MODIFIED RICE HUSK AND ACTIVATED CARBON FILTERS FOR THE REMOVAL OF ORGANICS AND HEAVY METALS IN WATER

ABDURRAHMAN GARBA

A thesis submitted in
fulfilment of the requirement for the award of degree of
Doctor of Philosophy in Science

Faculty of Science, Technology and Human Development
Universiti Tun Hussein Onn Malaysia

FEBRUARY, 2017
To Allah (S.W.T), then to my parents and all members of my extended family
ACKNOWLEDGEMENTS

In the name of Allah, the most beneficent, the most merciful. All praises be unto Him, the lord of the worlds for making it possible for me to come this far regarding the pursuit of PhD in Science. I would like to appreciate and thanks my main supervisor Dr. Hatijah Binti Basri for the support, guidance, advice and constructive criticism during the entire duration of this research. I also wish to extend my special gratitude to my co-supervisor Associate Professor Dr. Noor Shawal Nasri for his immense contribution towards making this research successful.

I wish to appreciate the financial support provided by the office for research, innovation, commercialization and consultancy management (ORICC) of University Tun Hussein Onn Malaysia for the financial support under GIPS Vot number 1253 for experimental and other aspects of this research. I also wish to thank the centre for graduate studies of UTHM for the assistance they rendered during conferences and other academic issues.

Special thanks to my parents, especially my mother for the constant prayers, care, love and encouragement. I appreciate the love, support, understanding and patience from my beloved wife Aisha Sani Muhammad and my children Abubakar, Hafsat and Abdullah. Special thanks to Mr. Ishak Ayub and his colleagues at food technology laboratory for the help and understanding they exhibited during the course of this work. Also special thanks to my brothers Bello, Abdullah and the entire extended family for their support. Special thanks to my friends at UTM – MPRC, UTM community and all others too numerous to mention.

Lastly, I acknowledge the support of my employer, Federal Ministry of Education, Abuja, Nigeria, for the study leave granted to me. Special thanks to all my colleagues at FGGC Bakori for their support and friendliness.
Discharge of untreated industrial effluents containing heavy metals and organics is hazardous to the environment because of their toxicity and persistent nature. At the same time, agricultural waste poses disposal challenges, which can be converted into value added products like adsorbents that could serve as tools for contaminants abatement. Previous findings proved that, adsorption was a sustainable, economical and lucrative separation technique for the removal of such contaminants. This thesis presents the fabrication of a filter for the removal of organics and heavy metals in water which was prepared from treated rice husk and modified activated carbon (AC). The analysis of AC via Brunauer-Emmett-Teller (BET) surface area and scanning electron microscopy evidenced porosity of 707 m²/g as surface and a pore volume of 0.31 cm³/g. The elemental and thermogravimetric analysis proved that AC contain 48.7% carbon, while the Fourier transform infrared spectroscopy shows that the surface contains functional groups such as O-H, C=C, C-O, C-O-C and C-H. The experimental results were fitted with fixed-bed adsorption models to understand the adsorbate-adsorbent relationship. Fixed-bed adsorption studies show that, the highest adsorption capacity of 248.2 mg/g and 234.12 mg/g for BPA and phenol respectively was obtained at 250 mg/L concentration and 9 mL/min flow rate. The results also revealed 73 % and 87 % as the highest removal capacity for heavy metal Pb and Cd respectively at 20 mg/L concentration and 9 mL/min flow rate. For sustainability, regeneration of the spent AC was carried out in a microwave which showed 75% yield after five cycles, while the rice husk was eluted with 0.1M hydrogen chloride and 37.8% efficiency was achieved after three successive cycles. The UV lamp incorporated in the filter shows total inactivation of E. coli after 7 minutes.
ABSTRAK

Pelepasan efluen industri tidak terawat yang mengandungi logam berat dan bahan organic adalah berbahaya kepada alam sekitar ekoran daripada ketoksikan bahan. Oleh itu, penyingkiran bahan daripada air minuman adalah sangat penting bagi melindungi kesihatan dan alam sekitar. Dalam masa yang sama, penyingkiran sisa pertanian juga merupakan cabaran, yang boleh ditukarkan menjadi produk berharga seperti penjerap yang boleh mengurangkan kuantiti bahan cemar ini. Kajian terdahulu menunjukkan teknik penjerapan adalah mesra alam, lestari, ekonomi dan boleh menjadi teknik pemisahan yang berharga bagi penyingkiran bahan cemar tersebut. Tesis ini membentangkan tentang fabrikasi penapis bagi tujuan penyingkiran bahan cemar organic dan logam berat yang disediakan daripada sekam padi terawat dan karbon teraktif terubahsuai (AC). Analisis luas permukaan dengan menggunakan teknik Brunauer-Emmett-Teller (BET) dan mikroskopi imbasan electron (SEM) menunjukkan keliangan AC adalah 707 m²/g dengan isipadu liang 0.31 cm³/g. Analisis unsur dan termogravimetri menunjukkan AC mengandungi 48.7% karbon, manakala spektroskopi infra-merah jelmaan fourier menunjukkan permukaan mengandungi kumpulan-kumpulan berfungsi O-H, C=C, C-O, C-O-C dan C-H. Keputusan eksperimen telah dipadankan dengan model penjerapan fixed-bed untuk memahami hubungi elemen dijerap dan penjerap. Kajian penjerapan fixed-bed menunjukkan kapasiti penjerapan tertinggi pada 248.2 mg/g dan 234.12 mg/g bagi BPA dan fenol masing-masing pada kepekatan larutan 250 mg/L dan kadar alir 9 mL/min. Keputusan juga menunjukkan kapasiti penyingkiran 73 % and 87 % bagi logam berat Pb dan Cd pada kepekatan 20 mg/L dan kadar alir 9 mL/min. Untuk kelestarian, penjanaan semula bagi AC terpakai yang dijalankan menggunakan ketuhar gelombang mikro menunjukkan 75% hasil setelah lima kitaran. Sekam padi yang dilalukan dengan larutan hidrogen klorida 0.1M menunjukkan kecekapan 37.8% yang berjaya dicapai setelah tiga kitaran. Lampu UV yang masukkan ke dalam penapis menunjukkan penyahaktifan semua E. coli setelah tujuh minit.
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td>CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xix</td>
</tr>
<tr>
<td>LIST OF ABREVIATIONS</td>
<td>xxi</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xxiii</td>
</tr>
</tbody>
</table>

## CHAPTER 1  INTRODUCTION

1.1 Research Background 1
1.2 Problem Statement 4
1.3 Research Objectives 5
1.4 Research Scope 6
1.5 Research Significance 7
1.6 Structure of the Thesis 8

## CHAPTER 2  LITERATURE REVIEW

2.1 Activated Carbon 10
2.2 Preparation of Activated Carbon 12
   2.2.1 Raw Materials for Carbon Production 13
   2.2.2 Carbonization Process 14
2.2.3 Activation Process 16

2.3 Types of Activated Carbon 21

2.4 Microwaves 23
  2.4.1 Microwave Heating 23
  2.4.2 Microwave Heating for Activated Carbon Regeneration 25

2.5 Activated Carbon Modification 26
  2.5.1 Acid Treatment 27
  2.5.2 Basic Treatment 28
  2.5.3 Heat Treatment 29
  2.5.4 Microwave Treatment 29
  2.5.5 Biological Treatment 30
  2.5.6 Miscellaneous Modification Methods 31

2.6 Activated carbon Properties 31
  2.6.1 pH 31
  2.6.2 Surface Area 31
  2.6.3 Ash Content 32
  2.6.4 Pore size distribution 33
  2.6.5 Chemical properties 33

2.7 Uses and applications of Activated carbon 34

2.8 Cost of activated carbon production 34

2.9 Adsorption Isotherms 37
  2.9.1 IUPAC Classification of isotherms 38

2.10 Fixed–bed adsorption models 42
  2.10.1 Clerk model 43
  2.10.2 Thomas model 43
  2.10.3 Adams–Bohart model 44
  2.10.4 Bed depth service time (BDST) model 44
  2.10.5 Yoon–Nelson model 45
  2.10.6 Wang model 46
  2.10.7 Wolborska model 46
  2.10.8 Dose – response model 47
  2.10.9 Modified dose–response model 47

2.11 Error Analysis 47
2.11.1 The sum of the squares of the error (ERRSQ) 48
2.11.2 Hybrid fractional error function (HYBRID) 48
2.11.3 Average relative error (ARE) 48
2.11.4 Sum of squares (SS) 49
2.11.5 Sum of absolute errors (EABS) 49
2.11.6 Marquardt’s percent standard deviation (MPSD) 49
2.11.7 Nonlinear chi–square test ($x^2$) 50
2.11.8 Sum of absolute error (SAE) 50
2.11.9 Root mean square error (RMSE) 50
2.11.10 Mean square error (MSE) 51

2.12 Rice Husk 51
2.12.1 Properties of Rice Husk 52
2.12.2 Rice Husk Pre-treatment 52
2.12.3 Uses and Applications of Rice Husk 54

2.13 UV Disinfection 55
2.13.1 Effectiveness of UVC Disinfection 57
2.13.2 Mechanism of UV Disinfection 59
2.13.3 Applications of UV radiation 61

CHAPTER 3 METHODOLOGY 62

3.1 Introduction 62
3.2 Activated Carbon (AC) Preparation 64
3.2.2 Carbonization Process 67
3.2.3 Activation Process 67
3.2.4 Physical Activation 69
3.2.5 Chemical Activation 70
3.2.6 Characterization of Activated Carbon 71
3.2.7 Field–Emission Scanning Electron Microscopy (FESEM) 71
3.2.8 Nitrogen Adsorption 72
3.2.9 Fourier Transform Infrared Spectroscopy (FTIR) 72
3.2.10 pH 72
3.2.11 Proximate Analysis 73
3.2.12 Ultimate Analysis 73
3.2.13 Thermogravimetric/Derivative Thermogravimetric Analysis (TG/DTG) 73
3.3 Ammonia Treatment 74
3.4 Fabrication of the filter 74
  3.4.2 Removal efficiency of Activated Carbon 77
  3.4.3 Fixed-Bed Adsorption Procedure 77
  3.4.4 Fixed-Bed Breakthrough Curves Modeling 79
  3.4.5 Error Analysis 79
  3.4.6 Regeneration Procedure 80
3.5 Rice Husk Preparation 82
  3.5.1 Materials 82
  3.5.2 Characterization of Rice Husk 84
  3.5.3 Treatment with Sodium Hydroxide 85
  3.5.4 Measurement of Pb^{2+} and Cd^{2+} Concentrations in water 85
  3.5.5 Removal efficiency of Rice Husk 85
  3.5.6 Fixed-bed Adsorption Procedure 85
  3.5.7 Breakthrough Curves modeling 86
  3.5.8 Error Analysis 87
  3.5.9 Regeneration Procedure 87
3.6 Sand Preparation 88
  3.6.1 Materials 88
3.7 Preparation of E. coli 88
  3.7.1 Materials 88
  3.7.2 Methods 89
  3.7.3 Gram Staining 89
  3.7.4 Preparation of inoculum 90
  3.7.5 Preparation of 0.5 McFarland standard 90
3.7.6 Use of McFarland’s standard in macro dilution procedure 91
3.7.7 Preparation of Serial dilutions of E. coli 92
3.7.8 Measurement of E. coli in water 93
3.7.9 Disinfection of E. coli by the UV lamp 93

CHAPTER 4 RESULT AND DISCUSSIONS 94

4.1 Introduction 94
4.2 Preparation of Activated carbon 95
  4.2.1 Proximate and Ultimate analysis of the precursor 95
  4.2.2 Effect of carbonization time and temperature on the carbon yield 96
4.3 Characterization of Activated Carbon 99
  4.3.1 Fourier Transform Infrared Spectroscopy 99
  4.3.2 Acid/base properties of activated carbon 100
  4.3.3 Field Emission Scanning Electron Microscopy 100
  4.3.4 Thermogravimetric analysis 102
  4.3.5 Zeta Potential Analysis 104
  4.3.6 Surface Area and Pore Volume Analysis 104
4.4 Regeneration and Adsorption/Desorption cycles of AC 105
4.5 Thermodynamic studies for Bisphenol A (BPA) and Phenol Adsorption 107
  4.5.1 Effect of temperature on BPA and Phenol Uptake 107
  4.5.2 Determination of free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) 109
  4.5.3 Estimation of activation energy 110
  4.5.4 Mechanism of Phenol Adsorption 111
4.6 Fixed-bed Adsorption Studies 112
4.6.1 Bisphenol A Uptake 112
4.6.2 Phenol Uptake 118
4.6.3 Phenol Breakthrough Curve Modeling 121
4.7 Comparison between synthesized and the commercially prepared carbon 124
4.8 Preparation of Rice Husk 126
4.8.1 Characterization of Rice Husk 126
4.8.2 Lead Uptake 129
4.8.3 Lead Breakthrough Curve Modeling 134
4.8.4 Cadmium Uptake 135
4.8.5 Cadmium Breakthrough Curve Modeling 139
4.8.6 Comparison between Pd and Cd uptake by the rice husk 141
4.8.7 Regeneration cycles of Rice Husk 145
4.9 Disinfection of E.coli using UV lamp 145
4.10 Cost of the filter production 146

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS 147

5.1 Conclusion 147
5.2 Recommendations 148

REFERENCES 150
APPENDIX 180
VITA 192
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Commercially Prepared AC with their Surface Area</td>
<td>32</td>
</tr>
<tr>
<td>2.2</td>
<td>Production cost of char in some parts of the world</td>
<td>36</td>
</tr>
<tr>
<td>2.3</td>
<td>Summary of some studies indicating dose response data for water disinfection using UV-LEDs</td>
<td>58</td>
</tr>
<tr>
<td>4.1</td>
<td>Proximate and ultimate analysis of raw palm oil shell use in this study</td>
<td>96</td>
</tr>
<tr>
<td>4.2</td>
<td>Proximate and ultimate analysis of this study compared with other studies</td>
<td>96</td>
</tr>
<tr>
<td>4.3</td>
<td>Effect of carbonization time on weight loss</td>
<td>98</td>
</tr>
<tr>
<td>4.4</td>
<td>Weight loss of oil palm shell and yield during carbonization</td>
<td>98</td>
</tr>
<tr>
<td>4.5</td>
<td>Acid–Base properties of the precursor, char and activated carbon</td>
<td>100</td>
</tr>
<tr>
<td>4.6</td>
<td>Thermodynamic parameters of BPA and phenol adsorption onto modified activated carbon</td>
<td>109</td>
</tr>
<tr>
<td>4.7</td>
<td>The Adams–Bohart, Thomas and Yoon–Nelson model constants for the BPA adsorption by modified activated carbon packed column</td>
<td>116</td>
</tr>
<tr>
<td>4.8</td>
<td>The Adams–Bohart, Thomas and Yoon–Nelson model constants for the phenol adsorption by modified activated carbon column.</td>
<td>122</td>
</tr>
<tr>
<td>4.9</td>
<td>Comparison of maximum adsorption capacity of some AC’s for BPA and phenol</td>
<td>125</td>
</tr>
<tr>
<td>4.10</td>
<td>The Adams–Bohart, Thomas and Yoon–Nelson model constants for the adsorption of lead by treated rice husk packed column</td>
<td>133</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.11</td>
<td>The Adams–Bohart, Thomas and Yoon–Nelson model constants for cadmium adsorption by treated rice husk packed column.</td>
<td>139</td>
</tr>
<tr>
<td>4.12</td>
<td>Regeneration efficiency at different cycles</td>
<td>145</td>
</tr>
<tr>
<td>4.13</td>
<td>Cost of producing 1 unit of the filter</td>
<td>146</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Internal structure of activated carbon adsorbent</td>
<td>12</td>
</tr>
<tr>
<td>2.2</td>
<td>Oil palm shell processing field</td>
<td>14</td>
</tr>
<tr>
<td>2.3</td>
<td>Carbonization reaction scheme of a carbonaceous material</td>
<td>15</td>
</tr>
<tr>
<td>2.4</td>
<td>Flowsheet for the production of activated carbon</td>
<td>16</td>
</tr>
<tr>
<td>2.5</td>
<td>The GAC Contactor</td>
<td>21</td>
</tr>
<tr>
<td>2.6</td>
<td>Types of activated carbon (A) PAC, (B) GAC and (C) EAC</td>
<td>22</td>
</tr>
<tr>
<td>2.7</td>
<td>The electromagnetic spectrum</td>
<td>23</td>
</tr>
<tr>
<td>2.8</td>
<td>The magnetic and electric fields of microwaves</td>
<td>24</td>
</tr>
<tr>
<td>2.9</td>
<td>Microwaves interactions with different materials</td>
<td>25</td>
</tr>
<tr>
<td>2.10</td>
<td>Thermal gradient for conventional (A) and microwave heating (B)</td>
<td>26</td>
</tr>
<tr>
<td>2.11</td>
<td>Type I isotherm plot for nitrogen adsorption</td>
<td>39</td>
</tr>
<tr>
<td>2.12</td>
<td>Type II isotherm plot for nitrogen adsorption</td>
<td>39</td>
</tr>
<tr>
<td>2.13</td>
<td>Type III isotherm plot for nitrogen adsorption</td>
<td>40</td>
</tr>
<tr>
<td>2.14</td>
<td>Type IV isotherm plot of nitrogen adsorption</td>
<td>40</td>
</tr>
<tr>
<td>2.15</td>
<td>Type V isotherm plot of nitrogen adsorption</td>
<td>41</td>
</tr>
<tr>
<td>2.16</td>
<td>Type VI isotherm plot of nitrogen adsorption</td>
<td>41</td>
</tr>
<tr>
<td>2.17</td>
<td>Uses of Rice husk</td>
<td>55</td>
</tr>
<tr>
<td>2.18</td>
<td>The types of UV radiations in the ultraviolet region</td>
<td>57</td>
</tr>
<tr>
<td>2.19</td>
<td>UVC Radiation disrupts DNA</td>
<td>60</td>
</tr>
<tr>
<td>2.20</td>
<td>Applications of UV radiations</td>
<td>61</td>
</tr>
<tr>
<td>3.1</td>
<td>Flow chart for the overall Methodology process</td>
<td>63</td>
</tr>
<tr>
<td>3.2</td>
<td>Oil Palm Shell sun dried after washing</td>
<td>65</td>
</tr>
<tr>
<td>3.3</td>
<td>Oven drying of Oil Palm Shell</td>
<td>65</td>
</tr>
<tr>
<td>3.4</td>
<td>The grinding machine</td>
<td>66</td>
</tr>
</tbody>
</table>
3.5 Sieves and shaker for size separation 66
3.6 Granulated oil palm shell after sieving 66
3.7 Oil palm shell char after carbonization process 67
3.8 Schematic diagram for carbonization and activation process 69
3.9 The pyrolysis set–up 70
3.10 Materials for impregnation 71
3.11 Magnetic stirrer for mixing the impregnated char 71
3.12 Schematic diagram of the fabricated filter 75
3.13 The PG Instruments UV–Vis Spectrometer 76
3.14 The Fixed–bed Adsorption set up 79
3.15 Modified microwave oven with glass reactor 81
3.16 Schematic diagram for microwave regeneration set–up 81
3.17 Rice Husk sun dried after washing 83
3.18 The drying of rice husk in hot air oven 83
3.19 The Milling Machine 83
3.20 The sieves and shaker 84
3.21 The Ground and Sieved Rice Husk 84
3.22 The Wickerham’s card 91
3.23 Serial dilution and plating of the bacteria 92
4.1 The FTIR spectra of the activated carbon samples 99
4.2 FESEM images of (A) RPS, (B) CPS and (C) PCAC 101
4.3 TG/DTG curves for RPS (A), CPS (B), and PCAC (C) 103
4.4 Zeta potential for the modified activated carbon 104
4.5 Type I isotherm plot from adsorption and desorption of nitrogen by PCAC 105
4.6 Desorption efficiency and Yield of PCAC-AM after five cycles 106
4.7 Effects of temperature on BPA and phenol removal at concentration of 50 mg/L, pH 6.5, 150 rpm and adsorbent dose of 0.1g 108
4.8 Linear plot of lnKc against 1/T at initial concentration of 50 mg/L, pH 6.5, steering speed of 150 rpm and adsorbent dose of 0.1g 111
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9</td>
<td>Effect of initial BPA concentration at constant bed height of 3 cm and flow rate of 6 mL/min</td>
</tr>
<tr>
<td>4.10</td>
<td>Effect of flow rate on adsorption of BPA at bed height of 3 cm and 50 mg/L concentration</td>
</tr>
<tr>
<td>4.11</td>
<td>Effect of adsorbent bed height at constant initial BPA concentration of 50 mg/L and flow rate of 6 mL/min.</td>
</tr>
<tr>
<td>4.12</td>
<td>Effect of initial phenol concentration at 3 cm bed height and flow rate of 6 mL/min</td>
</tr>
<tr>
<td>4.13</td>
<td>Effect of flow rate at bed height of 3 cm and 50 mg/L initial phenol concentration.</td>
</tr>
<tr>
<td>4.14</td>
<td>Effect of bed heights at constant phenol concentration of 50 mg/L and flow rate of 6 mL/min</td>
</tr>
<tr>
<td>4.15</td>
<td>FTIR spectra of the rice husk</td>
</tr>
<tr>
<td>4.16</td>
<td>SEM image of raw rice husk</td>
</tr>
<tr>
<td>4.17</td>
<td>EDS of Raw Rice Husk</td>
</tr>
<tr>
<td>4.18</td>
<td>SEM image of the rice husk after treatment</td>
</tr>
<tr>
<td>4.19</td>
<td>EDS of Rice Husk treated with NaOH</td>
</tr>
<tr>
<td>4.20</td>
<td>XRD result for the raw and treated rice husk</td>
</tr>
<tr>
<td>4.21</td>
<td>Effect of initial lead concentration at constant bed height of 2.8 cm and flow rate of 3 mL/min</td>
</tr>
<tr>
<td>4.22</td>
<td>Effect of lead solution flow rate at constant bed height of 2.8 cm and 5 mg/L concentration.</td>
</tr>
<tr>
<td>4.23</td>
<td>Effect of bed heights at constant lead concentration of 5 mg/L and 3 mL/min flow rate.</td>
</tr>
<tr>
<td>4.24</td>
<td>Effect of initial cadmium concentration at constant bed height of 2.8 cm and flow rate of 3 mL/min</td>
</tr>
<tr>
<td>4.25</td>
<td>Effect of cadmium solution flow rate at constant bed height of 2.8 cm and 5 mg/L concentration</td>
</tr>
<tr>
<td>4.26</td>
<td>Effect of bed heights at constant cadmium concentration of 5 mg/L and 3 mL/min flow rate</td>
</tr>
<tr>
<td>4.27</td>
<td>Effect of initial Pb or Cd concentration at constant bed height of 2.8 cm and flow rate of 3 mL/min</td>
</tr>
<tr>
<td>4.28</td>
<td>Effect of Pb and Cd solution flow rate at constant bed height of 2.8 cm and 5 mg/L concentration</td>
</tr>
</tbody>
</table>
4.29 Effect of bed heights at Pb and Cd concentrations of 5mg/L and 20 mg/L and constant flow rate of 3 mL/min

4.30 Percentage disinfection of E. coli with time
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometre</td>
</tr>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>BaCl</td>
<td>Barium Chloride</td>
</tr>
<tr>
<td>Ce</td>
<td>Concentration in equilibrium</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>Co</td>
<td>Initial Concentration</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>GHz</td>
<td>Giga Hertz</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Hydrogen sulphide</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrogen Chloride</td>
</tr>
<tr>
<td>K</td>
<td>Degrees Kelvin</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>Potassium Carbonate</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium Hydroxide</td>
</tr>
<tr>
<td>L</td>
<td>Litre</td>
</tr>
<tr>
<td>lbs</td>
<td>Pound-mass</td>
</tr>
<tr>
<td>m</td>
<td>Activated Carbon Dosage/ Mass</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
</tr>
<tr>
<td>Mins</td>
<td>Minutes</td>
</tr>
<tr>
<td>mm</td>
<td>Millimetre</td>
</tr>
<tr>
<td>n</td>
<td>Number Factors</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>N</td>
<td>Number of Experiment</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>Nitrogen Gas</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Nm</td>
<td>Nanometre</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre</td>
</tr>
<tr>
<td>q</td>
<td>Amount adsorbed</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>ZnCl\textsubscript{2}</td>
<td>Zinc Chloride</td>
</tr>
<tr>
<td>\lambda_{\text{max}}</td>
<td>Maximum Wavelength</td>
</tr>
</tbody>
</table>
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>BAC</td>
<td>Bead Activated Carbon</td>
</tr>
<tr>
<td>BDST</td>
<td>Bed Depth Service Time</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barret-Joyner-Helenda</td>
</tr>
<tr>
<td>BPA</td>
<td>Bisphenol A</td>
</tr>
<tr>
<td>CFU</td>
<td>Colony Forming Unit</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>CPS</td>
<td>Carbonized Palm Shell</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection Bye-product</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental Analysis</td>
</tr>
<tr>
<td>EAC</td>
<td>Extruded Activated Carbon</td>
</tr>
<tr>
<td>EBCT</td>
<td>Empty Bed Contact Time</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EMB</td>
<td>Eosin Methylene Blue</td>
</tr>
<tr>
<td>FCC</td>
<td>Federal Communications Commission</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Red Spectroscopy</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular Activated Carbon</td>
</tr>
<tr>
<td>GHG</td>
<td>Green House Gases</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
</tr>
<tr>
<td>PAC</td>
<td>Powdered Activated Carbon</td>
</tr>
<tr>
<td>PCAC</td>
<td>Furnace Prepared-Potassium Carbonate Activated Carbon</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>PCAC-AM</td>
<td>Ammonia treated-Potassium Carbonate Activated Carbon</td>
</tr>
<tr>
<td>RH-NaOH</td>
<td>Sodium Hydroxide treated Rice Husk</td>
</tr>
<tr>
<td>RPS</td>
<td>Raw Palm Shells</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet radiation</td>
</tr>
<tr>
<td>UV-LED</td>
<td>Ultraviolet – Light-emitting diode</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>List of publications and conferences attended</td>
<td>179</td>
</tr>
<tr>
<td>B</td>
<td>Instruments used for the characterization of the adsorbents</td>
<td>183</td>
</tr>
<tr>
<td>C</td>
<td>UV – Visible calibration data and curves</td>
<td>185</td>
</tr>
<tr>
<td>D</td>
<td>Structure of E. coli and differences between gram positive and gram negative bacterium</td>
<td>187</td>
</tr>
<tr>
<td>E</td>
<td>Pictorial presentation of the fabricated filter</td>
<td>189</td>
</tr>
<tr>
<td>F</td>
<td>Pictorial presentation of the UV lamp and its specifications</td>
<td>190</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Research Background

Water is colourless, odourless, tasteless and transparent liquid that without it, life is impossible. It is the only substance on earth that naturally exist in all the states of matter, and is also interchanging between this various forms. In comparison with other common liquids, water is unique because it has high absorption and retention capacity for heat due to hydrogen bonds that exist between its molecules. It is a valuable resource of outmost importance to both plants and animals for their survival. It is also a good liquid solvent because it can dissolve a great variety of compounds ranging from simple salts to complex organic compounds. Water is a natural resource that is essential to human survival. Therefore, there is need for its improvement and preservation continuously on daily basis. Although, about three-quarter of the earth was covered by water, not all of it is available for human consumption. This is because, only 3% of the water is fresh, while the rest are usually found in oceans and seas, which are saline in nature (Gleick & Ajami, 2014).

Water is of paramount importance to human beings in terms of both domestic and industrial use, its preservation from contamination at point and non-point sources is necessary (Garba, et al., 2016). The rapid growth in the area of human population and industries worldwide has increased the problems in the environment, specifically in the quality of water resources. Recently, the quality of water resources is declining on daily basis as a result of human activities such as indiscriminate disposal of pollutants into the water bodies through industrialization, civilization, environmental
changes and agricultural practices (Ali et al., 2012). Heavy metals pollution is one of the many causes of water pollution that brings about environmental degradation and deterioration which affects both humans and the aquatic system (Das et al., 2008). Heavy metals is a group name usually used for metals and metalloids that were associated with contamination and are toxic to both plants and animals. Commonly, they are the metallic and metalloid chemical elements that have a relatively high density values between 63.5 to 200.6 and a specific gravity greater than 5 (Fu & Wang, 2011; Zhao et al., 2016). They are non-biodegradable and toxic even at low concentrations. Thus, they could be harmful to most organisms at certain level of exposure and absorption. Common elements considered as heavy metals include Cu, Cd, Cr, Co, Pb, Hg, Se, Ni, Zn and As. Some researchers incorporate Ag, Be, Ba, Mn, Mg, Fe, Li, Ti, Ti, V, Sr and Sb as heavy metals (Fu & Wang, 2011; Park et al., 2016; Zhou & Haynes, 2010). It is a well-known fact that the anthropogenic sources of heavy metals into our water resources are power plants, extractive and metal ore processing, metallurgical, chemical, electronic, nuclear, agricultural practices and waste disposal. This pollution presents a serious problem that requires immediate attention and subsequent removal from water resources (Witek-Krowiak, 2013). Heavy metals are highly toxic as they were prioritized as the primary inorganic pollutants for surface water and groundwater as well as the environment due to their mobility in the aquatic ecosystem which affects both aquatic life and the other higher life forms. Water is the medium for and source of entry of this poisonous elements into the human body in which their intake beyond the permissible limits cause toxicity to the humans (Khan et al., 2008). Several methods were being used for heavy metals removal from water such as coagulation, precipitation, ion exchange, photocatalytic degradation, electrochemical deposition, flotation, membrane filtration and adsorption (Ahmed & Ahmaruzzaman, 2016; Barakat, 2011; Baruah et al., 2015; Duru et al., 2016; Goyal & Masram, 2015; Lofrano et al., 2016; Patil et al., 2016; Vunain et al., 2016).

In addition, organic pollutants is another group of pollutants that contaminate water bodies. They are carcinogenic, mutagenic, teratogenic, and have high bioaccumulation in nature if they are not removed from the water (Kümmerer et al., 2016). Therefore, organic pollutants were persistent in the environment because of such characteristics. Several types of organic pollutants were discovered in both surface and ground water bodies. These organic pollutants could be sourced from hydrocarbons, plasticizers, pesticides, oils, detergents, pharmaceuticals, greases,
biphenyls and phenols (Ali et al., 2012; Barceló, 2005; Tran et al., 2015). The pollutants have a general characteristics such as presence of a cyclic rings which are either of aromatic or aliphatic nature, absence of polar functional groups and substitution by a variable number of halogens in which chlorine was the preferred halogen substituted (Ali et al., 2012). Phenols and phenolic derivatives are other class of organic pollutants that were considered as priority pollutants because they are detrimental to humans even at low concentrations. Phenols and its derivatives can contaminate drinking water even at a low concentrations of 0.005 mg/L as it gives the water a significant bad taste and bad odour thereby making the water unfit for use (Aksu, 2005; Gupta & Balomajumder, 2015). Phenols and some of its derivatives were released from manufacturing industries such as pharmaceutical, plastic, paper, petroleum and petrochemicals, pesticides, and other manufacturers (Park et al., 2013). Literature reports several methods for organic compounds removal in aqueous media. The basic principles of their removal methods depends on their properties such as physical, chemical and biological. Some of the methods applied for the removal of phenols and its derivatives include reverse osmosis, chemical oxidation, electrochemical oxidation, ion exchange, solvent extraction, photocatalytic degradation, electro–dialysis, chemical coagulation and adsorption (Abussaud et al., 2015; Al-Rashdi et al., 2011; Ali et al., 2012; Bazrafshan et al., 2016; Cheng et al., 2016; Garba, et al., 2016; Singh & Balomajumder, 2016a, 2016b).

Furthermore, presence of infectious diseases that were caused by pathogenic bacteria such as E. coli were the most common health risk associated with drinking water. The waterborne pathogens were mostly introduced into the water bodies through human and animal faeces. In some instances, the bacteria can also exist naturally as autochthonous microorganism in the water. Cattles were considered as the main repository of E. coli where by the infected animals can approximately excrete between $10^2$ to $10^5$ CFU/g of faeces. Also, the introduction of fresh manure to the crops as fertilizer or for amendment of soil can basically enhance the spread of the pathogenic bacteria to the farmland and the environment at large. This is of great concern because, the bacteria may remain active from several days up to more than a year (Ongeng et al., 2011; Williams et al., 2007). The E. coli can easily be transported from the manure to the surface or groundwater by stormwater run-off, leaching, precipitation etc (Bradford et al., 2013; Mohanty et al., 2014; Zhang et al., 2014). The removal methods for pathogenic bacteria in water and wastewater is a complex process
that is significantly affected by some factors such as retention time, seasonal variations, vegetation and the composition of the water. The most frequently used and well established removal methods for pathogenic bacteria include starvation to death or predation, filtration, sedimentation and adsorption (Suzuki et al., 2014; Varga & Szigeti, 2016; Wu et al., 2016).

From all of the above listed methods for the removal of heavy metals, organics and bacteria from water, adsorption technology was the most commonly applied alternative. This is because, adsorption is cheap, green, sustainable, and can be regenerated. Fundamentally, adsorption is the accumulation of a substance on the surface or in the interface of an adsorbent. In the case of heavy metals, organics and bacterial removal, the process takes place between the surface and interface of a solid adsorbent and a contaminated water. The liquid contaminant is usually regarded as the adsorbate, while the adsorbing material is known as the adsorbent (Çeçen & Aktas, 2011).

### 1.2 Problem Statement

Presence of water pollutants such as heavy metals, organics and bacteria poses a serious problem that requires immediate attention. This is because, their ingestion and accumulation is dangerous to human health and the environment. For instance, heavy metals such as lead, cadmium, chromium, arsenic, mercury and others are serious common environmental pollutants that are generated from human activities. Heavy metals are toxic, can be incorporated into the food chain, and can exist in the environment as dissolved or free ions that could be absorbed into the soil, sediment or may bioaccumulate into the biota. Acute intoxication of these metals may trigger damage to the central nervous system, lungs, liver, kidney, cardiovascular and gastrointestinal system, bones and endocrine glands (Lakherwal, 2014; Liang et al., 2014).

Also, organic compounds such as phenols and its derivatives are water pollutants that were listed in the priority hazardous substances. These demonstrate their serious toxicities to human health and the ecology (Bazrafshan et al., 2012; Busca et al., 2008). The ingestion of water that is contaminated with phenol and its derivatives into the human body may result in protein degeneration and also damage
to the central nervous system, eye, heart, peripheral nerve, skin, kidney, liver, and pancreas (Asghar et al., 2014).

Furthermore, presence of pathogenic bacteria like *E. coli* in water is a public health hazard. These is because the microbes may lead to serious illnesses such as gastrointestinal, kidney failure, and urinary tract infections which is a significant cause of death in many parts of the world (Alshehri et al., 2014).

Adsorption using agricultural waste materials has been found to be undoubtedly one of the most popular and most widely used technology in water treatment, but most of filters that utilizes adsorption technology were still a little expensive. This is due to the fact that, commercially prepared activated carbon was incorporated into the filter.

It is on this note that this research focuses on fabrication of an efficient water filter that utilizes cheap activated carbon prepared from agricultural waste materials so as to convert the waste materials into value added products which helps to provide solution to agricultural waste disposal problem and at the same time using the products to remove contaminants in the environment. Although, fabrication of water filter is a highly researched area, but more has be done in the area so as to get filters that are less expensive, green, sustainable and have value for money. The novelty of this work is in preparation of a cheap water filter using cheap precursors that utilizes simple and efficient methods which does not require the usage of high energy or consumption of large amount of chemicals. Also, the filter was in modular form using cheap plastic containers as casing so as to give room for easy assembling and unlimited expansion. In addition, germicidal ultraviolet lamp was incorporated into the filter to ensure the total elimination of bacteria in the produced water.

1.3 Research Objectives

Based on the existing problem statement, the objectives of the research are summarized as follows;

i. To develop efficient adsorbents from low cost agricultural waste as adsorption media and to modify the adsorbents so as to improve their surfaces for higher adsorption of the contaminants.
ii. To characterize the adsorbents in terms of textural, thermal and chemical properties in order to understand their suitability and as well as their adsorption characteristics under fixed–bed adsorption mode.

iii. To evaluate the adsorption capacities of the regenerated adsorbents using microwave heating for activated carbon and elution with 0.1 M HCl for the rice husk.

iv. To evaluate the bacterial disinfection abilities of the incorporated UV lamp for their total elimination in the filter media.

1.4 Research Scope

To achieve the above mentioned objectives, the following scopes were drawn:

i. Adsorbents were prepared from low-cost agricultural waste materials. This include activated carbon prepared from palm oil shell by carbonization at 800 C and activation at the same temperature. Modification of the carbon was carried out using 6.6 M ammonia solution to improve its hydrophobic surface. The rice husk was prepared by treatment with 2 % NaOH in order to remove lignin and improve its adsorption capacity for heavy metals.

ii. The characterization of the adsorbents covers: surface chemistry (FTIR, and elemental composition), thermogravimetric analysis (TGA, fixed carbon, ash and volatile matter), surface morphology and texture (BET surface area SEM and XRD).

iii. Adsorptive capacities of the prepared adsorbents were investigated in a fixed – bed mode using synthetic solutions prepared from standard solutions of heavy metals for lead and cadmium analysis, phenol and bisphenol A for organic compounds analysis and E. Coli solution for bacterial analysis.
iv. Reusability of the adsorbents were determined after five successive adsorption/desorption cycles for activated carbon and three cycles for the rice husk.

v. Inactivation properties of the UV lamp was investigated and the results were expressed as percentage removal.

1.5 Research Significance

The main contribution of this study is fabrication of an inexpensive water filter from agricultural waste materials such as oil palm shell for the removal of organics, heavy metals and pathogenic bacteria from water. The fabricated filter demonstrated favourable adsorption capacity for the listed contaminants and the adsorbents in the filter media remain durable after reasonable successive regeneration cycles.

In Malaysia there is large amount of palm shells produced from oil palm processing industries. The use of this cheap and abundant precursor materials in production of adsorbents for subsequent use in the removal of heavy metals, organics and microbes from water will go a long way in reduction of environmental pollution which helps in environmental sustainability and in turn curb the potential health risks associated with this contaminants in water.

In addition, converting such agricultural waste into value added products such as adsorbents would serve as a way to mitigate the disposal challenges posed by this waste materials to the environment. Also, the industries involved in conversion of such waste materials would serve as an indirect way of revenue generation and simultaneously for job creation.

Furthermore, application of this cheap water filter would help in reduction of water shortages. This is because the filter could be used in recycling of grey water from (ablution water, laboratories, kitchens, etc). The filter could also help in harvesting rain water for areas that incorporate rain water as part of its source of domestic water.
1.6 Structure of the Thesis

The thesis comprises of five chapters and each chapter discusses specific areas of the research as presented below:

Chapter 1: Introduction
This chapter provides introduction to the research, background of the study, the problem statement, objectives of the research, scope of the research and as well how the thesis was organized.

Chapter 2: Literature Review
This chapter focuses on review of the relevant studies conducted in this area. The synthesis of the adsorbents and methods of modifications for a specific contaminant uptake from the water. The use of microwave heating for activated carbon regeneration.

Chapter 3: Methodology
This chapter discusses raw materials selection, experimental approaches, equipment employed for the research and general procedures followed in carrying out this research. These include the carbonization and activation processes, characterization and modification of the adsorbents, formulation of the synthetic heavy metals, organics and *E. coli* solutions in water and the fixed-bed adsorption process.

Chapter 4: Results and Discussion
This chapter presents the results of using oil palm shell for the production of AC under conventional heating method and as well the treatment of rice husk for heavy metals uptake. The chapter also discusses the characteristics of the prepared adsorbents and their applications for contaminants. The fixed–bed experimental results are also discussed and their correlations with the adsorption models and were respectively verified. Regeneration results of the spent adsorbents after five successive adsorption–regeneration cycles were also discussed.
Chapter 5: Conclusion and Recommendations
This chapter discusses the important inferences arrived at based on the results obtained from the research and it also present the recommendations for future studies in the area.
CHAPTER 2

LITERATURE REVIEW

2.1 Activated Carbon

Activated carbon (AC) is a microporous material that is predominantly amorphous solid with a highly developed internal surface area and pore volume. These unique properties are responsible for its high adsorption capacity which were exploited in many different liquid and gas phase applications (Adinata et al., 2007; Arami-Niya et al., 2010). Activated carbon has a slight positive charge on it which make it even more attractive to contaminants. When a liquid or gas passes over the positively charged surface of the carbon, the negatively charged ions from the contaminants were attracted to the surface of the carbon matrix (Alslaibi et al., 2013). The ease of regeneration of carbon gives it added advantage of making it economical and this significantly reduces the cost of purification process.

AC can be synthesized through carbonization followed by subsequent activation of the carbonaceous materials that contains lots of organic but few inorganic constituents like coal, wood, corn cobs, fruit shells and other agricultural wastes in an inert atmosphere (Mercier et al., 2014; Okman et al., 2014). AC is available in a various forms ranging from granular (GAC), powdered and extruded (EAC) activated carbon depending on their method of production and the prospective application.

Activated carbons are widely used in various applications for gas or liquid phase aqueous solutions such as portable water and treatment, industrial purification, air purification, chemical recovery operations, organic and inorganic contaminants removal from industries, toxins remediation by respirators, odour removal, natural and
hydrogen gas storage, catalyst support, pharmaceuticals and electrode materials in capacitors and batteries (Saygli et al., 2015; Tseng, 2006; Wang, et al., 2014). Various studies were published regarding the utilization of ACs as adsorbents mostly for environmental remediation. This processes were achieved due to well-developed porous nature of the carbons, large surface area and sufficient surface functionalities of the carbons. This physicochemical parameters (porous structure, large surface area and surface chemistry) can be enhanced by the type of raw material and the activation process employed (Inagaki, 2009).

Amongst the wide range of precursors used for activated carbon production (fruit shell, fruit stones, corn cobs, wood, coal bagasse, pulp etc.), oil palm shell is one of the most employed for water and wastewater uses because of its huge availability and effectiveness. Surface area of ACs ranges between 500 to 3000 m²/g depending on the composition of the precursor and the activation process used (Bandosz, 2006).

Among the AC properties, pore size distribution has been shown to play an instrumental role in its adsorption process as transportation of adsorbate from the aqueous medium to the internal structures or pores of the adsorbent is mainly through the mesopores and macropores. These distributions determines the adsorption capacity of the adsorbent (Bandosz, 2006). Hierarchically porous ACs comprised of interconnected pores such as micropores which has pore size between 0 – 2 nm (20 Å) and it determines the surface area of carbon as it constitutes about 95% of the carbon surface area, mesopores which are also known as transitional pores were responsible for adsorbates movement from the surface of AC to the internal pores with internal pores between 2 – 50 nm (20 - 500 Å) and macropores with pores above 50 nm (500 Å) respectively as presented in Figure 2.1 (Bhandari et al., 2015; Yamada et al., 2007).
2.2 Preparation of Activated Carbon

There are basically two processes involved in activated carbon production which are physical or chemical treatment. Each process involves two steps namely; carbonization and activation which were responsible for design of the shapes and sizes of the activated carbons (Al-Swaidan & Ahmad, 2011; Danish et al., 2011; Jun et al., 2010; Yahya et al., 2015). In physical treatment process, the precursor material is first carbonized, followed by activation step using either steam or carbon dioxide as activant. On the contrary, in chemical treatment process, the precursor material is impregnated with activating reagent, then heated under inert atmosphere to drive away the volatile components (Ahmad et al., 2013; Arami-Niya et al., 2010). The chemical reagents used in chemical treatment process could dissolve cellulosic components of the precursor material which initiates formation of cross-links (Örkün et al., 2012). Chemical activation has been shown to have more advantages over physical activation. This advantages include; chemical activation generally requires lower carbonization temperatures, produces carbons with higher yield, produce carbons with higher surface area, involves one step, and allows for tailoring the porosities of the produced carbons. However, there are some disadvantages associated with chemical activation such as thorough washing of the carbon produced is required so as to remove the impurities blended with the activating reagent and also the activating reagent could be corrosive (Hirunpraditkoon et al., 2011; Sing, 2014).
2.2.1 Raw Materials for Carbon Production

Any carbon-rich or lignocellulosic solid material can be a potential candidate for activated carbon production. However, the most crucial factors taken into consideration for the selection of an appropriate raw material are that the material must be non-hazardous, easily available, inexpensive with high carbon and low inorganic contents, highly resistant to abrasion, thermally stable, highly rich in volatile contents as their evolution during pyrolysis results into development of a porous char and must have small pore diameter which translates into higher exposed surface area and consequently high adsorption capacity (Ali et al., 2012; Kyzas & Deliyanni, 2015). Common raw materials used include agricultural waste (such as oil palm shell, coconut shell, coal, rice husk, corn cobs, waste tires, pulp mill residue, resins etc.) (Ioannidou & Zabaniotou, 2007).

Malaysia is the second largest palm oil producer and exporter with an annual estimation of about 73.74 million tons of biomass as residue. About 6 – 7 % of such biomass waste were left over as palm shells (as seen in Figure 2.2). Oil palm shell is one of the most common raw materials used for activated carbon production in Malaysia which could be due to its enormous availability and its demonstration of other good properties such as high fixed-carbon content, low ash and low inorganic materials. High carbon content in form of volatiles (usually above 50 %), helps to develop basic pore, while presence of inorganic materials influence the adsorption capacities of the carbon and high ash content make the carbon to be more hydrophilic (Mushtaq et al., 2015; Ohimain & Izah, 2017; Rafatullah et al., 2012; Yahya et al., 2015). It is also reported that oil palm shell based activated carbon have predominantly microporous pore structure and this accounts for its high available internal surface area that is found to be ideal for adsorption of small organic pollutant molecules (Ioannidou & Zabaniotou, 2007; Zhang et al., 2006).
2.2.2 Carbonization Process

Carbonization is a critical stage for activated carbon production because it is during this process that the micropores of the carbon starts to form. Carbonization can be defined as the thermal degradation of a carbonaceous material in the absence of oxygen which turn the material into different products that consist of solid (the char as residue), liquid (high molecular weights that condense after cooling) and gas in form of light molecular weights (Bandosz, 2006; Çeçen & Aktas, 2011). There are essentially two stages in a carbonization process namely; primary and secondary carbonization (Fernández et al., 2011).

The primary carbonization stage involved evolution of volatiles through thermal decomposition which is also known as devolatilization of the material. At this stage, the reactions that takes place were mainly dehydration, dehydrogenation, decarbonilation and decarboxylation (Bandosz, 2006). On the other hand, the secondary stage involved decomposition reaction that takes place within the solid matrix and as well further reaction between the released volatiles and the residue as presented in Figure 2.3.
At the secondary carbonization stage, the large molecular compounds or the char breaks further into smaller gas molecules such as carbon monoxide, carbon dioxide and hydrogen due to collision with gaseous materials from primary carbonization. The factors that play an important role in the above process include carbonization temperature, heating rate and residence time. Carbonization is also regarded as slow pyrolysis because it takes place at relatively lower heating rates at temperatures below 400 °C for a very long residence time that can take several hours or even days (Bandosz, 2006).

However, one of the primary products of pyrolysis that is in solid form (char) is a carbonaceous residue that mainly consist of elemental carbon that originates from the thermal decomposition of precursor material after the completion of the pyrolysis process. In other words, it could be regarded as the residue of an unconverted biomass material used in pyrolysis process. The char plays an important role in the pyrolysis as it has tendencies to catalyse or sometimes participate in secondary reactions. The applications of the char varies considerably according to its characteristics. It is widely applied as feedstock for production of activated carbon, nanofilaments, the gasification process to obtain hydrogen rich gas, producing high surface area catalyst used in electrochemical capacitors and also used in industries as solid fuel for boilers (Fernández et al., 2011). In this study, the char produced is mainly used for activated carbon synthesis.
2.2.3 Activation Process

Activation can be achieved thermally by heating the solid product (char) obtained from carbonization stage. Although, the char has started developing rudimentary pores as a result of carbonization process, it is unsuitable to be used as adsorbent until the porous structure is fully developed through activation. The activation process of char could be achieved by either physical or chemical means. In either case, heating of the char is required even though the temperature range is higher in physical activation due to absence of chemical activant. However, efficiency of activated carbon depends on modifications of its properties to increase its affinity towards certain contaminants (Çeçen & Aktas, 2011; Lu et al., 2012).

The functional groups at the surface of activated carbon were derived from the following sources namely; the precursor, thermal treatment, chemical treatment and activation methods (Li et al., 2011). Furthermore, activation process can be one-step or two steps. When carbonization and activation process are carried out simultaneously, then it is regarded as one-step activation. On the contrary, if the two processes were carried out one after the other, that is carbonization followed by activation process, then it is called two-step activation process as presented in Figure 2.4 (Bandosz, 2006; Nasri, et al., 2014).

Figure 2.4 Flowsheet for the production of activated carbon (Bandosz, 2006)
2.2.3.1 Physical Activation

For physical activation process, the raw material is first of all washed, dried and milled. It is then carbonized under oxygen deficient environment by flow of nitrogen to a temperature between 600 to 700 °C. The carbonized sample is then activated under flow of CO₂ or steam to a temperature of about 600 to 900 at 2 – 20 °C/min. The product is then washed with distilled water until the washing’s pH is close to 7, dried in oven and then stored in desiccator for use (Demiral et al., 2011).

The physical or thermal treatment method involved two stages; thermal decomposition otherwise known as carbonization of the precursor material followed by activation of the char. This process is basically referred to as dry oxidation which involved the reaction between the precursor and gaseous steam, gases and steam or mixture of CO₂ and air at temperature above 700 °C. A greater uniformity of the pores are usually achieved by activation with CO₂ compared to other physical activants. This process involved the removal of moisture and non-carbon portions of the material to produce a carbon skeleton with latent pore structure. The carbonization process converts the precursor to char with high fixed carbon content for activation purpose. Carbonization temperature is usually achieved at temperature range between 400 – 850 °C under nitrogen flow so as to create inert atmosphere within the system. On the other hand, activation temperature ranges from 600 – 900 °C which allow the conversion of the carbonized material to activated carbon (Yahya et al., 2015).

The activation process is usually carried out in the presence of activating gases such as carbon dioxide, steam or air, or combinations of any of the relevant gases mentioned above. The oxidizing gases reactions with the biomass give rise to the pore creation and development. During this process, if the carbon atoms were removed from inside of the rudimentary pores formed during carbonization, the opened micropores become enlarged and the closed micropores opened up. However, if the atoms were removed from the surface of the material, no new pores will be formed but it assist in the reduction of the particle size. In physical activation, gases were utilized as activating agents and does not produce waste water thereby making the process to be an environmental friendly technology. In brief, the activation process increases the pore volume and surface area of the precursor greatly through the removal of volatile
components and also from carbon burn-off (Ioannidou & Zabaniotou, 2007). The overall chemical reactions can be presented as follows;

\[
\begin{align*}
H_2O + C_X & \rightarrow CO + H_2 + C_{X-1} \text{ at (800 – 900 °C)} \\
CO_2 + C_X & \rightarrow 2CO + C_{X-1} \text{ at (800 – 900 °C)} \\
O_2 + C_X & \rightarrow 2CO + C_{X-2} \text{ at (800 – 900 °C)} \\
O_2 + C_X & \rightarrow CO_2 + C_{X-1} \text{ at (< 600 °C)}
\end{align*}
\]

However, the physical activation process for production of microporous activated carbon have some inherent drawbacks which include longer time of production and consumption of high energy. Another disadvantage of this method is that large amount of internal carbon mass is removed to obtain a well-developed internal structure which may translate to lower yield of product from the precursor material. The carbonization and activation procedure of the precursor materials are usually carried out in direct-fired rotatory kilns or furnaces. The materials used for constructing kilns and furnaces are usually steel and other refractories designed to withstand high temperatures during the processes. Recently, Microwave have also been employed for the activation of char with immense results of short heating period, simplicity of operation and cost effectiveness (Deng et al., 2010; Foo & Hameed, 2011; Liu et al., 2010). After the activation procedure, the reactor was cooled down to about 50 °C under nitrogen gas flow and the resultant AC produced is then washed with distilled water until washing’s pH is close to 7.

2.2.3.2 Chemical Activation

Chemical activation could be a single or two step process for the production of activated carbon. For a single step, the carbonization and activation of the precursor material takes place at the same time. Which means, the raw material is first impregnated with the chemical activant, followed by simultaneous carbonization and activation process. While for the two steps, the carbonization and activation are carried out consecutively in which the precursor is first carbonized in either furnace or microwave oven, the product (char) is then impregnated with the chemical activant and the activation is later carried out. In the chemical activation process, the precursor
is mixed with a solid chemical activant which is an acidic, basic or a salt containing alkali or alkali earth metals. The activating agents dehydrates the material and as such control its thermal decomposition by preventing the formation of the pyrolytic residue and thus improving the carbon yield. The temperatures applied during chemical activation process are usually lower than those used during carbonization process. Therefore, internal pore structure development is better achieved in the case of chemical activation process. Other advantages of chemical activation include; simplicity of use, lower activation temperatures, no need of previous carbonization of the precursor and development of good porous structure. Despite the above mentioned advantages, the chemical activation process has a disadvantage of post-activation washing of the carbon to remove residual reactants and inorganic materials (ash) which makes the process time and energy consuming, tedious and expensive (Abioye & Ani, 2015; Viswanathan et al., 2009).

Chemical activation is a process in which the raw material is impregnated by a chemical compound such as H$_2$SO$_4$, H$_3$PO$_4$, KOH, K$_2$CO$_3$, ZnCl$_2$ or any other inorganic chemical compound and the impregnated material is pyrolysed to degrade and dehydrate the organic materials content and then it is washed to remove the activating agents. The dehydration of the lignocellulosic material results into charring, aromatization and creation of the porous structure in the carbon skeleton (Kushwaha et al., 2012; Nor et al., 2013).

In chemical activation process, the raw material is first washed, dried and crushed into desired particle sizes before impregnation with the chemical activant. The activant concentration is adjusted to obtain a required mass ratio of the activant to the raw material, the mixture is then stirred until homogeneity, and it is then carbonized and activated in an inert atmosphere at temperatures between 400 – 800 °C. The product is then washed to remove residual activant. Washing is carried out using 0.1 M solution of HCl and followed by distilled water till the pH of the washings is constant and close to 7. The washed product is then dried and stored in desiccator. It is important to note that, adjusting operation conditions and parameters such as carbonization or activation temperature, duration of heating, activant-precursor ratio and the choice of activant allows for determination of the optimum operating conditions for the production of carbon with properties for a specific application (Foo & Hameed, 2012b). Studies revealed that, chemical activation process involved less soaking time and lower temperatures compared with physical activation process.
thereby reducing energy cost and consequently production cost, though chemical activation process requires treatment of residual waters from the washings. However, studies reports that adsorption capacity increases continuously with an increase of the activant-precursor ratio until a point where further increase has no effect on the activated carbon’s properties.

In short, the chemical activant play the following roles during chemical activation:

- Bond initiation and bond formation with the weakly connected bridges that translate to dehydration and elimination reactions that release volatiles to create a stronger cross-linked structure.

- Tar and other liquids (such as acetic acid and methanol) minimization and reduction of particles or volume shrinkages during thermal treatment resulting into an adsorbent with high yield and high porosity

- Modification of the adsorbent’s surface functionalities by forming surface complexes or functional groups (Viswanathan et al., 2009).

Similarly, a large number of carbonaceous materials often regarded as agricultural waste such as oil palm shell (Nasri et al., 2015), coconut shell (Nasri, et al., 2014), rice husk (Kalderis et al., 2008), cocoa shell (Ahmad et al., 2013), corn cobs and fruit waste (Ali et al., 2012) have all been converted successfully into activated carbon through physical or chemical activation process. Activated carbons with high surface area and a wide open structure have been synthesized through chemical activation of carbonaceous raw materials with chemicals such as potassium carbonate. In addition, it is important to note that the properties of the synthesized product depends on the starting raw material, carbonization conditions, and suitable activation process and post treatment methods employed.

Among the chemical activants employed, K₂CO₃ is very effective for activated carbon production. The reaction between carbon skeleton and K₂CO₃ in an inert atmosphere leads to reduction of the salt and oxidation of the carbon to generate porosity. However, chemical activants like KOH and NaOH were hazardous, expensive and corrosive, while others like ZnCl₂ were unfriendly to the environment and also poses waste disposal challenge (Adinata et al., 2007). Therefore, K₂CO₃ is employed in this study for purification of water and wastewater.
2.3 Types of Activated Carbon

Activated carbons are generally categorized and manufactured as either powdered, granular (GAC), extruded or pelletized (EAC), bead activated carbon (BAC) and polymer coated activated carbon. The most commonly used among the types were GAC and PAC. The PAC comprised of ground carbon that have very fine particle size. It is usually added to water treatment either in dry form or as slurry. The PAC’s adsorption capacity for the removal of tastes and odours depends on factors like adequate mixing, contact time, adsorbent dosage and concentration of the contaminants that brings about the taste/odour (Bandosz, 2006).

GAC has relatively larger particle size in comparison to PAC and this also made it to have a smaller external surface. PAC has disadvantages such as high operation cost when use continuously, cannot be regenerated, produces large amount of sludge and infiltrate through filters causing dirt in water (Bandosz, 2006). Also, GAC can remove organics as well as taste and odour causing compounds. The GAC is used in a filter medium as a layer or as separate filter known as GAC contactors. The GAC contactors are similar to filters as they are all designed to provide adequate contact time between the contaminants and the filter medium. The contact time can be determined by calculating the empty bed contact time (EBCT) which is also known as detention time by dividing the volume of the filter with flow rate. The calculation is coined as EBCT because the volume taken up by the GAC is not taken into consideration. However, GAC has advantage of regeneration after use compared to PAC (Bandosz, 2006). Below is a schematic diagram of a GAC contactor (Figure 2.5).

![Figure 2.5 The GAC Contactor](image-url)
In addition, most forms of activated carbon are non-polar in nature, which made them to have great affinity for non-polar compounds. Therefore, they are effectively employed in the removal of organic contaminants including phenolics (Bandosz, 2006). The different types of AC are presented in Figure 2.6.

Figure 2.6 Types of activated carbon (A) PAC, (B) GAC and (C) EAC (Bandosz, 2006)
2.4 Microwaves

Microwaves are between infrared radiation and radio waves in electromagnetic spectrum region. Microwaves have electromagnetic waves with wavelength in the range 0.001 to 1 m, which were equivalent to frequencies between 300 to 0.3 GHz. This range of electromagnetic spectrum were used for many applications such as radar, telecommunication, heating and various industrial processes (Fernández et al., 2011; Ranji, 2014). Figure 2.7 shows the electromagnetic spectrum

![Figure 2.7 The electromagnetic spectrum (Lam et al., 2016)](image)

2.4.1 Microwave Heating

Two frequencies were selected for heating purposes by the Federal Communications Commission (FCC) for microwave heating applications. The frequencies reserved were 0.915 and 2.45 GHz. Microwave heating is different from the conventional heating because energy is rather transferred to the material being heated. The material to be heated must have dielectric properties in which the heating is achieved when the dipoles in the dielectric material were exposed to alternating electromagnetic field that will make them to approximately realign themselves 2.5 billion times per second for a microwave operating at frequency of 2.45 GHz. This movement translate into rotation of dipoles and energy is released in form of heat from internal resistance to the rotation (Fernandez et al., 2014).
Materials are characterized based on their interactions with the microwaves. Microwaves consist of two components that are perpendicular to one another, namely electric and magnetic fields as shown in Figure 2.8. Different materials exhibit different dielectric properties and hence different interactions with the microwaves. Based on this factor, the materials are categorized into conductors, transparent, absorbers and mixed absorbers. The ability of any material to get heated by a microwave radiation depends on its loss factor where the high absorbing materials are regarded as having high loss factor, while those with low absorbance were categorized as low factor. Conductors such as metals cannot be heated with microwaves because as they interact with microwaves, their surfaces reflect off the radiation. On the other hand, transparent materials such as glass allow the radiation to pass it. The mixed absorbers such as composite materials display mixed characteristics of either absorption, reflection or transparency (Figure 2.9). Despite some materials were categorized as having low loss factor or poor microwave absorbers, sometimes do absorb and become heated in the process when heated in heated above their critical temperatures due to temperature dependent nature of microwave heating (Appleton et al., 2005). The only materials that perfectly absorbs microwave radiation and become heated during the process are those that have good dielectric properties.

Figure 2.8 The magnetic and electric fields of microwaves (Lam et al., 2016)
REFERENCES


from aqueous solution by NaOH-modified rice husk. *Desalination and Water Treatment*, 1-10.


and activated carbons derived from carbonized coconut shell chars. *Industrial Crops and Products, 28*(2), 190-198.


Masoumi, A., Hemmati, K., & Ghaemy, M. (2016). Low-cost nanoparticles sorbent from modified rice husk and a copolymer for efficient removal of Pb(II) and crystal violet from water. Chemosphere, 146, 253-262.


solutions using chemically modified moss biomass (Barbula lambarenensis).  
*Environmental Earth Sciences, 76*(1), 33.


column packed with Zr (IV) loaded dried orange juice residue. *Bioresour Technol, 146*, 713-720.


