



UNIVERSITI PUTRA MALAYSIA

***NUTRIENT RELEASE FROM RICE AND
RUBBER BIOCHAR TABLETS WITH AND
WITHOUT EMBEDDED FERTILIZERS***

LEE YIT LENG

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**NUTRIENT RELEASE FROM RICE AND RUBBER BIOCHAR TABLETS
WITH AND WITHOUT EMBEDDED FERTILIZERS**

By

LEE YIT LENG

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of
Philosophy.**

October 2021

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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October 2021

Chair : Prof. Ahmed Osumanu Haruna
Faculty : Agricultural Science and Forestry (Bintulu Campus)

An alternative to agricultural residues management is to convert them to biochar because this organic amendment can act as a superior soil conditioner that improves soil productivity. Nevertheless, the low density of biochar poses a challenge in the handling biochar. Tableting of biochar can mitigate the aforementioned problems associated with biochar. The objectives of this study were to determine the physico-chemical properties, nutrient release and soil ammonia volatilization of biochar tablets with and without embedded fertilizers. The different rates of biochar tablets with and without embedded fertilizers impact on selected soil chemical characteristics and nutrient use efficiency (NUE) of sweet corn (test crop) were also determined. Next planting cycle was conducted to determine the effects of combination biochar and fertilizers with and without tableting on selected soil chemical characteristics and NUE of sweet corn (test crop).

The composition of biochar mixture was 50% charred rice husk, 30% charred rice straw, and 20% charred rubber twigs. The NPK fertilizers used for this study were ammonium sulfate (AS), triple superphosphate (TSP), and muriate of potash (MOP). The biochar tablet (BT) was produced by blending a biochar mixture with starch followed by tableting using a single punch tablet press whereas the fertilizer embedded biochar tablet (BF) was prepared using the same procedure except that NPK fertilizers were added during blending. Similarly, a combination of biochar and NPK without tableting (Biochar + NPK) was prepared. The ratio of biochar to fertilizers mixture used for the BF and Biochar + NPK production was 2:1. Standard procedures were used to characterize BT, BF, Biochar + NPK, and NPK. The nutrient release of the biochar and fertilizers with- and without- tablets were determined using the water

incubation over 30 days. The daily loss ammonia was measured using a closed dynamic air flow system model for 10 days. A pot experiment with six fertilization treatments including control was carried out in an open field located in Perlis, Malaysia to determine the different rates of biochar tablets with- and without embedded fertilizers impact on selected soil chemical characteristics and NUE of the sweet corn (test crop). Sweet corn was cultivated for 53 days (tasselling) and after which the crops were harvested and partitioned into leaves, stems, roots and tassel flowers. The sweet corn plant tissues were analyzed for total C, N, P and K using standard procedures. Soil samples were taken from the pots after the sweet corn plants were harvested and the soil chemical properties were determined. Next planting cycle for the pot experiment with four fertilization treatments including control was conducted to determine effects of the combination biochar and fertilizers with and without tableting on the soil chemical characteristics and NUE of the sweet corn. The procedures used were the same as those used in the previous experiment.

Tableting the biochar produced increased the densities of BT (0.70 g cm^{-3}) and BF (0.90 g cm^{-3}). Higher density of BF can ease its handling and storage challenges. The blending of NPK fertilizers with the biochar produced, regardless of with and without tableting significantly increased the concentrations of N, P, K, and Ca, which are essential elements required for successful plant growth, development, and reproduction. The presence of NH bend (1614.26 cm^{-1}) in highly densified BF suggests that the nutrient compounds in BF is more stable against degradation and leaching. The water soluble nutrient release increased in the order of $\text{BT} < \text{BF} < \text{Biochar} + \text{NPK} < \text{NPK}$. However, combination of biochar and fertilizers regardless of with and without tableting increased soil ammonia volatilization relative to the NPK fertilizers. The first corn planting cycle demonstrated that co-application of biochar and fertilizers increased soil total C, N, but soil electrical conductivity reduced. Fertilizers only had the lowest effect on the total NUE of the sweet corn. Higher biochar tablet rate and lower rate of fertilizers increased the efficiency of the fertilizers used in the first corn planting cycle. The beneficial effects of tableting the combined use of biochar and NPK on the sweet corn plants' NUE were more evident in the second planting cycle. The findings suggest that the BF can slowly release embedded nutrients in synchrony with optimum nutrient uptake by the sweet corn. Therefore, transforming fertilizer embedded in biochar into tablet is recommended for sweet corn production following a long-term field study to confirm the findings of this pot study.

Keywords: Biochar; Tableting; Nutrient use efficiency; Ammonia volatilization; Tasseling; Binding

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGURAIAN NUTRIEN DARIPADA TABLET BIO-ARANG PADI DAN GETAH YANG TERSISIP DENGAN- DAN TANPA- BAJA

Oleh

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Oktober 2021

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Kaedah alternatif mengendalikan sisa pertanian adalah sisa pertanian ditukarkan ke bio-arang dimana bio-arang boleh bertindak sebagai perapi tanah yang mampu meningkatkan kesuburan tanah. Namun demikian, ketumpatan bio-arang yang rendah telah menyukarkan proses pengendalian, pengangkutan dan penyimpanan. Kaedah menghasilkan bio-arang dalam bentuk tablet mampu meningkatkan kecekapan pengendalian. Objektif kajian ini adalah untuk menentukan sifat kimia, fizikal, kadar penguraian nutrien dan volatilisasi amonia tanah dari tablet bio-arang yang dicampurkan dengan baja dan tanpa baja. Kadar penggunaan yang berbeza dan keberkesanan tablet bio-arang yang dicampurkan dengan baja dan tanpa baja ke atas ciri-ciri kimia tanah serta kecekapan penguraian nutrien pada tanaman jagung manis (tanaman ujian) juga ditentukan. Kitar tanaman yang seterusnya dijalankan untuk menentukan keberkesanan produk hasil pemampatan antara bio-arang dan baja serta produk tanpa pemampatan ke atas ciri-ciri kimia tanah dan kecekapan pengambilan nutrien jagung manis (tanaman ujian).

Antara komposisi campuran bio-arang termasuk sekam padi bakar 50%, jerami padi bakar 30% dan ranting getah bakar 20%. Baja NPK yang digunakan untuk kajian ini adalah ammonium sulfat (AS), triple superphosphate (TSP) dan muriate of potash (MOP). Tablet bio-arang (BT) dihasilkan daripada campuran bio-arang dengan kanji diikuti dengan pemampatan menggunakan pemampat tablet tunggal manakala tablet sebatian bio-arang dan baja (BF) dihasilkan dengan menggunakan prosedur yang sama kecuali baja NPK telah dimasukkan semasa pengadunan. Satu lagi produk telah dihasilkan dengan gabungan bio-

arang dan NPK tanpa pemampatan (Biochar + NPK). Nisbah campuran bio-arang ke baja yang digunakan untuk produk BF dan Biochar + NPK adalah 2:1. Prosedur standard telah diikuti untuk menganalisis ciri-ciri hasil produk BT, BF, Biochar + NPK dan NPK. Kaedah inkubasi air selama 30 hari telah dipraktikkan untuk mengenalpasti kadar penguraian nutrien antara produk tablet baja dan tanpa baja yang disalut dengan bio-arang sementara kadar pengewapan gas amonia telah diukur setiap hari bagi tempoh 10 hari dengan menggunakan model sistem aliran udara dinamik yang tertutup. Satu eksperimen merangkumi enam rawatan baja termasuk kawalan telah dijalankan menggunakan pasu dengan konsep terbuka bagi menentukan kadar penggunaan yang berbeza dan keberkesanan tablet bio-arang dicampurkan dengan baja dan tanpa baja ke atas ciri-ciri kimia tanah serta kecekapan penggunaan nutrien pada tanaman jagung manis (tanaman ujian). Tanaman jagung manis telah ditanam selama 53 hari dan dituai. Sampel tisu pokok jagung telah dihantar untuk analisis jumlah unsur C, N, P dan K. Sementara itu, sampel tanah juga diambil selepas tanaman dituai bagi menentukan sifat kimianya. Eksperimen pasu yang kitaran kedua seterusnya dijalankan merangkumi empat rawatan baja termasuk kawalan bagi menentukan keberkesanan antara produk hasil pemampatan dan tanpa pemampatan ke atas ciri-ciri kimia tanah dan kecekapan penggunaan nutrien pokok jagung manis. Prosedur yang sama seperti eksperimen sebelumnya digunakan untuk menuai pokok jagung manis dan menganalisis ciri-ciri kimia pada sampel tisu tanaman dan tanah.

Kajian menunjukkan proses pemampatan mampu meningkatkan ketumpatan BT (0.70 g cm^{-3}) dan BF (0.90 g cm^{-3}) yang memudahkan proses pengendalian dan penyimpanan. Pengadunan antara baja NPK dan bio-arang sama ada dalam bentuk tablet atau bukan telah menunjukkan peningkatan kadar N, P, K dan Ca. Sebatian nutrien dalam BF adalah lebih stabil dari segi degradasi dan larut lesap dengan kewujudan unsur NH (1614.26 cm^{-1}) yang terikat dalam BF yang mampat. Turutan kadar peningkatan penguraian nutrien larut air adalah $\text{BT} < \text{BF} < \text{Biochar} + \text{NPK} < \text{NPK}$. Kajian menunjukkan peningkatan kadar pengewapan gas amonia pada produk kombinasi bio-arang dan baja berbanding dengan baja NPK. Eksperimen menanam jagung kitaran pertama menunjukkan bahawa penggunaan bersama bio-arang dan baja meningkatkan jumlah karbon dan nitrogen dalam tanah, tetapi mengurangkan kekonduksian elektrik tanah. Rawatan baja sahaja telah mencatat kecekapan pengambilan nutrien yang paling rendah pada pokok jagung manis. Eksperimen menanam jagung kitaran pertama telah menunjukkan penggunaan tablet bio-arang yang lebih tinggi dan kadar baja yang rendah mampu meningkatkan kecekapan pengambilan baja. Eksperimen menanam jagung kitaran kedua telah menunjukkan sekali lagi bahawa kecekapan pengambilan nutrien yang lebih tinggi dengan menggunakan BF. Hasil kajian menunjukkan bahawa baja BF dapat menguraikan nutrien secara perlahan-lahan secara serentak dengan pengambilan nutrien optimum oleh jagung manis. Maka, penggunaan tablet baja dan biochar yang dimampatkan adalah disyorkan serta diikuti kajian eksperimen ladang yang jangka panjang untuk mengesahkan hasil kajian eksperimen pasu ini.

Kata kunci: Bio-arang; Pemampatan; Kerbekesanan penggunaan nutrien; Volatilisasi ammonia; Pembungaan; Pengikatan

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I certify that a Thesis Examination Committee has met on 5 October 2021 to conduct the final examination of Lee Yit Leng on her thesis entitled "Nutrient Release from Rice and Rubber Biochar Tablets With and Without Embedded Fertilizers" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENTS	v
APPROVAL	vi
DECLARATION	viii
LIST OF TABLES	xv
LIST OF FIGURES	xvii
LIST OF ABBREVIATIONS	xviii
CHAPTER	
1	
INTRODUCTION	1
1.1 Research background	1
1.2 Problem statements	2
1.3 General objectives	3
1.4 Significance of study	3
2	
LITERATURE REVIEW	4
2.1 Fertilizer consumption trend in Malaysia	4
2.2 Rice residues	4
2.2.1 Composition of rice straw and husk	5
2.3 Rubber crop production in Malaysia	5
2.3.1 Rubber wood residues	5
2.3.2 Composition of rubber wood	6
2.4 Best management of crop residues	6
2.4.1 Conversion of crop residues to biochar	7
2.5 Biochar of rice straw and husk	7
2.6 Biochar of rubber tree woods	8
2.7 Pyrolysis parameters and feedstock types on the composition of biochar	8
2.7.1 Temperature	9
2.7.2 Reaction residence time	10
2.7.3 Heating rate	10
2.7.4 Feedstock	10
2.8 Physical properties of biochar	11
2.8.1 Biochar yield	11
2.8.2 Biochar density	12
2.8.3 Surface area	12
2.8.4 Particle size distribution	12
2.9 Chemical properties of biochar	13
2.9.1 pH and electrical conductivity of biochar	13
2.9.2 Cation exchange capacity of biochar	13
2.9.3 Nutrient properties	14
2.9.3.1 Macronutrients	14
2.9.3.2 Micronutrients	15
2.9.3.3 Surface chemistry	15

2.10	Application of biochar to soil	16
2.10.1	Advantages of biochar application to soil	16
2.10.1.1	Soil pH improvement	16
2.10.1.2	Soil carbon sequestration	16
2.10.1.3	Effects of biochar amendment on soil nutrient availability	17
2.10.1.4	Effects of biochar amendment on growth yield and nutrient uptake	17
2.10.1.5	Biochar increases water holding capacity	19
2.10.1.6	Nutrient leaching	19
2.10.1.7	Effects of biochar amendment on ammonia volatilization	20
2.10.2	Disadvantages of biochar application to soils	20
2.11	Tableting of biochar	21
2.11.1	Moisture content	21
2.11.2	Particle size	22
2.11.3	Binder	22
2.11.4	Compression condition	23
2.12	Physical properties of pellet	23
2.12.1	Pellet density	23
2.12.2	Particle sizes and pellet durability	23
2.13	Nutrient release of biochar pellet	24
2.14	Factors limiting plant nutrient uptakes	24
2.14.1	Environmental factors	25
2.14.2	Soil nutrient deficiency	25
2.14.3	Soil ammonia volatilization	26
2.15	Factors affecting the soil ammonia volatilization	26
2.15.1	Soil characteristics	27
2.15.2	Types of nitrogenous fertilizer	27
2.16	Summary	28
3	CHARACTERISTICS OF BIOCHAR TABLETS WITH AND WITHOUT EMBEDDED FERTILIZERS	29
3.1	Introduction	29
3.2	Materials and methods	30
3.2.1	Samples collection and preparation	30
3.2.2	Biochar production and preparation	31
3.2.3	Biochar tablet production	31
3.2.4	Fertilizers embedded in biochar tablet and without tableting production	32
3.2.5	Types of NPK Fertilizers	32
3.3	Physical properties test	33
3.3.1	Unit density	33
3.3.2	Tablet durability	33
3.3.3	Moisture content	33
3.4	Chemical properties test	34

3.4.1	pH and electrical conductivity	34
3.4.2	Total carbon and nitrogen analysis	34
3.4.3	Total macronutrient analysis	34
3.4.4	Available ammonium and nitrate analysis	34
3.4.5	Available phosphorus analysis	35
3.4.6	Exchangeable potassium, calcium, magnesium and cation exchange capacity analysis	35
3.4.7	Fourier transform infrared spectra (FTIR) analysis	35
3.5	Statistical analysis	36
3.6	Results and discussion	36
3.6.1	Unit density, tablet durability, and moisture content	36
3.6.2	pH and electrical conductivity	37
3.6.3	Total carbon, nitrogen, phosphorus and potassium	38
3.6.4	Total calcium and magnesium	39
3.6.5	Available ammonium, nitrate, phosphorus, potassium	40
3.6.6	Exchangeable calcium, magnesium and cation exchange capacity	42
3.6.7	Fourier transform infrared spectra (FTIR) analysis	43
3.7	Conclusion	46
4	NUTRIENT RELEASE AND AMMONIA VOLATILIZATION OF BIOCHAR TABLETS WITH- AND WITHOUT EMBEDDED FERTILIZERS	47
4.1	Introduction	47
4.2	Materials and methods	48
4.2.1	Nutrient release analysis	48
4.2.2	Soil ammonia volatilization analysis	49
4.3	Statistical analysis	50
4.4	Results and discussion	51
4.4.1	Ammonium release analysis	51
4.4.2	Nitrate release analysis	53
4.4.3	Phosphorus release analysis	53
4.4.4	Potassium release analysis	54
4.4.5	Nutrient release during water incubation on the 30 th day	55
4.4.6	Selected soil chemical characteristics before the soil ammonia volatilization experiment	58
4.4.7	Daily loss of ammonia for 10 days of incubation	59
4.4.8	Effects of treatments on selected soil chemical properties after 10 days incubation of soil ammonia volatilization experiment	61
4.5	Conclusion	63

5	EFFECT RATES OF BIOCHAR TABLETS WITH- AND WITHOUT EMBEDDED FERTILIZERS ON THE SOIL CHEMICAL CHARACTERISTICS AND NUTRIENT USE EFFICIENCY OF SWEET CORN (<i>Zea mays</i>)	64
	5.1 Introduction	64
	5.2 Materials and methods	65
	5.2.1 Pot experiment	65
	5.2.2 Soil samples analysis	67
	5.2.2.1 Soil pH and EC analysis	67
	5.2.2.2 Soil exchangeable potassium, calcium, magnesium and cation exchange capacity analysis	67
	5.2.2.3 Soil available phosphorus analysis	67
	5.2.2.4 Soil total carbon and nitrogen analysis	68
	5.2.3 Plant samples analysis	68
	5.2.3.1 Total nitrogen analysis	68
	5.2.3.2 Total phosphorus and potassium analysis	68
	5.2.4 Statistical analysis	68
	5.3 Results and discussion	69
	5.3.1 Selected chemical characteristics of soil before planting sweet corn	69
	5.3.2 Selected soil chemical characteristics after 53 days of sweet corn planting	70
	5.3.3 Effect of treatments on the SPAD readings of sweet corn after 53 days planting	73
	5.3.4 Effect of treatments on dry weights of sweet corn after 53 days planting	74
	5.3.5 Effect of treatments on nutrients uptake in leaves, stems, roots and flowering tassels of sweet corn after 53 days planting	77
	5.3.6 Effects of treatments on nutrients use efficiency in leaves, stems, roots and flowering tassels of sweet corn after 53 days planting	79
	5.4 Conclusion	82
6	COMBINE USE OF BIOCHAR AND FERTILIZERS WITH AND WITHOUT TABLETING ON THE SOIL CHEMICAL CHARACTERISTICS AND NUTRIENT USE EFFICIENCY OF SWEET CORN (<i>Zea mays</i>)	83
	6.1 Introduction	83
	6.2 Materials and methods	84
	6.2.1 Pot experiment	84

6.2.2	Soil samples analysis	86
6.2.2.1	Soil pH and EC analysis	86
6.2.2.2	Exchangeable cations and cation exchange capacity determination	87
6.2.2.3	Soil available phosphorus analysis	87
6.2.2.4	Soil total carbon and nitrogen analysis	87
6.2.3	Plant samples analysis	88
6.2.3.1	Total nitrogen determination	88
6.2.3.2	Total phosphorus and potassium analysis	88
6.2.4	Statistical analysis	88
6.3	Results and discussion	89
6.3.1	Selected soil chemical characteristics after 53 days of sweet corn planting	89
6.3.2	Treatments on SPAD of sweet corn after 53 days planting	91
6.3.3	Treatments on dry weights of sweet corn at 53 days after planting	92
6.3.4	Treatments on nutrients uptake in leaves, stems, roots and flowering tassels of sweet corn at 53 days after planting	93
6.3.5	Treatments on nutrients use efficiency in leaves, stems, roots and flowering tassels of sweet corn at 53 days after planting	95
6.3.6	Treatments on total nitrogen, phosphorus, potassium use efficiency of sweet corn at 53 days after planting	97
6.4	Conclusion	98
7	GENERAL SUMMARY	99
8	GENERAL CONCLUSION AND RECOMMENDATION	100
	REFERENCES	101
	APPENDICES	132
	BIODATA OF STUDENT	146
	LIST OF PUBLICATIONS	147

LIST OF TABLES

Table		Page
3.1	Unit density, tablet durability and moisture content of biochar tablets (BT), biochar and fertilizers with (BF) and without tableting (Biochar + NPK)	37
3.2	pH, electrical conductivity, total content of carbon, nitrogen, phosphorus, potassium, calcium, and magnesium of biochar tablets (BT), biochar and fertilizers with (BF) and without tableting (Biochar + NPK)	38
3.3	Available ammonium, nitrate, phosphorus and potassium of biochar tablets (BT), biochar and fertilizers with (BF) and without tableting (Biochar + NPK)	41
3.4	Exchangeable calcium, magnesium and cation exchange capacity (CEC) of biochar tablets (BT), biochar and fertilizers with (BF) and without tableting (Biochar + NPK)	43
4.1	Soluble nutrient release of all the samples during water incubation on the 30 th day	57
4.2	Selected soil chemical characteristics before the soil ammonia volatilization experiment	58
4.3	Accumulation of ammonia volatilization over 10 days incubation	61
4.4	Selected soil chemical characteristics after the soil ammonia volatilization experiment	62
5.1	Selected chemical characteristics of soil before planting sweet corn	70
5.2	Selected soil chemical characteristics after 53 days of sweet corn planting	71
5.3	Effect of treatments on the SPAD readings of sweet corn after 53 days planting	74
5.4	Effects of treatments on dry weights of sweet corn after 53 days planting	76
5.5	Nitrogen, phosphorus and potassium uptake in leaves, stems, roots and flowering tassels of sweet corn	78

5.6	Nitrogen, phosphorus and potassium use efficiency in leaves, stems, roots and flowering tassels of sweet corn	80
5.7	Total nitrogen, phosphorus and potassium use efficiency of sweet corn	81
6.1	Selected soil chemical characteristics before planting the sweet corn	85
6.2	Selected soil chemical characteristics at 53 days of planting sweet corn	90
6.3	Effect of treatments on SPAD readings of sweet corn after 53 days planting	91
6.4	Treatments on the dry weights of sweet corn at 53 days after planting	92
6.5	Nitrogen, phosphorus and potassium uptake in leaves, stems, roots and flowering tassels of sweet corn at 53 days after planting	94
6.6	Nitrogen, phosphorus, and potassium use efficiency in leaves, stems, roots and flowering tassels of sweet corn at 53 days after planting	96
6.7	Treatments on total nitrogen, phosphorus, and potassium use efficiency of sweet corn at 53 days after planting	97

LIST OF FIGURES

Figure		Page
3.1	Steps for producing biochar tablets	32
3.2	FTIR spectra of biochar tablets (BT), biochar and fertilizer with (BF) and without tableting (Biochar + NPK) as well as NPK fertilizer	45
4.1	Ammonium release at every 5 days interval over 30 days of water incubation experiment	52
4.2	Nitrate release at every 5 days interval over 30 days of water incubation experiment	53
4.3	Phosphorus release at every 5 days interval over 30 days of water incubation experiment	54
4.4	Potassium release at every 5 days interval over 30 days of water incubation experiment	55
4.5	Daily loss of ammonia for 10 days of incubation. T1: Soil only, T2: NPK only, T3: Biochar + NPK, T4: BF	60

LIST OF ABBREVIATIONS

AS	Ammonium sulfate
TSP	Triple superphosphate
MOP	Muriate of potash
BT	Biochar tablets
BF	Fertilizers embedded with biochar tablet
Biochar + NPK	Combination of biochar and NPK without tableting
NPK	Nitrogen, phosphorus and potassium fertilizers
FTIR	Fourier Transform Infrared Spectroscopy
SPAD	Soil plant analysis development
GHG	Greenhouse gases
CO ₂	Carbon dioxide
CO	Carbon monoxide
SOC	Soil organic carbon
CH ₄	Methane
EC	Electrical conductivity
Na	Sodium
S	Sulfur
CEC	Cation exchange capacity
min	Minutes
BD	Bulk density
BET	Brunauer-Emmet-Teller
Fe	Iron
Zn	Zinc
Cu	Copper

Mn	Manganese
Cd	Cadmium
Se	Selenium
NUE	Nutrient use efficiency
NO ₃ ⁻	Nitrate
PO ₄ ³⁻	Phosphate
N ₂ O	Nitrous oxide
EFB	Empty fruit bunch
OPF	Oil palm frond
HCl	Hydrochloric acid
HNO ₃	Nitric acid
KCl	Potassium chloride
MgO	Magnesium oxide
NaHCO ₃	Sodium bicarbonate
NaOH	Sodium hydroxide
ICP-OES	Inductively couple plasma optical emission spectrometer
AAS	Atomic absorption spectrophotometer
AA	Autoanalyzer
K ₂ SO ₄	Potassium sulfate
ANOVA	Analysis of variance
SAS	Statistical analysis system
NH ₄ F	Ammonium fluoride

CHAPTER 1

INTRODUCTION

1.1 Research background

Large amount of agricultural residues such as rice husk, rice straw, green leaves, and rubber tree twigs are generated annually nationwide but they are barely reutilized. Malaysia is one of the Asean countries which largely produces oil palm (*Elaeis guineensis*), rubber (*Hevea brasiliensis*) and rice (*Oryza Sativa*). The growth rate of rubber cultivation in Malaysia is $15 \text{ m}^3 \text{ ha}^{-1} \text{ year}^{-1}$ (Ratnasingam et al., 2015), whereas rice cultivation covers approximately 688,770 ha (Agrofood Statistics, 2016). Approximately, four million tons of rice straw was produced in 2015 and 0.48 million tons of rice husk is produced annually in Malaysia (Shafie et al., 2014). The rubber tree twigs and rice residues generated from rubber pruning and rice production, respectively are commonly left to decompose in situ or burned in the field with consequent negative impact with environment, particularly greenhouse gas (GHG) emissions (Rondon et al., 2007). Therefore, these low cost renewable agricultural residues should be reused and valorized.

An alternative of agricultural residues management is to convert the rice residues and rubber tree twigs to biochar at the same time harvesting the energy (in the form of heat) produced during pyrolysis. Biochar is rich in aromatic carbon (C) which can act as a C sink. Nevertheless, higher ash and lower C content are reported in rice residue biochar compared with biochar derived from other feedstocks at the same pyrolysis conditions (Asadi et al., 2021). Singh et al. (2021) reported that the potential use of rice residue biochar on salinity stress reduction and crop yield improvement. During the charring process, the carboxylic acid and hydroxyl groups are formed on the carbonaceous surface of biochar (Sonkar and Sarkar, 2019). High large surface area during pyrolysis for the reactivity of biochar because it enables them to retain a significant amount of water and nutrients (Saxena et al., 2014; Vaughn et al., 2013). Although lignocellulosic biomass-derived biochar is a good soil amendment, mineral fertilizers are often required to sustain high agricultural yield. Some literature has suggested that biochar mixed with nitrogen (N), phosphorus (P), and potassium (K) to produce NPK fertilizers with bentonite clay as a binding agent increased rice yields by 15%–30% compared with chemical fertilizers applied at 500 kg ha^{-1} (Qian et al., 2014; Joseph et al., 2013). In another study, the N use efficiency of plant increased by biochar-amended from 7% to 261% compared with non-amended soils (Cao et al., 2019). Combination of biochar and fertilizers application can reduce wastage of chemical fertilizers and their accompanied environmental pollution.

Nitrogen is often the most limiting nutrient yet this nutrient is needed by crops in large amount for their growth and development and because of these reasons, N fertilizer is in high demand (Heffer and Prud'homme, 2015). However, excessive use of N fertilizer can lead to loss of N *via* soil ammonia (NH₃) volatilization and runoff and leaching during intense rainfall (Wang et al., 2018; Hou et al., 2018). Excessive N loss decreases nutrient use efficiency (NUE) and yield of crops. There are inconsistent data on the impacts of biochar addition on the soil NH₃ volatilization. Biochar application increased NH₃ volatilization in saline soil, as salt ions constrained NH₃/ammonium (NH₄⁺) adsorption capacity of biochar (Zhu et al., 2020). Higher rates of biochar increased soil NH₃ volatilization (Sun et al., 2017). In contrast, the using 5% biochar significantly reduced NH₃ volatilization in non-saline soils (Mandal et al., 2016). The potential of biochar to decrease NH₃ volatilization depends on its pyrolysis condition, biochar's pH, soil pH, soil moisture content, and soil temperature (Mandal et al., 2018).

However, biochar with high ash and low density makes it difficult in the handling process during soil application, transportation and storage. Husk and Major (2008) reported that approximately 25% of biochar are lost during application in the field. High rainfall can increase the loss of biochar by 20% and 53% through surface runoff (Major et al., 2010). Alternatively, tableting of biochar can impart the dense, uniform and durable properties, which reduce the loss of biochar in agricultural systems to offset the cost of handling, transporting, and storing biochar (Reza et al., 2012). The tableting is an important process by which the density of biomass is significantly increased (Soleimani et al., 2017). Tableting is one of the densification processes and its outcome depends on the initial raw material characteristics and the equipment used. Binder and temperature used for pellets production determine the nutrient release rate of biochar pellets (Kim et al., 2014). Fertilizer-embedded biochar pellets which are dried at 180 °C with increasing lignin content from 10 to 30 wt.% has a slower K and P release than pellets that are dried at 105 °C (Kim et al., 2014).

1.2 Problem statements

Although biochar tablet with embedded fertilizers is deemed as a potential cost-effective slow-release fertilizer in soils, there is lack of information on nutrient release and soil NH₃ volatilization from rice residues mix together rubber tree twigs-derived biochar tablet with embedded NPK fertilizers (BF). Also, there is dearth of information on the effect rates of BF on the growth and NUE of several crops. Several literature reported the effects of co-application biochar and fertilizers on the NUE of plants. Yet the effects of the combination of biochar and fertilizers with and without tableting on nutrient release and NUE are unknown. Therefore, this study was carried out to produce a BF as a more ecologically sound slow-release fertilizer. The biochar derived from thermal decomposition of rice straw, husk, and rubber tree twigs was blended with commercial fertilizers after which underwent with or without tableting process. This novel BF was evaluated for the quality in term of its ability to release nutrient and its effects on

NUE of plants relative to those without tableting and conventional fertilizers. We hypothesized that less voids in the BF is assumed to release the nutrients slowly and lower soil NH_3 volatilization ascribed to the close connection between the biochar particles and fertilizers. Minimal nutrient and NH_3 loss by applying the BF might have improved the soil quality and plant NUE.

1.3 General objectives

The objectives of this study were to determine the nutrient release and soil ammonia volatilization of blended biochar and fertilizer with- and without tableting which eventually impact on the soil chemical characteristics and NUE of sweet corn (test crop).

1.4 Significance of Study

Application of biochar and fertilizers is widely adopted to improve soil quality and plant yield performance but biochar is light density and hence incur much loss of nutrient during the handling and soil application. This study will provide information regarding which blended of biochar and fertilizers into tablet or without tablet is effective on the controlled nutrient release, soil NH_3 volatilization and eventually increases the plant NUE. Such information is valuable in the design of improved fertilizer application strategies. The results of the study will be of great benefit for the farmers to minimize the use of chemical fertilizers by blending fertilizers and biochar into tablet to improve soil quality and crop productivity while reducing negative impact to the environment.

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