Faculty of Manufacturing Engineering

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

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

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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 : ……………………….

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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 : ………………………………

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DEDICATION

To my beloved husband, children, mother, father and family,

for the understanding and moral support

throughout the years

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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.

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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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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

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LIST OF SYMBOLS

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

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