05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

FABRICATION AND CHARACTERIZATION OF GRAPHENE OXIDE-BASED ELECTRODES FOR WATER TREATMENT SYSTEMS APPLICATION

KHAYRI ZAID Z ALZALIT

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

UNIVERSITI PENDIDIKAN SULTAN IDRIS

2019

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

FABRICATION AND CHARACTERIZATION OF GRAPHENE OXIDE-BASED ELECTODES FOR WATER TREATMENT SYSTEMS APPLICATION

KHAYRI ZAID Z ALZLIT

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY OF SCIENCE (PHYSICS)
(DOCTOR BY RESEARCH)

FACULTY OF SCIENCE AND MATHEMATICS
UNIVERSITI PENDIDIKAN SULTAN IDRIS
2019

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

UPSI/IPS-3/BO 31
Pind.: 01 m/s:1/1

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

UNIVERSITI PENDIDIKAN SULTAN IDRIS
اونيۏرسيتي ڤنديديقن سلطان ادريس
SULTAN IDRIS EDUCATION UNIVERSITY

INSTITUT PENGAJIAN SISWAZAH /
INSTITUTE OF GRADUATE STUDIES

BORANG PENGESAHAN PENYERAHAN TESIS/DISERTASI/LAPORAN KERTAS PROJEK
DECLARATION OF THESIS/DISSERTATION/PROJECT PAPER FORM

Tajuk / ***Title*:**

FABRICATION AND CHARACTERIZATION OF GRAPHENE OXIDE-BASED ELECTRODES FOR WATER TREATMENT SYSTEMS APPLICATION

No. Matrik /*Matric No.*: **P20152002210**

Saya / *I* :

(Nama pelajar / *Student's Name*)

mengaku membenarkan Tesis/Disertasi/Laporan Kertas Projek (Kedoktoran/Sarjana)* ini disimpan di Universiti Pendidikan Sultan Idris (Perpustakaan Tuanku Bainun) dengan syarat-syarat kegunaan seperti berikut:-
acknowledged that Universiti Pendidikan Sultan Idris (Tuanku Bainun Library) reserves the right as follows:-

1. Tesis/Disertasi/Laporan Kertas Projek ini adalah hak milik UPSI.
   The thesis is the property of Universiti Pendidikan Sultan Idris

2. Perpustakaan Tuanku Bainun dibenarkan membuat salinan untuk tujuan rujukan dan penyelidikan.
   Tuanku Bainun Library has the right to make copies for the purpose of reference and research.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

3. Perpustakaan dibenarkan membuat salinan Tesis/Disertasi ini sebagai bahan pertukaran antara Institusi Pengajian Tinggi.
   The Library has the right to make copies of the thesis for academic exchange.

4. Sila tandakan (√) bagi pilihan kategori di bawah */ Please tick (√) from the categories below:-*

☐	**SULIT/*CONFIDENTIAL***	Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub dalam Akta Rahsia Rasmi 1972. / *Contains confidential information under the Official Secret Act 1972*
☐	**TERHAD/*RESTRICTED***	Mengandungi maklumat terhad yang telah ditentukan oleh organisasi/badan di mana penyelidikan ini dijalankan. / *Contains restricted information as specified by the organization where research was done.*
☐	**TIDAK TERHAD / *OPEN ACCESS***	

____
(Tandatangan Pelajar/ Signature)

____
(Tandatangan Penyelia / *Signature of Supervisor*)
& (Nama & Cop Rasmi / *Name & Official Stamp*)

Tarikh: ________________

Catatan: Jika Tesis/Disertasi ini **SULIT @ TERHAD**, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh laporan ini perlu dikelaskan sebagai **SULIT** dan **TERHAD**.

Notes: If the thesis is CONFIDENTAL or RESTRICTED, please attach with the letter from the related authority/organization mentioning the period of confidentiality and reasons for the said confidentiality or restriction.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

ACKNOWLEDGMENTS

I would like to thank my colleagues and friends from University Pendidikan sultan, for their great help in building up the laboratory facilities. I must thank Professor Dr. Suriani Abu Bakar for offering me laboratory facilities and necessary research materials.

My Ph.D. experience is very special as I spent half of my time working on my research in Tg malim, Malaysia. I had a great chance to work with Professor Dr. Suriani Abu Bakar her kindness and encouragement helped me overcome difficulties from academic also to my co-supervisor Associate Professor Dr. Azmi Mohamed. Many thanks go out to friends who have helped me stay focused and sane through the last couple of months. Their support and care are greatly valued, and I deeply appreciate their belief in me.

Finally, I must express my very profound gratitude to my country Libya for giving me chance to complete my PhD and very profound gratitude to my family providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without her.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

ABSTRACT

The aim of this study was to fabricate and characterize graphene oxide (GO) based electrodes for two types of home-developed water treatment system, namely electrodeposition (ED) and capacitive deionization (CDI) for copper ions (Cu^{2+}) and methylene blue (MB) dye removal. Electrochemical exfoliation was utilized to synthesize GO using custom-made triple-tails (TC14) surfactant. Hydrazine hydrate was utilized as reduction agent to produce TC14-rGO. The TC14-GO and TC14-rGO were then coated via spray coating method on stainless steel (SS) which further utilized as electrodes in ED water treatment system. Meanwhile for CDI system, the TC14-GO sample was sprayed and immersed in activated carbon fiber cloth (ACFC) electrodes. The TC14-GO-based electrodes were characterized using electron microscopy, energy dispersive X-ray, high resolution transmission electron microscopy, X-ray diffraction, fourier transform infrared spectroscopy, UV-Vis spectroscopy and micro-Raman spectroscopy. The atomic absorption spectroscopy and UV-Vis spectroscopy were used to determine the amount of Cu^{2+} and MB dye removal. The finding shows that the removal efficiency of Cu^{2+} reaches 98% for ED water treatment system assisted with constant magnetic field (CMF) using TC14-GO-/SS cylindrical electrode within reaction time of 6 hours. Meanwhile, for CDI flow through electrodes water treatment system, the TC14-GO-ACFC electrodes produced via immersion method have successfully removed Cu^{2+} from 100 ppm to 1.8 ppm. The TC14-GO-ACFC immersion electrodes for CDI flow through electrodes had successfully removed MB dye at various concentration level of 25, 50, 75 and 100 ppm within 3, 4, 5 and 6 hours respectively during the electrosorption process. In conclusion, the TC14-GO is a suitable material to be utilized as GO-based electrode for high Cu^{2+} removal in both ED and CDI application. TC14-GO also enhanced MB dye removal in CDI water treatment system. The implications of this study were a novel, green, cheaper and eco-friendlier concept for the fabrication of TC14-GO based electrodes to be used in both ED and CDI water treatment system.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

FABRIKASI DAN PENCIRIAN ELEKTROD GRAFIN OXIDA UNTUK APLIKASI SISTEM RAWATAN AIR

ABSTRAK

Kajian ini bertujuan memfabrikasi dan mencirikan grafin oxida (GO) berasaskan elektrod untuk dua jenis sistem rawatan air yang dibangunkan untuk premis-premis kediaman, yakni electrodeposisi (ED) dan kapasitif deionisasi (CDI) untuk penyingkiran logam tembaga (Cu^{2+}) dan pewarna biru metilena (MB). Pengelupasan elektrokimia telah digunakan untuk mensintesis GO menggunakan rantaian-buatan sodium tiga-cabang sulfonat surfaktan (TC14). Hidrazin Hidrat telah digunakan sebagai agen pengurangan untuk menghasilkan TC14-rGO. TC14-GO dan TC14-rGO kemudiannya disalut menggunakan kaedah semburan ke atas keluli tahan karat (SS) yang selanjutnya digunakan sebagai elektrod dalam sistem rawatan air ED. Manakala, untuk sistem CDI, sampel TC14-GO telah disembur dan direndam dalam karbon aktif serat kain (ACFC). TC14-GO yang berasaskan elektrod telah dicirikan menggunakan FESEM, EDX, HRTEM, Micro-Raman Spectroscopy, XRD, FT-IR, AAS, pH, UV-Vis, BET dan CV. Spektroskopi penyerapan atom dan spektroskopi UV-Vis telah digunakan untuk menentukan jumlah penyingkiran Cu^{2+} dan pewarna biru metilena (MB). Dapatan kajian menunjukkan bahawa kelancaran dalam penyingkiran Cu^{2+} mencecah 98% untuk sistem rawatan air ED, dengan dibantu medan magnetik tekal (CMF) menggunakan elektrod silindrikal TC14-GO-/SS dalam masa tindak balas 6 jam. Manakala, untuk aliran CDI melalui elektrod dalam sistem rawatan air, TC14-GO-ACFC yang dihasilkan melalui kaedah rendaman telah berjaya menyingkirkan Cu^{2+} daripada 100 ppm ke 1.8 ppm. Elektrod TC14-GO-ACFC untuk aliran CDI juga telah berjaya menyingkirkan pewarna biru metilena (MB) melalui kaedah rendaman pada tahap konsentrasi yang berbeza; 25, 50, 75 dan 100 ppm semasa proses elektrosorpsi, masing-masing dalam tempoh tindak balas 3, 4, 5 dan 6 jam. Kesimpulannya, TC14-GO merupakan bahan yang sesuai digunakan sebagai grafin oxida (GO) berasaskan elektrod untuk penyingkiran Cu^{2+} tahap tinggi dalam kedua-dua aplikasi ED dan CDI. TC14-GO juga meningkatkan penyingkiran pewarna biru metilena (MB) dalam sistem rawatan air CDI. Implikasi kajian ini adalah ia merupakan penyelidikan terbaharu dalam bidang sains, di samping menawarkan pendekatan yang lebih murah dan berkonsepkan mesra alam untuk pemfabrikasian elektrod TC14-GO yang perlu digunakan dalam kedua-dua sistem rawatan air ED dan CDI.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

TABLE OF CONTENTS

Page

DECLARATION OF ORIGINAL WORK ii

DECLARATION OF THESIS iii

ACKNOWLEDGEMENTS iv

ABSTRACT v

ABSTRAK vi

TABLE OF CONTENTS vii

LIST OF TABLES xv

LIST OF FIGURES xviii

LIST OF ABBREVIATIONS xxviii

LIST OF APPENDICES xxx

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

CHAPTER 1 INTRODUCTION

1.1 Introduction 1

1.2 Research Background 2

1.3 Research Problems 12

1.4 Research Objectives 15

1.5 Scope and Limitations of Study 16

1.6 Thesis Organization 17

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction 18

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

2.2 Water Treatment Techniques 19

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

2.2.1 Physical Treatment 19

2.2.1.1 Adsorption 20

2.2.2 Chemical Treatment 20

2.2.2.1 Electrodeposition 21

2.2.3 Basic Principle of Electrochemical Deposition 22

2.2.3.1 Basic Principle of Electrodeposition 25

2.2.3.2 Electrodeposition in Magnetic Field 26

2.2.3.3 Magneto-Electrolytic Deposition 27

2.2.4 Electrosorption of Ions 28

2.2.5 Graphene 29

2.2.5.1 Graphene Oxide 33

2.2.5.2 Reduced Graphene Oxide 36

2.2.6 Graphene Oxide and Reduced Graphene Oxide for Heavy Metals Ions Removal 37

2.2.6.1 Mechanism of Graphene Oxide Adsorption 40

2.3 Capacitive Deionization System for Water Treatment 41

2.3.1 Theory of Capacitive Deionization 42

2.3.2 Capacitive Deionization Technology 43

2.4 Development of Electrode Materials for Capacitive Deionization 46

2.4.1 Electrode from Activated Carbon 47

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

2.4.2 Electrodes from Activated Carbon Cloths 48

2.4.3 Electrodes from Composite of Carbon Fibre Cloth and Reduced 49

2.4.4 Electrodes from Carbon Nanotubes 50

2.4.5 Electrodes from Composite of Carbon Nanotubes and Activated Carbon 52

2.4.6 Electrodes from Composite of Carbon Nanotubes and Graphene 53

2.4.7 Electrodes from Graphene Sponge 55

2.5 Several Materials in Polluted Water 56

2.5.1 Heavy Metals Ions 56

2.5.2 Dye 56

2.6 Current Status of CDI in Pollutant Cu^{2+} ion and Methylene Blue Removal 59

2.7 Characterization of Graphene Oxide-based Electrodes and Activated Carbon Fibre Cloth with Graphene Oxide 60

2.8 Summary 75

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

CHAPTER 3 METHODOLOGY

3.1 Introduction 76

3.2 Fabrication of Graphene Oxide-based Electrode for Electrochemical Water Treatment System 77

3.2.1 Preparation of Substrate 77

3.2.2 Synthesis of Graphene Oxide 78

3.2.3 Production of Reduced Graphene Oxide 80

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

3.2.4 Substrate Preparation 81

3.2.5 Preparation of Constant Magnetic Field-Assisted Electrochemical Water Treatment System 83

3.2.6 Modification of Electrode for Electrodeposited Water Treatment System 85

3.2.6.1 Electrodeposited Water Treatment System with Typical Electrodes Arrangement 85

3.2.6.2 Fabrication Electrodeposited Water Treatment System by Utilizing Cylindrical Anode 86

3.2.6.3 Fabrication of Electrodeposited Water Treatment System by Utilizing Cylindrical Cathode 88

3.3 Fabrication of Three-Dimensional Active Carbon Fiber Cloth with Graphene Oxide for Capacitive Deionization 89

3.3.1 Electrodes Preparation Utilized in Capacitive Deionization Cells 89

3.3.2 Design and Fabrication of Electrodes in Capacitive Deionization Cells System 90

3.3.3 Capacitive Deionization Cells Flow between and through Electrodes System Components and Description 98

3.4 Samples of Characterizations 104

3.4.1 Field Emission Scanning Electron Microscopy and Energy Dispersive X-ray Analysis 104

3.4.2 High-Resolution Transmission Electron Microscopy 106

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

3.4.3 Micro-Raman Spectroscopy 107
3.4.4 X-Ray Diffraction 108
3.4.5 Fourier Transform Infrared Spectroscopy 110
3.4.6 Atomic Absorption Spectroscopy 111
3.4.7 pH Meter Measurement 112
3.4.8 Ultraviolet-Visible Spectroscopy 113
3.4.9 Brunauer-Emmett-Teller 114
3.4.10 Cyclic Voltammetry 116
3.5 Summary 117

CHAPTER 4 RESULTS AND DISCUSSIONS

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.1 Introduction 120
4.2 The Characterization of Graphene Oxide and Reduced Graphene Oxide 121
4.2.1 The Properties of Graphene Oxide 121
4.2.2 The Properties of Reduced Graphene Oxide 127
4.2.3 The properties of Graphene Oxide and Reduced Graphene Oxide on Stainless Steel Substrates 130
4.3 The Characterization and Performance of Electrodeposited Water Treatment System for Cu^{2+} Ion Removal by Utilizing Graphene Oxide and Reduced Graphene Oxide-based Electrodes 137
4.3.1 Effect of Constant Magnetic Field for the Enhancement of Cu^{2+} Removal in Electrodeposited Water Treatment System 137

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.3.2 Effect of Graphene Oxide-based Cathode on Electrodeposition of Cu^{2+} with and without Constant Magnetic Field in Electrochemical Water Treatment System 143

4.3.3 Effect of Reduced Graphene Oxide-based Cathode on Electrodeposition of Cu^{2+} with and Without Constant Magnetic Field in Electrochemical Water Treatment System 150

4.4 Effect of Graphene Oxide, Reduced Graphene Oxide, and Different Constant Magnetic Field In Electrodeposition Water Treatment System Utilizing Typical Plates, Cylindrical Anode and Cylindrical Cathode and for Cu^{2+} Ions Removal 158

4.4.1 Effect of Graphene Oxide, Reduced Graphene Oxide, and Different Constant Magnetic Field on the Cu2+ Removal Efficiency and the Solution pH Utilizing Typical plates in Electrodeposition Water Treatment System 158

4.4.2 The Reaction Mechanism of Graphene Oxide with Heavy Metals Cu^{2+} Ions Removal in Electrodeposition Process for Water Treatment System Utilizing Typical Electrode 167

4.4.3 Effect of Different Constant Magnetic Field in Electrodeposition Water Treatment System Utilizing Cylindrical Anode and Typical Cathode 171

4.4.4 Effect of Different Constant Magnetic Field in Electrodeposition Water Treatment System Using Cylindrical Cathode 178

4.5 The Characterization of Electrodes in Capacitive Deionization Water Treatment System 185

4.5.1 Activated Carbon Fiber Cloth-Graphene Oxide Electrodes by Spraying Method 185

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.5.2 Activated Carbon Fiber Cloth-Graphene Oxide Electrodes by Immersion Method 193

4.6 Cu^{2+} Ions Removal by Capacitive Deionization for Water Treatment System 201

4.6.1 The Cu^{2+} Ions Removal Performance Where the Solution Flowed Between the Electrodes in the Capacitive Deionization for Water Treatment System 201

4.6.2 The Cu^{2+} Ions Removal Performance Where the Solution Flowed Through the Electrodes in the Capacitive Deionization for Water Treatment System 208

4.7 Dye Removal Utilizing Capacitive Deionization Cells for Water Treatment System 216

4.7.1 Dye Removal Utilizing ACFC-GO Electrodes Fabricated by Spraying Method in Capacitive Deionization Single Cell Where the Solution Flowed Between Electrodes for Water Treatment System 216

4.7.2 Dye Removal Utilizing ACFC-GO Electrodes Fabricated by Immersion Method in Capacitive Deionization Cell Single Cell Where the Solution Flowed Between Electrodes for Water Treatment System 223

4.7.3 Dye Removal Utilizing ACFC-GO Electrodes Fabricated by Spraying Method in Capacitive Deionization Single Cell Where the Solution Flowed Through Electrodes for Water Treatment System 227

4.7.4 Dye Removal Utilizing ACFC-GO Electrodes Fabricated by Immersion Method in Capacitive Deionization Single Cell Where the Solution Flowed Through Electrodes for Water Treatment System 233

4.7.5 The Characterization of Electrodes Utilized in CDI Cell for MB Dye Removal 239

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.7.6 The Reaction Mechanism of Activated Carbon Cloths and Graphene Oxide as Electrodes for MB Dye Degradation in Capacitive Deionization System 244

CHAPTER 5 CONCLUSIONS AND FUTURE WORK

5.1 Conclusions 248

5.2 Future Work 252

REFERENCES 253

APPENDICES 282

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

LIST OF TABLES

Table No. **Page**

2.1 GO composite performance for heavy metal removal in water Treatment System 39

2.2 CDI performance for Cu^{2+} ions removal and MB dye in water Treatment System 59

3.1 The compositions of salts required for the preparation of metal ions solution 85

4.1 Micro-Raman Analysis of TC14-GO and TC14-rGO Film Grown on Stainless Steel Substrate 134

4.2 Various Cathodes Performance with Different ED Time for Heavy Metal Cu^{2+} Ions Removal 161

4.3 The pH Solution Containing Cu^{2+} Ions After ED Process with Various Cathodes 162

4.4 The Percentage of GO-CMF (46 and 69 G)/SS Typical Plate Cathode in Cu^{2+} Ions Removal during ED Process 164

4.5 The Performance of GO-CMF (46 and 69 G)/SS Electrodes during ED Time Utilizing Typical Plates Cathode in Cu^{2+} Ions Removal 165

4.6 The Changing of Solution’s pH Value during ED Process Utilizing GO-CMF (23, 46 and 69 G)/SS Typical Plates 166

4.7 The Percentage of GO-CMF (23and 46 G) and rGO-CMF (23 and 46 G)/SS Cylindrical Anode and Typical Cathode in Cu^{2+} Ions Removal during ED Process 172

4.8 The Performance of GO- and rGO-CMF (23 G)/SS Typical Cathode and Cylindrical Anode in Cu^{2+} Ions Removal during ED Process 173

4.9 The Performance of GO- and rGO-CMF (46 G)/SS Typical Cathodes and Cylindrical Anode in Cu^{2+} Ions Removal during ED Process 174

4.10 The Performance of GO-CMF (23, 46 and 69 G)/SS Typical Cathodes and Cylindrical Anode in Cu^{2+} Ions Removal After 6h ED Time 175

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.11 The Changing of Solution’s pH Value during ED Process Utilizing GO-CMF (23, 46 and 69 G)/SS and rGO-CMF (23 and 46 G)/SS Cathode and Cylindrical Anode 178

4.12 The Percentage of GO-CMF (46 and 69 G)/SS Cylindrical Cathode in Cu^{2+} Ions Removal during ED Process 181

4.13 The Performance of GO-CMF (46 and 69 G)/SS Cylindrical Cathode in Cu^{2+} Ions Removal during ED Process 182

4.14 The Changing of Solution’s pH Value during ED Process Utilizing GO-CMF (23, 46 and 69 G)/SS Cylindrical Cathode and Typical Anode 184

4.15 BET Analysis Results for Pristine ACFC and ACFC-GO Electrode Fabricated by Spraying Method 192

4.16 BET Analysis Results for ACFC-GO Electrode Fabricated by Immersion and Spray Method 200

4.17 The Cu^{2+} Ion Removal Performance during Electrosorption Process Utilizing ACFC-GO Fabricated by Spraying Method in CDI Cell where the Solution Flowed Between Electrodes 203

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.18 The pH Solution Value After Electrosorption Process with Different Applied Voltage Performed by CDI where the Solution Flowed Between the ACFC-GO Electrodes Fabricated by Spraying Method 204

4.19 The Cu^{2+} Ion Removal Performance during Electrosorption Process Utilizing ACFC-GO Fabricated by Immersion Method in CDI Cell where the Solution Flowed Between Electrodes 206

4.20 The pH Solution Value After Electrosorption Process with Different Applied Voltage Performed by CDI where the Solution Flowed Between the ACFC-GO Electrodes Fabricated by Immersion Method 208

4.21 The Cu^{2+} Ion Removal Performance during Electrosorption Process Utilizing ACFC-GO Fabricated by Spraying Method in CDI Cell where the Solution Flowed Through Electrodes 210

4.22 The pH Solution Value After Electrosorption Process with Different Applied Voltage Performed by CDI where the Solution Flowed Through the ACFC-GO Electrodes Fabricated by Spraying Method 211

4.23 The Cu^{2+} Ion Removal Performance during Electrosorption Process Utilizing ACFC-GO Fabricated by Immersion Method in CDI Cell where the Solution Flowed Through Electrodes 213

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.24 The pH Solution Value After Electrosorption Process with Different Applied Voltage Performed by CDI where the Solution Flowed Through the ACFC-GO Electrodes Fabricated by Immersion Method 216

4.25 The MB Dye Removal Percentage Electrosorption Process Utilizing ACFC-GO Electrodes Fabricated by Spraying Method Where the Flowed Between Electrodes 222

4.26 The MB Dye Removal Percentage During Electrosorption Process Utilizing ACFC-GO Electrodes Fabricated by Immersion Method Where the Solution Flowed Between Electrodes 227

4.27 The MB Dye Removal Percentage During Electrosorption Process Utilizing ACFC-GO Electrodes Fabricated by Spraying Method Where the Solution Flowed Through Electrodes 233

4.28 The MB Dye Removal Percentage During Electrosorption Process Utilizing ACFC-GO Electrodes Fabricated by Spraying Method Where the Solution Flowed Through Electrodes 238

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

LIST OF FIGURES

Figure No.		Page
2.1	Diagram of basic principle shape in the electrochemical deposition cell (Ammam, 2012).	22
2.2	Diagram of the electrochemical cell reaction	24
2.3	Diagram of Lorentz force during electrochemical process	28
2.4	GE forms (a) 0-D Bucky balls, (b) 1-D CNTs and (c) stacked of 2-D graphene (Zhen & Zhu, 2018).	30
2.5	Hexagonal lattice of GE (Zhen & Zhu, 2018)	31
2.6	(a) Representation of the electronic band structure and Brillouin zone of graphene. (b) The two graphene sub-lattices (red and blue) and unit cell (Avouris & Dimitrakopoulos, 2012).	32
2.7	Dispersion of GO in different solvents (Dreyer, Park, Bielawski, & Ruoff, 2010)	34
2.8	The changes of anodic exfoliation of the solution colour during the electrolysis process using sulfuric acid (Abdelkader et al., 2014)	36
2.9	(a) Diagram structure of GO and (b) interaction heavy metal with GO (Peng et al., 2017)	41
2.10	Schematic diagram of CDI system (khayri & Suriani 2017)	42
2.11	Timeline of scientific developments of CDI system since 1960 until 2012 (Porada, Zhao, Van Der Wal, Presser, & Biesheuvel, 2013)	44
2.12	Schematic diagram of CDI system flows between electrodes (Hou, Huang, & Hu, 2013)	45
2.13	FESEM images of MWCNTs (multiwall carbon nanotubes) with diameter range of (a) 10–20 nm (b) 20–40 nm (c) 41-55 nm and (d) 60-90 nm (Xiong, Yun, & Jin, 2013)	51
2.14	FESEM images of (a) CNTs paper electrode, (b) conventional AC electrode, (c) AC/CNTs binary composite electrode and (d) AC/CNTs ternary composite electrode (Lu et al., 2011)	53
2.15	SEM images of (a)-(b) graphene sponge (Yang et al. 2014)	54

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

2.16 Figure 2.16. chemical structure of MB Dye (Elmorsi, 2011) 58

2.17 HRTEM images of GO (Song, Yang, Fu, & Pan, 2017) 61

2.18 Micro-Raman spectra of graphite GO and rGO (Perumbilavil, Sankar, Priya Rose, & Philip, 2015) 63

2.19 Micro-Raman spectrum of pure ACFC (Roh, 2008) 64

2.20 Micro-Raman spectra of (a) low-growth and (b) high growth of ACFC-graphene (Tsuda et al., 2017). 65

2.21 Schematic Diagram of Bragg's Diffraction at Atomic Distance (d) and Incident Beam (θ) (Peiris, 2014) 66

2.22 XRD pattern of graphite, GO and rGO (Mishra, Tripathi, Choudhary, & Gupta, 2014) 67

2.23 Block diagram of FTIR spectrometer (Mbonyiryivuze, Mwakikunga, Dhlamini, & Maaza, 2015) 68

2.24 FTIR spectrum of graphene oxide and graphene (Çiplak et al., 2015) 69

2.25 (a) Nitrogen gas sorption isotherms at -196 °C and (b) calculated cumulative pore size distribution of activated carbon cloth ACC-507-15, ACC-5092-15, ACC-507-20, ACC-5092-20, and ACC-507-20 (Kim et al., 2017) 72

2.26 (a) One cycle of the triangular potential-excitation signal showed the initial potential and switching potential and (b) CV measurement of the peak currents and potentials (Mendoza, Bustos, Manríquez, & Godínez, 2015) 74

2.27 CV curve of carbon cloth treated by 1 M HNO3 for 9 h with voltage scan rate 1, 2 and 4mV/s (Thamilselvan et al., 2015) 75

3.1 Cleaning process of SS substrates in Power Sonic 410 ultrasonic cleaner (input: AC 230 V, 50 HZ and output: 500 watt) 77

3.2 The schematic diagram TC14-GO synthesis via electrochemical exfoliation method 78

3.3 The synthesis of TC14-GO via electrochemical exfoliation method 79

3.4 Schematic diagram of reduction process of TC14-GO in order to produce TC14-rGO 80

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

3.5 The reduction process of TC14-GO in order to produce TC14-rGO 81

3.6 (a) The transferring process of TC14-GO and TC14-rGO on the SS substrates in order to produce electrode thin films, (b) tubular furnace utilized to anneal the TC14-GO and TC14-rGO thin films on SS substrates. 82

3.7 The schematic of tubular furnace utilized to anneal the TC14-GO and TC14-rGO thin films 82

3.8 (a) Preparation of 120, 240 and 360 loops of copper wire in order to generate magnetic field, (b) electrodeposition system with TC14-GO and TC14-rGO-based electrodes with different CMF applied, (c) the schematic diagram of TC14-GO and TC14-rGO-based electrode with CMF-assisted EDTWS for Cu^{2+} removal and (d) the diagram of F_B resulted from CMF in electrodeposition process 84

3.9 The schematic diagram of EDWTS process with different CMF for Cu^{2+} removal utilized TC14-GO and TC14-rGO-based cathode with cylindrical anode 87

3.10 The EDWTS process with different CMF for Cu^{2+} removal utilized TC14-GO and TC14-rGO-based cathode with cylindrical anode 87

3.11 The schematic diagram of EDWTS process with different CMF for Cu^{2+} removal utilized TC14-GO and TC14-rGO-based cylindrical cathode 88

3.12 (a) Activated carbon fiber (HNCFF-1600) and (b) SS sheet (99.995% of iron) utilized as substrate in CDI system 89

3.13 External parts of CDI cell were designed by using Autodesk design software 2013. 91

3.14 (a)-(b) Plus 2-3D printer utilized to build CDI cell, print using 1.75 mm filament, print with ABS and PLA materials and (c)-(e) design of external parts of CDI cell 92

3.15 (a) Connection process of external part of the CDI cell utilized to flow in-out of solution, (b)-(c) preparation substrate of SS sheet (8 x 8) cm^2, (d) SS sheet as substrate (electrodes) and (e)-(f) preparation of ACFC (HNCFF-1600) 94

3.16 ACFC cloth was immersed in methanol and acetone 96

3.17 The fabrication process of ACFC electrodes for CDIWTS by TC14-GO spray and immersion methods assembled in CDI cells 97

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

3.18 The schematic diagram of CDI flows solution (a) CDI flows between the electrodes and (b) CDI flows through the electrodes 99

3.19 External parts of CDI cell flow through the gap between the electrodes 100

3.20 The complete schematic process of CDIWTS by ACFC-GO spray and immersion methods 100

3.21 Preparation of MB dye solution 101

3.22 Calibration curve of MB dye 102

3.23 CDIWTS for Cu^{2+} ion removal 103

3.24 FESEM (HITACHI SU8020) and EDX (HORIBA EMAX) instrument were utilized to observe the morphology structure and determine the elemental composition of SS electrode and ACFC before and after deposition of Cu and ACFC after filtration process by CDIWTS 105

3.25 HRTEM (JEOL-JEM 2100) utilized to investigate the structural of the TC14-GO and TC14-rGO 107

3.26 Micro-Raman spectroscopy utilized to analyze TC14-GO, TC14-rGO, and ACFC-TC14-GO electrodes 108

3.27 XRD (Bruker D8 Advance) utilized to investigate the crystallinity of electrode in water treatment and CDI system 109

3.28 FTIR (Nicolet 6700) spectroscopy utilized to investigate the chemical properties of ACFC/GO for CDI system 110

3.29 (a) AAS instrument (Perkin-Elmer) and (b) Varian 725-ES ICP utilized to determine the concentration of Cu element for water treatment application 111

3.30 The pH meter (Thermo scientific Orion 9107 NMD) utilized to measure the acidity concentration of water containing Cu in water treatment application 113

3.31 UV-Vis spectroscopy (Cary 60) utilized to investigate the absorbance of MB in water for CDI absorption system 114

3.32 High vacuum system of BET (V-SORB 4800P) at 120 °C 115

3.33 BET (V-SORB 4800P) was utilized to investigate the surface area and pore size 116

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

3.34 CV (Gamry potentiostat series-G750) utilized to study the electrochemical reaction and characterize the capacitive behaviour of SS electrode fabricated by spraying method and ACCF/TC14-GO fabricated by spraying and immersion method 117

3.35 Flow chart of research methodology for this study 119

4.1 (a) FESEM and (b) HRTEM images of the synthesized TC14-GO 122

4.2 Micro-Raman spectra of synthesized TC14-GO 123

4.3 (a) FTIR and (b) XRD spectra of the synthesized TC14-GO 125

4.4 UV-Vis spectrum of the synthesized TC14-GO 127

4.5 (a) FESEM image and (b) micro-Raman spectra of the produced TC14-rGO 128

4.6 FTIR spectra of fabricated TC14-rGO 129

4.7 Absorbance spectrum of TC14-rGO 130

4.8 FESEM images of (a)-(b) TC14-GO film grown on SS substrate 131

4.9 FESEM images of TC14-rGO film grown on SS substrate 132

4.10 Micro-Raman spectra of GO and rGO film grown on stainless steel substrate 134

4.11 CV curves of GO/SS electrode at (a) 2, (b) 4 and (c) 5 V during measurement 135

4.12 FESEM images with EDX analysis of (a)-(b) CMF/SS and (c)-(d) SS electrodes 138

4.13 XRD patterns of Cu deposited on; (a) SS and (b) CMF/SS electrodes 140

4.14 Micro-Raman spectra of Cu deposited on SS and CMF/SS electrodes 141

4.15 FTIR spectra of Cu deposited on SS and CMF/SS electrodes 142

4.16 FESEM images and EDX analysis of Cu deposited on; (a)-(c) GO-CMF/SS and (d)-(f) GO/SS cathode 145

4.17 XRD patterns of (a) Cu deposited on; GO-CMF/SS and GO/SS 147

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.18 Micro-Raman spectra of Cu deposited on GO-CMF/SS and GO/SS cathode 149

4.19 FTIR spectra of Cu deposited on GO-CMF/SS and GO/SS cathode 150

4.20 FESEM images with EDX analysis of (a)-(c) rGO-CMF/SS and (d)-(f) rGO/SS cathode 152

4.21 XRD patterns of Cu deposited on; (a) rGO-CMF/SS and (b) rGO/SS 154

4.22 Micro-Raman spectra of Cu deposited on the rGO/SS and rGO-CMF/SS cathode 156

4.23 FTIR spectra of Cu deposited on rGO-CMF/SS and rGO/SS cathode 157

4.24 The Cu^{2+} ions removal percentage by using various cathode during electrodeposition process 159

4.25 The percentage of Cu^{2+} ions in the solution during ED process utilizing typical plates coated by GO with 46 and 69 G CMF 163

4.26 The amount of Cu^{2+} Ions (mg/L) in the solution during ED process utilizing typical plates coated by GO with CMF 46 and 69 G 164

4.27 The pH solution during electrodeposition process for EDWTS utilizing GO-CMF (46 and 69 G)/SS typical plates 166

4.28 The schematic diagram of electrodeposition mechanism system by utilizing GO-CMF/SS cathode 168

4.29 The percentage of Cu^{2+} ions removal during ED process utilizing cylindrical anode and typical cathode coated by GO and rGO by utilizing 23 and 46 G CMF 172

4.30 The amount of Cu^{2+} ions (mg/L) in the solution after 6h ED process utilizing different CMF by utilizing cylindrical anode and GO-CMF/SS typical cathode 175

4.31 The pH solution during ED process for EDWTS utilizing GO-CMF (23, 46 and 69 G)/SS and rGO-CMF (23 and 46 G)/SS cathode and cylindrical anode 177

4.32 The percentage of Cu^{2+} ions removal during ED process utilizing cylindrical cathode coated by GO and utilizing 46 and 69 G CMF 179

4.33 The amount of Cu^{2+} ions (mg/L) in the solution during ED process utilizing cylindrical cathode coated by GO and utilizing 46 and 69 G CMF 180

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.34 The pH solution during ED process for EDWTS utilizing GO-CMF (23, 46 and 69 G)/SS cylindrical cathode and typical anode 184

4.35 FESEM images with EDX analysis of (a)-(b) ACFC-GO electrodes fabricated by spraying method 186

4.36 Micro-Raman spectra of pristine ACFC and ACFC-GO electrodes fabricated by spraying method 187

4.37 FTIR spectra of ACFC-GO electrodes fabricated by spraying method 188

4.38 CV curve of ACFC-GO electrode fabricated by spraying method at (a) 2, (b) 4 and (c) 5 V 190

4.39 BET adsorption and desorption isotherms with nitrogen on ACFC-GO electrode fabricated by spraying method at 77 K 192

4.40 FESEM images with EDX analysis of (a)-(c) ACFC-GO fabricated by immersion method 194

4.41 Micro-Raman spectra of ACFC and ACFC-GO electrodes fabricated by immersion method 195

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.42 XRD spectra of ACFC-GO fabricated by immersion method 196

4.43 CV curve of ACFC-GO electrode fabricated by immersion method at (a) 2 V, (b) 4 V and (c) 5 V 197

4.44 BET adsorption and desorption isotherms with nitrogen on ACFC-GO electrode fabricated by immersion method at 77 K 200

4.45 The percentage of Cu^{2+} ions removal during electrosorption process utilizing ACFC-GO sprayed method in CDI cell where the solution flowed between electrodes with various applied voltage 202

4.46 The pH solution value after electrosorption process with different applied voltage performed by CDI where the solution flowed between the ACFC-GO electrodes fabricated by spraying method 204

4.47 The percentage of Cu^{2+} ions removal during electrosorption process utilizing ACFC-GO immersion method in CDI cell where the solution flow between electrodes with various applied voltage 206

4.48 The pH solution value after electrosorption process with different applied voltage performed by CDI where the solution flowed between the ACFC-GO electrodes fabricated by immersion method 207

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.49 The percentage of Cu^{2+} ion removal during electrosorption arocess utilizing ACFC-GO fabricated by spraying method in CDI cell where the solution flowed through electrodes with various applied voltage 209

4.50 The pH solution value after electrosorption process with different applied voltage performed by CDI where the solution flowed through the ACFC-GO electrodes fabricated by spraying method 211

4.51 The percentage of Cu^{2+} ion removal during electrosorption process utilizing ACFC-GO fabricated by immersion method in CDI cell where the solution flowed thought electrodes with various applied voltage 213

4.52 The pH solution value after electrosorption process with different applied voltage performed by CDI where the solution flowed through the ACFC-GO electrodes fabricated by immersion method 215

4.53 UV-Vis spectra of MB dye removal solution after electrosorption process in CDI cell utilizing the ACFC-GO fabricated by spraying method where the solution flowed between electrodes for (a) 25, (b) 50, (c) 75, and (c) 100 ppm MB solution 218

4.54 The MB dye removal percentage during electrosorption process utilizing ACFC-GO electrodes fabricated by spraying method where the solution flowed between electrodes 221

4.55 UV-Vis spectra of MB dye removal solution after electrosorption process in CDI cell utilizing the ACFC-GO fabricated by immersion method where the solution flowed between electrodes for (a) 25, (b) 50, (c) 75, and (c) 100 ppm MB solution 223

4.56 The MB dye removal percentage during electrosorption process utilizing ACFC-GO electrodes fabricated by immersion method where the solution flowed between electrodes 226

4.57 UV-Vis spectra of MB dye removal after electrosorption process in CDI cell utilizing the ACFC-GO fabricated by spraying method where the solution flowed through electrodes for (a) 25, (b) 50, (c) 75, and (c) 100 ppm MB solution 229

4.58 The MB dye removal percentage during electrosorption process utilizing ACFC-GO electrodes fabricated by spraying method where the solution flowed through electrodes 232

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4.59	UV-Vis spectra of MB dye removal after electrosorption process in CDI cell utilizing the ACFC-GO fabricated by immersion method where the solution flowed through electrodes for (a) 25, (b) 50, (c) 75, and (c) 100 ppm MB solution	234
4.60	The MB dye removal percentage during electrosorption process utilizing ACFC-GO electrodes fabricated by immersion method where the solution flowed through electrodes	238
4.61	FESEM images and EDX analysis of (a)-(b) ACFC-GO cathode and (c)-(d) ACFC-GO anode	240
4.62	FTIR spectra of the ACFC-GO fabricated by immersion method (a) before and after electrosorption process where the solution flowed between the electrodes (b) anode and (c) cathode	242
4.63	The Schematic Diagram of Removal Mechanism of the MB Dye by Utilizing CDI Cell Where the Solution Flowed Between the Electrodes	245

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ACFC	Activated Carbon Fiber Cloth
ACFC-GO	Activated Carbon Fiber Cloth-Graphene Oxide Electrodes
BET	Brunauer-Emmett-Teller
C_0	are the initial and equilibrium concentration
C_e	Equilibrium Concentration
CDI	Capacitive Deionization
cm	Centimetre
CMF	Constant Magnetic Field
CMF/SS	Electrodes with Constant Magnetic Field
CNTs	Carbon Nanotubes
$C_3H_8O_2$	2-Metoxyethanol
Cu	Copper
Cu^{2+}	Copper Ion
C-O	Carboxylic
C=C	Carbonyl Group
C-V	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
D	Defect and Disorder Peak
DC	Direct Current
DI-water	De-Ionized Water
DWCNTs	Double-Walled Carbon Nanotubes
EDX	Energy Dispersive X-Ray
ED	Electrodeposition
EDL	Electrical Double Layer
EDWTS	Electrodeposition Water Treatment System
Fe	Iron
FESEM	Field Emission Scanning Electron Microscopy

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

$\overline{F}_L$	Lorentz Force
FT-IR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
G	Graphitic-Band
GE	Graphene
GO	Graphene Oxide
GO/SS	Graphene Oxide-based Stainless-Steel Electrode
GO-CMF/SS	Graphene Oxide-based Stainless-Steel Electrode Constant Magnetic Field
HRTEM	High Resolution Transmission Electron Microscopy
I	Current
I_D/I_G	Ratio of D and G peak
MF	Magnetic Field
MED	magneto-electrolytic deposition
MHD	magnetohydrodynamic
MB	Methyl Blue dye
ME	Magnetoelectrolysis
ml	Millilitres
Mins	Minutes
nm	Nanometre
O	Oxygen
O-H	Phenol Group
°C	Degree Celsius
pH	Meter measurement
ppm	Parts Per Million
rGO	Reduced Graphene Oxide
rGO/SS	Reduced Graphene Oxide-based Stainless-Steel Electrode
rGO-CMF/SS	Reduced Graphene Oxide-based Stainless-Steel Electrode Constant Magnetic Field
SS	Stainless Steel
T	Temperature

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

TC14	Sodium 1, 4-Bis (Neopentyloxy)-3-(Neopentyloxycarbonyl)-1, 4-Dioxobutane-2-Silphonate
UV-Vis	Ultraviolet-Visible Spectroscopy
V	Voltage
V	Volume of Solution
XRD	X-ray Diffraction
θ	Angle between Incident and Diffracted Rays
µm	Micrometre
ε_0	Permittivity Space

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

LIST OF APPENDICES

No	
A	Journal of Sci.Int Publishing (2017)
B	Journal of Sainmatika Publishing (2017)
C	International Conference on Life Sciences Revolution (2016)
D	International Conference on Sciences and Mathematics (2017)

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

CHAPTER 1

INTRODUCTION

1.1 Introduction

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

This chapter discusses the research background of graphene oxide (GO) and reduced graphene oxide (rGO) synthesized by utilizing custom-made triple-tail sodium 1, 4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1, 4-dioxobutane-2-silphonate (TC14) surfactant, as well as its application for water treatment. The research problems for this study were also intensively discussed. This chapter also covers research objectives, scope and limitation of study followed by thesis organization.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

1.1 Research Background

Nowadays, the widely developed industries, such as pharmaceuticals (Gaw et al., 2014), metal plating, batteries, fertilizer, pesticides, and printing industries (Fernández-luqueño et al., 2013) have caused water problem resulted from its waste released to the environment. Some heavy metals, such as copper (Cu), cobalt (Co), zinc (Zn), manganese (Mn) and molybdenum (Mo) (Nambatingar, Clement, Merle, Mahamat, & Lanteri, 2017; Azizi, Kamika, & Tekere, 2016) were commonly found in the polluted water and can caused serious health problem. They are easily affect the living organism metabolism and cause the damages on brain function (Torres-Sa´nchez et al., 2014), heart (Akpor & Muchie, 2010), liver (Parmar & Thakur, 2013), central nervous function (Verma & Dwivedi, 2013), or even death due to their toxicity and carcinogenic material. They were not biodegradable (Bobade & Eshtiagi, 2015) and could be decomposed or metabolized thus need special treatment to remove their presence in the water. Among them, the Cu^{2+} ions were mostly found in the industrial wastewater due to its high usage in many applications (Fakhru'l-Razi et al., 2009). However, recent empirical studies of GO reported that many methods were proposed to minimize the heavy metal (Cu^{2+} ions) in polluted water especially the physical and chemical techniques (Yang et al., 2019).

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

Both physical and chemical techniques can be utilized to treat the polluted water either from heavy metal ion or dye. The adsorption (Peng et al., 2011), evaporation (Li et al., 2016) and centrifugation (Retter & Schilp 1994; Kose & Genc, 2015) were belongs to the physical treatment process. The adsorption presents a

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

simple and low-cost method however its low adsorption efficiencies limits its usage (Khayri & Suriani, 2017). Meanwhile, the chemical oxidation (Li et al., 2016), chemical precipitation (Kornboonraksa, Lee, & Chiemchaisri, 2009), electroflotation (Ricordel, Darchen, & Hadjiev, 2010), electrocoagulation (Torres-Sa´nchez et al., 2014) and electrosorption (CDI) (Bhatluri, Manna, Ghoshal, & Saha, 2017) were included to the chemical treatment. Chemical precipitation treatment presents diverse heavy metal ion with different pH level (Oncel, Muhcu, Demirbas, & Kobya, 2013). However, it generates a high amount of sedimentation and caused disposal problems (Fu & Wang, 2011). Meanwhile, the electroflotation process was usually utilized to clean water surface by expulsion of polluted particles (Ricordel et al., 2010). This treatment shows high power consumption (high current) as compared to the another treatment (Bazrafshan, Moein, Mostafapour, & Nakhaie, 2013). The electrocoagulation process also reveals inefficient treatment due to the oxidation process occurred in the electrodes. Among chemical techniques, the ED presents low energy consumption (low applied temperature), wide range contaminant removal, sufficiently stable and efficient electrode materials (Padmaja, Cherukuri, & Reddy, 2014). Besides the advantages, it also presents a high cost and complex technology. The development of green, highly efficient and economical method was gained much attention.

The electrodeposition (ED) process offers easy, rapid, and efficient as an absorbent method to remove the heavy metals from wastewater especially Cu (Gunatilake, 2015). ED is a develop technology that is widely connected in different fields of electrochemistry (Giurlani et al., 2018), especially in material covering

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

(Amietszajew, Sridhar, & Bhagat, 2016; Kumar, Pande, & Verma, 2015; Schwarzacher, 2006) and fabrication of magnetic films (Zheng et al., 2017) however, only few studied that dealt with water treatment utilizing ED (Chen, 2004). ED is successful in recover heavy metals from wastewater. Previous studies have shown that up to 97.25 % of Cu^{2+} ion were successfully removed either by ED with iron electrode plates, and electrocoagulation/zonation with aluminum electrode set, followed by the process of zonation but it is not clear how much the primary concentration of Cu^{2+} ion and many treatment methods were utilized in this study (Orescanin, Kollar, Mikelic, & Nad, 2013). Moreover, Orescanin et al, have been tried to remove Cu^{2+} ion from water by their method for ED wastewater treatment utilizing waste by-product (ferrous-sulfate) and waste wood fly ash. The disadvantage of previous studies and techniques of wastewater treatment technology in recent decades, 80% of the electrodeposited technique for wastewater treatment uses chemical methods to treat copper in wastewater at home and abroad (Bai, Ying, Wang, & Lin, 2016). Developing electrodes that combine low electrical resistance, low-cost and mechanical flexibility is an ultimate goal in this field (Huh, Jeon, & Ahn, 2017).

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

The production of electrodes involves two main steps. First, the metal electrodes are prepared utilizing conventional microfabrication. In the second step, a thin layer of metal or metal oxide was electroplated above the existing model from an electrolyte solution. This result in the modification and improvement of surface properties (Patel, Bandre, Saraf, & Ruparelia, 2013). Moreover, the electrodes have been utilized for water treatment are either classified as inactive or active electrodes based on the stability of the electrode surface atoms to redox cycling. The active

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

electrodes, for example electrode Pt/IrO_2 continuously cycle the oxidation states during the electrochemical oxidation of the substrates. The inactive electrodes for utilized in water treatment it must be doped to obtain sufficient conductivity that allows it to function as an electrode for water treatment (Chaplin, 2018). As established in many studies, the nature of the anode material affects not only the efficiency of the process but also the selectivity of the electrode (Feng, Yang, Liu, & Logan, 2016a). Conventional electrode materials such as graphite electrodes and platinum electrodes still have broad applications in wastewater treatment. To improve efficiency of electrochemical processing researchers started to study and develop electrodes materials. Researchers aspire to get electrodes have greater catalytic activity, potential greater potentiality and greater stability (Feng et al., 2016). In change tactics traditional electrode matrix material pattern, Yang and her team (Yang, Wang, Zhou, Guo, & Li, 2016) decided to use aluminum as an in-core. Coat the outer layer with the titanium layered composite material constituent matrix material, electrode core as aluminum for fine conductivity and play an important role of reduction interface resistance and equalization current distribution, outer layer utilizing titanium the original electrochemical properties can still be maintained (Kang, Cha, Patel, Wu, & Choi, 2016).

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

Experimental results show that, changes in the electrode matrix material not only improve electrode performance, purpose of energy saving, and consumption reduction (Feng et al., 2016). For electrochemical treatment applications various electrode materials such as stainless steel (SS) (Szpyrkowicz et al., 1998), graphite, carbon aerogel (Rana-Madaria, Nagarajan, Rajagopal, & Garg, 2005) and vitreous

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

carbon (Ruotolo & Gubulin, 2009) have been developed. Metal electrodes for practical applications have good conductivity but are limited due to high energy consumption, low surface area, can easily damage and corrode which cannot give sufficient active sites to decrease or remove heavy metal form water. To resolve these issues, some composite electrode materials are being utilized conductive polymeric incorporated (Li et al., 2017) with metal materials (Pan et al., 2009). However, most materials of the composite electrode are synthesized utilizing polymeric binders that can block the surface of the electrode and improve the electrical resistance. In addition, graphene has a good ability to deliver electrons that can supply high current densities and accelerate the rate of heavy metal ions reduction. Other researchers have been utilized deposition of GO nanosheets on copper substrate for highly corrosion protective (Sahu et al., 2013). Li and his team (Li et al., 2017) have been synthesized reduced graphene Oxide on Stainless Steel Net Electrode. However, still need improving to use for electrochemical treatment water by developing the electrodes utilizing nanotechnology.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

Many research had been focused to improve the performance of CDI (Min, Choi, & Jung, 2018; Mitchison & Crick, 2017). The CDI has many designs such as flow between electrodes, flow through electrodes, membrane CDI, inverted-CDI and hybrid CDI. The major and important factor to enhance the performance of CDI is correct choice of electrodes material. Several studies were studied carbon materials as an electrode material in their researches. Moreover, many carbon materials including carbon aerogel (Quan et al., 2017), activated carbon powder (Blegur & Endarko,

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

2017), graphene (Nugrahenny et al., 2014) and carbon nanotubes (Wimalasiri & Zou, 2013) are studied as electrode materials for CDI.

The activated carbon fiber cloth (ACFC) is appropriate for CDI electrodes in that the surface area is large, variety in shaping, and the electrical conductivity is high (Chen, Huang, & Kang, 2014). As well has many functional groups on the surface. It can act as an ion adsorption site when an electric field is applied. However, many studies tried to modify ACFC to enhance its CDI performance by the reaction between polar groups on its surface and metal alkoxides of titanium, silicon, aluminum and zirconium. Meanwhile, Titania was effective in reducing the physical adsorption of NaCl, increasing the electric field adsorption and leading to a significant improvement in CDI performance (Ryoo & Seo, 2003). The effect of ACFC chemical activation on deionization properties was studied by Oh and his team (Oh et al., 2006). Other research studied a CDI electrode consisting of Nano/micro size ZnO_2/ACFC composite material, the ions removal efficiency up to 22% was observed compared to utilizing only ACFC (Tay, Myint, Al-harthi, & Dutta, 2014). Zhou and his team studied graphite and ACFC composite electrodes for enhance the performance of CDI. It was reported that the graphite and ACFC electrodes achieved high removal efficiency (Zhou et al., 2015). They had developed a new electrode composites based on reduced graphite oxide and activated carbon fiber and applied to CDI. The electrodes had shown high desalination capacity and good reversibility for CDI (Liu et al., 2017). The carbon materials and activated carbon fibre in CDI will be discussed in more detail later in chapter 2.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

The CDI had been applied aimed at removal of heavy metals. Only a few studies reported that CDI could remove the heavy metals (Cd^{2+}, Pb^{2+}, Cr^{3+}) and the performance was 32%, 43%, and 52%, respectively (Huang, Lu, Cai, & Ren, 2016). Other studies reported cadmium removal from aqueous solution by CDI (Peng et al., 2016). The results showed that Cd^{2+} was adsorbed on the surfaces of the electrodes and the maximum electrosorption capacity of Cd^{2+} was about 900.7 mg g^{-1} (Peng et al., 2016). Hu and coworkers have utilized CDI for removal Cu^{2+} ion from aqueous solution by activated carbon electrodes. Hu and her team (Hu, Liu, Lan, Liu, & Qu, 2015) have reported preparation of a manganese dioxide/carbon fiber (MnO_2/CF) electrode for utilized in CDI cell for removal Cu ion, the maximum removal was 90 % from Cu ion.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

Moreover, many water treatment techniques have been utilized for removing dyes from aqueous solution for example: electrochemical degradation (Weng, Zhou, & Zhang, 2013), photocatalytic degradation (Thao, Dang, Khanitchaidecha, Channei, & Nakaruk, 2017), adsorption/precipitation processes (Wang et al., 2012), ultra-filtration (Hammami, Charcosset, & Ben Amar, 2017), and biological degradation (Roy et al., 2018). The ACFC have been reported to be wonderful to treat contaminated water due to their porosity and large surface areas, however its desorption kinetics and regeneration is questionable (Nair, Joshi, & Geim, 2015). The variety and complication of the dyes have generated the necessity for modern methods of dye removal, which has been addressed by the development of Capacitive Dye Removal (CDR) method. As the methyl blue (MB) dye in water (aqueous solution) cannot be removed via conventional methods effectively, the removal of MB dyes on

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

cheap and effective by utilizing CDR cell has been reported to be suitable, promising and economically attractive method (Shi & Zhitomirsky, 2015).

The MB dye are widely utilized for numerous applications, for example textile industry (Singh & Arora, 2011), solar cells (Connell et al., 2015), medicine (Liu et al., 2013), sensors (Nishiyabu, Ushikubo, Kamiya, & Kubo, 2014) and other applications. In this study we have develop electrode CDI cell for the removal Cu ions and MB dye from aqueous solutions. The goal of this study was to develop the electrodes utilizing GO by sprayed and immersion method to coating ACFC for removal of MB dye.

However, recent empirical studies of GO reported that GO has been utilized in many application such as water treatment (Ping, & Dong, 2017), sensor, dye-sensitized solar cells (DSSCs) (Suriani, Fatiatun, et al., 2018) and supercapacitor (Masrom, 2015) due to its excellent properties such as high electrical conductivity (Chen et al., 2016), large specific surface area, and high thermal properties (Zhu et al., 2012). In addition, it also contains high amount of oxygen-functional groups, such as hydroxyl, carboxyl, carbonyl and epoxy (Dots & Ozonation, 2012) resulted from oxidation process during its synthesis. The GO can be synthesized by chemical approach such as Hummer’s and electrochemical exfoliation methods. Hummer’s method utilizes many hazardous chemical, complex synthesis step and expensive (Kaur, Kaur, & Kukkar, 2018). The electrochemical exfoliation offers much simpler, lower cost production and greener method as compared to Hummer’s method thus widely developed for GO synthesis (Suriani et al., 2018). By utilizing water-based

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

electrolyte, a surfactant is needed to assist the intercalation, exfoliation and stabilization of the exfoliated GO (Azmi Mohamed et al., 2016).

The commercially available single-tail sodium dodecyl sulphate (SDS) (Suriani, Fatiatun, et al., 2018, & Suriani, Muqoyya, et al., 2018) and poly(sodium 4-styrenesulfonate), double-tail sodium bis (3,5,5-trimethyl-1-hexyl) sulfosuccinate (Hensel et al., 2017), and custom-made triple-tail (TC14) surfactants were successfully utilized in electrochemical exfoliation method presented in the previous work (Azmi Mohamed et al., 2014).

The GO also poses a great absorbent thus has widely utilized for the heavy metals removal (Wu et al., 2012). Its high water solubility and high amount of oxygen-functional groups can directly react with the heavy metal ions and form metal ion complex thus promising in the heavy metals removal shows the optimum Cu removal was achieved by utilizing 1 mg/mL GO (Abdi & Kazemi, 2015; Zhao, Wang, Qiu, Lin, & Xu, 2014). The presence of magnetic field (MF) also proven to enhance the mass transport rate in the heavy metals deposition. By utilizing 1.2 T of MF, the optimum Cobalt- Nickel–Molybdenum (CoNiMo) deposition was achieved by (Aaboubi & Msellak, 2017). Meanwhile, Kolodziejski et al. developed external MF in the ED process known as magneto-electrolytic deposition (MED), Metals and alloys electrodeposited under constant MED have greater thickness and smoother surface with finest grains (Kołodziejczyk et al., 2018). It is proven that MHD enhanced the heavy metal ions removal due to faster ion transport (Krause el al, 2004).

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

Based on previous work, it is clearly proven that TC14 enhance the dispersion of multi-walled carbon nanotubes in latex nanocomposite (Azmi Mohamed et al., 2014). The GO assisted by TC14 (TC14-GO)-latex nanocomposite was also successfully produced by one-step electrochemical exfoliation and shows higher conductivity as compared to the SDS-GO-latex nanocomposite sample. Higher capacitance value was achieved and confirmed better quality of TC14-GO. Furthermore, the similar resistivity value of TC14-GO to the SDS-reduced GO (SDS-rGO) for the DSSCs counter electrode was also proven in the previous result (Suriani et al., 2017) investigated the type of electrode and obtained that iron (Fe)-Fe presents the best electrode (Suriani & Khayri zaid, 2017). Hence, in this work, TC14-GO was then utilized to coat the SS electrode for electrodeposition cathode since 90-95% of SS material composed of Fe. To the best of our knowledge, this is the first report which utilized the SS cathode utilizing GO assisted by TC14 surfactant for the heavy metal’s removal. The utilized of GO which contains of high oxygen-functional groups increases the cathode deposition surface area resulted higher Cu^{2+} ion removal concentration. In addition, it also supported by the presence of external MF which increase the mass transfer rate. This present work demonstrates a simpler, greener and highly efficient electrochemical system for removing heavy metals ions utilizing GO coated cathode with the MF presence.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

1.2 Research problems

The limitation of fresh water (Fogden, 2009; World Health Organization, 2017) and the increased of human activities in many industries cause an increase in contamination of a private nature of water resources (Ayangbenro & Babalola, 2017; Jenelapriscy & Jesvinshobini, 2017; Sewvandi & Adikary, 2011) increased the need of water treatment. The high cost in electrochemical treatment technologies (Wang & Chen, 2015) too, had urge the researcher interest to conduct a research for low cost of electrochemical water treatment. Besides, the limited study on Graphene oxide (GO) and reduced Graphene oxide (rGO-based SS electrode) utilized for the removal of heavy metal ions (Cu^{2+}) (Khayri Zaid & Suriani Abu Bakar, 2017) in water treatment has also contribute to the significance interest of the researcher to conduct the research.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

The researchers have been focused on development different forms of carbon-based material to utilize as electrodes in CDI technology. Since 2009, they have begun to utilize different materials as electrode in order to improve the performance and to increase the efficiency of ions removal (Chandrasekaran, Koh, Yamauchi, & Ishikawa, 2009). Most of the research efforts have focused on the development of new electrode materials and the improvement of its properties (Mossad & Zou, 2011).

Among the electrode materials that are being developed for CDI cell application are activated carbon (Ostafiychuk et al., 2015), carbon aerogels, nanostructured carbon cloth, graphene , carbon nanotubes and nanofibers. In general,

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

for the materials to be utilized as electrode in CDI they should be a conductive porous material with high surface area which will result in excellent absorption of fluids as well as able to absorb and remove odor. limited studies have studied CDI usage for Cu ions removal (Ostafiychuk et al., 2015). CDI has been focused to improve the performance by different materials as electrode in order to improve the performance and to increase the efficiency of Cu^{2+} removal.

The Cu^{2+} ion is considered a dangerous contaminate and has been introduced in large quantities in the aqueous medium from the different waste waters sources like for example metallurgy, mining, circuit printing and plating. Permission limits provided by the World Health Organization for Cu^{2+} downloaded inside surface water and drinking water are 3.0 mg/L and 0.05 mg/L, respectively (World Health Organisation, 2017). Excessive consumption of Cu^{2+} can cause gastrointestinal symptoms and liver toxicity. Therefore, it is very important to eliminate Cu^{2+} from water. Several treatment technologies have been suggested for the removal of Cu^{2+} from wastewater. To date, however, these processes are generally limited due to technical or economic constraints, especially at high and lower Cu concentrations (Huang, Fan, & Hou, 2014).

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

Currently, the electrosorption removal of metal ions from aqueous solution is still limited and need to be explored. The first study by Oda and Nakagawa. (Oda & Nakagawa, 2003) was the characteristic nature of the removal of Cu and Zn by utilizing a carbon electrode via applying 1 V. The second study by Zhan et al. have fabricated nanofiber film and carbon nanotube (CNT) electrodes for CDI to remove

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

Cu ions at different voltages (0–2 V) (Zhan, Pan, Nie, Li, & Sun, 2011). The third study was by Huang and He (Huang & He, 2013) whose modified activated carbon cloth electrodes for CDI and found that higher electrosorptive capacity of Cu ions was achieved at 0.3 V than that at open circuit. Furthermore, some study utilizing a CNT-chitosan composite electrode for electrosorption of Cu^{2+} and mesoporous carbon electrode, shows higher adsorption than conventionally activated electrodes (Ma, Huang, Chou, Den, & Hou, 2016).

Water pollution by MB dyes is a worldwide problem particularly in textile industry and many industries for example rubber and paper. Over the past few decades, substantial few of researchers have been focused to improve the performance of CDR for dye removal (Hidrovo et al., 2013). However, the studies about the removal of dye are quite limited (Annadurai Thamilselvan et al., 2018). Koparal and his team utilized commercial granular activated carbon for removal of acilan blau dye from textile effluents by electroadsorption (Koparal, Yavuz, & Ogutveren, 2002). Other study by Gercel has studied electroadsorption of textile (Burdem Orange II) dye utilizing activated carbon synthesized from waste material (Gerçel, 2016). The removal efficiency of textile dye was up to 98%. Ming Chen et al. (Chen, Wei, Chu, Hou, & Tong, 2017) have synthesized mesoporous amorphous B-N-O-H nanofoam as electrode for CDR cell for MB dye removal from water but this study was not shows the removal efficiency of MB dye. To the best of my knowledge, the ion removal of Cu^{2+} and MB dye by the TC14-GO based on active carbon fiber cloth utilized in CDI process has not been reported.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

1.3 Research Objectives

1. To synthesize the graphene oxide (GO) and reduced graphene oxide (rGO) by electrochemical exfoliation utilizing custom-made triple-tails surfactant (TC14) for water treatment systems application.

2. To develop constant magnetic field (CMF) assisted electrodeposition cell system with TC14-GO/SS and TC14-rGO/SS based electrodes for water treatment systems application.

3. To develop the CDI water treatment system utilizing GO-based active carbon fiber cloth (ACFC) electrodes for water treatment systems application.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

4. To determine the reaction of GO/SS electrodes mechanism with Cu^{2+} in electrodeposition process and ACFC-GO electrodes mechanism with methylene blue (MB) dye removal in CDI water treatment system.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

1.4 Scope and Limitation of Study

The utilization and characterization of GO and rGO was limited to the custom-made triple-tail surfactant (TC14) assisted electrochemical exfoliation method. This study was then actualizing on the coating of various type of GO/SS and TC14-rGO/SS electrodes via spray and immersion coating method to improve the removal of Cu ions utilizing CMF in electrodeposition water treatment system (EDWTS). Then, it also investigates the capability of TC14-GO and TC14-rGO on the development EDWTS.

The second part of the study focuses on the fabrication of CDI single cell system by developing the electrode materials utilizing ACFC with TC14-GO as electrodes for both CDI design flow between and through electrodes. It also, to investigates the viability of CDI in treating heavy metal (Cu ions). Moreover, the fabrication of CDI single cell system utilizing ACFC with TC14-GO as electrodes for both design (flow between and through electrodes) as electroadsorption for removing MB dye from aqueous solution utilizing the CDR electroadsorption process are also discussed.

Several analysis techniques were utilized for characterizations such as Field emission scanning electron microscopy (FESEM), energy dispersive X-Ray (EDX), High-Resolution Transmission Electron Microscopy, Fourier Transform Infrared Spectroscopy (FT-IR), micro-Raman spectroscopy, transmission electron microscopy (TEM), pH Meter measurement, Ultraviolet-Visible Spectroscopy, Brunauer-Emmett-Teller, Cyclic Voltammetry, and X-ray diffraction (XRD).

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

1.5 Thesis Organization

The thesis is organized in five chapters. Chapter 1 includes the introduction, background of study, research problems, research objectives, scope and limitation of studies. In chapter 2 deeper review of basic theories of ED, electroadsorption water treatment, theory of CDI, capacitive deionization technology, development of electrode materials for CDI, review on several materials in polluted water and application of GO in the water treatment as electrode material. The development of both ED and CDI system, the experimental work and characterization of samples were presented in chapter 3.

Chapter 4 presents the results of the both developed system for Cu^{2+} ions removal and MB dye removal from aqueous solution. Chapter 4 also covers the investigation on the mechanism of metal ions adsorption and dye removal from custom made system the finding was then summarized in chapter 5 and some suggested are also presented for future work.

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi