Faculty of Manufacturing Engineering

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

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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 ($p\text{-value} < 0.05$) 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 quadratik ANOVA. Penghasilan UF-MWCNTs yang sebati dengan ketiadaan struktur bergumpal MWCNTs dibuktikan melalui FESEM dan TEM. Pengimejan TEM juga telah menunjukkankan 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.

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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

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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.
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