



Faculty of Manufacturing Engineering

**FUNCTIONALIZED MULTIWALL CARBON NANOTUBES FOR
EFFICIENCY ENHANCEMENT USED OF NITROGENOUS
FERTILIZER IN PADDY**

Norazlina Binti Mohamad Yatim

Doctor of Philosophy

2016

**FUNCTIONALIZED MULTIWALL CARBON NANOTUBES FOR EFFICIENCY
ENHANCEMENT USED OF NITROGENOUS FERTILIZER IN PADDY**

NORAZLINA BINTI MOHAMAD YATIM

**A thesis submitted
In fulfilment of the requirements for the degree of Doctor of Philosophy**

Faculty of Manufacturing Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2016

DECLARATION

I declare this thesis entitled “Functionalized multiwalled carbon nanotubes for efficiency enhancement used of nitrogenous fertilizer in paddy” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

Name :

Date :

APPROVAL

I hereby declare that I have read this dissertation and in my opinion this dissertation is sufficient in terms of scope and quality as a partial fulfilment of Doctor of Philosophy of Manufacturing Engineering.

Signature :

Supervisor Name :

Date :

DEDICATION

To my beloved husband, children, mother, father and family,
for the understanding and moral support
throughout the years

ABSTRACT

The efficient use of urea fertilizer (UF) as an important nitrogen (N) source in the rice production has been a concern. The main problem is significant amount of the N fertilizer is lost during the year of application. Various studies that had adequately addressed the issue by using UF, which contains high amounts of N (47%) have so far had little success. Nanotechnology advancements in nutrition strategies involving multiwalled carbon nanotubes (MWCNTs) have attempted to provide solutions for N losses and low N use efficiency (NUE) by plants. However, agglomerates of MWCNTs limit their efficient mobility properties. Since a high degree of MWCNTs functionalization would lead to separation of nanotubes bundle, advanced N Nano-carrier is developed based on f-MWCNTs grafted with UF to produce urea-MWCNTs (UF-MWCNTs) for enhancing the nitrogen uptake (NU) and NUE. The grafted N can be absorbed and utilized by rice efficiently to overcome the N propensity for loss from soil-plant systems when UF-MWCNTs are applied as fertilizer. Screening process parameters were structured via Plackett Burman experimental design of experiment involving nine identified factors, which were the amount of MWCNTs, percentage of functionalization, stirring time, stirring temperature, agitation, sonication frequency, sonication temperature, sonication time and amount of ammonium chloride with corresponding response of Total N attached on the surface of MWCNTs. As a result, functionalization and amount of MWCNTs used were found to be the most significant factors and chosen for further optimization processes. Analyses were structured via the Response Surface Methodology based on a five-level Central Composite Design consisting of f-MWCNTs amount between 0.10–0.60wt% and functionalization reflux time varying from 12-24hrs as the design factors. The individual and interaction effects between the specified factors and the corresponding responses (NUE, NU) were investigated. The UF-MWCNTs with optimized 0.5wt% f-MWCNTs treated at 21hrs functionalization reflux time achieved tremendous NUE up to 96% and NU at 1180mg/pot. A significant model term (p -value < 0.05) for NUE and NU responses were confirmed by the ANOVA of two quadratic models. Homogeneous dispersion with non-agglomerate features was observed on UF-MWCNTs via FESEM and TEM. Direct evidence regarding the physical translocation of biodegraded f-MWCNTs through phospholipid bilayers into plant roots involving soil-plant interaction via mass flow route and direct penetration into the subcellular region of the plant cells were revealed via TEM imaging investigation. Surface functionalization was strongly suggested to have a bigger effect on the translocation of f-MWCNTs than the size factor. The chemical changes were monitored by FT-IR and Raman spectroscopy. Hence, this UF-MWCNTs approach provides a promising strategy in enhancing plant nutrition for rice.

ABSTRAK

Kecekapan baja urea (UF) sebagai sumber nitrogen (N) terpenting dalam perusahaan padi telah menjadi perhatian. Namun, kadar kehilangan N setiap tahun adalah tinggi. Pelbagai kajian melibatkan UF yang tinggi kandungan N (47%) telah dijalankan untuk mengatasi masalah ini masih belum sepenuhnya berjaya. Strategi pembajaan melalui penggunaan multiwalled carbon nanotubes (MWCNTs) telah menunjukkan penyelesaian kepada masalah ini. Namun, struktur MWCNTs yang bergumpal akan membataskan peranannya dalam membentuk sistem pengangkutan yang efektif. Oleh kerana kadar pembentukan kumpulan berfungsi yang tinggi pada permukaan MWCNTs boleh mengelakkan penggumpalan, N Nano-carrier dibangunkan melalui penggabungan f-MWCNTs dengan UF lalu menghasilkan urea-MWCNTs (UF-MWCNTs) untuk meningkatkan pengambilan N (NU) dan kecekapan penyerapannya (NUE). Gabungan ini menjadikan N dapat diambil dan diserap dengan lebih berkesan oleh padi dan mengatasi kehilangan N apabila UF digunakan. Proses pemilihan parameter telah distruktur dengan menggunakan model eksperimen Plackett Burman melibatkan sembilan faktor iaitu jumlah MWCNTs, peratusan kumpulan berfungsi, masa pengacauan, suhu pengacauan, kocakan, kekerapan sonikasi, suhu sonikasi, masa sonikasi dan jumlah ammonium klorida untuk melihat tindakbalas pada jumlah gabungan N yang dapat dihasilkan pada MWCNTs. Hasilnya, pembentukan kumpulan berfungsi pada MWCNTs dan jumlah MWCNTs didapati menjadi faktor paling ketara untuk langkah pengoptimuman. Analisis seterusnya telah distruktur dengan menggunakan Response Surface Methodology berdasarkan 5 peringkat Central Composite Design, melibatkan 2 faktor iaitu jumlah f-MWCNTs dari 0.10-0.60wt% dan masa pembentukan kumpulan berfungsi dari 12-24 jam. Kesan 2 faktor tersebut secara individu dan interaksi antara satu sama lain terhadap kadar NU dan NUE telah dikaji. Jumlah optimum 0.5wt% f-MWCNTs yang melalui pembentukan kumpulan berfungsi selama 21 jam untuk penghasilan UF-MWCNTs mencatatkan NUE dan NU yang memberangsangkan sehingga 96% dan 1180mg/pot. Model eksperimen bermakna (p -value < 0.05) untuk tindakbalas NU dan NUE telah disahkan oleh 2 model kuadratik ANOVA. Penghasilan UF-MWCNTs yang sehati dengan ketiadaan struktur bergumpal MWCNTs dibuktikan melalui FESEM dan TEM. Pengimejan TEM juga telah menunjukkan melalui interaksi akar tumbuhan dan tanah secara langsung, terdapat bukti jelas kemasukan f-MWCNTs yang telah terbiodegradasi melalui lapisan phospholipid akar dengan kaedah mass flow dan juga penembusan secara terus ke dalam ruang subcellular sel tumbuhan. Pembentukan kumpulan berfungsi pada sisi MWCNTs berkemungkinan menjadi faktor lebih penting kemasukan f-MWCNTs tersebut berbanding faktor saiz. Perubahan kimia juga telah dianalisis melalui FT-IR dan Raman spectroscopy. Oleh itu, UF-MWCNTs dilihat sebagai strategi yang meyakinkan untuk meningkatkan kaedah pembajaan untuk padi.

ACKNOWLEDGEMENTS

First and foremost, I am grateful to Allah, our Lord and Cherisher, for the guidance, wisdom and barakah through out my journey in life. My deepest gratitude goes to my supervisor, Assoc Prof Dr Azizah Shaaban, for essential supervision, guidance and encouragement towards the completion of this thesis. My co-supervisor, Mr. Mohd Fairuz Dimin, and my third supervisor Prof Dr Faridah Yusof, whose encouragement and guidance enabled me to develop a good understanding of the project work and successfully complete my research study. All the helpful lab technicians and staffs of Faculty of Manufacturing Engineering, Faculty of Mechanical Engineering, PPS and CRIM of Universiti Teknikal Malaysia Melaka (UTeM), Department of Land Management, Faculty of Agriculture, UPM, Pertubuhan Peladang Kawasan Melaka Tengah and Malaysian Nuclear Agency for the use of facilities and consultation throughout the duration of this research study. Likewise, lectures and members of Onebaja research group (UTeM, UTP, UPM and USM), sis Mastura, Mrs Noorismaliza, Mr Bahatiar and Mr Sarman for the help. My beloved husband, Mr Mohd Lokman, children, Auni, Yusuf, Yaseen and Yasser, parents, Mr Mohamad Yatim and Mdm Site Fatimah, and family for their endless love, patience and support. My lovely postgraduate colleagues for their kind assistance during the class, experimental work as well as dissertation writing. Lastly, may Allah s.w.t shower His Blessing upon all those who have been involved in making my research project a reality, directly or indirectly.

TABLE OF CONTENTS

| | PAGE |
|---|--------------|
| DECLARATION | |
| APPROVAL | |
| DEDICATION | |
| ABSTRACT | i |
| ABSTRAK | ii |
| ACKNOWLEDGEMENTS | iii |
| TABLE OF CONTENTS | iv |
| LIST OF TABLES | viii |
| LIST OF FIGURES | ix |
| LIST OF APPENDICES | xv |
| LIST OF ABBREVIATIONS | xvi |
| LIST OF SYMBOLS | xvii |
| LIST OF PUBLICATIONS | xviii |
| | |
| CHAPTER | |
| 1. INTRODUCTION | 1 |
| 1.1 Background | 1 |
| 1.2 Problem Statement | 5 |
| 1.3 Research Objectives | 6 |
| 1.4 Research Hypothesis | 7 |
| 1.5 Scope of research | 7 |
| 1.6 Dissertation organization | 8 |
| | |
| 2. LITERATURE REVIEW | 9 |
| 2.1 Nanomaterials in agriculture | 9 |
| 2.1.1 Nanomaterials for plant nutrition | 10 |
| 2.1.2 Carbon-based nanomaterials in plants | 12 |
| 2.2 Carbon nanotubes | 16 |
| 2.2.1 Background of CNTs | 16 |
| 2.2.2 The structure of CNTs | 17 |
| 2.2.2.1 Singlewalled carbon nanotubes | 17 |
| 2.2.2.2 Multiwalled carbon nanotubes | 19 |
| 2.2.3 Functionalization | 20 |
| 2.2.3.1 Nitrification process | 21 |
| 2.2.3.2 Non-covalent functionalization | 24 |
| 2.3 Nitrogenous fertilizer | 26 |
| 2.3.1 Nitrogen for plant growth | 27 |
| 2.3.2 Urea fertilizer as important N source | 29 |
| 2.3.2.1 Nitrification process | 32 |
| 2.3.2.2 Denitrification process | 33 |
| 2.3.3 N fertilizer use efficiency | 34 |
| 2.3.4 Yield and soil dynamics | 35 |
| 2.4 Plant nutrition | 36 |
| 2.4.1 Mechanisms of nutrients uptake by plant roots | 36 |
| 2.4.2 The plant growth and nutrient uptake relationship | 38 |

| | | |
|-----------|---|-----------|
| 2.5 | Nanomaterials mechanism of interaction for plant nutrition application | 40 |
| 2.5.1 | Mode of carbon nanomaterials entry into plants | 41 |
| 2.5.2 | Translocation of carbon nanomaterials into plants | 45 |
| 2.5.3 | Size and geometry dependent cellular uptake of carbon nanomaterials into plants | 46 |
| 2.5.4 | Activation of genes and photosynthetic activity in plants by carbon nanomaterials | 47 |
| 2.6 | Environmental concern of carbon nanomaterials | 48 |
| 2.7 | Specific equipment used in the study | 50 |
| 2.7.1 | Transmission electron microscope | 51 |
| 2.7.2 | Raman spectroscopy | 53 |
| 2.7.3 | X-Ray diffractometer | 54 |
| 2.7.4 | Field emission scanning electron microscope / Energy dispersive X-Ray | 56 |
| 2.7.5 | Fourier transform infrared spectroscopy | 57 |
| 2.8 | Summary of chapter 2 | 60 |
| 3. | METHODOLOGY | 61 |
| 3.1 | Characterization of MWCNTs | 63 |
| 3.1.1 | Graphitic structural analysis of MWCNTs via TEM | 63 |
| 3.1.2 | Chemical analysis of MWCNTs via Raman spectroscopy | 63 |
| 3.1.3 | Phase analysis of MWCNTs via XRD | 64 |
| 3.2 | Characterization of urea fertilizer | 64 |
| 3.2.1 | Morphology analysis via FESEM/EDX | 64 |
| 3.2.2 | Analysis of surface functional groups by FT-IR | 65 |
| 3.3 | Covalent functionalization through nitric acid treatment | 65 |
| 3.3.1 | Quantitative analysis of surface acidic functional groups via acid-base Boehm titration | 66 |
| 3.3.2 | Qualitative analysis of surface acidic functional groups via FT-IR spectroscopy | 66 |
| 3.4 | Parameter screening for grafting urea fertilizer onto multiwalled carbon nanotubes | 67 |
| 3.5 | Optimization process for grafting urea fertilizer onto multiwalled carbon nanotubes | 68 |
| 3.5.1 | Statistical analysis and modelling | 70 |
| 3.6 | Glasshouse application for MR219 local paddy variety | 70 |
| 3.6.1 | Paddy plantation | 71 |
| 3.6.2 | Analysis on paddy growth | 73 |
| 3.6.3 | Analysis on total N content | 73 |
| 3.7 | Isotopic techniques in N fertilizer use efficiency studies | 76 |
| 3.8 | Localization investigation of f-MWCNTs in plant root cells via TEM | 77 |
| 3.9 | Summary of chapter 3 | 78 |
| 4 | RESULTS AND DISCUSSION | 79 |
| 4.1 | Characterization of as purchased raw materials | 80 |
| 4.1.1 | Multiwalled carbon nanotubes (MWCNTs) | 80 |
| 4.1.2 | Urea fertilizer (UF) | 85 |

| | | |
|-----------|---|------------|
| 4.2 | Existence of surface acidic group on MWCNTs | 87 |
| 4.2.1 | Calculated values based on acid-base Boehm titration | 87 |
| 4.2.2 | Evaluation of surface acidic groups via FT-IR | 90 |
| 4.2.3 | Evaluation of surface acidic groups via XRD | 91 |
| 4.2.4 | Morphology analysis of f-MWCNTs via TEM | 93 |
| 4.3 | Grafting urea onto MWCNTs | 97 |
| 4.3.1 | Parameter screening by Plackett-Burman experimental design | 97 |
| 4.3.2 | Microstructural analysis of f-MWCNTs and MWCNTs grafted with UF | 102 |
| 4.3.2.1 | FESEM analysis | 102 |
| 4.3.2.2 | TEM analysis | 106 |
| 4.3.3 | Chemical analysis of f-MWCNTs and MWCNTs grafted with UF | 108 |
| 4.3.3.1 | FT-IR analysis | 108 |
| 4.3.4 | Paddy growth analysis of f-MWCNTs and MWCNTs grafted with UF | 110 |
| 4.3.4.1 | Evaluation of paddy height | 110 |
| 4.3.4.2 | Evaluation of total dry weight (TDW) | 113 |
| 4.3.4.3 | Evaluation of yield components | 115 |
| 4.3.4.4 | Total nitrogen (N) evaluation | 117 |
| 4.4 | Optimization via Response surface methodology experimental design | 120 |
| 4.4.1 | Treatment efficiency | 127 |
| 4.4.2 | Microstructural analysis of UF-MWCNTs fertilizer | 129 |
| 4.4.2.1 | TEM analysis | 129 |
| 4.4.2.2 | FESEM analysis | 132 |
| 4.4.3 | Chemical analysis | 134 |
| 4.4.3.1 | Raman spectroscopy | 134 |
| 4.5 | Glasshouse study on MR219 paddy growth | 137 |
| 4.5.1 | Paddy growth evaluation | 137 |
| 4.5.1.1 | Measuring paddy height | 137 |
| 4.5.1.2 | Measuring total dry weight (TDW) | 141 |
| 4.5.1.3 | Measuring yield | 143 |
| 4.5.2 | Efficiencies analysis using ¹⁵ N isotopic technique | 147 |
| 4.5.2.1 | Total N content analysis | 147 |
| 4.5.2.2 | N fertilizer uptake (NU) performance | 153 |
| 4.5.2.3 | N fertilizer use efficiencies (NUE) | 159 |
| 4.6 | Mechanism of N transfer in plant via f-MWCNTs nano carriers | 163 |
| 4.6.1 | Confirmation of f-MWCNTs uptake into plant roots | 164 |
| 4.6.2 | Mechanism of f-MWCNTs entry into plant roots | 167 |
| 4.6.3 | Localization of f-MWCNTs in plant root cells | 170 |
| 4.7 | Summary of chapter 4 | 175 |
| 5. | CONCLUSION AND RECOMMENDATIONS | 176 |
| 5.1 | Conclusion | 176 |
| 5.2 | Contribution to knowledge | 178 |
| 5.3 | Future recommendations | 179 |
| | REFERENCES | 181 |
| | APPENDICES | 223 |

LIST OF TABLES

| TABLE | TITLE | PAGE |
|-------|--|------|
| 2.1 | The application of carbon NMs holds great promise for the advancement of agricultural production | 12 |
| 2.2 | Nutrients required by plants | 27 |
| 3.1 | Specification of purchased MWCNTs | 63 |
| 3.2 | Experimental design matrix of Plackett Burman experimental design | 68 |
| 3.3 | Experimental codes and levels of independent variables for response surface methodological experiment | 69 |
| 3.4 | Experimental design matrix and results of CCD | 69 |
| 3.5 | Data needed to be recorded for ^{15}N direct technique calculation | 76 |
| 4.1 | Crystallites size of crude and nitric acid treated MWCNTs | 93 |
| 4.2 | Plackett-Burman Experimental design | 97 |
| 4.3 | Estimated effect, standard error, corresponding F and P values and confidence level for paddy height at 45 DAS in nine variables Plackett–Burman design experiment | 100 |
| 4.4 | Estimated effect, standard error, corresponding F and P values and confidence level for Total N content in nine variables Plackett–Burman design experiment | 102 |

| | | |
|------|--|-----|
| 4.5 | Number of panicles and grain yield of paddy for different UF-MWCNTs fertilizer | 115 |
| 4.6 | Total N content of different UF-MWCNTs fertilizer and paddy straw treated with different UF-MWCNTs | 118 |
| 4.7 | Results of CCD | 121 |
| 4.8 | Final equations in terms of coded and actual factors for parameters | 121 |
| 4.9 | Analysis of variance for NUE using CCD | 123 |
| 4.10 | Analysis of variance for NU using CCD | 124 |
| 4.11 | Analysis of variance for Total Dry Weight (TDW) using CCD | 126 |
| 4.12 | Optimization results for design factors of UF-MWNTs fertilizer | 129 |
| 4.13 | Optimization results for maximum responses of UF-MWNTs fertilizer | 129 |
| 4.14 | Sample identification according to design factors involved in grafting optimization process | 137 |

LIST OF FIGURES

| FIGURE | TITLE | PAGE |
|--------|--|------|
| 1.1 | Transverse cross section of the root absorption zone showing the differential nanoparticle interaction on exposure | 3 |
| 2.1 | TEM micrographs of (a) MWCNTs (b) SWCNTs (c) bundles of SWCNTs (d,e) Schematics of (d) MWCNTs and (e) SWCNTs | 16 |
| 2.2 | (a) Schematic honeycomb structure of a graphene sheet (b) armchair tubes (c) zigzag tubes (d) chiral tubes | 18 |
| 2.3 | Oxygen containing groups functionalized on CNTs surfaces | 22 |
| 2.4 | Covalent functionalization of CNTs | 23 |
| 2.5 | Strategies for noncovalent functionalization of CNTs: a) wrapping of polymers b) adsorption of aromatic and bio molecule | 25 |
| 2.6 | Growing stages of typical rice crop | 28 |
| 2.7 | Chemical structure of urea | 30 |
| 2.8 | Global nitrogen cycle | 31 |
| 2.9 | Mass flow mechanism | 37 |
| 2.10 | The ‘ideal fertilizer’: the nutrient release is synchronized with the crop’s nutrient requirements | 40 |
| 2.11 | Endocytosis and direct penetration of carbon nanotubes into the plant cell | 41 |

| | | |
|--------|---|----|
| 2.12 | The route of water sucked in by capillary force through two distinctive xylem cells (a) tracheid (b) vessel element | 43 |
| 2.13 | Figure 2.13 Digital image of different dispersion behaviour of (a) CNTs and (b) functionalized CNTs | 49 |
| 2.14 | Low and high-magnification TEM images of the MWCNTs | 51 |
| 2.15 | Schematic diagram when the electron beam passes through the samples in TEM machine | 52 |
| 2.16 | Schematic of a micro-Raman spectrometer where collection are performed through microscope objective | 53 |
| 2.17 | Raman spectroscopy analysis of MWCNT | 54 |
| 2.18 | Fundamentals of x-ray diffraction in material | 55 |
| 2.19 | XRD patterns of unmodified (CNT), oxidative functionalized (f-CNT) and aminosilanized (s-CNT) carbon nanotubes | 56 |
| 2.20 | FESEM schematic diagram | 57 |
| 2.21 | FT-IR spectrum of pure urea | 59 |
| 2.22 | Schematic diagram of FT-IR | 59 |
| 3.1(a) | Overall experimental works in 5 main sections, A, B, C, D and E | 61 |
| 3.1(b) | Details flowchart of the overall experiment | 62 |
| 3.2 | (a) Reflux apparatus and (b) vacuum filtration apparatus | 66 |
| 3.3 | Glasshouse study procedures for paddy growth | 72 |
| 3.4 | Healthy growth of paddies in a glasshouse after 110 days | 72 |
| 3.5 | Fresh paddy plants were harvested and separated from soil every 2 weeks for 5 times until 110 days after sowing | 73 |

| | | |
|------|--|-----|
| 3.6 | Both straw and root of paddy plants are used separately to measure the N content | 74 |
| 4.1 | TEM micrographs of multiwall carbon nanotubes | 80 |
| 4.2 | TEM micrographs of MWCNTs at higher magnification | 82 |
| 4.3 | The XRD analysis of MWCNTs | 83 |
| 4.4 | The Raman spectra of multiwall carbon nanotubes | 84 |
| 4.5 | FESEM micrograph of urea fertilizer | 85 |
| 4.6 | FESEM micrograph of urea fertilizer (a), coupled with EDX analysis (b) | 86 |
| 4.7 | FT-IR spectrum of urea | 87 |
| 4.8 | Concentration of acidic groups at varying reflux time between 3 and 24 hr | 89 |
| 4.9 | ATR-FTIR spectra of crude and nitric acid treated MWCNTs | 91 |
| 4.10 | XRD patterns of crude and nitric acid treated MWCNTs at 3h, 12h, 15h and 24 h (a) XRD patterns of samples zooming at 2θ values 20° to 30° | 92 |
| 4.11 | TEM micrographs of functionalized multiwall carbon nanotubes | 95 |
| 4.12 | Main effect on paddy height at 45 day after sowing | 98 |
| 4.13 | Main effect on Total N | 101 |
| 4.14 | FESEM micrographs of (a) MU and (b) FMU1 | 103 |
| 4.15 | FESEM micrographs coupled with EDX analysis of (a) MU, and (b) FMU | 106 |
| 4.16 | TEM micrographs of the (a-b) MU and (c-d) FMU | 108 |

| | | |
|------|---|-----|
| 4.17 | FT-IR spectra of f-MWCNTs, FMU2 with 0.6wt% f-MWCNTs, FMU1 with 0.1wt% f-MWCNTs and MU with 0.6wt% of MWCNTs | 109 |
| 4.18 | Paddy growth trend in different UF-MWCNTs fertilizer | 112 |
| 4.19 | Total Dry Weight of paddy for three types (FMU1, FMU2 and MU) of UF-MWNTs fertilizer | 114 |
| 4.20 | Amination process of f-MWCNTs | 119 |
| 4.21 | Design expert plot; normal probability plot of the standardized residual for NUE (a) and NU (b) | 127 |
| 4.22 | 3D Response surface plot of NUE (a) and NU (c) coupled with contour plots of NUE (b) NU (d) of paddy as a function of f-MWCNTs (%) and functionalization reflux time (hour) | 128 |
| 4.23 | TEM micrographs of (a-c) 21 hrs f-MWCNTs and (d-f) UF-MWCNTs | 131 |
| 4.24 | FESEM micrographs of UF-MWCNTs fertilizer at lower (a-b) and higher (c-d) magnification | 133 |
| 4.25 | Raman spectra of (a) 21 hrs f-MWCNTs in comparison to MWCNTs | 135 |
| 4.26 | Raman spectra of (a) UF-MWCNTs in comparison to (b) UF | 136 |
| 4.27 | Paddy growth trend for UF-MWCNTs at different functionalization time | 138 |
| 4.28 | Paddy growth trend for UF-MWCNTs compared to conventional UF | 140 |

| | | |
|------|---|-----|
| 4.29 | Paddy TDW for UF-MWCNTs at different functionalization reflux time | 142 |
| 4.30 | Paddy TDW for UF-MWCNTs compared to conventional UF | 143 |
| 4.31 | Trend of number of tiller per pot production for different UF-MWCNTs treatment | 144 |
| 4.32 | Tiller per pot production for UF-MWCNTs-21 treatment compared to conventional UF | 145 |
| 4.33 | Panicles per pot production for different UF-MWCNTs treatment compared to control | 147 |
| 4.34 | Trend of total N content in paddy straw for different UF-MWCNTs treatment | 148 |
| 4.35 | Trend of total N content in paddy roots for different UF-MWCNTs treatment | 150 |
| 4.36 | Trend of total N content in paddy straw and roots for UF-MWCNTs treatment compared to control | 152 |
| 4.37 | Trend of N fertilizer uptake by paddy straw for different UF-MWCNTs | 154 |
| 4.38 | Trend of N fertilizer uptake by paddy straw for UF-MWCNTs compared to control | 156 |
| 4.39 | Total N uptake by paddy straw and root at 11 weeks | 158 |
| 4.40 | Trend of NUE by paddy straw for different UF-MWCNTs | 160 |
| 4.41 | Trend of NUE by paddy straw for UF-MWCNTs compared to conventional UF | 163 |

| | | |
|------|--|-----|
| 4.42 | TEM micrographs showing the uptake of f-MWCNTs into paddies root at (a-d) 5 weeks and (e-f) 13 weeks of plant growth | 165 |
| 4.43 | Mass flow mechanism of f-MWCNTs entry into the plant cells | 168 |
| 4.44 | TEM micrographs on fresh plant root cells of UF-MWCNTs treatment shows (a-b) f-MWCNTs entry via a wound which resulted in leaking of plant organelles (c-d) | 170 |
| 4.45 | Localization of f-MWCNTs in the plant cells along the cell walls (a), near undamaged cell wall (b), independent of their size and geometry (c-d), and in the extracellular region of plant cells, evidenced by TEM observation | 172 |
| 4.46 | TEM micrographs on plant cells reveal dead and healthy plant cells | 174 |

LIST OF APPENDICES

| APPENDIX | TITLE | PAGE |
|----------|---|------|
| A | Certificate of analysis for safety of grains produced under UF-MWCNTs treatment | |

LIST OF ABBREVIATIONS

| | | |
|-----------|---|---|
| UF | - | urea fertilizer |
| CNTs | - | carbon nanotubes |
| MWCNTs | - | multiwalled carbon nanotubes |
| f-MWCNTs | - | functionalized multiwalled carbon nanotubes |
| UF-MWCNTs | - | urea-multiwalled carbon nanotubes |
| SWCNTs | - | singlewalled carbon nanotubes |
| NMs | - | nanomaterials |
| NU | - | nitrogen uptake |
| NUE | - | nitrogen use efficiency |
| TDW | - | total dry weight |
| TEM | - | transmission electron microscopy |
| FESEM | - | Field emission scanning electron microscope |
| EDX | - | Energy dispersive X-Ray |
| XRD | - | X-Ray diffraction |
| FT-IR | - | Fourier Transform Infrared |
| ATR | - | Attenuated total reflectance |
| RSM | - | Response surface methodology |
| CCD | - | Central composite design |
| ANOVA | - | analysis of variance |

LIST OF SYMBOLS

| | | |
|----------|---|------------------|
| θ | - | theta |
| d | - | crystal size |
| DAS | - | day after sowing |

LIST OF PUBLICATIONS AND AWARDS

1. **Norazlina M.Y.**, Azizah S., M.F. Dimin, Faridah Y., Rostam O. 2015. Influence of Nitric Acid Treatment on the Crystallographic Structure of Multiwalled Carbon Nanotubes. *Applied Mechanics and Materials*. 761, 369-373.
2. **Norazlina M.Y.**, Azizah S., Dimin M.F., Faridah Y. (2015). Statistical Evaluation of the Production of Urea Fertilizer-Multiwalled Carbon Nanotubes using Plackett Burman Experimental Design. *Procedia-Social and Behavioral Sciences*, 195, 315-323.
3. **Norazlina M.Y.**, Azizah S., Dimin M.F., Faridah Y., Jeefferie, A.R (2016). Application of Response Surface Methodology for Optimization of Urea Grafted Multiwalled Carbon Nanotubes in Enhancing Nitrogen Use Efficiency and Nitrogen Uptake by Paddy Plants. *Journal of Nanotechnology*. Vol. 2016, 14 pages.
4. Azizah S., **Norazlina M.Y.**, Dimin M.F., Faridah Y., Jeefferie, A.R. (2016). Urea Grafted Multiwalled Carbon Nanotubes Enhancing Nitrogen Use Efficiency and Nitrogen Uptake by Paddy Plants. Accepted to be publishing in *Jurnal Teknologi*.

Conferences

1. Influence of Nitric Acid Treatment on the Crystallographic Structure of Multiwalled Carbon Nanotubes. 3rd International conference on design and concurrent engineering (IDECON 2014). Norazlina M.Y., Azizah S., M.F. Dimin, Faridah Y., Rostam O. 22 - 23 September 2014. Avillion Legacy Hotel, Melaka, Malaysia.
2. Statistical Evaluation of the Production of Urea Fertilizer-Multiwalled Carbon Nanotubes using Plackett Burman Experimental Design. World Conference On Technology, Innovation and Entrepreneurship 2015. Norazlina M.Y., Azizah S., M.F. Dimin, Faridah Y. 28-30 May 2015. WOW Convention Center, Istanbul, Turki.
3. Urea Grafted Multiwalled Carbon Nanotubes Enhancing Nitrogen Use Efficiency and Nitrogen Uptake by Paddy Plants. 5th International conference on design and concurrent engineering (IDECON 2016). Azizah S., **Norazlina M.Y.**, Dimin M.F., Faridah Y., Jeefferie, A.R. 19 – 22 September 2016. Adya Hotel, Langkawi, Malaysia.