Faculty of Manufacturing Engineering

SYNTHESIS OF UREA IMPREGNATED RUBBER WOOD BIOCHAR
FOR RETENTION OF NITROGENOUS NUTRIENT IN SOIL

Se Sian Meng

Doctor of Philosophy

2015
SYNTHESIS OF UREA IMPREGNATED RUBBER WOOD BIOCHAR FOR RETENTION OF NITROGENOUS NUTRIENT IN SOIL

SE SIAN MENG

A thesis submitted in the fulfillment of the requirements for the degree of Doctor of Philosophy

Faculty of Manufacturing Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2015
DECLARATION

I declare that this thesis entitle “Synthesis of Urea Impregnated Rubber Wood Biochar for Retention of Nitrogenous Nutrient in Soil” is the results of my own research except as cited in the references. The thesis has not been accepted for any degree and not concurrently submitted in candidature of any other degree.

Signature :…………………………………………..

Name :………………………………………………

Date :………………………………………………
Approval

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Doctor of Philosophy.

Signature: ......................................................

Supervisor’s Name: ..............................................

Date: .............................................................
DEDICATION

To my late mother, beloved father and family,

For the understanding and moral support

throughout the years
Urea is one of the nitrogen sources for plants to grow. Upon its application to soil, mineralisation takes place, where urea \([(NH_2)_2CO]\) is hydrolysed and converted to an intermediate compound known as ammonium carbonate \([(NH_4)_2CO_3]\). Subsequently, it is converted to ammonium ions \((NH_4^+)\) by urease activities for plant uptake. The remaining hydroxide ions \((OH^-)\) increase the soil's pH and release ammonia \((NH_3)\), a greenhouse gas produced after the reaction with \(NH_4^+\). Some portions of \(NH_4^+\) will be oxidised by oxygen in the air and converted to nitrite \((NO_2^-)\) and nitrate \((NO_3^-)\) by bacteria. The mobility of \(NO_3^-\) causes leaching by the run-off of ground water and surface water that leads to eutrophication. Many efforts have been carried out to address this matter. However, there are still some research gaps and room for improvement. Biochar derived from rubber wood sawdust (RWSD) is introduced to be impregnated with urea to slow down the mineralisation and reduce nitrogen losses. The main objective of this research is impregnation of urea onto biochar for nitrogenous nutrient retention in soil. The characterisation of biochars focused on physiochemical characteristics such as X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, Fourier transform infrared (FT-IR) spectroscopy, Boehm titration, pH alkalinity, scanning electron microscopy (SEM) and SEM with energy-dispersive X-ray (SEM-EDX) spectroscopy. The porosities and acidic functional groups such as carboxylic \((-COOH)\) groups are hypothesised to enhance the physio-chemi adsorption of urea onto biochar. The impregnation of urea onto biochar is performed by urea dissolution and recrystallisation with biochars content ranging from 2 % to 15 %. The ammonium and nitrate retained in soil after four weeks incubation are analysed by the first order kinetic model. It is observed that the mineralisation rate constant of urea is 54.4 %/week, higher compared with that of the impregnated samples at 5 % biochar obtained at 300 °C, which is 25.9 %/week and urea impregnated biochar sample produced at 700 °C with 10 % of impregnation, which is 28.9 %/week. In addition, the result from the total nitrogenous nutrient retention show that the percentage of biochar produced at 300 °C ranging from 3 % to 7 % and those at 700 °C ranging from 2 to 10 % are able to retain 15 % more nitrogenous compound than pristine urea. Moreover, ammonia volatilisation also indicated significant reduction after impregnation with the biochars with percentage ranging from 4 to 10 %, and exhibited the maximum ammonia loss of 35 % at 7.5 % of biochar. The reduction of ammonia emission is due to better nitrogen retention in soil upon impregnation. In addition, the trend nitrogenous nutrient retention in soil shows inverse quadratic relationship for both biochar while the ammonia emission shows a normal quadratic relationship. Hence, the emission of nitrous oxide is reported very minimal compared to pristine urea. Finally, the water column analysis revealed that the influence of urea impregnation with urea is negligible for ammonium. Nevertheless, the leaching of nitrate declined in the urea impregnated biochar sample due to the biochar contribution in reducing the mobility of nitrate in soil.
ABSTRAK

Urea merupakan sumber nitrogen terpenting untuk tumbeseran tanaman. Apabila ia ditaburkan ke atas tanah, proses mineralisasi berlaku dimana urea akan dihidrolisis dan bertukar kepada bahan ammonium karbonat \([\text{NH}_4\text{CO}_3]\). Bahan ini ditukarkan kepada ion ammonium \((\text{NH}_4^+)\) oleh aktiviti urease untuk diambil oleh tumbuhan. Baki ion hidroksida yang tinggal pada tanah akan meningkatkan pH tanah dan bertukar dengan ion ammonium lalu membebaskan gas ammonia sebagai gas rumah hijau. Sebahagian \(\text{NH}_4^+\) akan dioksidakan di udara dan bertukar kepada ion nitrit \((\text{NO}_2^-)\) dan ion nitrat \((\text{NO}_3^-)\) oleh bakteria. Ion \(\text{NO}_3^-\) adalah gerak-bebas dalam tanah lalu berlaku resapan bersama air larian bawah tanah dan menyebabkan eutrofikasi. Pelbagai usaha telah dijalankan untuk mengatasi masalah ini, tetapi, masih terdapat jurang dan ruang untuk penambahbaikan. Biochar yang dihasilkan daripada serbuk kayu pokok getah diperkenalkan, untuk digabungkan bersama urea bagi memperlaikan penguraian urea dan mengurangkan pembebesan nitrogen. Objektif utama kajian ini adalah penghasilan baja urea impregnasi biochar untuk menambahkan kepengekalan nutrien nitrogen pada tanah. Pencirian sifat fizik-kimia biochar menggunakan X-ray diffraction (XRD), analisis luas permukaan Brunauer-Emmett-Teller (BET), Fourier transform infrared (FT-IR) spektroskopi, Boehm titration, kealkalian pH, scanning electron microscopy (SEM) and SEM energy-dispersive X-ray (SEM-EDX) spektroskopi. Porositi dan kumpulan berfungsi bersifat asidik seperti karboksilik (\(--\text{COOH}\)) pada permukaan biochar dihipotesis dapat meningkatkan penjerapan urea impregnasi biochar. Penyediaan impregnasi urea biochar dihasilkan melalui pembubaran dan penghabluran semula dengan kandungan biochar dari 2 % hingga 15 %. Jumlah kandungan ammonium dan nitrat yang dikekalkan selepas 4 minggu pengeraman pada tanah telah dikaji dan dianalisis menggunakan Kinetik Model Perintah Pertama. Kadar mineralisasi konstan untuk urea didapati paling tinggi sebanyak 54.4 %/minggu berbanding dengan urea yang diimpregnasi dengan biochar 25.9 %/minggu untuk biochar yang dihasilkan pada suhu 300 °C sebanyak 5 % dan 28.9 %/minggu untuk biochar yang dihasilkan pada suhu 700 °C. Jumlah simpanan kandungan nitrogen bagi sampel yang impregnasi dengan urea menunjukkan biochar yang dihasilkan pada suhu 300 °C dengan 3 % hingga 7 % biochar mengekalkan 15 % nitrogen lebih daripada sampel urea. Biochar yang dihasilkan pada suhu 700 °C dengan kandungan 4 % hingga 10 % dapat mengekalkan nitrogen nutrien yang melebihi 15 %. Pembebasan gas ammonia berkurang dengan jelas selepas impregnasi dengan biochar dari 4 % hingga 10 %, dan mencapai pengurangan yang maksimum sebanyak 35 % dengan 7.5 % kandungan biochar. Selain itu, didapati hubungan antara jumlah nitrogen yang kekal pada tanah dengan kandungan biochar adalah kuadratik songsang, manakala pembebasan ammonia menunjukkan kuadratik normal. Gas nitrus oksida yang dibebaskan didapati pada tahap yang sangat minimal untuk sampel urea impregnasi biochar berbanding dengan sampel urea. Keputusan analisa air larut lesap menunjukkan kesan urea impregnasi biochar tidak memberi kesan yang ketara untuk larut resapan ammonium. Namun, larut resapan nitrat telah berkurangan pada sampel urea impregnasi biochar dimana biochar telah mengurangkan mobility nitrate pada tanah.
ACKNOWLEDGEMENTS

First and foremost, I would like to take this opportunity to express my sincere acknowledgement to my supervisor Associate Professor Dr. Azizah Binti Shaaban from the Faculty of Manufacturing Engineering Universiti Teknikal Malaysia Melaka (UTeM) for her essential supervision, support and encouragement towards the completion of this thesis.

I would also like to express my greatest gratitude to Mr. Mohd Fairuz Bin Dimin @ Mohd Amin, co-supervisor of this project for his advice and suggestions. Special thank to Long Term Research Grant Scheme, Ministry of Education Malaysia awarded to Universiti Teknikal Malaysia Melaka LRGS/2011/FKP/TK02/1R00001 under the OneBaja Project (Universiti Teknologi Petronas) and MyBrain 15 scholarship funded under Ministry of Education Malaysia.

Particularly, I would also like to express my deepest gratitude to Mr. Azhar and Mr. Hairul Hisham, the technicians from material laboratory Faculty of Manufacturing Engineering, Mr. Ismail technician from chemistry lab Faculty of Mechanical Engineering. Professor Dr. Mohd. Khanif Yusof and Mr Mohd Mu’az Hashim from the Faculty of Agricultural, Universiti Putra Malaysia (UPM) for their assistance, time spent and efforts in all the laboratory analyses.

Special thanks to all my peers, my late mother, beloved father and siblings for their moral support in completing this degree, with the strength given by Buddha, Dharma and Sangha Triple Gems. Without them it would seem impossible to complete this project. Lastly, thank you to everyone who had been to the crucial parts of realisation of this project. Not forgetting, my humble apology as it is beyond my reach personally mentioned those who are involved directly or indirectly one to one.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>DECLARATION</th>
<th>APPROVAL</th>
<th>DEDICATION</th>
<th>ABSTRACT</th>
<th>ABSTRAK</th>
<th>ACKNOWLEDGEMENTS</th>
<th>TABLE OF CONTENT</th>
<th>LIST OF TABLES</th>
<th>LIST OF FIGURES</th>
<th>LIST OF APPENDICES</th>
<th>LIST OF ABBREVIATIONS</th>
<th>LIST OF SYMBOLS</th>
<th>LIST OF PUBLICATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>i</td>
<td>ii</td>
<td>iii</td>
<td>iv</td>
<td>vii</td>
<td>ix</td>
<td>xv</td>
<td>xvi</td>
<td>xvii</td>
<td>xix</td>
</tr>
</tbody>
</table>

## CHAPTER

### 1 INTRODUCTION

1.1 Background 1
1.2 Problem Statement 6
1.3 Research objective 8
1.4 Research Hypothesis 8
1.5 Thesis overview 9

### 2 LITERATURE REVIEW

2.1 Biomass 12
2.1.1 Biomass content 15
2.2 Pyrolysis of biomass 21
2.2.1 Slow pyrolysis in biochar production 24
2.2.2 Physiochemical properties of biochar 26
2.2.3 Pyrolysis process parameters screening 31
2.2.4 Analysis of Variance 33
2.3 Application of biochars in soil 35
2.4 Application of urea in soil 37
2.4.1 Mineralisation of urea in paddy soil 40
2.4.2 Kinetic model of urea mineralisation 43
2.5 Slow release fertiliser 45
2.5.1 Function and mechanism of slow release fertiliser 46
2.6 Urea-biochar fertiliser for nutrient retention in soil 47
2.7 Environmental complications by urea 49
2.7.1 Emission of gas ammonia 50
2.7.2 Emission of nitrous oxide 52
2.7.3 Water contamination by ammonium and nitrate via leaching 53
3 METHODOLOGY

3.1 Experimental approaches
3.2 Characterisation of rubber wood sawdust
   3.2.1 Determination of ash content
   3.2.2 Determination of fixed carbon content of RWSD
   3.2.3 Determination of carbon, hydrogen and nitrogen (CHN) content
3.3 Pyrolysis and Impregnation process
   3.3.1 Design of experiment (DoE) by Design-Expert
   3.3.2 Slow pyrolysis
   3.3.3 Urea impregnation
3.4 Characterisations of biochar and urea impregnated biochar
   3.4.1 Crystallinity phase analysis
   3.4.2 Quantitative measurement of surface area using Brunauer-Emmett-Teller
   3.4.3 Microstructural and compositional analysis using SEM/EDX
   3.4.4 Quantitative measurement of surface functional groups using FT-IR spectroscopy
   3.4.5 Quantitative measurement of acidic surface functional groups using Boehm titration
   3.4.6 Determination of alkalinity
   3.4.7 Chemisorption of ammonia gas by biochar
   3.4.8 Thermal stability by differential scanning calorimetry (DSC)
3.5 Nitrogenous nutrient retention in soil
   3.5.1 Incubation for unconverted urea in soil
   3.5.2 Incubation for mineralised ammonium and nitrate
3.6 Emission of greenhouse gasses from the paddy soil
   3.6.1 Ammonia (NH₃) emission via volatilisation
   3.6.2 Nitrous oxide (N₂O) emission via denitrification
3.7 Water column leaching test
3.8 First order kinetic model for determination of mineralization rate constant

4 RESULTS AND DISCUSSION

4.1 Characteristics of raw materials
   4.1.1 Proximate analysis of rubber wood sawdust
   4.1.2 Ultimate analysis of rubber wood sawdust
   4.1.3 Characterisation of urea
4.2 Characteristics of biochars
   4.2.1 Specific surface area using BET technique guided by factorial design
   4.2.2 Acidic functional groups by Boehm titration guided by factorial design
4.3 Influence of pyrolysis temperature and holding time on physiochemical properties of biochar
   4.3.1 Phase analysis by X-ray diffraction (XRD)
   4.3.2 Thermal analysis by thermogravimetric analysis (TGA)
   4.3.3 Surface porosities by Brunauer-Emmett-Teller (BET) analysis
4.3.4 Morphology analysis by Scanning Electron Microscopy (SEM) and SEM-EDX
4.3.5 Surface functional groups by Fourier transform infrared (FT-IR) spectroscopy
4.3.6 Negative surface charge by Boehm titration
4.3.7 pH alkalinity
4.3.8 Chemisorption of biochar surface with ammonia gas
4.4 Characteristics of urea-impregnated biochar
4.4.1 Pore filling analyses of urea fertiliser
4.4.2 Thermal stability of urea impregnated biochar fertiliser by Differential scanning calorimetry (DSC)
4.4.3 Elemental analysis by CHN
4.4.4 Formation of chemical bonds by FT-IR
4.5 Soil test of urea biochar-urea fertiliser
4.5.1 Urea retention as un-converted urea in soil
4.5.2 Mineralisation of fertiliser to exchangeable minerals ammonium and nitrate in soil
4.5.3 Mineralisation rate of urea and urea impregnated biochar fertiliser using first order kinetic model
4.5.4 Total nitrogen retention in soil
4.5.4.1 The effect of biochar negative surface charge on nitrogenous nutrient retention
4.5.4.2 The effect of biochar specific surface area on nitrogenous nutrient retention
4.6 Ammonia emission by urea fertilisers
4.7 Nitrous oxide (N₂O) loss via volatilities
4.8 Leaching of ammonium and nitrate by water column
4.8.1 Ammonium content in leachate
4.8.2 Nitrate content in leachate

5 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES
5.1 Conclusions
5.2 Contributions to knowledge
5.3 Future recommendations

REFERENCES
APPENDICES
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Several types of popular biomass available in Malaysia</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>(Source: Sustainable Energy Development Authority Malaysia, 2012)</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>Composition of lignocellulose originated from five sources of biomass in Malaysia (Maria et al., 2011)</td>
<td>19</td>
</tr>
<tr>
<td>2.3</td>
<td>Linkages between monomers in lignocellulose biomass (Harmsen and Huijgen, 2010)</td>
<td>20</td>
</tr>
<tr>
<td>2.4</td>
<td>Functional groups in lignocellulose biomass (Harmsen and Huijgen, 2010)</td>
<td>21</td>
</tr>
<tr>
<td>2.5</td>
<td>Pyrolysis process control and typical parameters (Atkinson et al., 2010; Ahmad et al., 2014)</td>
<td>23</td>
</tr>
<tr>
<td>2.6</td>
<td>Classification of nanoporosity by IUPAC (IUPAC, 1985)</td>
<td>26</td>
</tr>
<tr>
<td>2.7</td>
<td>Biochar physiochemical properties reported by previous researchers</td>
<td>32</td>
</tr>
<tr>
<td>2.8</td>
<td>Arrangement of a standard two-way ANOVA with two factors (Sahai and Ageel, 2000)</td>
<td>33</td>
</tr>
<tr>
<td>2.9</td>
<td>Total ammonia loss over 6 weeks (Junejo et al., 2009)</td>
<td>52</td>
</tr>
<tr>
<td>3.1</td>
<td>Factors and levels for pyrolysis</td>
<td>61</td>
</tr>
<tr>
<td>3.2</td>
<td>Recommended process parameter for pyrolysis of dried RWSD</td>
<td>61</td>
</tr>
<tr>
<td>3.3</td>
<td>Sample identification and parameters involved in pyrolysis</td>
<td>62</td>
</tr>
<tr>
<td>3.4</td>
<td>Sample identification and parameters involved in impregnation</td>
<td>63</td>
</tr>
<tr>
<td>4.1</td>
<td>Sample identification and parameters involved in pyrolysis</td>
<td>88</td>
</tr>
<tr>
<td>4.2</td>
<td>Sample identification and parameters involved in impregnation</td>
<td>88</td>
</tr>
<tr>
<td>4.3</td>
<td>Proximate analysis of RWSD</td>
<td>90</td>
</tr>
<tr>
<td>4.4</td>
<td>Ultimate analyses of raw RWSD</td>
<td>92</td>
</tr>
<tr>
<td>4.5</td>
<td>Physical properties of urea</td>
<td>93</td>
</tr>
</tbody>
</table>
4.6 Specific surface area of biochars measured by BET method at parameters recommended by factorial design
4.7 ANOVA of specific surface area with four factors
4.8 Negative surface charge values of biochars at parameters recommended by factorial design
4.9 ANOVA of negative surface charge with four factors
4.10 ANOVA of main factor (A) and interaction factor (B)
4.11 ANOVA of main factor (A) and interaction factor (C)
4.12 ANOVA of main factor (A) and interaction factor (D)
4.13 Specific surface porosities of biochar samples obtained from pyrolysis temperature 300 °C – 700 °C with holding time 1 and 3 hours
4.14 Surface functional groups on biochar
4.15 BET surface area analysis of biochar samples and urea-impregnated biochar fertiliser
4.16 pH level of paddy soil
4.17 Amount of fertilisers, biochar and negative surface charge added to soil
4.18 Amount of fertilisers, biochar and total surface area added to soil
4.19 Mineralisation rate constant, mineralisable potential and t1/2 of urea and fertiliser samples
4.20 Total nitrogen accumulate in soil after 4 weeks
4.21 Ammonia emission of urea and urea-impregnated biochar fertiliser to environment
4.22 Statistical summary of total nitrogenous retention and ammonia emission to the environment
<table>
<thead>
<tr>
<th>FIGURE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>World urea consumption of top 20 countries year 2011 (Source: Food and Agricultural Organisation of the United Nations)</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>Types and sources of biomass in Malaysia (Source: Sustainable Energy Development Authority Malaysia)</td>
<td>13</td>
</tr>
<tr>
<td>2.2</td>
<td>Various technologies involved in biomass utilisation (Harmsen and Huijgen, 2010)</td>
<td>15</td>
</tr>
<tr>
<td>2.3</td>
<td>A typical biomass composition and the chemical structures (Singh et al., 2012)</td>
<td>16</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic of cellulose, hemicellulose and lignin in biomass (Yang et al., 2007)</td>
<td>17</td>
</tr>
<tr>
<td>2.5</td>
<td>TGA curves of cellulose, hemicellulose and lignin (Yang et al., 2007)</td>
<td>18</td>
</tr>
<tr>
<td>2.6</td>
<td>The composition of fractions obtained by various types of pyrolysis (Ronsse et al., 2013)</td>
<td>22</td>
</tr>
<tr>
<td>2.7</td>
<td>Decomposition of each component via pyrolysis (Parthasarathy and Narayanan, 2014)</td>
<td>24</td>
</tr>
<tr>
<td>2.8</td>
<td>The yield of biomass process by combustion and pyrolysis (Bolan et al., 2012)</td>
<td>25</td>
</tr>
<tr>
<td>2.9</td>
<td>SEM micrograph of biochar obtained from wood based biomass via slow pyrolysis at 400 °C and 1-hour holding time showing the pores on biochar surface upon pyrolysis (Shaaban et al., 2014)</td>
<td>27</td>
</tr>
<tr>
<td>2.10</td>
<td>(a) Acidic and (b) base functional groups commonly found on biochar surface (Brennan et al., 2001)</td>
<td>29</td>
</tr>
<tr>
<td>2.11</td>
<td>Surface negative charge on biochar surface (Shafie et al., 2012)</td>
<td>31</td>
</tr>
<tr>
<td>2.12</td>
<td>A statistic showing the grain yield increase by biochar compared to</td>
<td>36</td>
</tr>
</tbody>
</table>
types of organic carbon contents in different type of soil (Ernsting, 2011)

2.13 The nitrogen cycle (Rosenstock et al., 2013)

2.14 Simplified process flow of (a) ammonia production, and (b) urea production (Haber-Bosch, 1999)

2.15 Mineralisation of urea in soil

2.16 Zoning of flooded paddy soil modified from (Chowdary et al., 2004)

2.17 Mechanism of control release fertiliser modified from (Trenkel, 2010)

2.18 Mechanism of slow release fertiliser (Trenkel, 2010)

2.19 Mechanism of urease and nitrification inhibitors (Trenkel, 2010)

2.20 Environmental losses of nitrogen (Ruark, 2012)

3.1 Plate-like shape of rubber wood sawdust as receiving

3.2 (a) Overall experimental works in section A, B, C and D, (b) Details on experimental works in section A, B, C, and D

3.3 Schematic diagram for the process of urea-impregnated biochar (a) biochar before impregnation (b) urea-impregnated biochar

3.4 Fundamentals of x-ray diffraction in material

3.5 General shape of sorption isotherms (Andrade et al., 2011)

3.6 Classification of adsorption isotherms (IUPAC)

3.7 Classification of adsorption hysteresis (Wang et al., 2012)

3.8 Electron interaction in SEM (Allwar, 2012)

3.9 Schematic diagram of chemisorption analysis chamber

3.10 A typical pulse of chemisorption profile

3.11 Incubation experiment setup (a) a plastic pot containing the mixture of paddy soil, fertiliser and distilled water, (b) 3 replicates of each treatment for 4 weeks

3.12 Method of determining the amount of ammonium and nitrate in soil solution (a) distillation of soil solution, (b) distillate with indicator, and (c) titration for ammonium and nitrate quantification

3.13 Schematics diagram of experiment setup for ammonia loss measurement

3.14 The soil incubation setup for measurement of nitrous oxide emission
4.15 (a) SEM micrograph of biochar sample BC 300-1, (b) SEM micrograph of biochar sample BC 300-3
4.16 (a) SEM micrograph of biochar sample BC 700-1, (b) SEM micrograph of biochar sample BC 700-3
4.17 SEM micrographs of (a) as received RWSD, (b) sample BC 300-1, (c) sample BC 400-1, (d) sample BC 500-1, (e) sample BC 600-1, (f) sample BC 700-1
4.18 Semi-quantitative of percentage of localised carbon and oxygen content by SEM-EDX analyses
4.19 FT-IR spectra for RWSD and biochar samples
4.20 Effect of pyrolysis temperature on negative surface charge at holding time 1-hour and 3-hours, temperature 300°C to 700 °C
4.21 Alkalinity of biochars obtained at temperature 300 °C to 700 °C with holding time 1-hour and 3-hours
4.22 Potassium and total minerals content in biochars obtained at temperatures 300 °C to 700 °C with holding time 1-hour and 3-hours
4.23 Ammonia gas molecule chemisorbed to the surface functional groups on biochar, modified from Briones, 2012 (Briones, 2012)
4.24 Chemisorption pulse TCD vs time of biochar sample BC 300-1
4.25 Amount of NH$_3$ adsorbed on biochar obtained at temperatures ranged from 300 °C to 700 °C for 1-hour holding time
4.26 Isotherms of adsorption and desorption of biochar samples obtained from (a) BC 300- and UBC 300-10, and (b) BC 700-3 and UBC 700-10
4.27 SEM micrographs of (a) RWSD, (b) biochar BC 700, and (C) urea impregnated biochar
4.28 SEM micrographs and SEM-EDX analysis of biochar sample UBC 300-10
4.29 SEM micrographs and SEM-EDX analysis of biochar sample UBC 700-10
4.30 DSC endothermic peaks of urea, biochar BC 300 and fertiliser samples UBC 300-5 and UBC 300-10
4.31 DSC endothermic peaks of urea, biochar BC 700 and fertiliser
samples UBC 700-5 and UBC 700-10

4.32 Nitrogen content of urea-impregnated biochar fertilisers

4.33 FT-IR spectra of urea, BC 300 and UBC 300

4.34 Urea retention in soil of urea and urea impregnated biochar BC 300-1 at week 1, week 2, week 3, and week 4 (Appendix B for data)

4.35 Urea retention in soil of urea and urea impregnated biochar BC 700-3 at week 1, week 2, week 3, and week 4 (Appendix B for data)

4.36 Ammonium and nitrate retention in soil of urea and urea impregnated biochar BC 300-1 at week 1, week 2, week 3, and week 4 (Appendix B for data)

4.37 Ammonium and nitrate retention in soil of urea and urea impregnated biochar BC 700-3 at week 1, week 2, week 3, and week 4 (Appendix B for data)

4.38 Log (No-Nt) vs time plots of urea and urea impregnated biochar BC 300-1

4.39 Log (No-Nt) vs time plots of urea and urea impregnated biochar BC 700-3

4.40 One-way ANOVA of urea impregnation samples with BC 300-1 at various percentages

4.41 Total nitrogen in soil by urea-impregnated biochar BC 300-1 at various percentages after 4 weeks

4.42 Total nitrogen in soil at various percentages of biochar and negative surface charge

4.43 (a) 3D scatter plot and (b) 3 D surface plot of nitrogen retention in soil at various percentages of biochar and negative surface charge

4.44 One-way ANOVA of fertiliser samples with BC 700-3 at various percentages

4.45 Total nitrogen in soil by urea-impregnated biochar BC 700-3 at various percentages after 4 weeks

4.46 Total nitrogen in soil at various percentages ages of biochar and BET surface area

4.47 (a) 3 D scatter plot and (b) 3 D surface plot of nitrogen retention in xiii
soil at various percentages of biochar and BET surface area

4.48 Ammonia emission of urea and urea-impregnated biochar BC 300-1 and BC 700-3 after 8 weeks 164

4.49 One-way ANOVA of ammonia emission for urea and urea-impregnated biochar BC 300-1 at various percentages of biochar 165

4.50 One-way ANOVA of ammonia emission for urea and urea-impregnated biochar BC 700-3 at various percentages of biochar 165

4.51 Regression plot of ammonia emission for urea and urea-impregnated biochar BC 300-1 at various percentages of biochar 166

4.52 Regression plot of ammonia emission for urea and urea-impregnated biochar BC 700-3 at various percentages of biochar 167

4.53 Ammonia emission at various percentages of biochar and negative surface area 172

4.54 (a) 3D scatter plot (b) 3D regression plot of ammonia emission at various percentages of biochar and negative surface charge 173

4.55 Nitrous oxide emission of urea and UBC 300-5 for 12 days 174

4.56 Calibration curve of ammonium by standard solution by UV-Vis 175

4.57 Graph of ammonium content in leachate for urea and urea-impregnated biochar BC 300-1 over 4 weeks 176

4.58 Graph of ammonium content in leachate for urea and urea-impregnated biochar BC 700-3 over 4 weeks 176

4.59 Graph of nitrate content in leachate for urea and urea-impregnated biochar BC 300-1 over 4 weeks 178

4.60 Graph of nitrate content in leachate for urea and urea-impregnated biochar BC 700-3 over 4 weeks 178
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Deriavations of First Order Kinetics Model</td>
<td>190</td>
</tr>
<tr>
<td>B</td>
<td>Experimental raw data of soil analyses</td>
<td>193</td>
</tr>
</tbody>
</table>
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>Biochar</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CHN</td>
<td>Carbon-Hydrogen-Nitrogen</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-Dispersive X-ray</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Ammonium</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Nitrate</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>Nitrite</td>
</tr>
<tr>
<td>N₂O</td>
<td>Nitrous oxide</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
</tr>
<tr>
<td>RWSD</td>
<td>Rubber wood sawdust</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature and Pressure</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

°C - Degree Celsius

°C/min - Degree Celsius per minute

ml/min - Milliliter per minute

g - Gram

mg - Milligram

W - Weight

% - Percentage

h - Hour

%/min - Degree per minute

C_{Ir} - Crystallinity Index

P - Pressure

Po - Relative Pressure

m^2/g - Meter square per gram

N_A - Avogadro’s number 6.023 x 10^{23} molecules/mol

Pa - Pascal

kV - Kilo volt

cm^{-1} - Wave number

nm - Nano meter
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>Normality</td>
</tr>
<tr>
<td>$M$</td>
<td>Molarity</td>
</tr>
<tr>
<td>mmol/g</td>
<td>Mili Mole per gram</td>
</tr>
<tr>
<td>$\mu g, N, g^{-1}$</td>
<td>Micro gram nitrogen per gram</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
</tr>
<tr>
<td>$K$</td>
<td>Kinetic constant</td>
</tr>
<tr>
<td>$g/cm^3$</td>
<td>Gram per centimetre cube</td>
</tr>
<tr>
<td>$2\theta$</td>
<td>Bragg angle</td>
</tr>
<tr>
<td>$cm^3/g$</td>
<td>Centimetre cube per gram</td>
</tr>
<tr>
<td>wt %</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>$mW$</td>
<td>Miliwatt</td>
</tr>
<tr>
<td>$\mu g/g$</td>
<td>Microgram per gram</td>
</tr>
<tr>
<td>Log</td>
<td>Logarithm</td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>Half-life</td>
</tr>
<tr>
<td>ppm</td>
<td>Part per million</td>
</tr>
<tr>
<td>mole</td>
<td>Mole</td>
</tr>
<tr>
<td>wt.%/ºC</td>
<td>Weight percentage per Degree Celsius</td>
</tr>
<tr>
<td>gmol$^{-1}$</td>
<td>Gram per Mole</td>
</tr>
</tbody>
</table>

