Faculty of Manufacturing Engineering

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

Se Sian Meng

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

SE SIAN MENG

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

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DECLARATION

I declare that this thesis entitle “Synthesis of Urea Impregnated Rubber Wood Biochar for Retention of Nitrogenoues 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

ABSTRACT

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 ºC, which is 25.9 %/week and urea impregnated biochar sample produced at 700 ºC 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 ºC ranging from 3 % to 7 % and those at 700 ºC 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 [$(NH_4)_2CO_3$]. Bahan ini ditukarkan kepada ion ammonium (NH_4^+) oleh aktiviti urease untuk diambil oleh tumbuhan. Baki ion hydroksida yang tinggal pada tanah akan meningkatkan pH tanah dan bertindakbalas dengan ion ammonium lalu membebaskan gas ammonia sebagai gas rumah hijau. Sebahagian NH_4^+ akan dioksidakan di udara dan bertukar kepada ion nitrit (NO_2^-) dan ion nitrat (NO_3^-) oleh bakteria. Ion NO_3^- adalah gerak-bebas dalam tanah lalu melarut 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 memperlahankan penguraian urea dan mengurangkan pembebesan nitrogen. Objektif utama kajian ini adalah penghasilan baja urea impregnasi biochar untuk menambaik pengekalan nutrient 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 dand kumpulan berfungsi bersifat asidik seperti karboksilik (--COOH) pada permukaaan 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 tinngi sebanyak 54.4 %/minngu berbanding dengan urea yang diimpregnasikan dengan biochar 25.9 %/minngu untuk biochar yang dihasilkan pada suhu 300 ºC sebanyak 5 % dan 28.9 %/minggu untuk biochar yang dihasilkan pada suhu 700 ºC. Jumlah simpanan kandungan nitrogen bagi sampel yang imregnasi dengan urea menunjukkan biochar yang dihasilkan pada suhu 300 ºC dengan 3 % hingga 7 % biochar mengekalkan 15 % nitrogen lebih daripada sampel urea. Biochar yang dihasilkan pada suhu 700 ºC dengan kandungan 4 % hingga 10 % dapat mengekalan 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 kandung 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.

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LIST OF ABBREVIATIONS

BC	-	Biochar
BET	-	Brunauer-Emmett-Teller
CHN	-	Carbon-Hydrogen-Nitrogen
DSC	-	Differential Scanning Calorimetry
EDX	-	Energy-Dispersive X-ray
FT-IR	-	Fourier Transform Infrared
HCl	-	Hydrochloric Acid
IUPAC	-	International Union of Pure and Applied Chemistry
N	-	Nitrogen
NaOH	-	Sodium Hydroxide
NH_4^+	-	Ammonium
NO_3^-	-	Nitrate
NO_2^-	-	Nitrite
N_2O	-	Nitrous oxide
NH_3	-	Ammonia
RWSD	-	Rubber wood sawdust
SEM	-	Scanning Electron Microscopy
STP	-	Standard Temperature and Pressure
TGA	-	Thermogravimetric analysis
UV	-	Ultra voilet
XRD	-	X-ray diffraction

LIST OF SYMBOLS

^oC	-	Degree Celsius
$^oC/min$	-	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	-	Avogrado's number 6.023 x 10^{23} molecules/mol
Pa	-	Pascal
kV	-	Kilo volt
cm^{-1}	-	Wave number
nm	-	Nano meter

N	-	Normality
M	-	Molarity
$mmol/g$	-	Mili Mole per gram
$\mu g\ N\ g^{-1}$	-	Micro gram nitrogen per gram
V	-	Volume
K	-	Kinetic constant
g/cm^3	-	Gram per centimetre cube
2ϑ	-	Bragg angle
cm^3/g	-	Centimetre cube per gram
$wt\ \%$	-	Weight percentage
mW	-	Miliwatt
$\mu g/g$	-	Microgram per gram
Log	-	Logarithm
$t_{1/2}$	-	Half-life
ppm	-	Part per million
$mole$	-	Mole
$wt.\%/^oC$	-	Weight percentage per Degree Celsius
$gmol^{-1}$	-	Gram per Mole

LIST OF PUBLICATIONS AND AWARDS

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