Problem Statement

MFC technology is currently gaining international attention as a rapidly expanding bio-electrochemical system capable of converting the chemical energy contained in wastewater into electricity while also degrading the pollutant in the wastewater as well as the organic substrate for microbes [24]. However, the transport of electrons from the microbes to the anode surface has remained poor over the years, suppressing MFC power performance progress. As a result, there have been several

attempts to improve electron transport between the anodic biofilms and electrodes, thereby gradually increasing the efficiency of MFC. To achieve this goal, a wide range of materials had been used to fabricate highly improved electron transferable anodes for high energy generation and MFC durability [25]. Although biowaste-derived graphene oxide (GO) materials have been shown to provide an effective platform as the anode in MFC, there is still a need to improve electron transport from microbial cells to the anode electrode. For example, Yaqoob et al. [10] achieved a low voltage of 91 mV in 57 days of MFC operation using a GO anode made from biowaste material. This is due to a low rate of electron transport issues. However, studies have shown that transforming of GO to a reduced graphene oxide (rGO) can improve the electrical conductivity of the GO material, resulting in a significant improvement in extracellular electron transport as well as microbial biocompatibility [26]. Therefore, this study employs the use of palm kernel shell (PKS) as a precursor for the synthesis of GO and the subsequent preparation of rGO for fabrication into anode electrodes. Furthermore, we thought of improving the anode properties of the rGO material by further hybridizing the material with metal oxides such as ZnO and TiO_2. According to one recent study, biomass modification with metal oxide (such as ZnO, TiO_2) is one of the best options for improving electron transport rate [27]. Metal oxide-based materials such as cobalt oxide, zinc/cobalt oxides, and iron oxide have recently been used as anode electrode modifiers in MFC [28, 29]. Because of their distinctive electrical, high electrocatalytic capacity, semiconductor, and optical activities, metal oxides are regarded as a promising material for anode modification [27, 30]. Hence, these measures may improve electron transport rates in MFC applications. Furthermore, Xu et al. [31] reported that metal oxide anode modifications provided adequate exo-electrogenic microbial enrichment in the MFC. The anode material should, in general,

have a large surface area for microbial adhesion, be electrically conductive, have good hydrophilicity, be durable and stable, and have good microbial biocompatibility [2]. Therefore, it is crucial to develop a high durable, stable, and low-cost anode to improve electron transport and anodic biofilm development on the anode's surface. Using metal oxide hybridized with carbon-based materials can help to improve the electrocatalytic activities and electron transport rate of the anode in MFC. The use of PKS-derived GO derivatives as anode in electrochemical cells is not a novel idea. Even though it is well known that this material is high in carbon and has been used in a variety of waste recovery and treatment studies [32]. PKS carbon has also been used as an electrode in other electrochemical cells, including carbon fuel cells, lithium batteries, and supercapacitors [33, 34]. To the best of our knowledge, we are the first to use PKS-derived GO and rGO/metal oxide composites in MFC anode formulation. Additionally, much has been reported in recent years about toxic metal remediation via MFC; this study fills some research gaps in MFC application by focusing on organic pollutant degradation, which has not been adequately studied in previous MFC works. There has been no adequate clarity on the organic pollutant degradation mechanism or their interaction with microbes in the MFC. This study proposes the mechanism routes and microbial interactions with organic pollutants for the various MFC system studied. Furthermore, phylogenetic trees of the anodic biofilms were adequately presented in the studies conducted. The environmental friendliness, long-term sustainability, and green approach features of MFC make it more suitable for organic pollutant degradation. We believe that this study will spark new research interests in the field of organic pollutant degradation using MFC. In a nutshell, the TiO_2 and ZnO metal oxides as modifiers into the PKS-derived rGO may improve the microbial biocompatibility thereby improving the electron transport rate of the MFC.

1.3 Research Objectives

1. To synthesize and characterize GO, rGO, rGO/TiO_2 and rGO/ZnO materials derived from PKS waste.
2. To fabricate the PKS-derived materials into anode electrodes (PKS-GO, PKS-rGO, PKS-rGO/TiO_2 and PKS-rGO/ZnO anodes).
3. To evaluate and compare the performances of the anodes through MFC application in terms of power generation and organic pollutant degradation.
4. To investigate the microbial community of individual anodes after completion of the MFC operation.

1.4 Scope of Study

1. Palm kernel shell (PKS) waste was used as the primary source for the synthesis of GO and its derivatives such as rGO, rGO/TiO_2, and rGO/ZnO. The GO was first synthesised from carbonised PKS, and it was then used to prepare the rGO via thermal reduction. Furthermore, the rGO/TiO_2 and rGO/ZnO composite materials were prepared via a simple solvothermal process. Consequently, the materials were given the designations PKS-GO, PKS-rGO, PKS-rGO/TiO_2, and PKS-rGO/ZnO.
2. The prepared PKS-GO, PKS-rGO, PKS-rGO/TiO_2 composite and PKS-rGO/ZnO composite are used to fabricate the anode electrodes for MFC application. Throughout the study, commercial graphite electrodes were employed as cathodes for the MFC application. A single chamber MFC with a 1 kΩ external resistor was employed. Rotten sweet potato (RSP) juice was processed and used in the MFC as the organic substrate.

3. Several techniques were used to accomplish different anode material characterization processes. Fourier transform infrared (FTIR), energy disperse x-ray (EDX), x-ray diffraction (XRD), Brunauer-emmett-teller (BET), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscopy (AFM) are the techniques used in the materials studies.
4. The manufactured anodes were applied to a single MFC system, and their evaluation in terms of energy generation and organic pollutant degradation was evaluated and compared to a commercial graphite anode. Electrochemical measures such as daily voltage outputs, electrochemical impendence spectroscopy (EIS), cyclic voltammetry (CV), and polarization behaviour were used to examine performance. The maximum current and power densities for each anode electrode were calculated using voltage trends to assess the cell's power output.
5. The microbial analysis was also performed on the electrodes after the MFC operation. This is done to identify the microbial species actively responsible in the anode biofilms. In this case, SEM and EDX were employed to examine the microbial biocompatibility towards the anodes. Furthermore, the pure cultures were isolated and microbial identification study was conducted. The phylogenetic tree for the microbial isolates were constructed.
6. The organic pollutants formaldehyde (FA) and naphthalene are the target pollutants in this project.

1.5 Organization of Thesis

This thesis consists of five chapters. Chapter 1 provides detailed information about the background of the study. The problem statements highlighting the research gaps and contribution of the research were presented. The goals, objectives and scope of the study were also presented in Chapter 1. Chapter 2 provides in-depth overview of the current study with review of several recent literatures in the field. The scalability of utilizing biowaste materials as anode electrode in MFC was extensively researched. Utilization of MFC for organic pollutants degradation was also explored. The organic pollutant interaction with microbes in the MFC was comprehensively reported. The methodology and workflow procedure for synthesizing PKS-GO and PKS-rGO, as well as the modification with metal oxide for assembling the anode electrode, are presented in Chapter 3. This chapter explicitly describes the chemicals and apparatus utilized for this investigation. The performance of the GO-derivative anodes as an efficient source of electron transfer and organic pollutant degradation supports via MFC was thoroughly examined. The results of the material characterizations were thoroughly detailed in Chapter 4. This chapter also critically examined the electrochemical and degradation performance of the employed anode electrodes. SEM, AFM, TEM, EDX, Raman, XRD, FTIR, BET, XPS, TGA, UV, EIS, and CV were among the material characterizations presented. The biological analysis, which included microbial identifications, was investigated and reported. The findings and outcomes of this study are outlined in Chapter 5. Chapter 5 also includes ideas to improve future research and direction.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The ongoing global industrialization has contributed to a significant increase in the release of toxic pollutants into the environment, the majority of which are primarily organic pollutions. When organic pollutants more than permissible limits are in the environment, they pose a serious threat to aquatic life and humans. Various bioremediation and degradation techniques for organic pollutants removal from the environment have been reported; however, their sustainability and efficacy remain insufficient. The overarching goal of this literature review is to unravel the effectiveness of using the microbial fuel cells (MFC) technique to degrade organic pollutants while improving the energy generation performance of the system. Furthermore, this literature review extensively reports on the scalability of utilizing biowaste materials as anode electrodes in MFC, thereby improving the system's overall performance.

A microbial fuel cells (MFC) is a technique in which microbes, in the form of bacteria, absorb nutrients from a carbon source (usually called a substrate) to produce electrons, thereby converting chemical energy into electrical energy. This is done by successive reactions in which the generated electrons are transferred to the anode electrode and then to the terminal electron acceptor via an external circuit, where electric current is generated in the process [35]. In a traditional MFC system, microbes live in the anodic chamber, forming biofilms around the anode and requiring organic substrates as a carbon source for survival and growth. Electrons and protons are produced as a result of the metabolic process. **Figure 2.1** shows a schematic diagram

of a typical double chamber MFC system. The electrons are transferred to the anode through any of the electron transfer methods which are subsequently transported to the cathode, while the protons enter the cathodic chamber via the proton exchange membrane (PEM) [24, 36, 37]. However, the single chamber MFC does not have the PEM to separate the two regions, the protons move freely towards the cathodic region. The MFC technique is designed to simultaneously generate electricity and biodegrade pollutants that are present in the anodic chamber of the system [38]. These functions make MFC an emerging technology and the most widely studied type of bioelectrochemical technique, which has recently attracted the interest of many researchers for the simultaneous production of green energy and the biodegradation of pollutants. [39, 40]. The technique has made good progress in removing toxic metals from wastewater [10]. Recently, however, researchers have begun to apply MFC technology to the degradation of organic pollutants [22]. There have been various conventional techniques used in degrading organic pollutants; such methods include photocatalytic degradation [41], adsorption techniques [42], chemical precipitation [43], electrochemical degradation [44], advanced oxidation [45] among others. These methods have made good advances in removing organic pollutants from wastewater and soil samples; however, there are some significant drawbacks such as cost ineffectiveness, high energy requirements, lack of environmental friendliness, and process difficulties. As a result, it is critical to investigate greener approaches to organic pollutant degradation. For example, Umar et al. [46] was faced with some of these issues while studying the photocatalytic degradation of organic pollutants like ketoprofen and chlorothalonil. They proposed a complex novel synthesis route for synthesising the photocatalyst, which was capable of reducing the total organic carbon

(TOC) content of the pollutants. Photocatalytic processes are time-consuming and environmentally unfriendly.

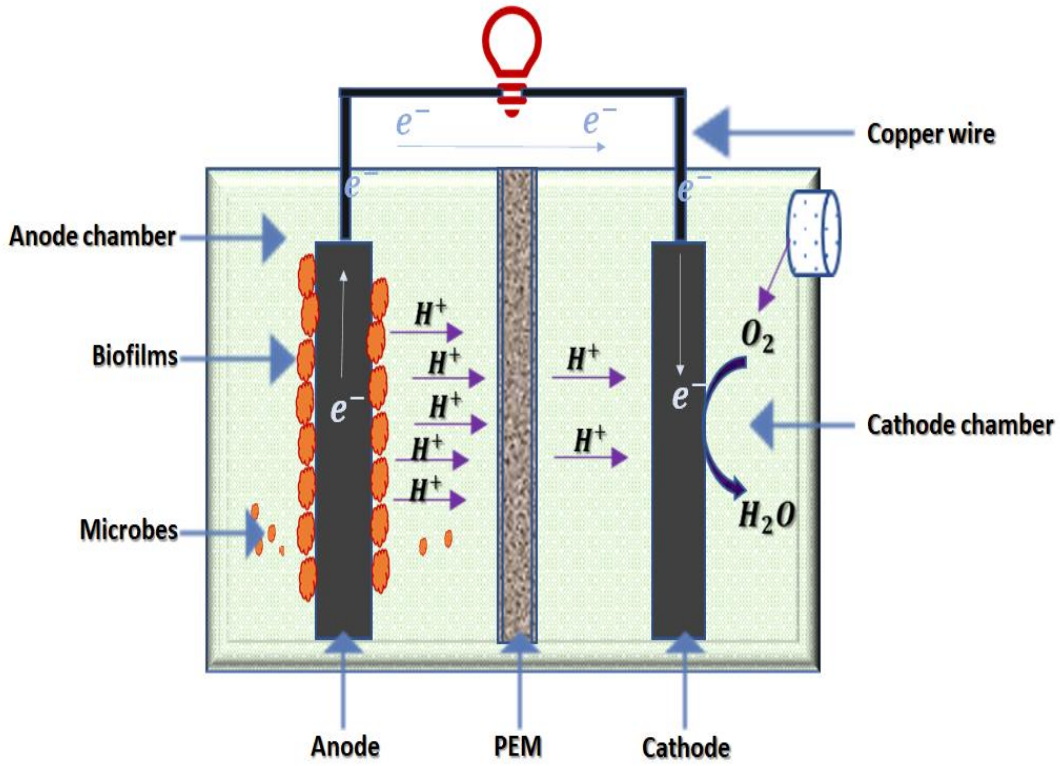

Figure 2.1: Schematic presentation of a typical double chamber MFC with the components.

Despite all of the advancements in MFC, the power output performance is still very low for commercial application. Efforts are being made to improve the performance of MFCs while lowering their set-up and operating costs. According to a review of the literature, the transfer of electrons from anode to cathode is critical in improving MFC performance. Electron transportation is hampered as a result of the utilization of a poor material as an anode. For example, metal-based anode electrodes can transfer electrons more effectively, but after a while, they create corrosion, which inhibits bacterial growth and activity. Similarly, other common carbon materials such as graphite, carbon rods, and so on, have failed to transport the electrons, despite the

fact that carbon, with the exception of carbon nanotubes (CNTS), is not hazardous to bacterial species. According to recent research, carbon derivatives can be a beneficial strategy to address such a problem [8, 9]. Yaqoob et al. [10] comprehensively researched the graphene oxide-based anode derived from biowaste in MFC application and achieved considerable good results with no hazards. Commercial graphene is not an ideal solution due to economic feasibility. Fabricating anodes through biomass waste has provided a promising alternative for cost-effectiveness. Insight on the synthesis routes and modification can provide wider knowledge on its large-scale application for MFC. However, this literature review aims to discuss the effectiveness of enhancing energy generation and in MFC through the application of biowaste-derived anodes as well as studying their organic pollutant degradation potentials.

2.2 Advances in Electrodes for MFC Application

The electrode materials used in MFC have certain generic characteristics as well as their own. The foundation materials for all types of electrodes must have good conductivity, good chemical stability, strong mechanical properties, and low cost. Carbon compounds and non-corrosive metals are currently the most extensively utilized base materials since they can meet the broad standards outlined above. Some electrode material surface properties, such as high surface roughness, strong biocompatibility, and rapid electron transport between microbes and electrode surface, are required for high bio-catalytic activity. In MFC, there are two basic types of electrodes: anode electrodes and cathode electrodes. The anode electrode is of critical importance because of its crucial role in the performance of the MFC. The anode electrode material can influence microbial activity and increase electron mobility in

the MFC system. This thesis literature review, on the other hand, concentrates on the most recent improvements in anode electrode technology in MFC applications.

2.2.1 Significance of Anode Electrode in MFC

The anode is established as a very significant part of the MFC, both functionally and structurally, due to the major role that it plays in improving the performance of the MFC. The materials mostly used for anode fabrication are from carbon-based origin, such as graphite felt, graphite fiber brush, graphite rod, carbon cloth, carbon felt, carbon paper, and reticulated vitreous carbon (RVC), graphite granules (GGs), or granular activated carbon (GAC). They have also been widely used for the anode due to the certain favourable properties they possess, ranging from stability in bacterial cultures, high conductivity, and a good surface area [47, 48]. Modifying the material surfaces before fabricating the anode is one way to improve the performance of MFC. In this way, adhesion to bacteria cells, the potentiality of the cell, and extracellular electron transfer are improved [49]. Recently, MFC scientists have begun to modify the anode material using various modification techniques to improve the electron transfer [50]. Griškonis et al. [49] studied the voltage dependence of MFC that utilizes different anodes and observed that MFC with an anode modified with ethylenediamine produced a slightly larger voltage than the MFC with the anode prepared from ordinary GF (graphite felt), whereas the MFC with an anode made of GF, which was treated with paraphenylenediamine, produced about 32% higher voltage than the control MFC when the circuits of the studied MFCs were connected with resistors of 659 Ω. The power density of the latter MFC was about 1.75-fold higher than in the control. Another feasible way to enhance MFC output power is using modified carbon such as graphene derivatives and metal-based anodes with conductive

polymers. The structure of the anode and its materials are capable of affecting the oxidation process as well as the bacteria adhesion [51]. Materials used for anode fabrication in MFC usually encompass the following essential factors, the compatibility of the material is influenced by a few several reasons, including low price and high biocompatibility, chemical stability, and electrical conductivity. However, compatibility issues can occur even if the anode material selection and design are superficially correct. This is a major reason for the low efficiency of some prototype MFC and remains a significant barrier to their practical application [52]. In the biochemical and electrochemical aspects of the anode surface, the oxidation reaction in MFC takes place at the anode, thereby electrons are released. The bacterial species rely on the energy produced by fuel oxidation. For energy conversion, microbes use two metabolic pathways: respiration and fermentation. Bacterial species undergoes respiration via the respiratory or oxidative pathway, in which electrons circulate through a respiratory chain before leaving the microbial cell via membrane-bound electron acceptors [53]. The bacterium produces CO_2 and H_2O in the presence of oxygen during the decomposition of the substrate. However, the presence of oxygen is inhibitory and as such, anode chambers are made anaerobic. In these anaerobic conditions, the bacteria decompose the organic matter into only CO_2 [54].

2.2.2 Metal Oxide Decorated Anode Electrodes

While metal/metal oxides are also frequently used as anode materials in MFC, their corrosion can limit their compatibility with microbes, which hinders their widespread application in MFC systems [52]. This issue highlights the need for more stable and environmentally friendly anode materials to enhance the sustainability and performance of MFC. The modification of electrodes with metal or metal oxide

nanocomposite greatly increased MFC performance due to a reduction in ohmic loss caused by improved microbial cell adherence [52]. Oxides of titanium (Ti), zinc (Zn), manganese (Mn), iron (Fe), and other elements have been combined with carbonaceous material to generate nanocomposite materials that have been used as anode electrode modifiers. TiO2's biocompatibility and chemical stability make it an attractive candidate for use as MFC electrode material [55]. Recently, TiO_2 nanotubes vertically orientated on carbon paper were shown to improve MFC performance [56]. This was attributed to the creation of vertically penetrating 3D pores, which provide a large contact area for direct electron transfer and are highly biocompatible, allowing for molecular diffusion and good electron transport conduits. TiO_2 or ZnO is a promising material for anode modification because of its high biocompatibility, anti-corrosion capabilities, optical and dielectric qualities, and lower cost when compared to other metals [57]. Thus, this metal oxide is a promising material for altering anode electrodes. Some metal-based modifications and power generation have been reported [31].

2.3 Biowaste Materials as Anode Electrodes

In previous years, biomass derived materials have been receiving more and more attention as high-performance and low-cost materials for the fabrication of anode in fuel cells. With the increasing demand for green energy, anode electrodes have been fabricated from recyclable and renewable materials, especially with waste materials rather than high-cost precursors to obtain more high-performance anode materials. Therefore, due to their low-cost and recyclable characteristics, waste-derived carbon derivatives from available bio-waste are considered a very promising alternative to conventional anodes [58-61]. Recently, researchers are introducing this concept of

waste materials for anode fabrication in MFC application as summarized in **Table 2.1.** For example, Yaqoob et al. [10] studied the use of lignin-graphene derived anode (L-GO) obtained from bio-waste (oil palm) in an MFC to generate energy. The authors improved the electron transportation rate of the anode by introducing a zinc oxide composite-based anode (L-GO/ZnO). MFC system featured with L-GO/ZnO anode displayed a higher removal efficiency (91.07%) of the toxic metal (Pb^{2+}), whereas a removal efficiency of 85% was observed when L-GO anode was used. Also, the lignin-based anode (L-GO/ZnO) supported a higher maximum current density (1.350 mW/m^2) with a corresponding current density (142.98 mA/m^2) compared to the values exhibited by the anode (L-GO), which displayed a power density of 0.020 mW/m^2 with a current density of 17.54 mA/m^2. The authors agreed that oil palm material can be used as a promising and cost-effective waste to improve the anode properties for enhanced performance of MFC. Similarly, Hung et al. [62] showed that coffee waste-activated carbons (CWAC) can be used as material to form anode in a *Escherichia coli* based MFC. The pore size of CWAC was modified to achieve a power density of 3927 mW/m^2, which was greater than that of commercial activated carbon (975 mW/m^2). The authors attributed the increased power density of CWAC to its high conductivity and appropriate pore size distribution, which resulted in a rapid electron transfer and bacterial attachment. Furthermore, bamboo charcoal was prepared by Zhang et al. [63], which was discovered to present better electrode characteristics than that of a conventional graphite rod. The SEM image derived from the carbonized bamboo charcoal is shown in **Figure 2.2**. The observed benefits of this electrode material include low internal resistance, improved biocompatibility, and a rougher surface that promotes biofilm adhesion. According to the findings, the addition of C=N bonds facilitated electron transfer from the bacteria through the anode. As a result, the

anode made of bamboo charcoal was 50 % more efficient than the anode made of graphite tube [63]. The reachability of bacterial species to the large surface area of the anode improves kinetics and performance significantly. The SEM scan shows that the surface was rough, with many apparent fissures. **Figure 2.3** shows different biomass materials and their FE-SEM micrographs used as anodes in MFC.

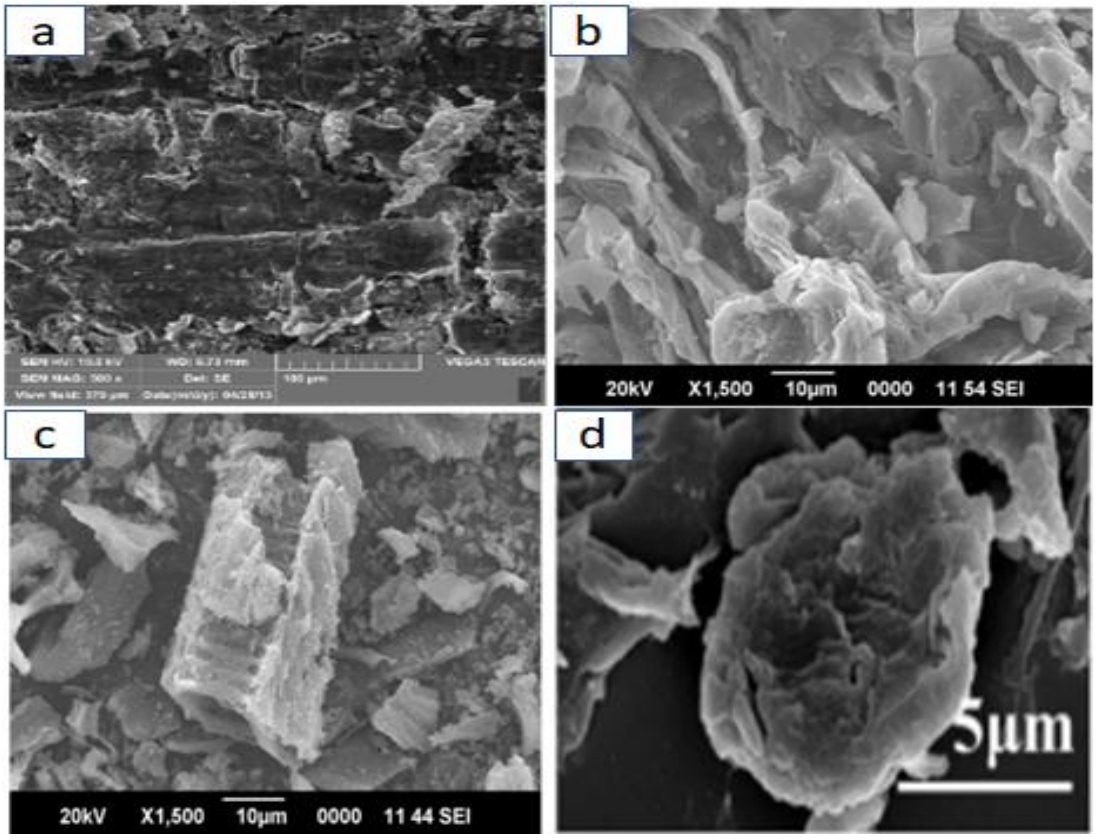

Figure 2.2: SEM image of biomass carbon derivative materials. (a) bamboo charcoal tube surface (b) orange peels biochar (c) cauliflower leaves biochar (d) almond shell carbon (adapted from reference [63-65] with permission from Elsevier)

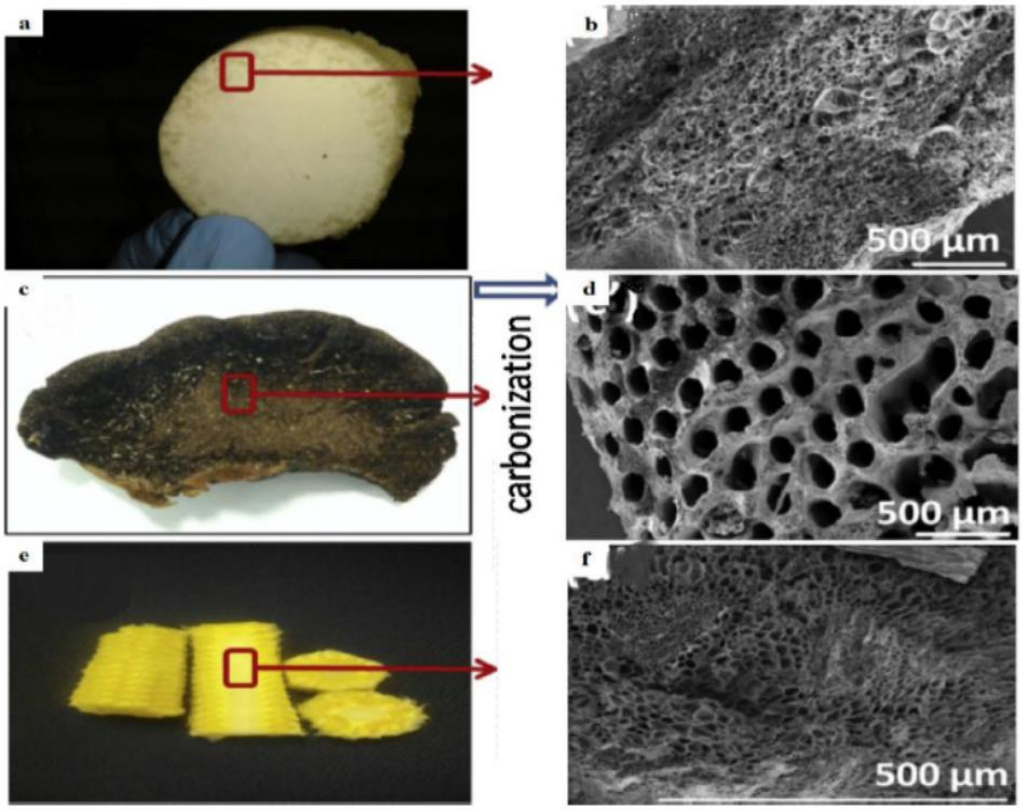

Figure 2.3: Samples of biomass that have been recently used for anode fabrication in MFC (a, b) king mushroom, FE-SEM micrographs of carbonized king mushroom (c, d) wild mushroom, FE-SEM micrographs of carbonized wild mushroom and (e, f) corn stem, FE-SEM micrographs of carbonized corn stem. (Adapted from Reference [66, 67] with permission of copyright from Elsevier)

Table 2.1: Summary of recently used biowaste materials for anode electrodes fabrication in MFC.

Biowaste Material	Surface area (cm^2)	Electrode size (cm^2)	Strain/Inoculum source	Power density (mW/m^2)	Reference
Oil palm	76.0	8.0 × 1.3	Pb^{2+} wastewater	1350×10^{-3} 20×10^{-3}	[10]
Coffee waste	1.0	-	*Escherichia coli*	3927	[62]
Waste tires	1.0	-	-	-	[68]
Oil palm	76.0	8.0 × 1.3	Synthetic wastewater	-	[69]
Cellulose waste	0.71	7.5 × 1.2	Synthetic wastewater	-	[70]
Palm kernel shell AC	0.5	-	Fecal sludge	1730	[71]
Corn stem	-	-	Anaerobic sewage	-	[66]
Sludge mixed with fly ash	12	1.8 × 0.8	Sodium acetate	-	[72]
Municipal sludge	-	3.0 × 2.0	*Shewanella oneidensis*	568.5	[73]
Municipal sludge	0.5	3.0 × 3.0	Artificial wastewater	615.2	[74]
Mango wood	75.3	2.0 × 3.0	Inoculum bacteria	589.8	[75]
Onion peels	7.0	10 × 2.0	Mixed sludge	742	[76]
Compress mill residue	10.99	0. 5 × 3.0	Anaerobic sludge	532	[77]

Table 2.1: (Continued)

Biomass Material	Surface area (cm^2)	Electrode size (cm^2)	Strain/Inoculum source	Power density (mW/m^2)	Reference
Barbed chestnut shell	91	2.7 × 2.7	Mixed sludge	759	[78]
Loofah sponge	11	0.5 × 3.0	Anaerobic sludge	701	[79]
Silk cocoon	7.0	-	Mixed sludge	5.0	[80]
Coconut shell/ sewage sludge	10.99	0.5 × 3.0	Mixed sludge	1069	[81]
Bamboo Charcoal	59.21	2.4 × 1.57	Anaerobic Mix sludge	1652 ± 18	[63]

There are vast numbers of available waste materials useful for anode fabrication, few among them include palm kernel shells, coconut shells, almond shells, chestnut shells, cashew nut shells, wooden wastes, waste papers, corn straw, etc. The availability of these materials is based on locations and geographical regions. Most countries around the world are introducing several green policies to save the ecosystem and to attenuate the complicating effects of environmental pollution. For instance, Malaysian government has demonstrated its intention to develop the palm biomass industry since 2001 as a measure of supporting the country's green policy. The Small Renewable Energy Program (SREP), introduced in Malaysia in 2001, promotes the use of renewable energy sources [82]. Palm tree-based biomass waste is a major bio-waste source that is readily and abundantly available in Malaysia [83]. Hence, this can serve as a source of raw material to researchers in Malaysia for utilization as biomass-

derived anode for MFCs system. Yaqoob et al. [69] developed a self-assembled and modified anode electrode. Local waste material (oil palm biomass) was used to produce GO anodes. The bioinspired modified GO anodes exhibited more than eight times larger energy output (135.96 mA/m^2) than unmodified GO anodes (15.65 mA/m^2). It shows that the waste material converted to an anode delivered a great support for transporting electrons. Furthermore, the modified GO anode supported a higher utilization of waste-derived organic waste (oil palm trunk sap) as the carbon source substrate in the removal of Cd^{2+} from synthetic wastewater. Also, graphene/polyaniline nanocomposite anode derived from cellulosic biomass was utilized for the removal of toxic metals with electricity production via benthic microbial fuel cell (BMFC) as studied by Yaqoob et al. [70]. In the experiment, 87.71 mA/m^2 was observed to be the maximum current density. This demonstrated that the altered graphene anode performed four times better than the unmodified one. The remediation efficiency was also higher for the modified graphene anode than for the unmodified graphene anode.

The utilization of biochar material for anode electrodes in MFC has been reported in several research articles. Bio-char is an economic material containing high content of carbon with a large specific macro-surface area as well as mesopores, and nanopores [84]. Chakraborty et al. [85] reviewed the applications of waste-derived biochar in MFC. It was reported in the review that different raw material sources used to produce biochar can be derived from cellulosic-based biowaste, microalgae, fruit waste like the peel wastes from banana and watermelon fruits. They further stated that the application of sludge derived from sewage and the fraction of organics from landfills have also been investigated as start-up material in making biochar. Huggins et al. [77] synthesized biochar from residues obtained from mills and forestry activities

at a carbonization temperature of 1000 ˚C, which was explored as an anode in MFC. MFC performance using biochar as the applied anode was compared to the MFC performance utilizing granular activated carbon (GAC) and graphite granules as an anode. Milling residue and forestry biochar presented the highest power densities of 532 and 457 mW/m^2, respectively, whereas the outcome of MFC using GAC was the highest, with a value of 674 mW/m^2. Biochar derived from a variety of biomass/waste materials such as shells, sewage sludge, fruit peels, corncob, food husk, wheat straw, etc., have demonstrated essential anodic properties [86-89]. The production of biochar from waste raw materials and a simple synthesis method makes biochar an economic-effective and alternative to metals and other commercial material for use as electrodes.

Over time, there is a rapid increase in research interest towards the synthesis and use of biomass-derived carbon in energy applications. This perhaps is due to the cost-effectiveness, sustainability, and of course the ease of fabrication from their various bio-precursors [90]. Due to their intrinsic nano porous and hierarchical structures, biomass-derived graphene outperforms the contrived nanostructured carbons such as graphene in terms of capacitance, performance, and stability in supercapacitor applications [91-93]. Long et al. [94] synthesized porous layer-stacking graphene-like carbon (PGC) materials from biomass as carbon precursors. The layer-stacking PGC prepared presented a high surface area (1103 m^2/g), high bulk density (about 0.96 g/cm^3), and hierarchically interconnected porous framework, that provides adequate storage sites with short transport paths for electrolyte ions, and enhances the overall conductivity of the electrode. However, the technicalities of the process to synthesize carbon base from biomass/waste that will present a high yield of carbon content and high energy density remains a challenge for researchers [90]. Biomass wastes or agricultural products are an alternative starting material for preparing