



Faculty of Engineering

**Synthesis of Tapioca Starch/Palm Oil Encapsulated Urea-Impregnated
Peppercorn Biochar Controlled-Release Fertilizer for Soil Amendment**

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Synthesis of Tapioca Starch/Palm Oil Encapsulated Urea-Impregnated Peppercorn Biochar Controlled-Release Fertilizer for Soil Amendment

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

The slow-release property of biochar-based fertilizer is still facing limitation and it can be overcome by integrating encapsulating technology and biochar-based fertilizer. Starch has been introduced as an encapsulating material due to its low-cost and biodegradable nature, but the slow-release property is limited by its hydrophilicity. Hence, this study aimed to formulate the tapioca starch/PO encapsulated urea-impregnated peppercorn waste derived biochar controlled-fertilizer pellet (EUIB pellet), followed by investigation of the effect of EUIB pellet on the nitrogen release rate and kinetic, nitrogen leaching, water retention and okra plant growth. The CCD was utilized to investigate the effect of pyrolysis temperature, residence time and urea:biochar ratio on the nitrogen content. The optimum condition to synthesize urea-impregnated peppercorn derived biochar-based fertilizer powder (UIB powder) was 400 °C pyrolysis temperature, 120 minutes residence time and 0.6 urea:biochar ratio which resulted in a nitrogen content of 16.07%. The acidic surface functional groups and hydrophilicity decreased with increasing pyrolysis temperature. In contrast, the changes of acidic surface functional group and hydrophilicity were insignificant when residence time increased. The biofilm formulated using 8g of tapioca starch and 0.12 μ L showed the lowest water absorption ability and was employed to encapsulate the urea-impregnated biochar-based. The EUIB pellet had the greater crushing strength than urea-impregnated peppercorn derived biochar-based fertilizer pellet (UIB pellet). The UIB and EUIB pellets achieved complete nitrogen release after 90 minutes and 330 minutes, respectively. The Korsmeyer-Peppas model best described the nitrogen release mechanism of UIB and EUIB pellets. The enhancement of water retention ratio of UIB and EUIB pellets were more significant in the sandy-textural soil than clayey-textural soil. The nitrogen content of pure urea and UIB pellet was completely leached from the sand after two and three leaching activities while the

nitrogen of EUIB pellet was completely leached from the sand after five leaching activities. The EUIB pellet has enhanced the shoot length, root length, number of leaves, area of leaves, wet weight and dry weight of the okra plant as compared to UIB pellet, pure urea and control experiment. In conclusion, the EUIB pellet formulated in this study has the potential to be utilized as a slow/controlled-release fertilizer for soil amendment.

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Keywords: Peppercorn waste biochar; tapioca starch/palm oil biofilm; slow/controlled-release fertilizer; leaching; water retention

**Sintesis Kanji Ubi Kayu/Minyak Sawit Terkapsul Urea Diresapi Lada Biochar Baja
Pelepasan Terkawal untuk Pindaan Tanah**

ABSTRAK

Sifat pelepasan lambat bagi baja berasaskan biochar masih terbatas dan ia boleh diatasi dengan menyepadukan teknologi pembungkusan dan baja berasaskan biochar. Kanji telah diperkenalkan sebagai bahan pembungkus kerana sifat kos rendah dan boleh terbiodegradasi, tetapi sifat pelepasan perlahan dihadkan oleh hidrofiliknya. Oleh itu, kajian ini bertujuan untuk merumuskan kanji ubi kayu/PO terkapsul urea-impregnated lada jagung yang diperolehi pelet baja terkawal biochar (EUIB pellet), diikuti dengan penyiasatan kesan pelet EUIB ke atas kadar pelepasan nitrogen dan kinetik, larut lesap nitrogen, air, pengekal dan pertumbuhan pokok bendi. CCD digunakan untuk menyiasat kesan suhu pirolisis, masa tinggal dan nisbah urea:biochar ke atas kandungan nitrogen. Keadaan optimum untuk mensintesis serbuk baja berasaskan biochar (serbuk UIB) yang diresapi urea biji lada adalah suhu pirolisis 400 °C, masa tinggal 120 minit dan nisbah 0.6 urea:biochar yang menghasilkan kandungan nitrogen sebanyak 16.07%. Kumpulan berfungsi permukaan berasid dan hidrofilik menurun dengan peningkatan suhu pirolisis. Sebaliknya, perubahan kumpulan berfungsi permukaan berasid dan hidrofilik adalah tidak penting apabila masa tinggal meningkat. Biofilem yang dirumus menggunakan 8g kanji ubi kayu dan 0.12 µL menunjukkan keupayaan penyerapan air yang paling rendah dan digunakan untuk membungkus berasaskan biochar yang diresapi urea. Pelet EUIB mempunyai kekuatan penghancuran yang lebih besar daripada pelet baja berasaskan biochar (pelet UIB) biji lada yang diresapi urea. Pelet UIB dan EUIB mencapai pelepasan nitrogen lengkap selepas 90 minit dan 330 minit, masing-masing. Model Korsmeyer-Peppas menggambarkan mekanisme pelepasan nitrogen bagi pelet UIB dan EUIB. Peningkatan

nisbah pengekalan air bagi pelet UIB dan EUIB adalah lebih ketara dalam tanah bertekstur berpasir berbanding tanah bertekstur liat. Kandungan nitrogen urea tulen dan pelet UIB telah larut lesap sepenuhnya daripada pasir selepas dua dan tiga aktiviti larut lesap manakala nitrogen bagi pelet EUIB terlarut sepenuhnya daripada pasir selepas lima aktiviti larut lesap. Pelet EUIB telah meningkatkan panjang pucuk, panjang akar, bilangan daun, luas daun, berat basah dan berat kering pokok bendi berbanding pelet UIB, urea tulen dan eksperimen kawalan. Kesimpulannya, pelet EUIB yang dirumus dalam kajian ini berpotensi untuk digunakan sebagai baja pelepasan perlahan/terkawal untuk pindaan tanah. .

Kata kunci: *Biochar sisa lada; biofilem kanji ubi kayu/minyak sawit; baja perlahan/pelepasan terkawal; larut lesap; pengekalan air*

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LIST OF ABBREVIATIONS

AAc	Acrylic acid
Aam	Acrylamide
APS	Ammonium persulfate
BCN	Corn cob biochar impregnated with nutrient
BCRNF	Biochar/bentonite/PVA/urea
CCD	Central composite design
CEC	Cation exchange capacity
DAP	Diammonium phosphate
EC	Electrical conductivity
EUIB	Tapioca starch/PO encapsulated urea-impregnated peppercorn waste derived biochar controlled-release fertilizer
IPDI	Isophoronediiisocyanate
KPS	Potassium persulfate
MAP	Monoammonium phosphate
MBA	N,N'-Methylenebiscarylamide
MMt	Montmorillonite
NUE	Nutrient Use Efficiency
PHG-g-CNT/urea	Polymer hydrogel-g-natural cotton ball microfiber/urea
PLB	Poultry litter biochar
PMDI	Polymethylenediisocyanate
PO	Palm oil
PVA	Polyvinyl alcohol
PVP	Polyvinylpyrrolidone

RSE	Relative standard error
Si-PU	Poldimethylsiloxane-polyurethane
TDI	2,6-diisocuanatotoluene
TSP	Triple superphosphate
UIB	Urea-impregnated peppercorn waste derived biochar fertilizer

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Soil fertility often refers to the ability of soil to support the growth of agricultural plants. Typically, soil fertility is governed by the physical, biological and chemical properties of the soil (Igalavithana et al., 2017). Low soil fertility is a major concern in most of the region around the world. For instance, the soil from the arid and semi-arid regions usually has very low water retention capacity and nutrient contents (Khalifa & Yousef, 2015). Anthropogenic activities such as agricultural practices and rapid industrialization may lead to low soil fertility by degrading the soil. Climate change has also resulted in low fertility soil. Degradation of soil could affect the soil quality such as nutrient depletion, salinization and reduce the water retention capacity which restrict the food production. According to the United Nation Food and Agriculture Organization (FAO, 2011) and El-Naggar et al. (2019), 25% of the global agricultural land is classified as highly degraded, 44% is moderately degraded and around 10% is recovered from degradation. Improvement of water retention in the soil could enhance the plant available water content in the soil for the plant growth during drought season. Additionally, it also reduces the water surface run-off which can retain nutrient from leaching (Zheng et al., 2013). Low available nutrient content and water retention in low fertility soil are the main challenges faced by agricultural sector as these factors could reduce the crop production as well as increase the frequency of the irrigation and decrease the fertilizer efficiency. Organic and inorganic fertilizers are widely used to improve soil quality, however long-term use of inorganic fertilizers for soil fertility and crop yield could affect the environment while organic fertilizers mineralize rapidly and need to

be replenished frequently to support the plant growth (Syuhada et al., 2016; Oladele et al., 2019). Besides, excessive fertilizer application causes air and groundwater pollution through leaching and volatilization, thus it reduces the nutrient use efficiency by the crops and limits the growth performance.

The rapid population and industrial growth in Malaysia over the years have gradually increased the generation of solid waste. Among the various industries, the agricultural sector is one of the largest contributors of solid waste. The rapid expansion of the agricultural industry has affected the environment with abundant of the solid waste. According to Fadzil & Othman (2021), 998 million tonnes of agricultural waste were generated per year globally and about 15% of the total waste produced in Asia consisted of agricultural waste. Moreover, it has been reported that about 0.122 kg/cap/day of agricultural waste is produced in Malaysia, and the generation of the agricultural waste has been predicted to increase to 0.210 kg/cap/day by 2025 (Fadzil & Othman, 2021). Pepper waste is one of the agricultural wastes abundantly produced from the pepper plantation and pepper production industry which needs to be properly managed. The disposal of the accumulated pepper waste by open burning would cause environmental pollution (Holilah et al., 2021).

Several technologies have been used to reduce the agricultural solid waste which include landfill, thermal, thermochemical and biochemical methods. The biochemical method consists of composting, anaerobic digestion and fermentation; thermal method consists of incineration whereas thermochemical method includes combustion, pyrolysis and gasification. Conventionally, landfilling is the most common practice to manage the solid waste, yet it requires a high capacity of space. It has been reported that 40 hectare of land area is required for landfilling (Owusu-Nimo et al., 2019). Furthermore, it also contributes

to pollution hazards and discomfort due to emission of bad odour (Sonibare et al., 2019). On the other hand, incineration of solid waste also causes negative impacts on the environment as it generates airborne pollutants such as nitrogen oxide and sulphur oxide. These airborne pollutants result in acid rain and particulate matter, thus incineration method has been restricted by the Department of Environment (Lahijani & Zainal, 2011; Baharuddin et al., 2010; Bakar et al., 2011). The biochemical method such as composting has been widely used to reduce the solid waste as it can minimize the negative impacts on the environment by reducing the greenhouse gases emission. However, aerobic composting requires a longer reaction time to degrade the solid waste compared to other methods, which is one of the disadvantages.

Recently, pyrolysis has gained more attention as it is one of the promising methods for converting solid waste into three valuable products which are biochar, syngas and bio-oil (Hameed et al., 2019). Biochar possesses various applications including for soil fertility improvement, acts as an adsorbent to remove pollutant in wastewater treatment as well as acting as fuel source for power generation (Tripathi et al., 2016; El-naggar et al., 2019; Agegnehu et al., 2017). Among the conversion technologies, thermochemical conversion is preferred, as it does not any pre-treatment and require long reaction time (Stöcker, in press; Sutejo et al., 2022). As compared to other thermochemical methods, pyrolysis has more advantages as it is more flexible with either feedstock type or operating condition. Furthermore, pyrolysis process retards the emission of harmful gases (Tripathi et al., 2016). Thus, pyrolysis is the best option selected to convert biomass to biochar.

Biochar has been used for soil amendment in agriculture to improve the soil fertility. Moreover, the application of biochar onto the soil also serves as a tool for climate change

mitigation through carbon sequestration. Shen et al. (2017) stated that biochar application reduced the CO₂ emission and promoted crop yield in semiarid soil. Furthermore, adding biochar in soil could also enhance the CEC, pH level, plant available water content, bulk density and porosity of the soil (Geng et al., 2022; Sadowska et al., 2023; Alkharabasheh et al., 2021). Simiele et al. (2022) reported that the application of biochar increased the overall plant growth. Moreover, Ye et al. (2019) observed that the increment of the plant growth was not significant when high application rate of biochar was applied. Despite the application of biochar has been proven to improve the soil properties and plant growth, high dosage of biochar application into the soil is not agronomically and economically feasible as the nutrient content especially macronutrients such as nitrogen, phosphorus and potassium present in the biochar are not sufficient for plant growth (Liu et al., 2019b). Thus, modification of biochar is necessary. Due to the unique properties of the biochar such as high surface area and diverse functional group, biochar can be used as a nutrient carrier by impregnating the nutrient into the biochar matrix (Sashidhar et al., 2020). The nutrient-loaded biochar not only improves the soil properties, but it also increases the nutrient use efficiency by the plants as well as reducing the nutrient loss. Ndoung et al. (2021) also observed that biochar-based fertilizer was more effective in improving the crop yields as relative to pristine biochar and conventional fertilizer. Schmidth et al. (2017) and Hagemann et al. (2017) demonstrated that nutrient loaded biochar with low application rate was able to enhance the crop yield as compared to high application rate of pristine biochar. The slow-release mechanism property of biochar-based fertilizer still has certain limitations for the plant growth, and therefore an in-depth study is needed to overcome the limitations. Integration of encapsulating material and biochar-based fertilizer is therefore introduced as

one of the novel methods to improve the slow-release mechanism of the biochar-based fertilizer.

1.2 Problem Statement

The disposal of huge amounts of peppercorn waste generated during the pepper plantation and processing by open burning could cause environmental pollution. The conversion of peppercorn waste into biochar is a sustainable waste management practice as biochar can be used as a soil amendment to alleviate the soil properties. Recently, biochar has been used as a nutrient carrier to synthesize fertilizer as it can enhance the nutrient use efficiency by the crops. Biochar-based fertilizer exhibits slow-release property, but the slow-release property still needs to be improved as it is restricted by the weak van der Waals bonding, hydrogen bonding and intermolecular force (An et al., 2021a; Wang et al., 2021b). The integration of encapsulating technology and biochar-based fertilizer has been proven to enhance the slow-release property (An et al., 2021a), but the release performance of the encapsulated biochar-based fertilizer is influenced by the formulation of the encapsulating materials. Bio-based encapsulating materials such as biopolymer, superabsorbent (combination of organic and inorganic/pure natural) and bio-based polyurethane have been used to replace pure synthetic polymers due to their biodegradability. The drawback of preparation methods of superabsorbent and bio-based polyurethane as encapsulating materials is costly (An et al., 2021a). Additionally, the diisocyanate used in the synthesis of bio-based polyurethane is toxic (Lu et al., 2022). Meanwhile, biopolymer such as starch has been widely used as an encapsulating material due to its biodegradability, non-toxic nature and low cost. However, the high hydrophilicity of starch has restricted its application in slow-release fertilizer (Fertahi et al., 2021). To alleviate these issues, this study therefore aimed to explore the feasibility of blending the tapioca starch with green additives such as

palm oil to enhance its hydrophobicity and applied it as an encapsulating material to formulate a low cost and environmentally friendly peppercorn waste-based encapsulated urea-impregnated biochar as a controlled-release fertilizer.

1.3 Research Objectives

- i. To synthesize urea-impregnated peppercorn waste derived biochar with high nitrogen content by varying the pyrolysis temperature, residence time and urea:biochar ratio,
- ii. To formulate tapioca starch/PO biofilm encapsulated urea-impregnated biochar controlled-release fertilizer,
- iii. To investigate the effect of encapsulated urea-impregnated biochar controlled-release fertilizer on nitrogen release rate in water, release kinetic, nitrogen leaching, water retention and plant growth.

1.4 Research Gap

The studies on the effect of synthesis conditions on the urea retention capacity using impregnation followed by direct heating method have been very limited as most of the studies only focused on single variable or chemical treatment/modification to synthesize biochar. Besides, peppercorn waste has not been investigated as the precursor for preparing of biochar. To date, no study has investigated the optimization study of the nitrogen content of urea-impregnated biochar derived from peppercorn waste using response surface methodology (RSM). Starch-based encapsulating material blended with bentonite, nano-silica and eggshell as additives has been used as an encapsulating material to synthesize slow-release fertilizer with enhanced hydrophobicity, however, none has reported on

blending tapioca starch and palm oil biofilm to be utilized as an encapsulating material in synthesizing slow-release fertilizer. Since much fundamental knowledge on tapioca starch/PO biofilm encapsulated urea-impregnated biochar controlled-release fertilizer still remains unknown, a systematic in-depth study on the effect of the application of the formulated fertilizer on the nutrient release rate, water retention, nutrient leaching, plant growth and their release kinetic mechanisms is crucial to be explored.

1.5 Hypothesis

The nitrogen content of urea-impregnated peppercorn waste derived biochar is influenced by the synthesis condition. The tapioca starch/PO biofilm encapsulated urea-impregnated biochar controlled-release fertilizer with low water absorption capacity could be formulated by regulating the amount of starch and PO concentration. The application of the formulated encapsulated urea-impregnated biochar controlled-release fertilizer would improve the nutrient release rate, water retention, nutrient leaching and plant growth.

1.6 Research Questions

- i. What is the optimum condition to synthesize urea-impregnated peppercorn waste derived biochar-based fertilizer with high nitrogen content?
- ii. How to formulate tapioca starch/PO encapsulated urea-impregnated biochar-controlled-release fertilizer?
- iii. How does tapioca starch/PO encapsulated urea-impregnated biochar controlled-release fertilizer affect the nitrogen release rate, release kinetic, nitrogen leaching, water retention and plant growth?

1.7 Scope of Study

This research intended to synthesize biochar using pepper waste as feedstock. Besides, this study also investigated the synthesis conditions to synthesize urea-impregnated biochar-based fertilizer with high nitrogen content by varying the pyrolysis temperature, residence time and urea:biochar ratio. The characteristics such as pH, EC level, elemental composition, surface morphology and surface chemistry of the peppercorn waste-based biochar and UIB powder were studied. The biofilm was formulated with the lowest absorption capacity through water absorption analysis and the surface chemistry of the biofilms (8g of pristine starch and 8g and 0.12 μ L of tapioca starch/PO only) were also studied. The biofilm with the lowest water absorption ability was selected as the encapsulating material for coating the UIB pellet. The synthesized UIB and EUIB pellets were then characterized for their surface morphology, surface chemistry, elemental composition (before and after nitrogen release in water) and crushing strength. The nitrogen release rate in water, nitrogen leaching in sand and water retention in sandy and clayey-textural soil were conducted to study the performance of the EUIB pellet. Moreover, the zero order, first order, Higuchi and Korsmeyer-Peppas kinetic models were applied to evaluate the release mechanism of the EUIB pellet. Lastly, the effect of EUIB pellet on the growth performance of the okra plant was determined. The shoot length, root length, number of leaves, leaf area as well as wet and dry weight of the okra plant were measured. The okra plant was planted in a sandy-textural soil and 100 ml of water (controlled condition) was used to irrigate the okra plant.

CHAPTER 2

LITERATURE REVIEW

2.1 Agricultural Wastes

According to United Nation Development Programme (UNDP), 821 million of people have suffered from hunger and malnutrition, with Asia region accounted 63%. To overcome this global issue, Malaysia has collaborated with other countries to establish Sustainable Development Goal (SDG2) to end hunger, achieve food security, improve nutrition and promote sustainable agriculture by 2030. Focus has therefore been given to the agriculture and agro-food sectors, with billions of Ringgit spent on fertilizer subsidy mainly to increase crop productivity and ensure food security. The rapid growth of the agriculture sector generates abundant of solid waste which faces waste disposal problem. It has been reported that about 0.122 kg/cap/day of agricultural waste is produced in Malaysia and is predicted to increase to 0.210 kg/cap/day by 2025. Improper management of the agricultural waste leads to various adverse environmental issues (Koul et al., 2022). Therefore, a suitable remedy is imperative to decrease the volume of agricultural waste in order to conserve the environment. Malaysia is the fifth largest producer of pepper in the world with 23500 metric tonnes of pepper production (Izzah & Wan Asrina, 2019). Due to pepper's is a perennial crop that can be grown and harvested throughout the year, the abundant quantity of waste it produces necessitates proper management (Holilah et al., 2021). The world production of black pepper was 432,607 metric tonnes in 2021 (International Pepper Community, 2021). It was estimated that 6,575.63 metric tonnes of black pepper waste were generated (Bosa et al., 2021; Izzah & Wan Asrina, 2019). Unfortunately, the practice of disposing accumulated

damaged or undeveloped peppercorn (peppercorn waste) through open burning has significant detrimental effect on the environment.

2.2 Solid Waste Treatment Technologies

There are several technologies which can be used to reduce the vast amount of solid waste, which include landfill, thermochemical and biochemical methods. Thermochemical method utilizes heat and chemical catalyst to generate energy from the biomass. The thermochemical method can be classified into four types of technique/process which are combustion, gasification, torrefaction and pyrolysis. Combustion is a process in which the biomass is directly burnt under the presence of oxygen or air, and results in the chemical energy stored in the biomass which is converted into thermal energy (Elkhalifa et al., 2019; McKendry, 2002; Tripathi et al., 2016). The combustion process of the biomass takes place within the temperature range of 800 °C to 1000 °C. This process can be applied to any type of biomass, however, the feasibility of the combustion process is affected by available moisture content in the biomass. Gasification process converts the carbonaceous contents of different type of biomass into gaseous fuel under the presence of oxidizing agent such as oxygen, air, nitrogen, carbon dioxide, steam or a consolidation of these gases at a raised temperature between 700 °C to 900 °C (Tripathi et al., 2016; Elkhalifa et al., 2019). Torrefaction is achieved by slow heating of the biomass under the inert condition at a relatively low temperature of 200 °C to 300 °C, causing decomposition and devolatilization reactions to occur. It is also known as mild pyrolysis. Pyrolysis is another thermochemical process which thermally degrades the biomass under low oxygen or absence of oxygen atmosphere with temperature ranging from 350 °C to 1200 °C. Pyrolysis offers less pollution and converts biomass into three useful products which are biochar, bio-oil and syngas.

Besides, pyrolysis can be optimized to produce desired products as compared to other thermochemical processes (Tripathi et al., 2016).

2.3 Biochar

Biochar is a material with a high carbon content that can be synthesized through thermochemical treatment of organic materials under the absence of oxygen condition (Banitalebi et al., 2019). Animal manure, sludges, food waste, green waste and agricultural waste can be utilized as biochar precursors (Abrishamkesh et al., 2015). Biochar has been recognized as a promising organic material for soil amendment to improve fertility of soil. Some studies demonstrated that biochar had potential to enhance the pH, CEC, nutrient retention, water retention, bulk density and porosity of the soil (Bayu et al., 2016; Nyambo et al., 2018; Han et al., 2019; Bohara et al., 2019). The physical, chemical as well as biological properties of biochar are highly variable, which are determined by the origin of feedstock and the biochar synthesis condition.

2.4 Factors Affecting Biochar Yield and Characteristic

In pyrolysis, the reaction condition and process parameters play an important role as the biochar produced from the pyrolysis is influenced by certain process parameters, which include temperature, retention time and heating rate. Manipulation of the operating condition can be used to control the char yield and quality of the pyrolysis products.

2.4.1 Feedstock

The origin of feedstock plays an important role in determining the biochar characteristics. The physical structure as well as the elemental composition of the original biomass are reflected on the outcome of the final products (Kloss et al., 2012). Biochar can be generated from different organic biomass such as manure (Tomczyk et al., 2020),

agricultural waste including wheat straw, peanut shell, sweet potato, corn (Sun et al., 2016), wood biomass (Kloss et al., 2012), switchgrass (Ashworth et al., 2014) and biosolid (Yang et al., 2018). The composition of the biomass such as hemicellulose, cellulose, lignin, extractive and minerals are differing widely with the type of biomass (Mohan et al., 2006). For instance, biomass with low content of lignin will produce less biochar than the biomass with a high content of lignin. Besides that, the elemental composition of the biochar after pyrolysis highly depends on the raw feedstock. Wang et al. (2015) reported the biochar derived from woody biomass had high carbon content and low ash content, In contrast, Feola Conz et al. (2017), Yang et al. (2018) and Wang et al. (2015) verified that biochar derived from biomass such as switchgrass and alfalfa, poultry manure and biosolid had low carbon content but had much greater ash content and nutrient content (nitrogen, phosphorus, potassium and sulfur) than biochar derived from woody biomass. Besides that, wood-derived biochar had higher surface area and pore volume than biochar derived from manure and herbaceous biomass. This was due to the degradation of the lignin and hemicellulose content and formation of channel structure and vascular bundle in the woody biomass. The physical and chemical properties of the biochar are associated with water retention, nutrient retention and pollutant removal and these properties can affect the properties of the soil. According to Weil et al. (2020), peppercorn biomass consists of 9% cellulose, 4% lignin and 3% hemicellulose. Peppercorn biomass is usually disposed by open burning which causes air pollution. Pepper stem biomass has been utilized as a feedstock to produce biochar (Liu et al., 2021). The utilization of peppercorn biomass to produce biochar is a sustainable waste management solution which is still scarcely reported in the literature.

2.4.2 Pyrolysis Temperature

Many studies have revealed that pyrolysis temperature could impact the biochar yield as well as the characteristic of the biochar. Increasing the temperature in pyrolysis causes a decrease in biochar yield. This is because increase the pyrolysis temperature allows thermal cracking of heavy hydrocarbon, thus results in increased liquid and gaseous and decreased biochar yield. Zhao et al. (2018) reported that an increase in pyrolysis temperature from 300 °C to 700 °C caused a reduction of approximately 60% in the biochar yield for rapeseed stem. Sun et al. (2017) verified that the pH level of different biochar was greatly increased at pyrolysis temperature of 300 °C to 400 °C and then began to slow down with a further increase in pyrolysis temperature. Southavong et al. (2018) also reported the pH level of rice straw biochar increased from 8.69 to 10.18 when pyrolysis temperature was elevated from 300 °C to 600 °C. This was probably due to the formation of the ash-containing alkaline material such as carbonates compound (CaCO_3 and MgCO_3), inorganic alkalis such as K, Na, Ca and Mg as well as the concomitant decrease in acidic functional groups (-COOH and -OH).

CEC is a crucial property of biochar as it indicates the capacity to absorb water and cation nutrient. A study conducted by Claoston et al. (2014) reported that the CEC decreased from 10.80 cmol kg^{-1} and 21.50 cmol kg^{-1} to 8.35 cmol kg^{-1} and 12.03 cmol kg^{-1} for rice husk biochar and empty fruit bunches biochar, respectively when the pyrolysis temperature was increased from 350 °C to 650 °C. Yang et al. (2018) found that the ash content increased with increased pyrolysis temperature. Furthermore, Zhao et al. (2018) showed that the volatile matter decreased with elevated temperature. Several studies (Zhao et al., 2017; Southavong et al., 2018; Rafiq et al., 2016) reported a reduction of oxygen and hydrogen content in biochar with increasing the pyrolysis temperature whereas carbon content in

biochar increased as pyrolysis temperature rose. The H/C ratio indicates the stability of biochar whereas O/C ratio indicates the polarity as well as the abundance of polar oxygen-containing functional groups in the biochar (Bai et al., 2017). High O/C ratio can increase the CEC, hence facilitates nutrient retention (Bai et al., 2017).

Some studies claimed that pyrolysis temperature showed significant effects on surface area and pore development in the biochar during pyrolysis. Wang et al. (2018) verified that when the temperature in pyrolysis rose from 300 °C to 750 °C, the surface area, total pore volume, and microporous pore volume were all increased. This was due to the degradation of the organic matter such as hemicelluloses, cellulose and lignin and inorganic matter as well as reduction of carbonyl and phenolic functional groups (Zhao et al., 2017; Yang et al., 2018; Bai et al., 2017). Nevertheless, according to Angin and Sensor (2014) reported that if pyrolysis temperature was too high, the surface area and pore volume will be decreased. This was due to shrinkage of biochar and realignment of biochar structure caused by sintering effect.

2.4.3 Residence Time and Heating Rate

Residence time and heating rate in pyrolysis have slight impacts on biochar characteristic and biochar yield. Both factors decrease the biochar yield with increased retention time and heating rate in pyrolysis. Zhao et al. (2018) demonstrated that the effect of residence time had less impact on biochar yield compared to pyrolysis temperature. Agrafioti et al. (2013) stated that increase in residence time did not significantly influence the sewage sludge biochar yield. On the other hand, Aysu & Küçük (2014) reported that the increase in heating rate from 15 °C/minute to 50 °C/minute increased the biochar yield. High heating rate improved the depolymerization process and assisted in the secondary reaction

to form gaseous component which led to low biochar yield. Zhao et al. (2018) verified that the surface area of biochar increased with increasing residence time from 10 minutes to 60 minutes, but decreased with further prolonged residence time (100 minutes) whereas the surface area increased with increasing heating rate from 1 °C/minute to 20 °C/minute. Rafiq et al. (2016) stated that prolonged residence time could shift the micropore to mesopore and macropore.

2.5 Effect of Biochar on Soil Properties and Plant Growth

This section presents and discusses the effect of pristine biochar on the physical and chemical properties of the soil as well as plant growth.

2.5.1 Bulk Density and Porosity

Biochar has a significant influence on the physical and hydrological properties of the soil as it affects the plant growth by changing the root penetration as well as plant available water content in the soil. The reduction of the bulk density of the soil is important as it improves the porosity and aggregation of the soil for root elongation. Generally, the bulk density of the biochar is lower than the bulk density of the soil. The bulk density of the biochar is $< 0.6 \text{ g/cm}^3$ whereas the bulk density of the soil is about 1.25 g cm^{-3} . Therefore, addition of biochar probably decreases the bulk density of the soil through dilution effect (Baiamonte et al., 2019; Faloye et al., 2019). The biochar application decreases the bulk density in fine-textural soil and course-textural soil. Xiao et al. (2016) found that low application rate which was $< 10 \text{ Mg/ha}$ had no effect on the bulk density of the clay loam soil. de Jesus Duarte et al. (2019) verified that biochar with small particle size ($< 0.15 \text{ mm}$) amended with soil could increase the bulk density in either sand soils or loamy soils. The

soil porosity and bulk density were inversely proportional to each other. The reduction of bulk density of the soil resulted in an increase in soil porosity.

2.5.2 Saturated Hydraulic Conductivity

Soil hydraulic conductivity is an important parameter as it impacts and controls the partitioning of precipitation between groundwater recharge and surface runoff, plant water uptake as well as plant growth (Jarvis et al., 2013). Saturated hydraulic conductivity can be defined as the degree of resistance of the soil particle when water flows through the saturated porous media (Kumar & Mittal, 2008). Increasing in saturated hydraulic conductivity (K_{sat}) indicates the fluid allows to flow through the soil pores whereas decreasing in saturated hydraulic conductivity would result in restriction of fluid flows through the soil pores. Low saturated hydraulic conductivity contributes to the surface runoff which reduces the available water in deeper soil for plant growth (Fischer et al., 2019). However, low saturated hydraulic conductivity can assist in water retention and prevent nutrient from leaching (Fischer et al., 2019; Devereux et al., 2013). Barnes et al. (2014) found that the changes of the saturated hydraulic conductivity depended on the soil texture and biochar properties.

2.5.3 pH

The application of biochar into the soil could improve the soil pH level, but the changes in the pH level depend on two factors which are the liming effect (biochar type) and the type of soil (acidic soil or alkaline soil). The liming effect of biochar is related to its high base cation such as K, Ca and Mg, carbonates alkaline, Al and H (Nyambo et al., 2018; Mensah & Frimpong, 2018; Nigussie et al., 2012; Tian et al., 2018). In general, low pH in the soil usually restrains the plant growth. Cornelissen et al. (2018) observed that application of alkaline biochar into acidic soil could neutralize the pH level in the soil which

consequently increased the soil pH level. In contrast to alkaline soil, the liming effect could have adverse effect (Albuquerque et al., 2014). Liu and Zhang (2012) mentioned that the pH level of the alkaline soil decreased with the application of low pH biochar.

2.5.4 Nutrient Content

Minerals play an important role in plant growth. Minerals content such as N, P, K, S, Ca, Mg, Mn, Fe and Zn are required for the plant growth. The improvement of soil nutrient and nutrient use efficiency can be enhanced through improved nutrient retention and the addition of nutrients contained in the biochar. Gao et al. (2018) reported that application of biochar in the soil increased the available nutrient in the soil (N, P and K). Manolikaki & Diamadopoulos (2019) and You et al. (2019) also observed that the addition of wood, manure, poultry litter and biochar in soil showed positive effect on the soil nutrient content. Basically, the extent of the increment of the nutrient contents and the ability to retain nutrient in the soil depends on the type of biochar. Firdaus & Abdul (2017) observed that the nutrient content of two biochar (empty fruit brunch and rice husk) produced at fixed temperature were varied with each other. Both types of biochar improved the nutrient content in the soil, but empty fruit brunches derived biochar increased nutrient content (phosphorus, potassium, calcium and magnesium) in the soil more significantly than rice husk derived biochar. Furthermore, Yao et al. (2012) found that addition of biochar reduced the leaching of nutrient content.

2.5.5 Plant Growth

Plant growth and nutrient uptake are also influenced by the addition of biochar. As reported by Nigussie et al. (2012), the application of maize stalk biochar enhanced the plant nutrient uptake of N, P and K content in polluted soil and unpolluted soils. Wang et al. (2018)

also observed that the enhancement of plant growth was due to addition of bamboo biochar provide large amounts of potassium and molybdenum to the soil. Albuquerque et al. (2014) reported that olive tree prunings and wheat straw biochar enhanced the overall plant growth while pine wood biochar, olive stone biochar and almond shell biochar did not show any significant effect on the plant growth. Taherymoosavi et al. (2018) proposed that mixed feedstock increased the nutrient content of the biochar (a combination of wheat straw and basalt powder) and had potential to improve the plant growth compared to single feedstock. Mensah and Frimpong (2018) also reported that the combination of compost and biochar increased the maize growth. Besides, Wang et al. (2022a) mentioned that biochar itself did not have enough fertilizing elements for plant growth. Moreover, applying a high application rate of biochar was found to be impractical from both agronomic and economic perspectives, thus resulted in low profit gained for farmers. Hence, modification of biochar is required in order to meet the desired performance in soil.

2.6 Categorization of Slow/Controlled-release Fertilizer

In the past decade, there has been significant exploration and advancement in the development of various formulations of slow/controlled-release fertilizers. The categorization of these fertilizer is based on the method of synthesis and the material used for the encapsulation or coating. The encapsulation or coating material serves as a physical barrier, regulating the release of the nutrients from the fertilizer (Bley et al., 2017). Generally, slow/controlled release fertilizers (matrix/carrier or coated type) can be classified into three categories which are inorganic mineral-based, polymer-based, and superabsorbent-based fertilizer.

2.6.1 Inorganic Mineral-based Fertilizer

In the formulation of controlled-release fertilizer, coating or encapsulation materials like sulfur, zeolite, gypsum, dolomite, diatomite and bentonite, which are inorganic minerals, are frequently used (Dubey & Mailapalli, 2019). Among these, pure sulfur has been traditionally employed as a coating/encapsulation material in the production of controlled-release fertilizer due to its ability to reduce the solubility of the conventional fertilizers. The impact of atomizing air, spouting air temperature and liquified sulfur flow rates on the nutrient release rate was investigated by Ayub et al. (2001). The authors discovered the nutrient release rate of sulfur-coated fertilizer was affected by the spouting air temperature, while no significant effect was observed when varying the atomizing air. Urea dissolution rates of 100% and 95.61% was achieved at spouting air temperatures of 69 °C and 82.5 °C, respectively, along with atomizing air flow rates of 1.0 and 1.4 m³/h. The quality of the sulfur coating varied with different spouting air temperatures, the sulfur droplet solidified before coating the urea, while at high spouting air temperature, a uniform film coating was observed. Although the sulfur coating could extend the release of nutrients, it tended to crack easily due to its brittleness. In order to overcome this issue, modification of sulfur and sealant are usually employed to enhance the quality of the coating. Liu et al. (2008) conducted a study where the authors utilized dicyclopentadiene (DCPD), an organic resin, to enhance the sulfur coating. The results indicated that the incorporation of the DCPD into the sulfur coating led to improvements in mechanical strength, resistance of moisture and abrasive resistance. The study reported that the release rate of urea from modified sulfur -coated fertilizer was 53.5% after 28 days, whereas the pure sulfur-coated fertilizer achieved a release rate of 82.9% after 7 days.

According to Mehmood et al. (2019), the incorporation of sulfur in combination with gypsum, starch or bentonite as coating/encapsulation materials resulted in a decrease in the urea release rate. The study demonstrated that sulfur/gypsum-coated urea exhibited a lower urea release rate compared to sulfur/bentonite and sulfur/starch-coated urea. The higher urea release rate observed in sulfur/starch-coated urea was attributed to the hydrophilic nature of starch, while the sulfur/bentonite-coated urea displayed uneven coating, leading to inconsistent release. Furthermore, increasing the amount of binder in sulfur/gypsum-coated urea was found to reduce the urea release rate. Another study by Dubey & Mailapalli (2019) studied the impact of different binders on the ammonium release rate of zeolite-coated urea. The authors revealed that uncoated urea exhibited the highest ammonium release rate compared to zeolite-coated urea with various binders. Moreover, the use of different binders on zeolite-coated urea resulted in varying release rates. Among the binders tested, the zeolite-coated urea with acrylic polymer demonstrated the lowest ammonium release rate compared to the other binders. Moreover, all zeolite-coated urea with binder possessed higher crushing strength as compared to the zeolite-coated urea without a binder.

2.6.2 Biopolymer-based Fertilizer

Sulfur coating/encapsulation material suffers from certain limitations as highlighted by Zhang & Yang (2021a). One major drawback is the sulfur film formed on the fertilizer granules' surface is fragile, making it susceptible to the formation of pores and cracks. Moreover, the sulfur film is also prone to disruption by soil bacteria. Furthermore, the production of sulfur-coated fertilizer requires expensive conditioners and sealants to improve the quality of coating, thereby increased the production costs (Behin & Sadeghi, 2016). Another concern associated with sulfur coating/encapsulating material with sulfur film is its potential contribution to soil acidification, as mentioned by Ma et al. (2020). In

order to overcome these problem, polymeric coating/encapsulating materials were adopted. The polymeric materials usually employed as a coating/encapsulating films include polyurethane (Li et al., 2012), polysulfone, polyacrylonitrile, cellulose acetate (Jarosiewicz and Tomaszewska, 2003), polyolefin (Zvomuya et al., 2003) and polyvinyl chloride (Sarkar et al., 2018). Jarosiewicz and Tomaszewska (2003) developed three types of coated NPK fertilizers utilizing polyacrylonitrile, polysulfone and cellulose acetate. The authors observed that an increase in coating thickness and polymer concentration led to reduced coating porosity. Among the three materials, cellulose acetate possessed higher porosity as relative to polysulfone and polyacrylonitrile. Moreover, the study also demonstrated that multilayer coating o higher polymer concentration resulted in a decrease in nutrient release rate. After 5 hours of dissolution, the NPK release rate was the lowest for polysulfone-coated fertilizer and the highest for cellulose acetate-coated fertilizer. The low NPK release rate of polysulfone and polyacrylonitrile coatings was attributed to their low porosity and high hydrophobicity characteristic of the film.

Dai et al. (2020) discovered that by incorporating polydimethylsiloxane as a modifier in the polyurethane film improved the hydrophobic nature of the film. This enhancement of the hydrophobicity of the film was due to the hydrophilic propyl ether bond of the polyol segment was partially replaced by the hydrophobic dimethyl siloxane structure of polydimethylsiloxane. Their research study demonstrated that urea coated with the modified polyurethane exhibited a reduced release rate as compared to unmodified polyurethane during the initial stage. Besides, the authors also found that increasing the amount of the polydimethylsiloxane from 1% to 3% in the uniform film-coated urea did not significantly affect the urea release rate. The release rate of urea was influenced by the water contact angle of the polyurethane film, with higher water contact angles resulting in lower release rates

compared to lower water contact angles. In addition to uniform film-coated urea, a gradient hydrophobic planar film-coated (InHL-OutHB and InHB-OutHL) urea was also produced in the study. This involved coating the urea layer by layer with varies different formula which included polyurethane, 1% Si-PU, 2% Si-PU, and 3% Si-PU. It found that InHL-OutHB was slower than InHB-OutHL and uniform film coated urea in terms of the urea release rate, as depicted in **Figure 2.1**.

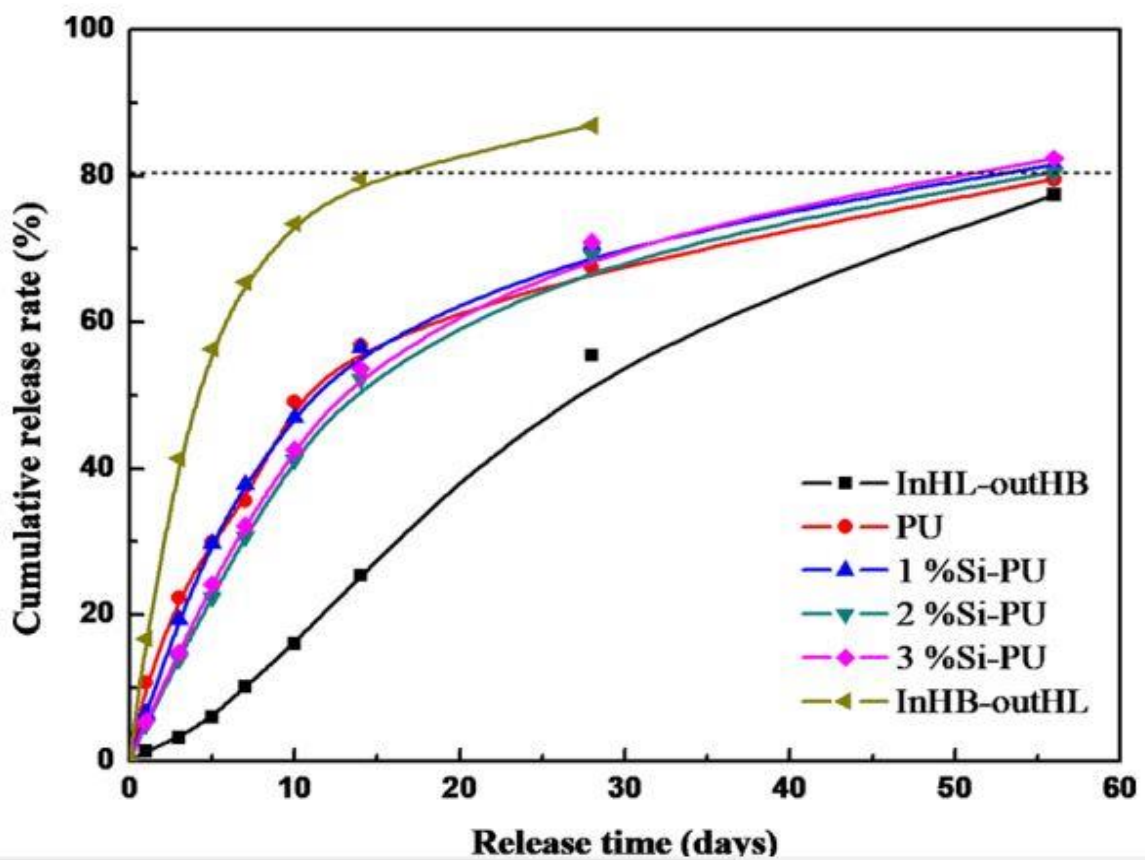


Figure 2.1: Release performance of urea for (a) InHL-outHB, (b) uniform coating, and (c) InHB-outHL (Dai et al., 2020).

Numerous research studies have indicated that employing the organic/petroleum-derived polymers as coating/encapsulating materials to produce slow/controlled-release fertilizer is not environmentally friendly. This is primarily due to the non-biodegradable,

high cost (Ibrahim et al., 2020) as well as might cause toxicity toward the soil (Mukerabigwi et al., 2015). Hence, bio-based coating/encapsulating materials has been introduced by the researchers to manufacture more environmentally friendly slow/controlled-release fertilizer. Starch, cellulose and lignin are among the most commonly utilized bio-based materials for synthesizing slow/controlled-release fertilizer. However, the bio-based polymers as a coating/encapsulating material has certain drawbacks such as numerous hydrophilic groups and microholes, thus the release lifetime are usually shorter. To overcome this problem, modified or incorporate additives could be considered to enhance the hydrophobicity of the bio-based polymers. Behin & Sadeghi (2016) developed modified lignin-based controlled-release urea fertilizer to enhance the hydrophobicity of the unmodified lignin and this was achieved by modifying the kraft and sulphite lignin extracted from plants, using acetic acid and sodium metabisulfite. The results of the study demonstrated that both modified kraft and sulphite lignin-coated fertilizers exhibited a reduced dissolution rate of urea compared to unmodified lignin-coated fertilizers. In contrast, unmodified lignin-coated fertilizer completely releases the urea within one hour when exposed to water. The reduction of release rate for modified lignin-coated fertilizer was attributed to its hydrophobicity through the modification process. Furthermore, the pore size of the coated fertilizer reduced when increasing the percentage of the coating on the surface of the urea fertilizer which reduced the urea release rate. Besides, the study also found that the urea release rate of modified lignin-coated urea fertilizers in soil were slower than sulfur-coated urea fertilizer without any sealant and conditioner. The study also concluded that hydrophobic and adhesion surface properties of the coating materials governed the urea release rate in the fertilizer.

Bio-based polyurethane is another environmentally friendly coating/encapsulating materials which has also been employed to synthesize slow/controlled release fertilizer

instead of using non-biodegradable synthetic polyurethane. The polyol can be produced by various feedstock as the hydroxyl number of polyol varied different from each other. Liang et al. (2019) utilized castor oil-based polyurethane as coating/encapsulating material to synthesized controlled release fertilizer. The study investigated the impact of different diisocyanates, the hydroxyl number of castor oil and the hydroxyl/isocyanate molar ratio on the release rate of urea in the coated fertilizer. The results indicated that the urea release rate of IPDI and TDI-based polyurethane-coated urea were faster as compared to PMDI. The faster urea release observed in IPDI and TDI was because to the higher reactivity of PMDI, which possessed a higher crosslinking density due to its two aromatic rings. Besides, PMDI-based polyurethane film also exhibited greater hydrophobicity and a more rigid network film structure as relative to IPDI and TDI. The study also observed that polyol derived from castor oil with higher number of hydroxyl groups resulted in a lower urea release rate and prolonged release longevity as compared to polyol derived castor oil with lower number of hydroxyl groups. Furthermore, increasing the hydroxyl/isocyanate molar ratio led to a lower initial urea release. The hydrophobicity and crosslinking density of the coating materials were the main factor that resulted in lower release rate and longer urea release longevity of the produced controlled-release fertilizer. One of the drawbacks of utilize bio-based polyurethane is the diisocyanate (crosslinking agent) was costly.

2.6.3 Superabsorbent Hydrogel-based Fertilizer

The superabsorbent hydrogel, alternatively referred to as a superabsorbent polymer, is a water-loving polymer capable of absorbing substantial quantities of water and aqueous solution (Klinpituksa & Kosaiyakanon, 2017). Generally, the superabsorbent is a hydrophilic polymer that forms a three-dimensional structure through crosslinking. The superabsorbent can be utilized as a coating material or a carrier/matrix. The hydrogel based-

fertilizer come in several variants, including synthetic hydrogel-based fertilizer, hybrids combining of synthetic and natural materials (inorganic/organic) hydrogel-based fertilizer and pure natural hydrogel-based fertilizer. The most common synthetic hydrogel-based fertilizer was produced from AAm and AAc. Cheng et al. (2018) demonstrated the successful attainment of a delay urea release by employing Poly(AAm) with urea. The authors observed that the synthesized Poly(AAm) hydrogel-based fertilizer was able to release the urea progressively over a period of 40 days when immersed in distilled water. Another study by Teoderescu et al. (2009) investigated the NPK release rate of Poly(AAc)-based hydrogel fertilizer in distilled water at room temperature. The authors observed that the release rate of NPK was dependent on MBA/AAc ratio, with a higher MBA/AAc ratio indicating a slower release rate. The increased network density was caused by the high concentration of the crosslinking agent. Urbano-Juan et al. (2019) conducted a study to examine the release of nitrate in water and saline solution from acrylamide-co-itaconic acid-based hydrogel with two distinct crosslinking agents, namely ethylenglycol dimethacrylate and MBA. The authors revealed that the behaviour of nitrate release was found to depend on the type of the crosslinking agent. According to Helaly et al. (2005), the release rate of urea in water for Poly(AAm)/maleic acid and Poly(AAc)/maleic acid-based hydrogel fertilizers was found to be prolonged up to four months. Notably, the release of urea from Poly(AAc)/maleic acid-based hydrogel fertilizer was slower than Poly(AAm)/maleic acid-based hydrogel fertilizer. Given the high cost of production, poor mechanical and thermal characteristic and limited biodegradability of petroleum-based hydrogel, researchers have turned to a combination of natural materials (organic and inorganic) with synthetic polymers to fabricate hydrogel-based fertilizers. The incorporation of natural material into the synthetic polymer yielded

enhancement in the swelling ratio, release behaviour of nutrient, biodegradability as well as thermal and mechanical characteristic of the hydrogel-based fertilizer.

Sugarcane bagasse-g-Poly(AAm)/attapulgit was employed as a matrix to control the release of urea by Kenawy et al. (2020). The findings showed that augmenting the attapulgit concentration in the formulation, the release rate of urea was slowed, thereby enhancing the sustained release property of the formulated hydrogel-based fertilizer. According to Liang and Liu (2007) also reported that the hydrogel-based fertilizer with the highest kaolin concentration (30%) exhibited a low urea release rate. This was due to the aggregation of kaolin, which obstructed the pores or channels within the polymer matrix. The study also observed that other variables such as AAm concentration, crosslinker amount and temperature also influenced the quantity of urea release rate. Rashidzadeh & Olad (2014) also discovered that incorporation MMt into sodium alginate-g-Poly(AAc-co-AAm)/NPK hydrogel-based fertilizer can decreased the rate of NPK release compared to pristine sodium alginate-g-Poly(AAc-co-AAm)/NPK hydrogel. This was due to the formation of tortuous path when MMt was incorporated into the pristine hydrogel.

Natural polysaccharides are often used to synthesis pure natural hydrogel-based fertilizer (Klein & Poverenov, 2020). Perez & Francois (2016) developed a chitosan//starch hydrogel-based fertilizer and found that the mass ratio of the chitosan and starch had an impact on the potassium nitrate release rate. After 14 days, the potassium nitrate release rate ranged between 73% and 95% depending on the mass ratio of chitosan and starch. The highest release rate of potassium nitrate was observed in pure chitosan (100:0) based-hydrogel fertilizer whereas the release rate of potassium nitrate was the lowest when chitosan

and starch were mixed in a ratio of 30:70. The nutrient release behaviour of various type of slow/controlled release fertilizer is summarized in **Table 2.1**.

Table 2.1: Nutrient release behaviour of various slow/controlled release fertilizers

	Nutrient	Nutrient release performance in water	Nutrient release performance in soil	References
Corncob-g-Poly(AAm)/Bent/PVP/urea	Urea	-	Urea release rate was 56.6% after 30 days	Wen et al. (2017a)
Urea-biochar (UB), urea-hydrochar (UH), urea-zeolite (UZ), U-hydroxyapatite (U-HAP)	Urea	-	Urea release of UB, UH, UZ and U-HAP was 93.5% after 260s, 95.5% after 180s, 92% after 360s and 88% after 460s, respectively	Maghsoodi et al. (2020)
Bio-based epoxy coated urea (EPCU)	Urea	-	Urea release lasted more than 60 days with optimum LB/BDE ratio and 7.5% coating content	Li et al. (2018b)
Starch acetate/glycerol/PVA coated DAP	Diammonium phosphate	Release of nutrient for all formulations were lower than uncoated DAP	-	Sofyane et al. (2021)

Table 2.1 continued

Sulfonated corn starch-g-Poly(acrylamide)/phosphate rock (SCS-g-Poly(AAm)/PHR)	Phosphate rock	Release of P was 71% after 30 days. More P was released from SCS-g-P(AAm)/PHR compared to other treatments	-	Zhong et al. (2013)
Chitosan/MMt/Polyethylene glycol 4000-inner/ParrafinWax-outer coated DAP	Diammonium phosphate	-	P release of coated DAP was the lowest (<40%) compared to uncoated DAP (100%) after 30 days	El Assimi et al. (2020)
Mixed vegetable oil (castor oil and hydroxylated soybean oil)/polymethylene polyphenylene isocyanate coated NPK (MVO/PPI coated NPK)	NPK	-	Nutrient release for 5:4 ratio of MVO:PPI with 6% of mass percentage (thickness) lasted for 164.14 days	Sun et al. (2019)

Table 2.1 continued

Zein coated porous carboxymethyl starch/iron/phosphorus	Iron and monoammonium phosphate (P)	P release of zein-coated PCS/Fe/P and uncoated PCS/Fe/P was 18% and 28% lower than pristine monoammonium phosphate, respectively after 30 days	-	Qi et al. (2020)
Lignin-coated U-hydroxyapatite, cellulose-coated U-hydroxyapatite, bagasse-coated U-HAP and U-HAP	Urea	Urea release of lignin-coated U-HAP, cellulose-coated U-HAP, bagasse-coated U-HAP and U-HAP after 30 days was 21.64%, 45.48%, 59% and 78.8%, respectively. Urea release of all coated U-HAP was slower than pristine urea	-	Elhassani et al. (2019)

Table 2.1 continued

Starch-g-Poly(AAm) (SBSAPs)	Urea	Urea release of SBSAPs exceeded 80% after 30 days and lasted for more than 45 days	-	Xiao et al. (2017)
Polyolefin wax/castor oil/polymethylene polyphenylene isocyanate-coated DAP	Diammonium phosphate	P release of all formulated polyolefin wax/castor oil/PPI-coated DAP was lower than castor oil/PPI DAP (without wax modification). Increasing the wax content improved the P release longevity	-	Lu et al. (2019)
Ethylcellulose-inner/Polyacrylic acid-co-acrylamide)-outer coated PCU/sodium alginate/urea (DSWU)	Urea	-	N release of DSWU was 72.8% in soil after 30 days	Ni et al. (2009)

Table 2.1 continued

Tamarind gum/diatomite coated urea, xanthan gum/diatomite coated urea, guar gum/diatomite coated urea and xanthan gum/diatomite/poly(methacrylic acid)-coated urea	Urea	-	N release of TUD, XUD and GUD slow-release fertilizer in 24 h was 78%, 74% and 68%, and after 28 days was 98%, 92% and 98%, respectively. N release rate of XUDM was the lowest compared to uncoated XUDM which was 43% and 79.5% after 24 h and 28 days, respectively	Mukerabigwi et al. (2015)
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Table 2.1 continued

Gypsum/dolomitic limestone/sulfur-coated urea	Urea		Urea release rate of gypsum/dolomitic limestone/sulfur with ratio 1:1:0 was the lowest, but higher than pure sulfur. Addition of 1.1% polyol improved the release resistance while it decreased with 1.6% polyol	Eghbali Babadi et al. (2015)
Cassava starch-g-P(AN)	Urea	-	N release in sandy clay loam soil of cassava starch-g-P(AN) was lower than uncoated urea which ranged between 69.8%-78.3% after 108 days of incubation while 100% was observed after 28 days of incubation for uncoated urea	Jyothi et al. (2018)

2.7 Nutrient Release Behaviour of Slow/Controlled-release Fertilizer in Different Soil Type

Nitrogen is extremely vulnerable to leaching, especially in sandy soil and tropical climates experience greater overall nitrogen losses. In contrast, phosphorus loss primarily occurs through the fixation in alkaline (calcareous) and acidic P-fixing soils, whereas potassium loss is greater in sandy soil and highly weather tropical soil. As a result, the use of slow/controlled-release fertilizers can effectively mitigate the losses of nutrient as well as prevent P fixation. Several factors such as type of soil (textural and pH), irrigation frequency and volume, temperature and coating/encapsulating/matrix formulation were influencing the release properties of the slow/controlled release fertilizers. Chen & Chen (2019) studied the impact of temperature on the nutrient release rate of methylcellulose-based with and without K₂SO₄ (M-O.25 and M2) and hydroxypropyl methylcellulose-based hydrogel with and without addition of K₂SO₄ (H-0.25 and H2). The study revealed that the nutrient release rate of all the synthesized hydrogel-based fertilizer reduced when the temperature rose from 25 °C to 35 °C. Moreover, M2, M-0.25 and H-0.25 nutrient release rate increased with rising pH level, whereas H2 showed minimal responsiveness to changes in pH. The authors also stated that at various temperatures and pH level, all the formulated hydrogel-based fertilizer exhibited slower release rate of nutrient as compared to conventional fertilizer. According to Lohmousavi et al. (2020), the behavior of N and P release of banana peel cellulose-g-Poly(AAc)/PVA/layered double hydroxide (LDH) hydrogel-based fertilizer varied across pH range of 2-12. The study found that the release of N decreased from pH 2 to 7 but subsequently increased, while the release of P exhibited an inverse pattern compared to N release. Olad et al. (2018) revealed that the hydrogel-based fertilizer demonstrated slow-release as compared to conventional fertilizer in sandy loam soil. Furthermore, Qi et al. (2020) found that both zein coated PCS/Fe/P and uncoated PCS/Fe/P exhibited enhanced

diffusion and release characteristic of P in red soil and silt loam soil which the diffusion and release characteristic of P were superior to monoammonium phosphate. Based on the study, both synthesized slow/controlled release fertilizers were able to regulate the pH level in red and silt loam soil.

From the literature findings, it is suggested that the effect of slow/controlled release fertilizer on different soil types and diverse environmental conditions should be investigated because majority of previous research studies focused on investigating the nutrient release behaviour on either one type of soil or in water.

2.8 Synthesis Method of Slow/Controlled-release Fertilizer

The production method of slow/controlled release fertilizer can be classified into two main types which are coating/encapsulating-based and matrix/carrier-based method. For the synthesis of the superabsorbent hydrogel-based fertilizer, a variety of polymerization techniques can be employed. The solution polymerization (Sarmah & Karak, 2020), inverse suspension polymerization (Liu et al., 2007), ultraviolet light irradiation (Wu et al., 2020), ionizing radiation (Abd El-Rehim, 2006) and microwave irradiation (Wen et al., 2017b) are among the polymerization techniques. There are two techniques that can be employed to incorporate liquid fertilizer into the matrix of hydrogel which are in situ and two steps (Rabat et al., 2014). The in-situ method involves the fabricate of hydrogel-based controlled-release fertilizer by entrapping the liquid nutrient within the matrix of the hydrogel. During the polymerization process, the liquid fertilizer and other substances including monomer, co-monomer, crosslinker and initiator are combined in the reaction mixture. Zonatto et al. (2017) synthesized hydrogel-based fertilizer utilizing Arabic gum as the base material through a two-step method. In the first step, the modified arabic gum, AAm and APS were

mixed to form the hydrogel. Subsequently, the dried hydrogel made from arabic gum was placed in the solution containing fertilizer to enable the hydrogel to absorb the nutrient. The nutrient enriched hydrogel was then dried to produce final arabic gum hydrogel-based fertilizer. Rabat et al. (2014) carried out research to investigate the growth performance of rose balsam flower by synthesizing the hydrogel-based fertilizer using in situ and two steps method. It was found that the growth performance of the balsom rose flower was better and more favourable when in-situ method was utilized. The distinction between the two method was that in-situ method require single drying stage, while the two steps method required two drying stages.

In addition to matrix/carrier type fertilizer, coated type fertilizer has also been investigated by the researchers in an effort to reduce the rate of nutrient release. The coated type of fertilizer employs solid form fertilizer which is conventional fertilizer as its core materials such as urea (Wu & Liu, 2008), NPK (Ni et al., 2009) and DAP (Sofyane et al., 2021). The rotary drum coating, pan coating, fluidized bed coating and dip coating are the coating techniques used. The granules of the conventional fertilizer typically coated with a layer of mineral, superabsorbent polymer or synthetic or natural polymer film. Moreover, researchers have recommended that double coating or multilayer coating on fertilizer granules could lead to a further decrease in the release rate of nutrient as relative to single coating. In order to produce slow/controlled release fertilizer with water retention ability, superabsorbent hydrogel coating/encapsulating materials was utilized to coat on the final or outer layer of the granule's fertilizer. The researches had employed various coating materials to coat the fertilizer granules. Noppakundilograt et al. (2015) produced a three-layered coated fertilizer from PVA, chitosan and Poly(AAc-co-AAm). Firstly, the NPK fertilizer were immersed in a PVA solution and dried to form the first layer. Subsequently, the second

layer was formed by soaking the PVA-coated fertilizer in a chitosan-acetic solution and crosslinking it with glutaraldehyde in a closed system L-chamber. In the next step, the PVA/chitosan-coated fertilizer and APS were subsequently added to a four-necked flask containing span 80 and cyclohexane equipped with a mechanical stirrer, condenser and dropping funnel. Then, a mixture of AAm, AAc, MBA and N,N,N',N'-tetramethyl ethylenediamine was added to the flask and the mixture was heated, agitated and dried to obtain the PVA/chitosan/poly(AAc-co-AAm) tri-layered fertilizer. **Table 2.2** provides a summary of various synthesis method employed for slow/controlled release fertilizers.

Table 2.2: Synthesis methods of slow/controlled release fertilizers

Type of fertilizer	Classification	Preparation method	References
Hydroxypropyl methylcellulose/K ₂ SO ₄ and methylcellulose/K ₂ SO ₄ -based hydrogel fertilizer	Matrix/carrier; In-situ	Hydroxypropyl methylcellulose/K ₂ SO ₄ or methylcellulose/K ₂ SO ₄ fertilizer was mixed in distilled water in cold water bath and kept at 4 °C.	Chen & Chen (2019)
PHG-g-CNT/urea	Matrix/carrier; Two steps	AAC and water were mixed in three round neck flasks equipped with condenser and nitrogen line in a thermostated water bath and heated (60 °C). CNT, MBA and APS were added under inert condition while stirring. After polymerization, product was washed, dried and immersed in urea solution and dried again.	Laftah & Hashim (2014)
Sulfur/bentonite-coated urea, sulfur/gypsum-coated urea and sulfur/starch-coated urea	Coated	Urea was heated to remove moisture content and sulfur/bentonite, sulfur/gypsum or sulfur/starch mixture was sprayed on the pre-heated urea. Liquid binder and demineralise water were added and transferred to ball mill (7 min, 52 rpm), coated granule was then dried.	Mehmood et al. (2019)

Table 2.2 continued

Banana peel cellulose-g-Poly(AAc)/PVA/LDH	Matrix/carrier; In-situ	Banana peel cellulose and water were mixed and stirred in three round neck flasks (50 °C, 10 min). LDH, urea and ammonium dihydrogen phosphate were added while stirring. AAc and APS were added under inert condition, MBA was added and heated (60 °C). After polymerization, product was washed and grinded.	Lohmousavi et al. (2020)
Kraft lignin-coated urea, sulphite lignin-coated urea, modified kraft-coated urea and modified sulphite lignin-coated urea	Coated	Modified kraft lignin and sulphite lignin were dissolved in ethanol/dichloromethane and acetic acid while unmodified kraft and sulphite lignin were dissolved in water, urea granule was sprayed with prepared coating solution by using fluidized bed coater and dried.	Behin & Sadeghi (2016)
Castor oil-based polyurethane-coated urea (castor-oil/PMDI coated urea)	Coated	Castor oil and PMDI were mixed and degassed, urea was coated with prepared solution by using rotary drum machine (40 rpm, 10 min) and dried.	Liang et al. (2019)

Table 2.2 continued

Polyacrylic acid/urea (Poly(AAc)/urea)	Matrix/carrier; In-situ	AAC, urea and MBA were mixed and transferred into three neck round flask equipped with mechanical stirrer, nitrogen line and condenser and KPS was added under inert condition. After polymerization, product was dried and grinded.	Cheng et al. (2018)
Wheat straw-g-Poly(AAc)/urea (WS-g-Poly(AAc)/urea)	Matrix/carrier; Two steps	Wheat straw powder and water were mixed in four necked flasks equipped with nitrogen line, thermometer, condenser and mechanical stirrer and heated (95 °C, 30 min) under inert condition. APS was added at 60-65°C, AAC and MBA were added and heated (70 °C, 3 h). After polymerization, product was washed, dried, grinded and soaked in urea solution (12 h) and then dried again.	Liang et al. (2009)
Poly(acrylic acid)/phosphorus (Poly(AAc)/P)	Matrix/carrier; In-situ	AAC and potassium hydroxide were mixed and cooled (30°C). P, MBA and APS were added into the mixture, polymerization was performed by using microwave irradiation.	Tyliszczak et al. (2009)

Table 2.2 continued

Natural rubber-inner/ natural rubber-g-poly(acrylic acid) (NR-g-Poly(AAc)-outer coated urea/dipotassium phosphate/attapulgate	Coated	Urea (powder and granules), dipotassium phosphate and attapulgate were granulated in a pan granulator (core), natural rubber was dissolved in carbon tetra chloride and sprayed on fertilizer core to form first coating. NR-g-Poly(AAc) was prepared via radical solution, NR-g-Poly(AAc) was grinded and adhered on the surface of natural rubber coated fertilizer to form second coating.	Cui et al. (2020)
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2.9 Biochar-based Fertilizer

Other than inorganic, polymer and superabsorbent hydrogel-based fertilizer, biochar-based fertilizer has been introduced by the researchers to increase the crop production and nutrient use efficiency, owing to its potential as slow-release fertilizer. Due to its different chemical and physical characteristic, biochar can be employed as a carrier for nutrient delivery and allow various type of nutrient to be incorporated into its matrix. A few studies showed that biochar-based fertilizer could reduce the loss of nutrient and increase the nutrient use efficiency by the crops in the long term compared to conventional fertilizer. Lateef et al. (2019) found that biochar derived from corncobs when impregnated with macronutrients and micronutrient extended the duration of the release of nutrient. The rate of nutrient release was found to be affected by pore size, ion binding capacity and absorption level. Shi et al. (2020) stated that biochar-urea composite improved the growth of maize and nitrogen use efficiency. The study also stated that only 39% of nitrogen was leached out from biochar-urea composite as compared to urea which was 70% in the first day. El Sharkawi et al. (2018) synthesized biochar-based fertilizer composed of rice husk, H_3PO_4 and ammonia gas, it was found that the N release rate of the synthesized biochar-based fertilizer was more consistent and steadier than mineral fertilizer, thereby minimizing the N loss. According to Zhong et al. (2018) observed that biochar infused with molten urea of varying diameter exhibited a slow-release property and decreased the rate of N release in the soil compared to pure urea. An et al. (2020) found that the P and K release rate synthesized from cotton straw/bentonite/tripotassium phosphate biochar-based fertilizer through co-pyrolysis was slower than cotton straw/tripotassium phosphate biochar-based fertilizer. The authors also claimed that the inclusion of bentonite into the formulated biochar-based fertilizer enhanced the sustained release of nutrient. This was due to the presence of bentonite

during co-pyrolysis, which decreased the formation of channels and pore of the biochar, resulting in the formation of stable P and hydrophobic compounds. Vendra Singh et al. (2020) executed a comparison of nutrient release performance between two type of biochar-based fertilizer from different feedstock. The authors claimed that the urea-impregnated biochar derived from rice husk exhibited the highest release rate, with 98% of the urea being released after 72 h. In contrast, the urea-impregnated biochar showed the urea release rate was slightly slower which is 91% after 72 h of incubation in water. Li et al. (2018a) observed that the application of biochar-based fertilizer reduced the loss of total nitrogen in the soil by 8.69% compared to conventional fertilizer. The formulation of biochar-based fertilizers with an undesirable pH level could restrict their use in soil. Zhao et al. (2016) synthesized P enriched biochar-based fertilizer made from bone meal and TSP and it was observed that the pH was the lowest (ranging from 4.96 to 5.12) as relative to the fertilizer with bone meal and pristine biochar. To address this issue, incorporating alkaline source into the formulation could be utilized as a solution. Lustosa Filho et al. (2017) incorporating magnesium oxide into the formulation to synthesize biochar-based fertilizer and revealed that magnesium oxide successfully neutralized acidulated phosphate which led to decreasing P release in water. Additionally, it enhanced the pH level of tropical soil, hence decreasing P absorption by the soil. This was due to the fact that P bonded to soil more strongly at pH 4-6 (Borges et al., 2020). Besides, the biochar-based fertilizer with high alkalinity did not substantially alter the pH level of the alkaline soils such as calcareous soil (Zheng et al., 2017).

The direct discharge of wastewater or effluent sludge into the environment has adverse effect due to high organic matter. The nutrient-rich wastewater or effluent sludge or anaerobic digestate can be combine with biochar via impregnation and co-pyrolysis. Kizito et al. (2019) utilize wood/corn biochar and digestate to synthesized biochar-based fertilizer

via impregnation method. The biochar impregnated with liquid anaerobic digestate improved the soil fertility as it increased the soil organic matter (232%-514%) and macronutrient (110%-230%) as relative to pristine biochar and control. In addition, it also assisted in the immobilization of heavy metals in soil and increased biomass yield. The results indicated that this innovative biochar-based fertilizer could contribute to a zero-waste agricultural production system while reduce the reliance on chemical fertilizer in biochar-based fertilizer formulation. Haddad et al. (2021) used cypress sawdust and olive mill wastewater to synthesize biochar-based fertilizer know as ICS-OMW-B. The dry mass of ryegrass and K bioavailability in the soil was improved by the ICS-OMW-B. The ICS-OMW-B has the potential to suppress various microorganism present in the studied agricultural soil. The ICS-OMW-B can be applied in acidic soil due to its alkaline property.

El-Bassi et al. (2021) investigated the effect of variable application rates of a biochar-based fertilizer on soil characteristic, activities of the enzyme and the growth of tomato. The findings revealed that as the application rate of the fertilizer (I-OMWS-B) increased, the pH level and urease and phosphatase activity increased proportionally. However, the highest dehydrogenase and protease activities were found when application rate of 2.5% was utilized. Moreover, the optimum growth of tomato plants was observed when I-OMWS-B was applied at application rate of 5%. This was attributed to the I-OMWS-B improved the characteristic of soil and enzyme activities. Karim et al. (2019) carried out a study in which they use banana peduncle and effluent sludge to develop biochar-based fertilizer. The authors found that the developed biochar-based fertilizer contain high levels of toxic component which was unsuitable for crop production. Although wastewater and effluent sludge have the potential to be replace the use of chemical fertilizer in the formulation, the toxic constituents such as heavy metals and fluoride present may restrict their use in the

development of biochar-based fertilizer. Overall, the release of nutrients from biochar-based fertilizer is dependent on factors such as type of feedstock, type of additives used and the synthesis method. It is recommended that extensive research be conducted on the impact of the synthesized biochar-based fertilizer on various soil type and soil-plant system. Dominguez et al. (2020) reported that nutrient leaching in water was the highest for nutrient loaded oil palm kernel shell derived biochar as relative to agroblen (slow-release fertilizer). The study also claimed that encapsulating the nutrient loaded biochar with suitable coating materials is required to improve the nutrient release property. In another study by Piash et al. (2022) synthesized biochar-based fertilizer by mixing Ca-bentonite and nutrient-rich chicken manure through co-pyrolysis method. The authors found that P and K of the synthesized biochar-based fertilizer possessed slow-release fertilizer in quartz sand and clay loam soil due to orthophosphate forming less soluble P (Ca/Mg-phosphate) and K is strongly bound in the crystalline bentonite's exchange sites during co-pyrolysis. In contrast, the synthesized biochar-based fertilizer could not retard the N release. They also claimed that combination of suitable environmentally friendly coating with co-pyrolysis is required to be studied to further retard N release.

Biochar-based fertilizer has many benefits beyond its exceptional slow-release performance compared to traditional fertilizer, some of the additional benefits including enhance water holding capacity, immobilized heavy metals in soil and utilized as a carbon sequestration material (Lateef et al., 2019, Chen et al., 2018, Dominguez et al., 2020).

2.10 Synthesis Methods of Biochar-based Fertilizer

Three synthesis methods can be utilized for the production of biochar-based fertilizer which included the impregnation method (include solid-liquid/gas adsorption), mixed

granulation method, co-pyrolysis method as well as in-situ method. In general, in-situ method utilizes nutrient-rich feedstocks such as sewage sludge as a precursor and then undergo pyrolysis to obtain biochar-based fertilizer. For impregnation method, the nutrient is mixed with biochar by submerging the biochar into the liquid solution, after which the nutrient-rich biochar is dried. For instance, a biochar-based fertilizer was synthesized by Lateef et al. (2019) by mixing the biochar with a solution of macronutrient and micronutrients. The synthesis steps were: (i) submerging in a nutrient-rich solution for few hours or days to facilitate maximum absorption and (ii) the nutrient impregnated biochar was dried. In mixed granulation method, solid fertilizer either one type or more type of fertilizer and the biochar are usually blended and ground to make it into powder form with uniform particle size and the powdered mixture is granulated or pelletized using granulator or pelletizer (Shin & Park, 2018). On the other hand, co-pyrolysis method includes mixing of feedstock and other additive or nutrient before undergoing pyrolysis process. For example, Zhao et al. (2016) utilize co-pyrolysis method to synthesize biochar-based fertilizer. The authors mixed the plant-based biomass together with TSP and bone which act as an additives/nutrient with a ratio of 4:1 (w/w) and then undergo pyrolysis to synthesize P enriched biochar-based fertilizer. Normally, the biochar-based fertilizer, which is usually in powder form and it has been observed by Shin & Park (2018) as roughly 30% of the biochar experience loss due to expose to strong wind and roughly 20% of the biochar is gone due to heavy rainfall. In order to solve the loss of nutrient enriched biochar-based fertilizer, pelletization and granulation can be adopted (Chen et al., 2018). Additionally, various type of binders such as sepiolite, bentonite clay, modified lignin, starch (Xiang et al., 2020), molasses and ammonium nitrate (Briens et al., 2020) have been utilized during the pelletization and granulation to assist the process due to biochar's hydrophobicity (Zhong et

al., 2018). Gwenzi et al. (2017) produced NPK impregnated biochar-based fertilizer by utilize sawdust biochar as a nutrient carrier while starch/PVA as a binder to assist the granulation process. The NPK impregnated biochar-based fertilizer was granulated using granulator to produce NPK impregnated biochar-based fertilizer granules. In **Figure 2.2**, schematic diagram is displayed which illustrating the synthesize of biochar-based fertilizer via impregnation method, co-pyrolysis method and mixed granulation method.

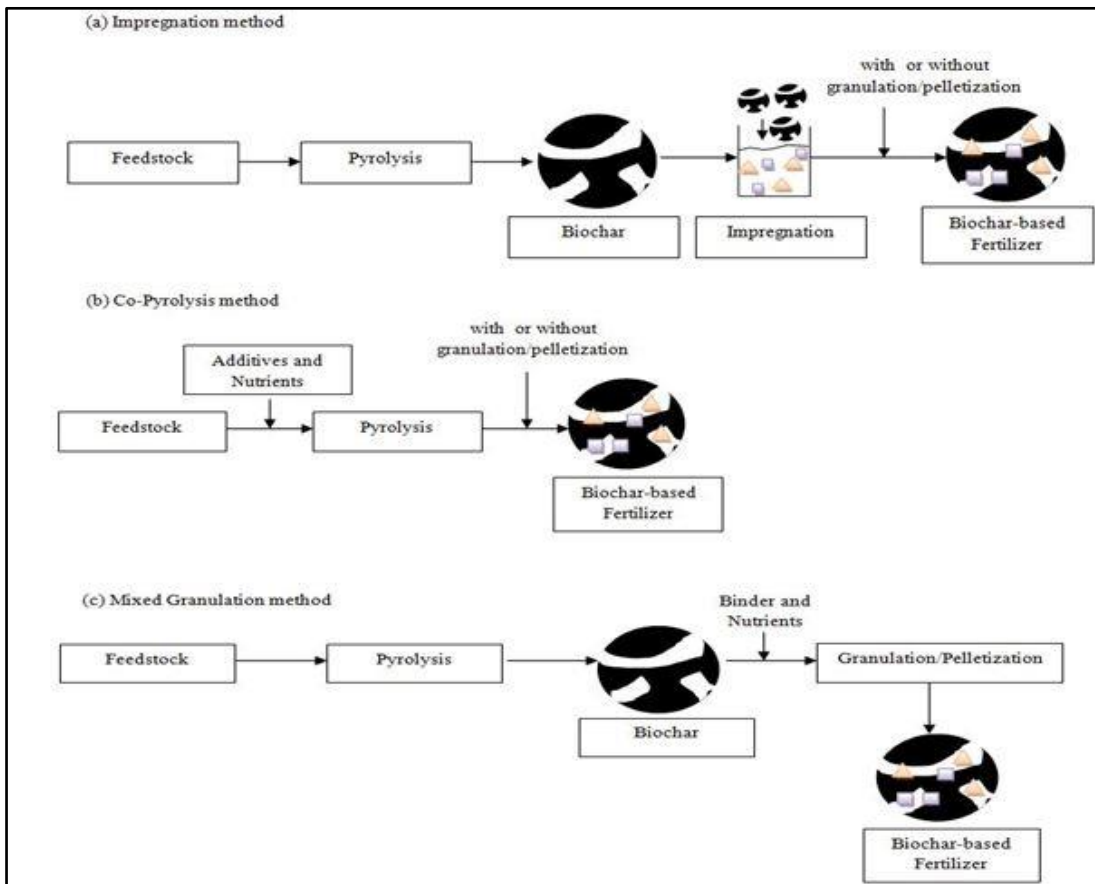


Figure 2.2: Schematic diagram of biochar-based fertilizer synthesis via (a) impregnation method, (b) co-pyrolysis method, and (c) mixed granulation method.

2.11 Encapsulated Biochar-based Fertilizer

Although biochar-based fertilizers can reduce the loss of nutrient, their slow-release still have limitation. Thus, combination of encapsulating or coating technology with the

biochar-based fertilizer is one innovative method that can be used to enhance their slow-release property in order to further reduce the nutrient leaching and increase the nutrient use efficiency. For an example, a study by Ye et al. (2019) synthesized encapsulated biochar-based fertilizer with bio-oil as an encapsulating material by using fluidized spraying device with 1.0-3.0 m/s gas velocity observed that bio-oil coated biochar-based fertilizer improve the sustain release property by further reducing the nutrient release rate. It indicated the bio-oil coated biochar greatly improve the sustained release ability compared to pristine biochar-based fertilizer. The authors were also found that the nutrient release mechanism of the bio-oil encapsulated biochar-based fertilizer synthesized from anaerobic pyrolysis atmosphere of water in gas form and carbon dioxide was greater than nitrogen gas. Liu et al. (2019b) synthesized biochar-based fertilizer made by coating urea loaded biochar with bentonite and PVA. This fertilizer possessed low nutrient release rate and high water retention relative to pristine biochar-based fertilizer. Another study by An et al. (2021b) prepared an encapsulated biochar-based fertilizer by integrate encapsulating technology and biochar-based fertilizer (co-pyrolysis) to synthesized encapsulated biochar-based fertilizer (sodium alginate/bentonite (CSRFs) based encapsulated biochar fertilizer and starch-g-Poly(AA)/PVP (PSRFs based biochar fertilizer) with slow-release and water retention properties. It was found that both encapsulated biochar-based fertilizer demonstrated slow-release property compared to unencapsulated biochar-based fertilizer (Monopotassium phosphate impregnated biochar and liquid absorption-MSRFs and co-pyrolysis of magnesium phosphate, bentonite and cotton straw-BSRFs). Besides, An et al. (2021a) fabricate a bio-based polyurethane encapsulated biochar-based fertilizer by employing cotton stalk derived bio-based polyurethane and P impregnated biochar. The study found that the bio-based polyurethane encapsulated biochar-based fertilizer can reduce the P

release rate as compared to unencapsulated biochar-based fertilizer. This was due to cotton stalk derived bio-based polyurethane possess high hydrophobicity. It was also found that increasing the thickness of the bio-based polyurethane can further reduce the P release rate from the synthesized fertilizer. Based on the past studies, it can be found that the nutrient release rate of encapsulated biochar-based fertilizer was depended on the encapsulating material's formulation.

Encapsulated biochar-based fertilizer is an example of a precise agriculture-friendly fertilizer with slow-release property. The encapsulated biochar-based fertilizer not only provide slow/controlled-release of nutrient but also offer other benefits over some of the other slow/controlled-release fertilizer. Once the encapsulating/coating material degraded, the residual biochar might be able to assist in soil physical, chemical and biological properties of the soil and also and also helps to immobilize soil heavy metals in soil. Additionally, the residual biochar also serves as a carbon sequestration material to help to curb emission of carbon dioxide to mitigate the global climate change. As a result, it may be concluded that biochar-based fertilizer and encapsulated biochar-based fertilizer are outperform to most of the other slow/controlled-release fertilizer. Moreover, the biochar-based and encapsulated biochar-based fertilizer are made of different waste sources which it contributes to the sustainable waste management. Furthermore, encapsulated biochar-based fertilizer possessed dual mechanisms (biofilm and biochar-based fertilizer) of slow-release effect which could reduce the cost of extensive modification of the encapsulating materials in conventional fertilizer as well as making the chemical preparation process simpler (An et al., 2021a). The methods utilized by earlier researchers to synthesize biochar-based and encapsulated biochar-based fertilizers are summarized in **Table 2.3**. **Figure 2.3** compares the attributes of the conventional fertilizer, biochar-based fertilizer and encapsulated

biochar-based fertilizer whereas **Figure 2.4** represents the schematic diagram of various form of slow/controlled-release fertilizers. As much fundamental knowledge on encapsulated biochar-based controlled release fertilizer remains unknown, therefore a detailed study on this precision fertilizer needs to be explored.

Table 2.3: Synthesis methods of biochar-based and encapsulated biochar-based fertilizers

Biochar-based/Encapsulated biochar-based fertilizers	Preparation methods	Findings	References
PLB/TSP/MgO and PLB/H ₃ PO ₄ /MgO	Co-pyrolysis	Movement of P in soil for TSP was limited while biochar-based fertilizer was less vulnerable to this problem due to slow-release property. P uptake by plant was higher in TSP compared to biochar-based fertilizer either in granular or powder form due to fast dissolution of P. PLB/H₃PO₄/MgO in granular form was recommended as smart fertilizer. Long-term effect of this fertilizer on P use efficiency needed to be evaluated as only small portion of P was diffused out from the fertilizer.	Lustosa Filho et al. (2019)
Maize cobs biochar/digestate (Dig-BC)	Impregnation	Soil pH and C/N ratio for biochar treatment increased compared to treatment without biochar. Shoot biomass, leaf area and total biomass were greater for Dig-BC than other treatments.	Dietrich et al. (2020)

Table 2.3 continued

Date palm waste biochar/potassium phosphate (BCP)	Impregnation	BCP enhanced the soil P, plant growth, P uptake compared to other treatments. BCP and pristine biochar immobilized heavy metals.	Ahmad et al. (2018)
PLB/TSP/MgO, PLB/TSP, PLB/H ₃ PO ₄ /MgO and PLB/H ₃ PO ₄	Co-pyrolysis	All biochar-based fertilizers increased shoot dry matter (SDM) yield in second and third cropping compared to TSP, but lower than TSP when in first cropping except PLB/H ₃ PO ₄ /MgO at the highest application rate. All biochar-based fertilizers significantly enhanced SDM yield when summing up all the harvest compared to TSP. Increasing the application rate of biochar-based fertilizer increased the SDM yield. Biochar-based fertilizers enhanced relative agronomic efficiency compared to TSP due to slow-release of P, as P formed precipitation with Ca and Mg (water insoluble P). Biochar-based fertilizers increased Mg bioavailability in soil due to addition of MgO.	Lustosa Filho et al. (2020)

Table 2.3 continued

Cotton stalk-g-Poly(AAc-co-AMPS)/bentonite encapsulated nitrogen impregnated biochar (cotton stalk-g-Poly(AAc-co-AMPS)/Bent/N-BC)	Impregnation and encapsulating/coating	Water retention capacity, N use efficiency and N release rate was the highest and lowest, respectively for cotton stalk-g-Poly(AAc-co-AMPS)/Bent/N-BC compared to N-BC and ammonium chloride. High water retention capacity of encapsulated biochar-based fertilizer was due to the hydrophilic group of Poly(AAc-co-AMPS) and biochar.	Wen et al. (2017b)
Maize stalk biochar/potassium phosphate (B300P and B600P)	Impregnation	AEM-P (soil P) of B600P was the greatest compared to TSP, B300+TSP, B600+TSP and B300P after four weeks of incubation while B300, B600 and control showed no major variation in the evolution of AEM-P.	Li et al. (2020)
Biochar/urea/bentonite/sepiolite	Mixed granulation	Biochar/urea/bentonite/sepiolite improved the growth of maize and N use efficiency. Biochar/urea/bentonite/sepiolite reduced the N loss compared to conventional fertilizer.	Shi et al. (2020)

Table 2.3 continued

Empty fruit bunches biochar/zeolite/DAP/potassium chloride/magnesium sulfate (char- NPK)	Mixed granulation	Char-NPK with magnesium sulfate and without magnesium sulfate enhanced the production of red onion compared to conventional NPK.	Finalis et al. (2020)
Cotton straw/H ₃ PO ₄ (PBC)	Co-pyrolysis	Adsorption of lambda-cyhalothrin for PBC (55.9 mg/g) was higher than pristine biochar (42.71 mg/g). Adsorbed lambda-cyhalothrin was useful for improvement of slow-release property of PBC, due to lambda- cyhalothrin filled the pore of PBC and enabled slow- release of P from PBC.	An et al. (2021d)
Cellulose acetate (CA), sodium alginate (SA), ethylcellulose (EC) encapsulated biochar-based fertilizer	Impregnation and encapsulating/coating	All encapsulated biochar-based fertilizers retarded urea hydrolysis at the first day compared to pristine urea. Maize growth and N uptake of encapsulated biochar-based fertilizers were lower than pristine urea and commercial slow-release fertilizer, but N uptake for EC was slightly lower than commercial slow-release fertilizer.	González et al. (2015)

Table 2.3 continued

Sodium alginate/vegetable oil (VO), starch/VO, chitosan/VO, cellulose/VO and maltodextrin/VO hydrogel encapsulated biochar-based fertilizer	Co-pyrolysis and encapsulating/coating	All encapsulated biochar-based fertilizers had lower P release rate than unencapsulated biochar-based fertilizer due to hydrophobic surface. P release rate depended on encapsulating materials. Encapsulated biochar-based fertilizers enhanced germination ratio, plant height, root length, dry and wet weights compared to other treatments. Encapsulated biochar-based fertilizers showed reduced P leaching compared to other treatments.	An et al. (2021c)
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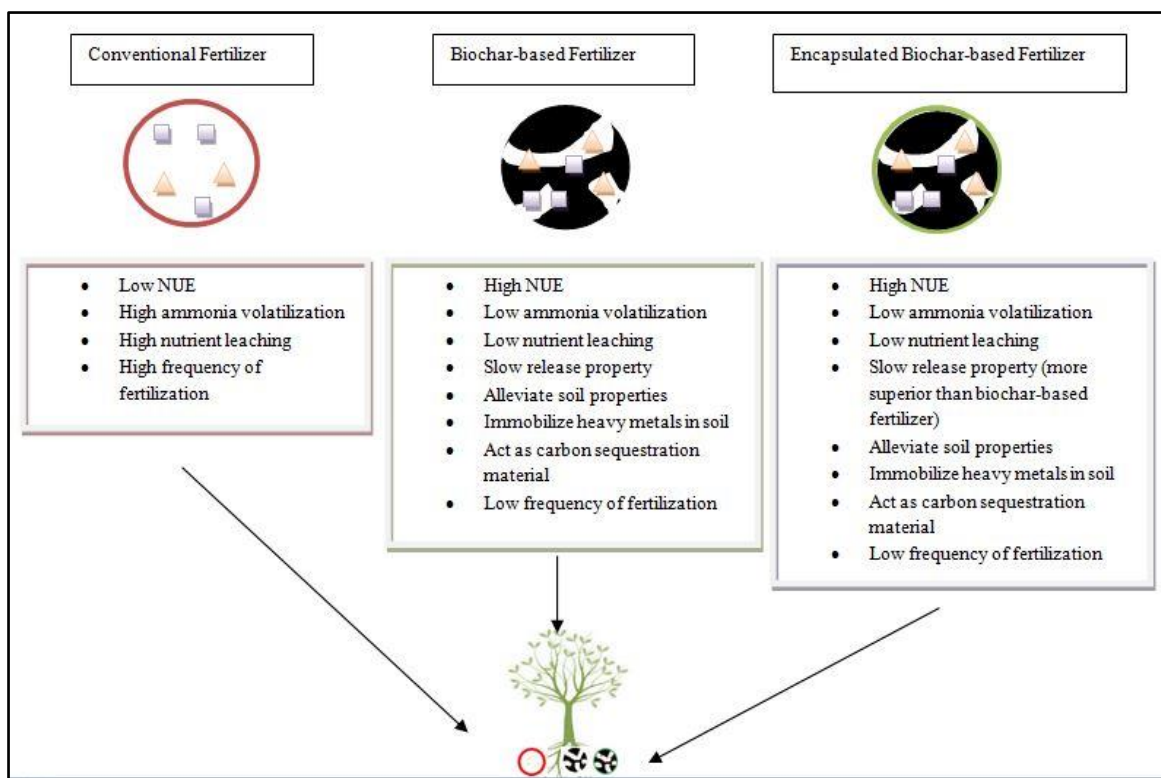


Figure 2.3: Comparison of conventional, biochar-based and encapsulated biochar-based fertilizers.

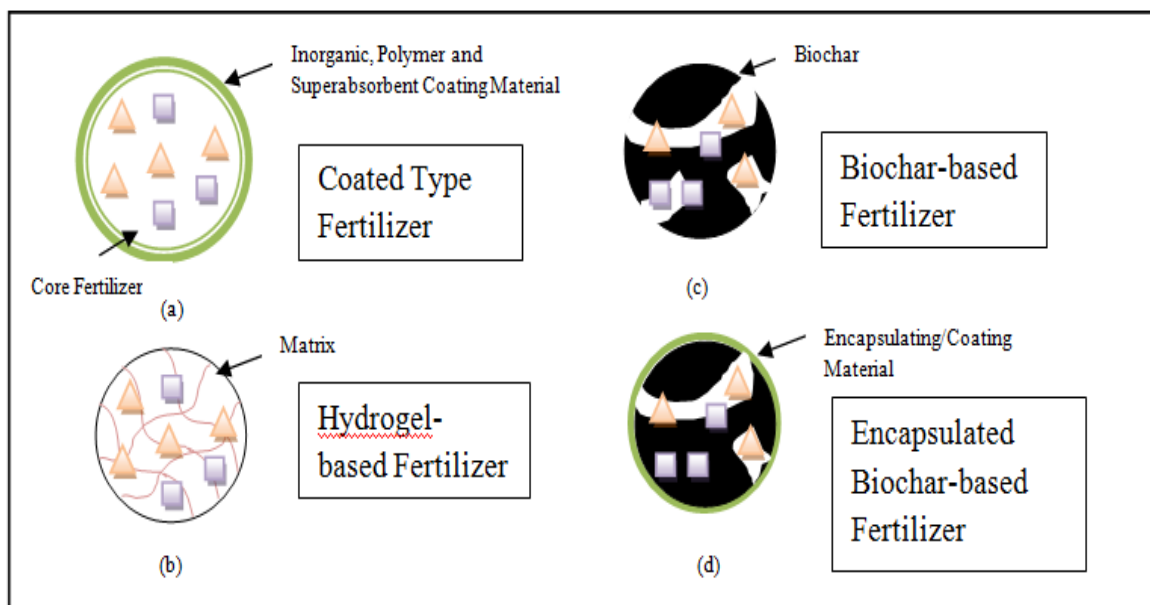


Figure 2.4: Schematic diagram of various slow/controlled release fertilizers: (a) coated type fertilizer, (b) hydrogel-based fertilizer, (c) biochar-based fertilizer, and (d) encapsulated biochar-based fertilizer.

2.12 Nutrient Bonding and Release Mechanism

Biochar is able to effectively retain nutrients via physisorption and chemisorption mechanism due to its porous structure and diverse functional group present within the biochar. Numerous studies have investigated the interaction effect between biochar and nutrients, focusing on the dynamics of interaction between different macronutrient such as nitrogen compounds like urea, ammonium (NH_4) and nitrate (NO_3^-); potassium (K^+); phosphorus (PO_3^-) as well as micronutrient such as zinc (Zn^{2+}), manganese (Mn^{2+}) and copper (Cu^{2+}). For example, divalent cations such as Mg^{2+} , Fe^{3+} , Al^{3+} and Ca^{2+} of the biochar could bind with PO_3^- ions and create bridge bond on the surface of biochar (Ahmad et al., 2018). Moreover, Zhao et al. (2016) observed that during co-pyrolysis, the C and O atom of the biochar could bound with P through chemical. Zhang et al. (2015) demonstrated that the oxygen-containing functional groups (polar moieties) such as $\text{C}=\text{O}$, $-\text{COOH}$ and phenolic OH can form hydrogen bond with the $-\text{NH}_2$ and $\text{C}=\text{O}$ group in urea. Besides that, Shi et al. (2020) revealed that the amide groups were formed owing to the reaction of $\text{C}=\text{O}$ and $-\text{NH}_2$ in the biochar-urea composite. Ye et al. (2019) observed that PO_4^{3-} and NO_3^- ions were found to be absorbed into the biochar matrix via electrostatic attraction which formed bonds with COOH_2^+ and $\text{R}-\text{OH}_2^+$ and formed hydrogen bond with $-\text{COOH}$, $\text{OH}[\text{C}-\text{H}]_n-\text{COOH}$ and $\text{R}-\text{OH}$. In contrast, the Ye et al. (2019) also observed that K^+ ion was able to bond with $-\text{COOH}$, SiO_4^- , OH , $-\text{COO}^-$ and $\text{R}-\text{O}^-$ in the biochar through co-precipitation, surface complexation, inner-sphere complexation and electrostatic attraction. Additionally, Wen et al. (2017b) also stated that NH_4^+ could bound with the biochar via electrostatic attraction and hydrogen bonding between NH_4^+ and the oxygen functional group of biochar. Liu et al. (2019b) found that the sorption of nutrients into the matrix of biochar was due to chemisorption mechanisms which involved both polar and non-

polar interaction and hydrophobic bonding, electron donor-acceptor interactions and weak unconventional hydrogen bonds were among these interactions. Deng et al. (2020) found that the Cu^{2+} ion could bind with the surface functional group of biochar via cation-interactions, cation exchange processes ($-\text{COR}$ and $-\text{COOR}$), complexation ($-\text{COOH}$ - and $-\text{OH}-$) and precipitation (OH^- and CO_3^{2-}). It was also found that physical adsorption was one of the mechanisms in binding Cu^{2+} . The Mn^{2+} were absorbed into the biochar's matrix via physical absorption and chemisorption such as cation-exchange ($-\text{COOR}$ and COR) and precipitation (CO_3^{2-} and OH^-) whereas for Zn^{2+} ions were absorbed through mechanism like cation- π interaction, cation-exchange ($-\text{COOR}$, $-\text{COR}$), precipitation (CO_3^{2-} , OH^-) as well as via physical adsorption. The biochar porosity and surface functional group varied depending on the feedstock type and synthesis condition utilized. Therefore, while designing biochar-based and encapsulated biochar-based fertilizers, it is important to understand the nutrient bonding and mechanism which could help in tailoring the biochar characteristics to optimize the nutrient retention capacity.

The concept of nutrient release mechanism in precision agriculture aims to solve the issues such as nutrient leaching, surface runoff and volatilization, yet the release of nutrient of the biochar-based fertilizer and encapsulated biochar-based fertilizer is difficult to conceive and remain challenging and ongoing. The zero-order release kinetic, first-order release kinetic, Higuchi model, Hixson-Crowell model, Baker- Lansdale model, Parabolic diffusion, Elovich model and Korsmeyer-Peppas model are some of the mathematical models that have been utilized to describe the release kinetics and mechanism of biochar-based fertilizer and encapsulated biochar-based fertilizers. A recent study by An et al. (2020) found that the Higuchi model was best in describing the release mechanism of cotton straw/bentonite/ K_3PO_4 biochar-based fertilizer synthesized by co-pyrolysis. The release of

P and K of the cotton straw/bentonite/K₃PO₄ biochar-based fertilizer was governed by diffusion mechanism. In addition, the Higuchi model was best fitted for cotton straw/trimagnesium phosphate (Mg₃(PO₄)₂)/bentonite biochar-based fertilizer as demonstrated by An et al. (2021c) which observed that the P release mechanism of the synthesized fertilizer was dominated by dissolution and diffusion mechanism. The study also observed that the Hixson-Crowell model best described the P release of the encapsulated biochar-based fertilizer and the mechanism of the P release was governed by diffusion of the nutrient through the encapsulating/coating material, instead of dissolution of fertilizer. According to Lustosa Filho et al. (2017), the P release from PLB/H₃PO₄/MgO, PLB/MAP/MgO, PLB/TSP and PLB/TSP/MgO was found to be slower as relative to PLB/MAP and PLB/H₃PO₄, and the slow P release was dominated by diffusion mechanism. On the other hand, PLB/MAP and PLB/H₃PO₄ was dominated by dissolution mechanism. The slow P release from PLB/H₃PO₄/MgO, PLB/MAP/MgO was attributed to the less soluble P compound formed. Besides, Gwenzi et al. (2017) observed that the nutrient release of the synthesized fertilizer was high at the initial stage due to rapid dissolution and washout from the synthesized fertilizer. After equilibrium, the rate of nutrient release typically slowed down and was presumably controlled by the solute diffusion from the porous solid biochar phase into the aqueous phase. Additionally, Vendra Singh et al. (2020) revealed that the release mechanism of the nutrient from urea-impregnated biochar-based fertilizer involved a mix of nutrient particle dissolution and nutrient particle diffusion under concentration gradient.

Figure 2.5 represents a schematic diagram depicting the release mechanism of encapsulated biochar-based fertilizer. The release mechanism of encapsulated biochar-based fertilizer encompasses three phase which are transportation of water into the

encapsulating/coating material and biochar, dissolution of nutrients attached or bound to the biochar and nutrient gradually release out from the encapsulating/coating material. Liu et al. (2019b) proposed a multi-stage diffusion model to describe the release mechanism of urea of the synthesized encapsulated biochar-based fertilizer. According to the model, the following steps helped to illustrate the release mechanism: (i) the water absorbed by bentonite and swelling at the channels and orifice pores of the biochar, (ii) gradually release of dissolved nutrient via diffusion under concentration or pressure gradient or a combination of both under concentration and pressure gradient and (iii) the nutrient solution and water diffused out and then diffused into the soil when dehydration of bentonite occurred during water shortage in soil. Owing to the slow-release characteristic of biochar-based fertilizer and encapsulated biochar-based fertilizer, they possess higher potential to prevent nutrient leaching, volatilization and surface run-off as relative to conventional fertilizers because of their slow/controlled-release characteristic.

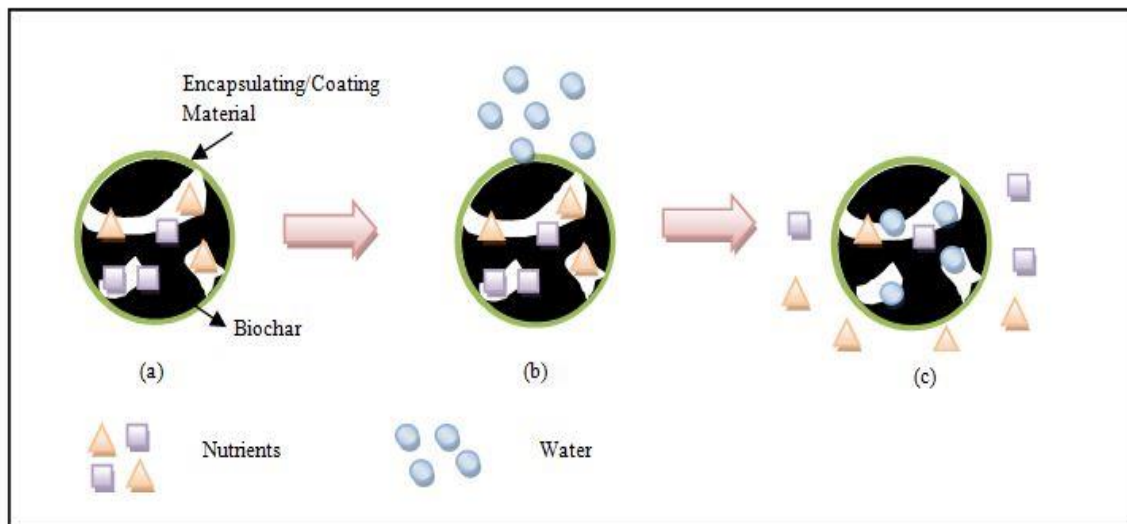


Figure 2.5: Diffusion mechanism of encapsulated biochar-based fertilizer: (a) biochar-based fertilizer with encapsulating material, (b) water molecules move or penetrate into the capsule, and (c) nutrient released through the encapsulating material.

2.13 Economic Assessment

The factors such as mineral depletion, high energy usage and high labour consumption have a negative impact on the overall economic balance of the entire agrochemical production process (Lubkowski, 2016). This problem can be improved by utilizing biochar-based fertilizer and encapsulated biochar-based fertilizer. The economic assessment of the cost of production for biochar-based and encapsulated biochar-based fertilizer still need to be continuously investigated and studied as the information regarding to production cost of these fertilizers is still very little. In general, the cost of production of the biochar-based fertilizer and encapsulated biochar-based fertilizer are influenced by many factors such as cost of feedstock, operating cost, additives and others. For instance, An et al. (2020) investigated the production cost of the biochar-based fertilizer made by cotton straw/bentonite/ K_3PO_4 via co-pyrolysis. It was found that the cost of production of the biochar-based fertilizer was \$206.997/tonne while commercial chemical PK fertilizer was \$830.98/tonne which the production cost is much lower as compared to commercial chemical PK fertilizer. The study also claimed that the production cost reduced with increasing the bentonite content as presence of bentonite reduced the consumption of the energy to synthesize the biochar-based fertilizer. The production cost of encapsulated biochar-based fertilizer might increase as it combined encapsulating/coating materials with biochar-based fertilizer. Nonetheless, it was able to alleviate the release performance of the biochar-based fertilizer, as demonstrated by An et al. (2021c) and An et al. (2021a). Therefore, it could potentially contribute to the reduction of cost of fertilization by decreasing the frequency of fertilization as well as the time and labour consumption. The economic assessment of biochar-based and encapsulated biochar-based fertilizers is

important as agricultural industry can benefit greatly from the economic analysis particularly in terms of future up-scaling by the agricultural industry.

2.14 Slow/Controlled-release Fertilizer for Soil Amendment

This section represented and discussed the effect of the slow/controlled release fertilizer including the inorganic based fertilizer, polymer-based fertilizer, superabsorbent based fertilizer, biochar-based fertilizer and encapsulated biochar-based fertilizer on water retention capacity, ammonia volatilization, nutrient leaching and plant growth.

2.14.1 Water Retention

The enhancement of water retention ability of agricultural soil is crucial as it helps in reducing the frequency of irrigation and enhance the plant growth. It accomplishes this by enhancing the plant available water during periods of water scarcity. The utilization of slow/controlled-release fertilizer can enhance the soil's water retention capacity. Superabsorbent hydrogel-based fertilizer is a type of slow/controlled release fertilizer which can effectively enhanced the water retention capacity of the soil because it was able to absorb and hold a large amount of water within its matrix. According to Chen & Chen (2019) had synthesize superabsorbent hydrogel-based fertilizer made by hydroxypropyl methylcellulose/potassium sulfate and methylcellulose/potassium sulfate. It was designed to enhance the water retention capability and regulate the nutrient release. The water retention performance in sandy soil of hydroxylpropyl methylcellulose and methylcellulose-based hydrogel without incorporating potassium sulfate was better than Poly(AAm)-based hydrogel. As demonstrated in **Figure 2.6**, the water retention capacity was enhanced with the increment of application rate of the synthesized superabsorbent-based fertilizer.

Additionally, the water retention capacity of the superabsorbent hydrogel-based fertilizer was slightly reduced with the incorporate of potassium sulfate.

There are several studies that had highlighted the addition of inorganic nanoparticle can further increased the water retention ability of hydrogel. Lohmousavi et al. (2020) stated that addition of layered double hydroxide in banana peel cellulose-g-Poly(AAc)/PVA could held more water in loamy sand soil as relative to banana peel cellulose-g-Poly(AAc)/PVA and banana peel cellulose-g-Poly(AAc). Similar findings were found by Olad et al. (2018) and Shen et al. (2020). On the other hand, biochar-based fertilizer has been acknowledged for its ability to increase the water retention capacity of soil and this was attributed to its highly porous structure. For instance, a study by Lateef et al. (2019) observed that the water retention performance in soil with application of BCN had enhanced as relative to soil without the application of BCN. The authors claimed that the water retention in the soil with addition of BCN was 67.17% while only 55.50% was observed in the soil without addition of BCN. Similar results were observed by Liu et al. (2019b), who discovered that water retention of the soil treated with encapsulated biochar-based fertilizer was better than the untreated soil. Based on the authors, this was attributed to the hydrophilic functional group and porous structure of biochar and bentonite as well as the polymer network of PVA on the biochar's surface. Another study by An et al. (2021b) also observed that sodium alginate encapsulated biochar-based fertilizer and starch-based hydrogel encapsulated biochar-based fertilizer enhanced the water retention capacity of desert soil as compared to uncoated treatment. This was due to sodium alginate and starch possessed a stronger hydrophilicity.

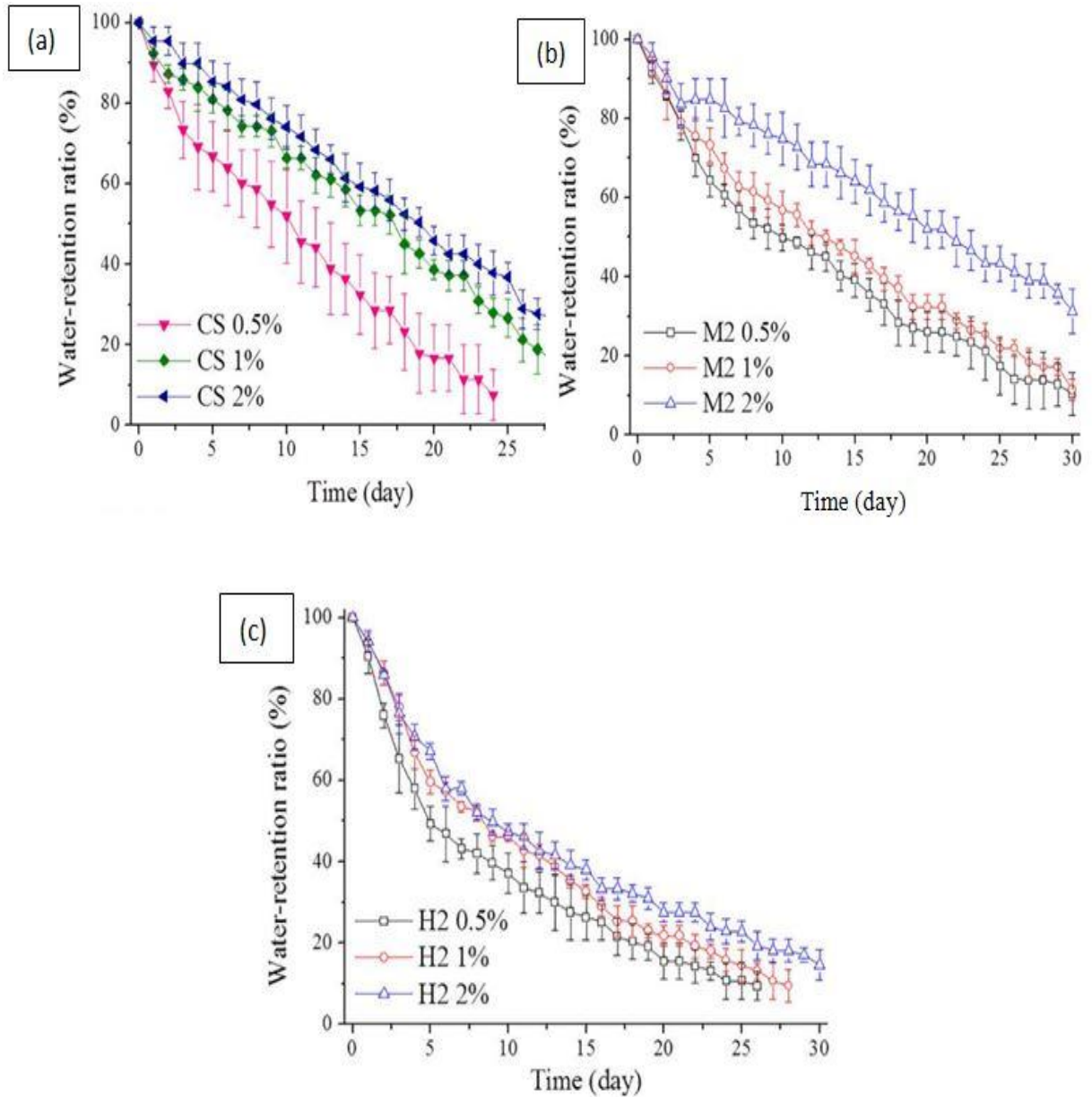


Figure 2.6: Water retention capacities of sandy soils mixed with (a) commercial conditioner, (b) methylcellulose-based hydrogel, and (c) hydroxypropyl methylcellulose-based hydrogel (Chen and Chen, 2019).

2.14.2 Nutrient Leaching

Low NUE by the crops is the outcome of nutrient deficiency in the soil which caused by nutrient leaching. The utilization of slow/controlled-release fertilizer can help in mitigating the nutrient loss because it releases nutrient gradually over the period. Past

researchers have utilized various methods and conditions to conduct the nutrient leaching analysis. However, because of differences in variables such as irrigation water volume and duration, initial fertilizer concentration (nutrient rate), moisture content of the soil same and soil type, thus a direct comparison between the studies is challenging. For instance, Wen et al. (2017a) utilized irrigation water volume of 200 mL every four days while Chen et al. (2018) used 100 mL of irrigation water daily. Additionally, the nutrient rate or the initial concentration employed in the leaching analysis were not stated in most of the studies. As a result, direct comparisons of the findings (% leached or mg leached) could not reveal the actual efficiencies of the fertilizers. In order to obtain a more precise comparison, certain enhancement could be employed, for example by using the same irrigation volume and duration, same initial nutrient rate or maintaining the same moisture content of the samples at the same percentage. In a field experiment involving the cultivation of potatoes, Zvomuya et al. (2003) showed that the use of polyolefin-coated urea fertilizer resulted in a reduction of leaching of nitrate by 34%-39% as relative to conventional fertilizer. Wen et al. (2017a) found that the synthesized corncob-g-Poly(AAm)/bentonire/PVP/urea superabsorbent hydrogel-based fertilizer greatly decreased the loss of urea through leaching. The urea leaching loss for corncob-g-Poly(AAm)/bentonire/PVP/urea was 13.2% which was lower than conventional urea (44.50%). Similar findings were observed by Li et al. (2015) who claimed that the nutrient leaching loss was reduced when wheat straw cellulose-g-Poly(AAc)/PVA/NP superabsorbent hydrogel-based fertilizer was utilized as relative to conventional fertilizer. Moreover, Chen et al. (2018) claimed that when compared to pure urea hydrogen peroxide, biochar-based fertilizer synthesized from biochar/kaolin/urea hydrogen peroxide reduced the cumulative urea leaching by 74.32%. It was found that biochar-based fertilizer possessed slow-release characteristic mainly because of the capillary

effect displayed by the small pores of biochar and the strong urea molecules adsorption, therefore a reduction of cumulative urea release was observed. Besides, Li et al. (2018a) also found that the effect of application rate of biochar-based fertilizer impacted the amount of nutrient being leached. The study showed that the biochar-based fertilizer with 3% application rate reduced the loss of total N and total K respectively by 8.36% and 9.18%, biochar-based fertilizer with 9% reduced the loss of total N and total K by 6.72% and 9.31% while at application rate of 15%, the total N and total K loss were decreased by 6.45% and 11.82% respectively. The study also claimed that the total N was adsorbed into the biochar due to its high cation-exchange capacity while the high surface area, porous structure and negative charge potential of the biochar were responsible for the reduction of total K. In contrast, the leaching of P was not greatly impacted by the application rate of the biochar-based fertilizer. Another study by Wang et al. (2021b) also revealed that the leaching loss of urea of urea-impregnated biochar-based fertilizer synthesized at different synthesis condition was less than the conventional urea.

2.14.3 Volatilization of Ammonia

The loss of N via volatilization could result in low soil fertility. In double rice production system, the ammonia loss via volatilization with for polyolefin-coated fertilizer treatment was 4%-8% which was lower than conventional urea (16%-30%) (Xu et al., 2013). Tian et al. (2017) investigated the impact of two distinct type of slow/controlled-release fertilizer which are polymer-coated fertilizer and polymer/sulfur coated fertilizer on ammonia volatilization. Both slow/controlled-release fertilizer showed lower level of ammonia volatilization as compared to conventional urea. The reduction of ammonia volatilization of both slow/controlled-release fertilizer was due to polymer and polymer/sulfur coatings prevent the direct contact of soil's moisture and urea. Souza et al.

(2018) was also found that conventional urea and tablet urea had the higher loss of ammonia as relative to clinoptilolite/urea-based fertilizer. According to Puga et al. (2020b), who found that the loss of ammonia through volatilization for biochar-based fertilizer and acidified biochar-coated urea was lower than conventional urea and unacidified biochar-coated urea. The reduction of the ammonia loss through volatilization of the biochar-based fertilizer was because ammonia was adsorbed into the biochar via physical and chemical adsorption. In addition, the slow-release characteristic of the biochar-based fertilizer was also one of the factors that contributes to the reduction loss of ammonia through volatilization by gradually release the nutrient. Additionally, the biochar:nitrogen ratio also plays an important factor in controlling the amount of ammonia loss through volatilization. The higher ratio of biochar:nitrogen producing more ammonia release than the lower biochar:nitrogen ratio. It was also found that the biochar-based fertilizer synthesized with more alkaline could increase the ammonia loss through volatilization. Another finding from Puga et al. (2020a) revealed that biochar-based fertilizer had higher loss of ammonia as relative to conventional urea. The authors also noted that the biochar-based fertilizer utilize six days to volatilize 50% of its maximal loss. In contrast, conventional urea took five days. This delay of the ammonia loss through volatilization is important because it raises the possibility that the biochar-based fertilizer would come into contact with rainwater which could resulted in ceased volatilization process. The authors also mentioned that the experimental set-up for ammonia volatilization might overestimate the process because the chamber used in the experimental set-up were not allowed wind and rain to get into the fertilizer within them, the precision of the findings might have been impacted.

2.14.4 Plant Growth

The use of slow/controlled-release fertilizer has been demonstrated to enhance the yield of the crops and improve the agricultural products' quality. The parameters such as plant height, root length, leaf width, fresh weight and dry weight of the plant are frequently utilized to assess the growth performance of the plant by comparing the soil treated with slow/controlled-release fertilizer and untreated soil (Abd El-Rehim, 2006). According to Laftah & Hashim (2014), the sandy soil treated with PHG-g-CNT/urea superabsorbent hydrogel-based fertilizer had greater growth performance as compared to PHG-g-CNT without urea, conventional urea and blank after twelve weeks of okra planting. In the study of Wen et al. (2016), it showed that the growth of cotton plant improved with the cotton stalk-g-Poly(AAc)/bentonite/PVP/urea superabsorbent hydrogel fertilizer treatment. When, the synthesized superabsorbent hydrogel-based fertilizer was used, the germination rate and height of the cotton plant enhanced by 25.23% and 22.04%, respectively. According to the research done by Wen et al. (2017b), they found that utilizing cotton stalk-g-Poly(AAc-co-AMPS)/bentonite/N-BC led to a better growth performance of cotton plant as compared to utilizing conventional fertilizer and N-BC. It was observed that the NUE of the cotton plant enhanced. This was attributed to the slow-release behaviour of N supplied from the stalk-g-Poly(AAc-coAMPS)/bentonite/N-BC which matched the growth requirement of the cotton plant. Besides, the oilseed rape plant biomass during various stages such as seedling, bolting, flowering and harvest stages improved with the application of encapsulated biochar-based fertilizer (BCRNF) as relative to conventional urea, combination of biochar and urea, pristine biochar and control system (Liao et al., 2020). Among the treatments, the application of BCRNF had the highest grain yield, rape growth and NUE. This was due to the slow-release of N and also enhanced the nitrification process via AOB activity while decreasing

the denitrification during later phases. Chew et al. (2020) claimed that the dry and wet shoot of the rice plants were found to increase by 67% and 82%, respectively with the use of biochar-based fertilizer. Furthermore, Ye et al. (2019) also stated that the growth of plant was improved by the bio-oil encapsulated biochar-based fertilizer as compared to conventional fertilizer and unencapsulated biochar-based fertilizer due to the enhanced slow-release property by the bio-oil. Puga et al. (2020a) also claimed that the maize yield was enhanced by biochar-based fertilizer (BN_{51/10} and BN_{40/17}) which was attributed to the slow-release of N from the biochar-based fertilizer. The BN_{51/10} showed the highest NUE and the differences in NUE observed in the study were related to the biochar-based fertilizer's slow-release characteristic. An et al. (2021a) found that the root length, plant height, dry and wet weight of the maize plant of cotton stalk derived bio-based polyurethane encapsulated biochar-based fertilizer with the lowest coating thickness was the greatest as compared to the control, conventional fertilizer, uncoated biochar-based fertilizer and encapsulated biochar-based fertilizer with higher coating thickness. This increment of the plant growth was due to slow-release property. Moreover, the authors observed that encapsulated biochar-based fertilizer with higher coating thickness resulted in decline maize growth was due to the slower nutrient release rate as compared to low coating thickness which it unable to provide sufficient nutrient to the plant.

2.15 Summary

Malaysia is one of the largest producers of pepper around the world. In order to minimize the pepper waste such as peppercorn waste produced from the pepper plantation and processing, converting the pepper waste into valued-add product can be employed. The conversion of peppercorn waste into biochar has been scarcely reported. Biochar can be utilized as a soil amendment and carbon sequestration material to enhance soil fertility and

mitigate climate change. Due to low quantity of nutrient content in the pristine biochar, incorporating nutrient into matrix of biochar to produce biochar-based fertilizer has been discovered by researchers to resolve the low nutrient content present in pristine biochar. Nonetheless, their slow-release mechanism is still facing limitation. Therefore, the combination of encapsulation technology with biochar-based fertilizer could be employed to overcome this issue. Despite the slow/controlled release property could be enhanced by encapsulating, their sustained release property is influenced by the formulation of the encapsulating materials. Biopolymer such as starch has been utilized as encapsulating or coating material due to its low-cost and environmentally friendly. The limitation of utilizing pure starch as encapsulating material is due to their high hydrophilicity. Therefore, blending with other additives can be one of the solutions to enhance its hydrophobicity. The formulation of tapioca starch/PO biofilm as an encapsulating material in synthesize slow/controlled-release fertilizer is still unknown. From the literature review, there is a lack of study in investigating the effect of tapioca starch/PO biofilm encapsulated urea-impregnated biochar-based fertilizer on nitrogen release behaviour, water retention behaviour, nitrogen leaching and growth performance of plant.

CHAPTER 3

METHODOLOGY

3.1 Outline of Methodology

This chapter outlines the stages of methodology to accomplish the research objectives of this study, as illustrated in **Figure 3.1**.

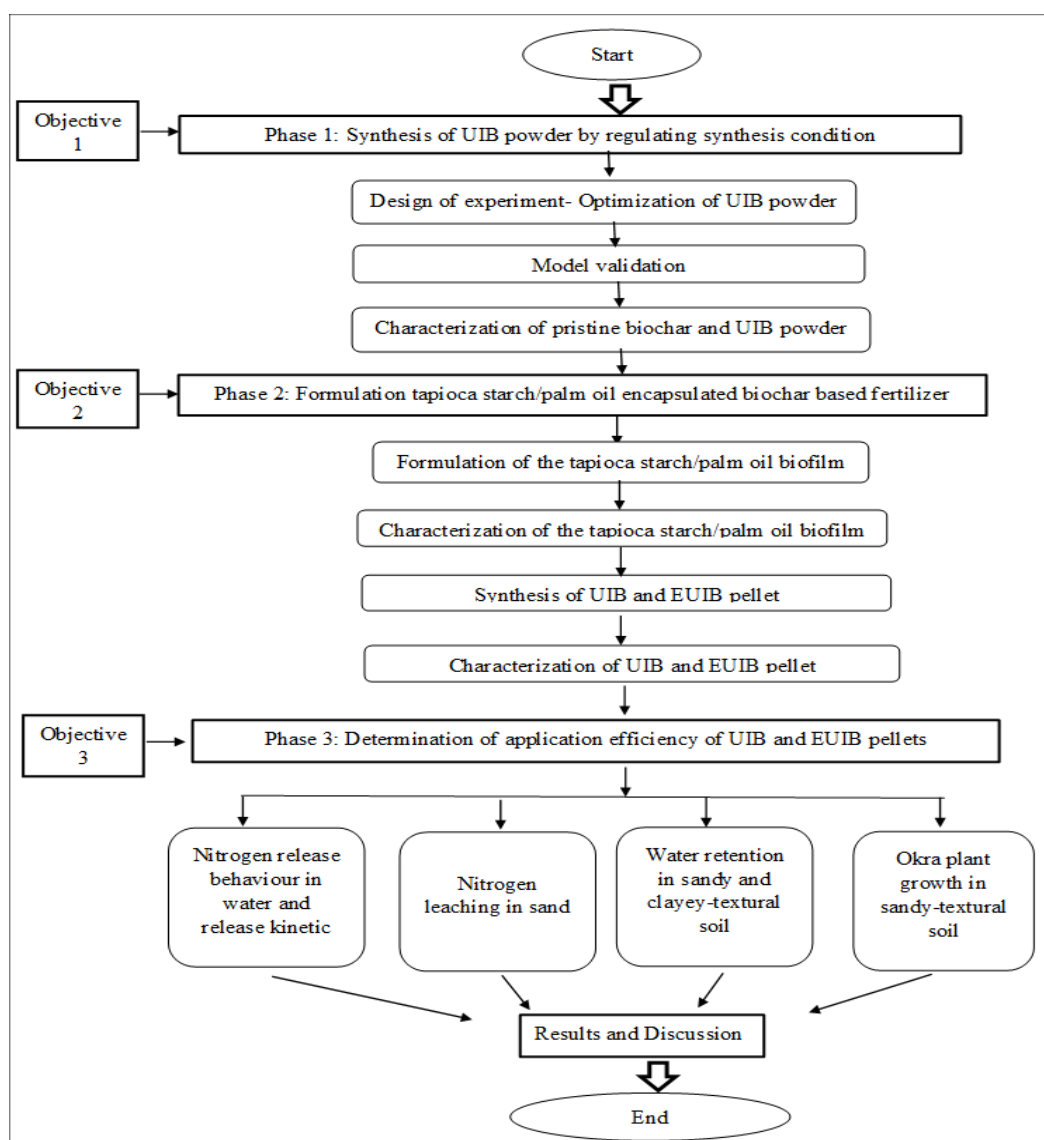


Figure 3.1: Experimental Flow Chart

This study comprised of three primary phases that were aligned with the research objectives. The first phase referred to objective 1 was conducted to synthesize the urea-impregnated peppercorn waste derived biochar-based fertilizer by regulating the pyrolysis temperature, residence time and urea:biochar ratio. The experimental work consisted of the synthesis and characterization of the peppercorn waste derived biochar and UIB powder as well as to optimize the UIB powder using response surface methodology and model validation. The second phase was to formulate the tapioca starch/PO biofilm encapsulated biochar-based fertilizer by varying the concentration of tapioca starch and PO. The experimental works involved synthesis and characterization of biofilm, UIB pellet and EUIB pellet. The third phase was associated with objective 3 which was to investigate the effect of the formulated encapsulated biochar-based fertilizer on nitrogen release in water, release kinetics, nitrogen leaching in sand, water retention in sandy and clayey-textural soil and okra plant growth in sandy-textural soil.

3.2 Materials

The peppercorn waste utilized in this study as the precursor for synthesis of biochar was provided by Malaysian Pepper Board, Kuching, Sarawak. The tapioca starch and palm oil (Harvis) were obtained from local store, urea (ACS grade, 99.00% - 100.50%) was obtained from JT Baker, selenium (ACS grade, 99.00%) and methyl red indicator (ACS grade) were obtained from Bendosen, glycerol (Ph.Eur, 85.00%) was obtained from Supelco, sodium hydroxide (AR grade, $\geq 97.00\%$) obtained from Fisher Chemical, sulfuric acid (95.00%-98.00%, ACS grade) was obtained Merck, silica was obtained from Witeg, copper sulfate (AR grade, $\geq 99.00\%$), potassium sulfate (ACS grade, $\geq 99.00\%$, boric acid (ACS grade, $\geq 99.50\%$), bromocresol-green indicator (ACS grade, $\geq 95.00\%$) were obtained from Sigma-Aldrich and nitrogen gases were obtained from Big Industrial.

3.3 Phase 1: Synthesis of UIB Powder

3.3.1 Design of Experiment

The synthesis of fertilizer with a high nutrient content is crucial because it ensures an adequate supply of nutrient to plants while reducing the bulk of material farmers have to handle (Bakshi et al., 2021). Therefore, the synthesis of UIB-based fertilizer with high loading of nitrogen is crucial. To achieve this, an optimization study was conducted by using the Design Expert software version 11.1.2 (STAT-EASE Inc, Minneapolis, USA). Central composite design (CCD) was employed as an experimental design model to determine the optimum condition for synthesizing the UIB. The CCD consisted of three types of points including $2n$ axial points, $2n$ factorial points and n_c center points. The UIB was synthesized by adjusting the parameters with the CCD. The independent variables chosen were pyrolysis temperature (A), residence time (B) and urea:biochar ratio (C). The variables and values were selected based on the studies of Menya et al. (2019), Sahoo et al. (2021), Azman et al. (2022) and preliminary studies. To study the three independent variables, a 2^3 full factorial was implemented, comprising of 8 factorial points, 6 axial points and 6 replicates at the center. In total, 20 experiments were formed based on the CCD, as determined by Equation (3.1):

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \quad \text{Equation 3.1}$$

where N denoted the number of experiments to be carried out whereas n presented the number of independent variables. The nitrogen content was analyzed using central composite rotary design (Senthilkumar et al., 2005). **Table 3.1** displays the full design matrix for the experiments that need to be conducted. The experimental order was randomized to minimize the influence of uncontrolled variables. Each response of nitrogen content was also

presented in **Table 3.1** was utilized to develop an empirical model by using a second-order degree polynomial model to correlate the nitrogen content to the UIB powder synthesis variables, as presented in Equation (3.2) (Zainudin et al., 2005):

$$Y = b_o + \sum_{i=1}^n b_i x_i + (\sum_{i=1}^4 b_{ii} x_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad \text{Equation 3.2}$$

where Y represented the estimated response, b_o denoted the constant regression coefficient, b_i represented the coefficient of linearity, b_{ij} represented the coefficient of interaction, b_{ii} denoted the coefficient of quadratic whereas the UIB synthesis variables were represented by x_i and x_j as the coded values.

The optimum condition predicted for synthesizing the peppercorn waste derived UIB in this study was determined using the numerical optimization function. In order to validate the model, the experiment condition with the highest level of desirability was chosen. Duplicate experiments were carried out to replicate the predicted optimum condition and to compare the experimental values with the predicted values. The accuracy of the predicted values was assessed using the RSE, which is the fraction of the estimate and is typically expressed as a percentage as illustrated in Equation. (3.3):

$$RSE = \left| \frac{x_1 - x_2}{x_2} \right| \times 100\% \quad \text{Equation 3.3}$$

where x_1 was the experimental value and x_2 was the predicted value.

Table 3.1: Central composite design matrix and results

Run	Pyrolysis temperature (°C) (A)	Pyrolysis residence time (minutes) (B)	Urea:biochar ratio (C)
1	500.00	39.55	0.425
2	331.82	90.00	0.425

Table 3.1 continued

3	600.00	120.00	0.250
4	500.00	90.00	0.425
5	500.00	140.45	0.425
6	668.18	90.00	0.425
7	500.00	90.00	0.425
8	500.00	90.00	0.719
9	500.00	90.00	0.131
10	600.00	120.00	0.600
11	600.00	60.00	0.250
12	500.00	90.00	0.425
13	400.00	60.00	0.250
14	400.00	120.00	0.250
15	500.00	90.00	0.425
16	600.00	60.00	0.600
17	400.00	120.00	0.600
18	400.00	60.00	0.600
19	500.00	90.00	0.425
20	500.00	90.00	0.425

3.3.2 Regression and Statistical Analyses

The experimental results were utilized to conduct the regression analysis and fit the equation established using Design Expert software version 11.1.2 (STAT-EASE Inc., Minneapolis, USA). In addition, analysis of variance (ANOVA) was performed to assess the

statistical significance of the model as determined by the *f*-value and *p*-value (Zhou et al., 2020).

3.3.3 Synthesis of Peppercorn Waste-based Biochar and UIB Powder

The raw feedstock was washed several times and dried in an oven at 105 °C (Model Binder FD 115) for 24 hours to remove the moisture content and other impurities. Next, 5 g of the feedstock was placed into a clean crucible and pyrolyzed in a tubular furnace (Model Berkeley Scientific BSG-1200X) with heating rate of 10 °C/minute under inert condition by flowing nitrogen gas through the furnace (Zhang et al., 2022b). After that, the biochar was cooled to room temperature (± 28 °C), crushed and sieved to 300 μ m. The urea solution was prepared by mixing urea powder at different weight in 20 mL of distilled water, according to the urea:biochar ratio (weight/weight). Then, 0.2 g of the synthesized biochar was mixed into the urea solution and heated at 65 °C in a hot air oven (Model Binder FD 115) (Manikandan & Subramanian, 2013). The UIB was kept in an air-tight bottle for further analysis.

3.3.4 Determination of Nitrogen Content of Urea-Impregnated Biochar-based Fertilizer

Before pelletization and encapsulation process, the micro-Kjeldahl method was used to determine the nitrogen content of the UIB (Abu et al., 2021). Kjeldahl method was classified into three stages including digestion, distillation and titration. In the digestion stage (**Figure 3.2**), 1 mg of N of biochar was placed into a micro-Kjeldahl flask. Next, 3 mL of 98% sulfuric acid was added into the flask overnight. Then 1.10 g of catalyst (copper sulfate, potassium sulfate and selenium) was added and heated in a heating mantle with an angle of 45 ° until the colour of the solution became light green. Thereafter, it was heated for 3 hours. After that, the micro-Kjeldahl flask was cooled to room temperature (± 28 °C).



Figure 3.2: Digestion process

In the distillation stage (**Figure 3.3**), 20 mL of distilled water was added into the flask and swirled gently after the solution was cooled. The solution was then transferred into a distillation flask and the micro-Kjeldahl flask was rinsed three times with 10 mL of distilled water. Next, 20 mL of 50% sodium hydroxide solution was added into the distillation flask and 30 mL of distilled water was added to top up the solution to 80 mL. Then, 5 mL of 2% boric acid was added to trap the ammonia gases. After collected about 35 mL of the distillate, the distillation process was stopped (Bremner & Mulvaney, 1982).



Figure 3.3: Distillation process

In the titration stage (**Figure 3.4**), the 35 mL of distillate was then titrated with 0.01 N of hydrochloric acid until the solution became slightly pink (Abu et al., 2021). The nitrogen content of the urea-impregnated biochar-based fertilizer was calculated by using Equation (3.4) (Gao et al., 2015):

$$\text{Nitrogen, \%} = \frac{(s-b), \text{ml} \times 0.01N \text{ HCl} \times 1.4N}{\text{weight of sample, g}} \times 100 \quad \text{Equation 3.4}$$

where s represented the titrant volume of the sample while b represented the titrant volume of blank.



Figure 3.4: Titration process

3.3.5 pH and EC

The pH and EC of the biochar synthesized at 400 °C, 60 minutes; 400 °C, 120 minutes and 600 °C, 120 minutes was measured using a pH meter and EC meter, respectively with ratio of 1 g :20 mL (Tang et al., 2023). About 1 g of the biochar was placed in conical flask with 20 mL of distilled water. The conical flask containing the solution was shaken by using orbital shaker. After that, the solution was filtered using a filter paper and the filtered solution was tested by using pH and EC meter.

3.3.6 Surface Morphology and Elemental Composition

The peppercorn waste-based biochar synthesized at 400 °C and 60 minutes, 400 °C and 120 minutes and 600 °C and 120 minutes and UIB powder were characterized for their

surface morphology and the elemental composition by using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Model TM4000Plus, Hitachi, Japan) with accelerating voltage of 15 kV (Adeniyi et al., 2021).

3.3.7 Surface Chemistry

The peppercorn waste-based biochar synthesized at 400 °C and 60 minutes; 400 °C and 120 minutes and 600 °C and 120 minutes and UIB powder were characterized for their surface chemistry by using Fourier transform infrared spectroscopy (FTIR) (Model IRAffinity 1S, Shimadzu, Japan) under 400-4000 cm^{-1} and wavelength of 4 cm^{-1} (Maghsoodi et al., 2020).

3.3.8 Surface Area and Total Pore Volume

The surface area and pore volume of biochar synthesized at 400 °C and 60 minutes; 400 °C and 120 minutes and 600 °C and 120 minutes and UIB powder were determined from the adsorption isotherms of nitrogen at 77 K onto the samples using Brunauer Emmett Teller method (Quantachrome ASIQC0000-3) (Tan et al., 2017).

3.4 Phase 2: Formulation of Tapioca Starch/PO Encapsulated Biochar-based Fertilizer

3.4.1 Synthesis of Biofilm

The casting method was used to synthesize the tapioca starch/PO biofilm (Wang et al., 2021a). Three different concentrations of tapioca starch which were 4 g, 6 g and 8 g were mixed with 100 mL of distilled water. Next, the tapioca starch solution was added with 30 wt% of glycerol (based on the weight of tapioca starch). Subsequently, two different amounts of PO (0.04 μL and 0.12 μL) and 20 wt% of tween 80 (based on the weight of the PO) were separately added into the solution. The mixture was then heated at 90 °C using a hotplate

and stirred at 500 rpm with an overhead stirrer for 45 minutes. Subsequently, 25g of the mixture was casted into a 9 cm x 9 cm petri dish. After that, it was dried in an oven at 50 °C (Guo et al., 2022). The pure tapioca starch biofilm (4 g, 6 g and 8 g) was synthesized using the same step but without the inclusion of PO and Tween80.

3.4.2 Water Absorption Analysis of Biofilm

The water absorption ability of the biofilm is an important factor for slow-release as low water absorption ability of the biofilm could reduce the release rate of nutrients. The method described by Guo et al. (2022) was used to ascertain the biofilm's capacity to absorb water. The dried biofilm was measured 2cm by 2cm was submerged in 100 mL of distilled water for 24 hours. The biofilm was then weighed and the water absorption was calculated by using Equation (3.5):

$$\text{Water absorption, \%} = \frac{W_w - W_d}{W_d} \times 100 \quad \text{Equation 3.5}$$

Where W_d (g) represented the weight of the dried biofilm before submerged in the distilled water whereas W_w (g) represented the weight of the biofilm after submerged in the distilled water.

3.4.3 Surface Chemistry of Selected Biofilm

The lowest water absorption ability of pure tapioca starch biofilm and tapioca starch/PO biofilm were characterized for their surface chemistry by using Fourier transform infrared spectroscopy (FTIR) (Model IRAffinity 1S, Shimadzu, Japan) under 400-4000 cm^{-1} and wavelength of 4 cm^{-1} (Maghsoodi et al., 2020).

3.4.4 Synthesis of UIB and EUIB Pellets

To produce UIB pellet, 0.3g of UIB powder was mixed with 150 μ L of methylcellulose solution, pelletized using a pellet press and then dried in an oven at 65 °C. For synthesis of EUIB pellet, the dip-coating approach was utilized to obtain EUIB pellet (An et al., 2021a). The biofilm with the lowest water absorption was chosen as the coating material to encapsulate the UIB pellet. Firstly, the UIB pellet was immersed into the tapioca starch/PO solution for 10 seconds and then carefully retrieved from the solution by using a pinset. After that, it was placed on the parchment paper and dried for three hours at 65 °C in the oven. The schematic diagram of the synthesis process was shown in **Figure 3.5**. The process was repeated four times to achieve a sufficient coating thickness, ensuring effective sustained-release characteristic and complete coverage of the UIB pellet with the tapioca starch/PO (Ghumman et al., 2021).

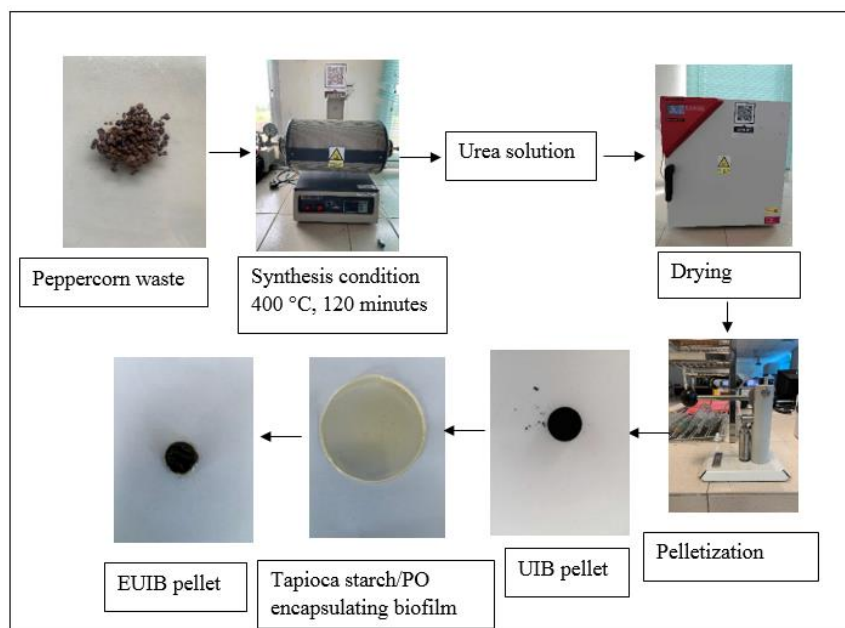


Figure 3.5: Schematic diagram of the synthesis process of EUIB pellet

3.4.5 Surface Morphology and Elemental Composition

The UIB and EUIB pellets were characterized for their surface morphology and elemental composition (before and after nitrogen release in water-presented in result and discussion in phase 3) by using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Model TM4000Plus, Hitachi, Japan) with accelerating voltage of 15kV (Adeniyi et al., 2021).

3.4.6 Surface Chemistry

The UIB and EUIB pellets were characterized for their surface chemistry using Fourier transform infrared spectroscopy (FTIR) (Model IRAffinity 1S, Shimadzu, Japan) under 400-4000 cm^{-1} and wavelength of 4 cm^{-1} (Maghsoodi et al., 2020).

3.4.7 Crushing Strength

Compression test was performed on the synthesized fertilizers to assess their resistance to impact, in order to ensure the durability of the synthesized fertilizers from the synthesis phase until their packaging and transportation (Beig et al., 2020b). The UIB pellet and EUIB pellet were subjected to compression test by using universal testing machine (AGS-50kNX). The crosshead speed of the compression was set to 1 mm/min. The amount of stress that caused the UIB pellet and EUIB pellet to disintegrate was recorded (Beig et al., 2020b).

3.5 Phase 3: Determination of the Effect of EUIB Pellet on Nitrogen Release in Water, Release Kinetic, Nitrogen Leaching in Sand, Water Retention in Sandy and Clayey-Textural Soil and Plant Growth in Sandy-Textural Soil

3.5.1 Nitrogen Release Behaviour in Water

To investigate the nitrogen release behaviour in water, about 29 mg of N of each sample including pure urea, UIB pellet and EUIB pellet was placed separately into teabags. Then, the sample was soaked separately in 100 mL of distilled water in a 250 mL beaker. After that, 5 mL of the distilled water was withdrawn by using a pipette at different time intervals (1 minute, 3 minutes, 15 minutes, 30 minutes, 60 minutes, 90 minutes, 240 minutes and 330 minutes). Next, another 5 mL of fresh distilled water was added into the solution to maintain the solution level at 100 mL. The nitrogen content in the water was measured using Kjeldahl method (Liu et al., 2019b). The nitrogen content in mg/L and the cumulative nitrogen release in percentage was determined by using Equations (3.6) - (3.7):

$$\text{Nitrogen content, mg/L} = \frac{(s-b), \text{ml} \times 0.01N \text{ HCl} \times 14 \text{ N} \times 1000}{\text{weight of sample, ml}} \quad \text{Equation 3.6}$$

where s denoted the titrant volume of the sample while b denoted the titrant volume of the blank.

$$\text{Cumulative nitrogen release, \%} = \frac{Q_t}{Q_o} \times 100 \quad \text{Equation 3.7}$$

where Q_t (mg) represented the nitrogen release from pure urea, UIB pellet and EUIB pellet at time t whereas Q_o (mg) indicated the total nitrogen in the pure urea, UIB pellet and EUIB pellet.

3.5.2 Nitrogen Release Kinetic Model

The release mechanism of the UIB pellet and EUIB pellet was assessed using four release kinetic models including the zero-order model, first-order model, Higuchi model and Korsmeyer-Peppas model. The experimental data were analyzed by fitting the data into the mathematical models as depicted in Equations (3.8) – (3.11) (Padmaa Paarakh et al., 2018; An et al., 2021b):

Zero-order release kinetic model:

$$Q = k_o t \quad \text{Equation 3.8}$$

First-order release kinetic model:

$$\log M_t = \log M_o - \frac{k_t}{2.303} \quad \text{Equation 3.9}$$

Higuchi release kinetic model:

$$\frac{M_t}{M_o} = k_H t^{\frac{1}{2}} \quad \text{Equation 3.10}$$

Korsmeyer-Peppas release kinetic model:

$$\frac{M_t}{M_o} = k_{kp} t^n \quad \text{Equation 3.11}$$

where M_t and M_o indicated the amount of nitrogen in solution at time t (min^{-1}) and initial amount of nitrogen at time t (min^{-1}), respectively, Q represented the the amount of nitrogen released of UIB and EUIB pellet at time t (min^{-1}), $\frac{M_t}{M_o}$ indicated the release percentage of nitrogen in different time intervals, n represented the exponent indicative of the transport mechanisms whereas k_o (min^{-1}), k_t (min^{-1}), k_H (min^{-1}) and k_{kp} (min^{-1}) indicated the release rate constant for zero-order model, first-order model, Higuchi model and Korsmeyer-Peppas model, respectively.

3.5.3 Water Retention Behaviour

The water retention behaviour of the UIB pellet and EUIB pellet was investigated through the method demonstrated by Wang et al. (2021d). About 0.6g of the samples were buried separately into 100 g of clayey-textural and sandy- textural soil in a plastic cup and weighed. Next, 25 mL and 50 mL of the distilled water was poured into the plastic cup containing the sandy-textural and clayey-textural soils with the samples, respectively and then weighed again. The control treatment (without UIB and EUIB pellet) was employed as a reference for comparing the soil treated with UIB pellet and EUIB pellet. The water retention ratio in percentage of control, UIB pellet and EUIB pellet was calculated using Equation (3.12) (Wang et al., 2021d):

$$WR, \% = \frac{W_t - W_o}{W_i - W_o} \quad \text{Equation 3.12}$$

where W_o (g) indicated the weight of sample, plastic cup and soil, W_t (g) indicated the weight of sample, plastic cup, distilled water and soil at regular time interval while W_i (g) indicated the weight of sample, plastic cup and soil after distilled water had been added.

3.5.4 Nitrogen Leaching in Sand

The sand column leaching method was utilized to study the nitrogen leaching behaviour of pure urea, UIB pellet and EUIB pellet, as displayed in **Figure 3.6**. The nitrogen leaching was carried out by using a syringe with 3 cm diameter and 12 cm height. The bottom of the syringe was covered with a 160-wire mesh to prevent the loss of soil followed by glass beads and sand. Next, an equivalent amount of N (about 29 mg of N) sample was added and then covered again with sand, wire mesh and glass beads, as illustrated in **Figure 3.7**. To simulate natural raining environment, 110 mL of distilled water at a flow rate of 10 mL/minute was pumped into the syringe by using a peristaltic pump (LongerPump YZ1515x). The leaching activity was performed every 24 hours in a reagent bottle. The nitrogen content in the leachate was then measured using Kjeldahl method (Liu et al., 2019b).

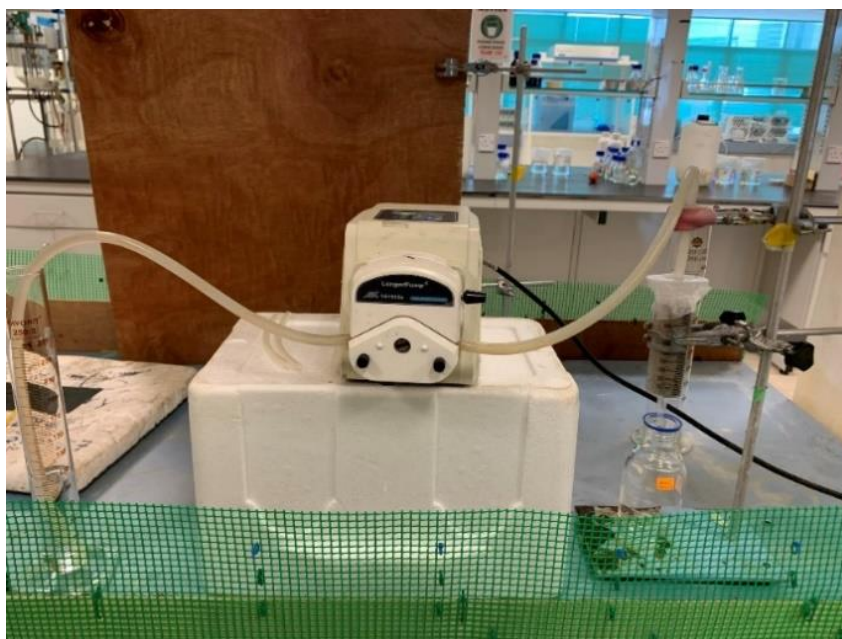


Figure 3.6: Sand column leaching set-up

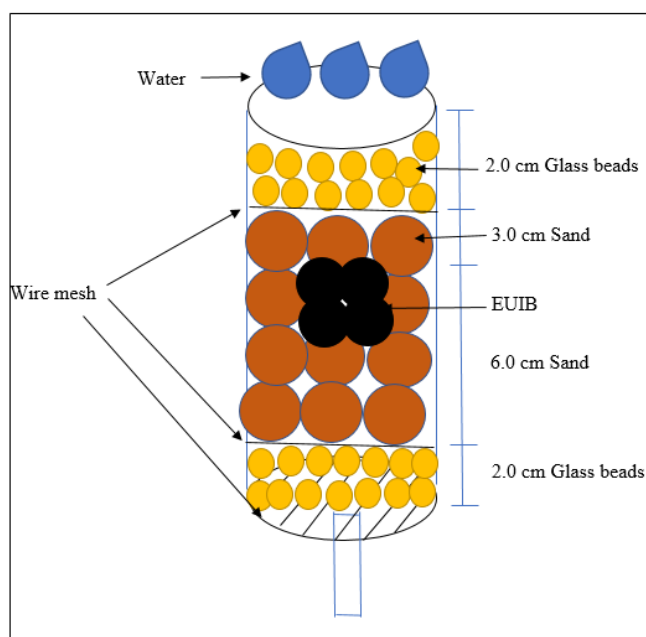


Figure 3.7: Schematic diagram of the sand column leaching

3.5.5 Plant Growth

The sandy-textural soil was used in this study as nitrogen tended to be lost in sandy-textural soil. The pH and EC levels of the sandy-textural soil were 6.09 and 0.02 ms cm^{-1} .

Plastic pots with diameter of 12 cm and 9 cm height were used to conduct the experiment. 600 g of the soil was added into the plastic pot and okra seed was planted at a depth of 2 cm. When the okra seed started seedling, about 60 mg of N of pure urea, UIB pellet and EUIB pellet was buried around the roots of the okra plant (about 4 cm depth in the soil) in separate pot. The plant in each pot was watered with 100 mL of distilled water every two days. After sowing for 30 days, the plants were carefully removed from the pots. The shoot length, root length, leaves area as well as the dry and wet weight of the plants were measured (Salimi et al., 2021; Salem & Hassan, 2020). Besides, the number of leaves were also counted. The shoot and root length of the okra plant were measured using a ruler and the data was recorded. The dry and wet weight of the okra plant were measured using the weighing balance and the weight was recorded. The height and the width of the leaves was measured by using a ruler to obtain the area of the leaves.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

This chapter presents and discuss the findings relevant to the study's goals and objectives. The results and discussion sections are structured into three main phases that align with the objectives in Chapter 1.

4.2 Phase 1: Synthesis of Urea-Impregnated Biochar-based Fertilizer

The empirical model was developed in this study to correlate synthesis variable to nitrogen content in order to obtain optimum synthesis condition to synthesize UIB powder by using Design Expert software. Besides, model validation was performed. The characteristic of the peppercorn waste-based biochar and UIB powder was also evaluated.

4.2.1 Regression Model Development and Analysis of Variance

The relationship between the synthesis variables of UIB powder and nitrogen content was correlated using CCD. The range of urea retention capacity in relation to nitrogen content was between 4.70 % and 17.00 %, as shown in **Table 4.1**. Both linear and quadratic models were suggested, however the quadratic model was chosen due to the higher correlation coefficient (R^2). The Equation (4.1) presents the final empirical equation expressed in terms of coded factors:

$$Y_{1(\text{Nitrogen content, \%})} = 13.23 - 0.8425A + 0.3506B + 2.77C - 0.2412AB - 0.6788AC + 0.2113BC - 0.9087A^2 - 1.02B^2 - 0.5074C^2 \quad \text{Equation 4.1}$$

The positive coefficient value in the equation represented the synergistic effect whereas the negative coefficient value indicated the antagonistic effect. The model's quality was assessed based on the R^2 value. Generally, a decent model fit typically has R^2 of at least 0.8 (Ahmad et al., 2020). The R^2 obtained from Equation 4.1 was 0.8428 which indicated that the model was well fitted. In the meantime, the adjusted R^2 was 0.7013 which was considered to be reasonably high in order to confirm the significance of the model. Since it would forecast a response value that was more closely aligned with the actual value, the model would perform better if the R^2 was nearer to unity and the standard deviation was smaller. In order to ensure adequate precision, the signal to noise ratio was evaluated in which the ratio superior than 4 was preferred. The model developed in this study had an adequate precision of 7.96, indicating that the model discrimination was deemed satisfactory (Singh et al., 2015). In order to further support the suitability of the model, analysis of variance (ANOVA) was performed. **Table 4.2** depicts the ANOVA of the quadratic model for nitrogen content. The F -value was 5.96, indicating that it was significant and there was only 0.50% chance that an F -value this large could be caused by noise. The model terms were considered significant if the p -value was less than 0.0500 (Ahmad et al., 2021). The model terms C and B^2 were significant in this case whereas A and A^2 were moderately significant as the p -value was lower than 0.100. In other words, the urea:biochar ratio and pyrolysis temperature played an important role in affecting the nitrogen content of the UIB. The urea:biochar ratio was significant probably due to more available nitrogen for the active site of the biochar. The effect of pyrolysis temperature in this study was moderately significant. This was probably due to the quantity of the acidic functional group present in the peppercorn waste was moderate. It was noteworthy that the quantity of the acidic functional group of biochar varied with different precursor. Sun et al. (2017) found that dry

leaves derived biochar had more acidic functional group (0.40 mmol g^{-1}) than reed derived biochar (0.21 mmol g^{-1}) at pyrolysis temperature of 400°C . Meanwhile, the effect of residence time was insignificant due to the changes of the amount of acidic functional group was not significant with the increase of the residence time. Sun et al. (2017) also claimed that the changes of the total acidic functional group of fresh leaves was insignificant from 0.73 mmol g^{-1} to 0.68 mmol g^{-1} respectively at 1 hour and 4 hours of residence time. **Figure 4.1** shows the diagnostic for the model's statistical features, including the normal probability plot and predicted versus actual plot. The normal plot of residuals in **Figure 4.1(a)** shows the assumption of normality was satisfied because the residual plot roughly followed a straight line. **Figure 4.1(b)** shows the predicted values versus actual value for nitrogen content. As can be observed, the predicted values obtained fitted quite well with the actual values, showing that the model successfully captured the relationship between the variables used in the production of urea-impregnated biochar and the nitrogen content.

Table 4.1: Central composite design matrix and results

Run	Pyrolysis temperature ($^\circ\text{C}$) (A)	Pyrolysis residence time (minutes) (B)	Urea:biochar ratio (C)	Nitrogen content (%) (Y)
1	500.00	39.55	0.425	9.08
2	331.82	90.00	0.425	10.40
3	600.00	120.00	0.250	9.50
4	500.00	90.00	0.425	12.00
5	500.00	140.45	0.425	9.210
6	668.18	90.00	0.425	8.500
7	500.00	90.00	0.425	14.100

Table 4.1 continued

8	500.00	90.00	0.719	16.470
9	500.00	90.00	0.131	4.700
10	600.00	120.00	0.600	12.380
11	600.00	60.00	0.250	8.560
12	500.00	90.00	0.425	14.280
13	400.00	60.00	0.250	9.500
14	400.00	120.00	0.250	10.000
15	500.00	90.00	0.425	12.100
16	600.00	60.00	0.600	12.000
17	400.00	120.00	0.600	17.000
18	400.00	60.00	0.600	14.25
19	500.00	90.00	0.425	13.80
20	500.00	90.00	0.425	13.50

Table 4.2: Analysis of variance (ANOVA) for quadratic regression model for nitrogen content of urea-impregnated biochar

Source	Sum of squares	Degree of freedom (d.f.)	Mean square	F value	Prob>F
Model	146.88	9	16.32	5.96	0.0050
A	9.69	1	9.69	3.54	0.0894
B	1.68	1	1.68	0.6128	0.4519
C	104.98	1	104.98	38.32	0.0001

Table 4.2 continued

AB	0.4656	1	0.4656	0.1699	0.6889
AC	3.69	1	3.69	1.35	0.2731
BC	0.3570	1	0.3570	0.1303	0.7256
A ²	11.90	1	11.90	4.34	0.0638
B ²	14.89	1	14.89	5.44	0.0420
C ²	3.71	1	3.71	1.35	0.2715
Residual	27.40	10	2.74		
Lack of fit	22.38	5	4.48	4.46	0.0633
Pure error	5.02	5	1.00		
SD	1.66		R ²	0.8428	
Mean	11.57		Adjusted R ²	0.7013	
C.V. %	14.31		Adequate precision	7.9679	

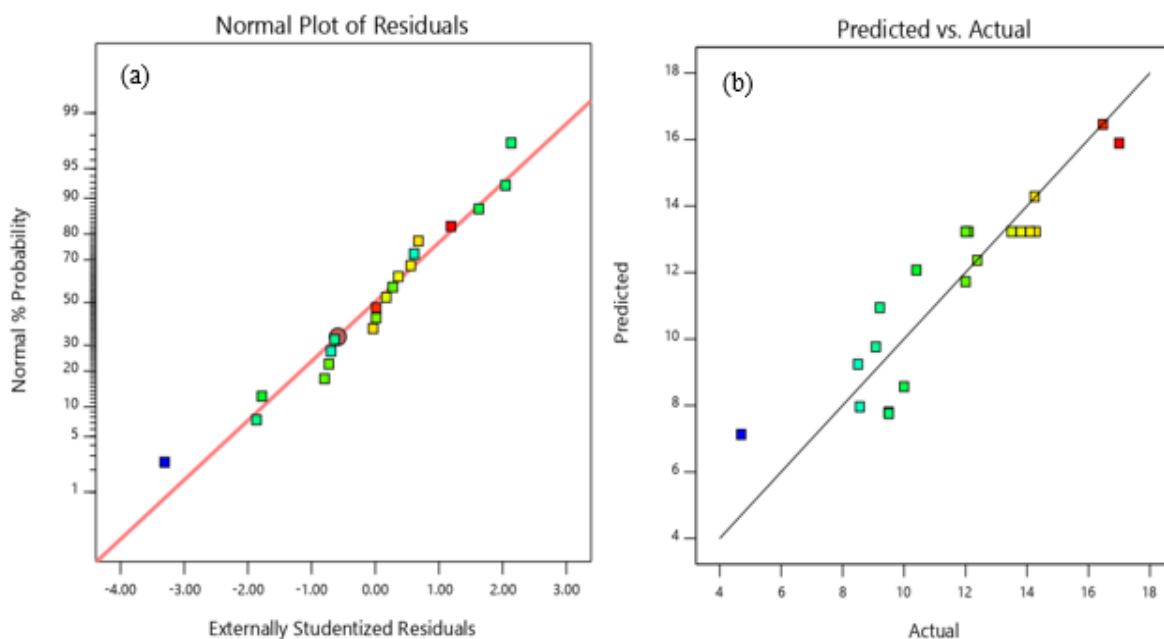


Figure 4.1: Diagnostics plot for nitrogen content using (a) normal plot of residuals and (b) predicted versus actual value

4.2.2 Interactive Effect of Pyrolysis Temperature and Residence Time on Nitrogen Content of UIB Powder

The response surface plot of the interactive effect of pyrolysis temperature and residence time on the nitrogen content of UIB is displayed in **Figure 4.2**. It was demonstrated that the lower temperature of pyrolysis and longer residence time were preferable for achieving a higher nitrogen content. The higher nitrogen content observed might be due to the acidic functional group and hydrophilicity of the biochar. The results were supported by Liu et al. (2019b) and Zhang et al. (2015) which reported that urea could react with the acidic functional group, and the hydrophobic property of the biochar could retard the urea molecules from diffusing into the pores. The interaction of urea and acidic functional group of biochar is shown in **Figure 4.3**. The studies observed that the acidic functional group of the biochar reduced by increasing the temperature of pyrolysis. Zhang et al. (2021) observed that by increasing the pyrolysis temperature from 300 °C to 700 °C, it resulted in a decrease

in the total acidic functional group of cow manure-based biochar from 4.41 mmol g⁻¹ to 0.96 mmol g⁻¹. Moreover, Cantrell et al. (2012) also observed that by increasing the temperature of pyrolysis from 300 °C to 700 °C, it caused a reduction or loss of the -COOH and C=O groups in all types of manure-based biochar. In the other hand, the residence time showed a less significant impact on the nitrogen content. The acidic functional groups and C-O would not always be reduced by a longer residence time. In this study, the biochar synthesis at longer residence time had slightly increased the acidic functional groups (C=O and -COOH) and C-O as compared to shorter residence time. However, the changes of acidic functional groups were insignificant. Sun et al. (2017) observed that the total acidic functional group of plantae wood biochar increased from 0.75 mmol g⁻¹ to 0.80 mmol g⁻¹ at residence time of 0.5 hours and 24 hours, respectively. The total acidic functional group of the plantae wood biochar significantly reduced from 0.75 mmol g⁻¹ to 0.02 mmol g⁻¹ when the pyrolysis temperature was increased from 300 °C to 600 °C. The study revealed that the residence time demonstrated a less significant impact on the acidic functional group as compared to pyrolysis temperature.

Design-Expert® Software
Factor Coding: Actual

Nitrogen Content (%)

● Design points above predicted value

○ Design points below predicted value

4.7 17

X1 = A: Pyrolysis Temperature

X2 = B: Residence Time

Actual Factor

C: Urea:biochar ratio = 0.425

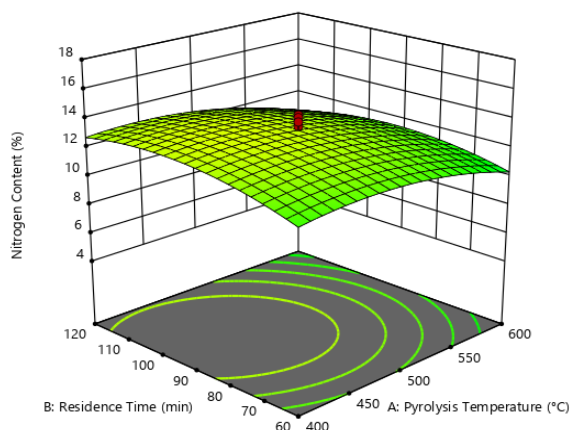


Figure 4.2: Response surface plot of pyrolysis temperature and residence time on nitrogen content

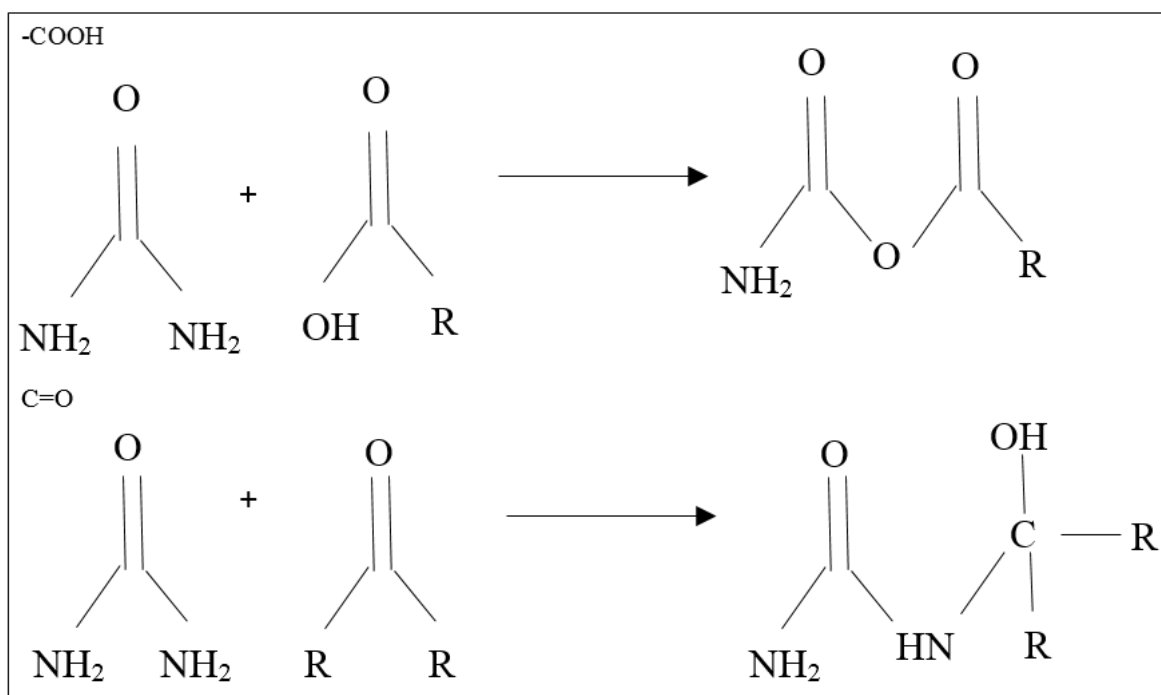


Figure 4.3: Interaction of urea and acidic functional groups of biochar(Wang et al., 2021b)

4.2.3 Interactive Effect of Pyrolysis Temperature and Urea:Biochar Ratio on Nitrogen Content of UIB Powder

Based on the response surface plot (**Figure 4.4**) of the interactive effect of pyrolysis temperature and urea:biochar ratio on the nitrogen content, the nitrogen content enhanced with increasing urea:biochar ratio. However, the nitrogen content declined as the temperature of pyrolysis raised. This indicated that the increase in the temperature of pyrolysis could have a negative influence on the nitrogen impregnation. The biochar synthesized at a lower pyrolysis temperature and higher urea:biochar ratio exhibited a higher nitrogen content. This could be explained by the peppercorn waste-based biochar having a more acidic functional group such as C=O, C-O and -COOH, and also being less hydrophobic as compared to peppercorn waste-based biochar synthesized at higher pyrolysis temperature which can be seen in **Figure 4.7** and **Table 4.5**. This provided more sites accessible and less urea diffusional resistance for urea molecules to be impregnated onto the biochar, therefore resulted in a higher nitrogen content. Moreover, high pyrolysis temperature improved the hydrophobicity of biochar and retarded the urea molecules from diffusing into the pores on the surface of the biochar. Although the biochar synthesized at 600 °C had more surface area which shown in section 4.2.10, but the hydrophilicity and acidic functional groups decreased with increasing pyrolysis temperature. Thus, it resulted in low nitrogen content than lower pyrolysis temperature. Zhang et al. (2015) also found that corncob-based biochar synthesized at 600 °C had lower urea adsorption capacity when compared to 300 °C, as the low adsorption capacity was attributed to the low polar moieties (acidic functional group) such as carbonyl, carboxyl and phenolic-OH as well as its hydrophobicity.

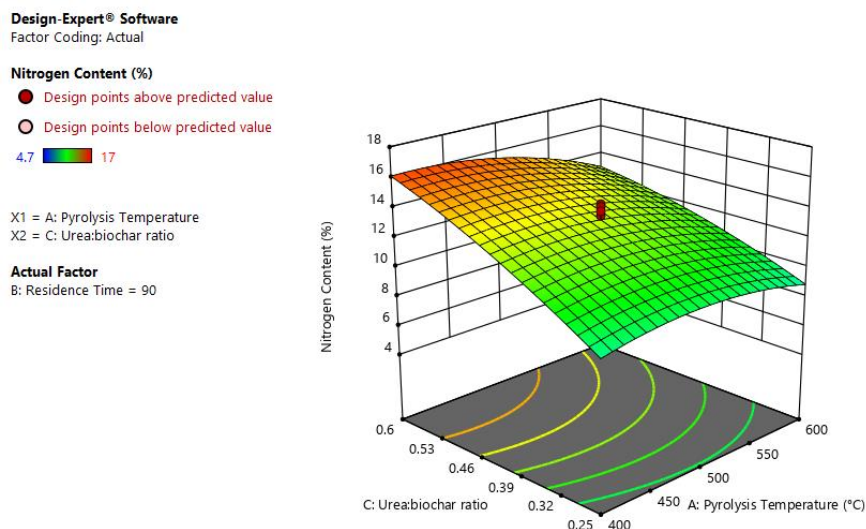


Figure 4.4: Response surface plot of pyrolysis temperature and urea:biochar ratio on nitrogen content

4.2.4 Interactive Effect of Residence Time and Urea:Biochar Ratio on Nitrogen Content of UIB Powder

The response surface plot of the interactive effect of residence time and urea:biochar ratio on the nitrogen content is displayed in **Figure 4.5**. It showed that by increasing the urea:biochar ratio, it increased the nitrogen content whereas increasing the residence time did not affect the nitrogen content significantly. This might be due to the changes of acidic functional group, polar functional group (hydrophilicity) and surface area were not significant with the increasing residence time. Sun et al. (2017) also found that the changes of acidic functional group of plantae wood biochar was insignificant. As shown in section 4.2.10, the surface area of the biochar synthesis at longer residence time was slightly higher than shorter residence time which higher surface area also contributes to the higher nitrogen content as more urea was bound and recrystallize within the pores of the biochar. Although, the surface area increased with increasing residence time, but the changes of surface area were insignificant. Overall, the surface chemistry and surface area of the biochar produced

in this study was found to be minimally affected by the residence time, which subsequently posed an insignificant impact on the nitrogen content.

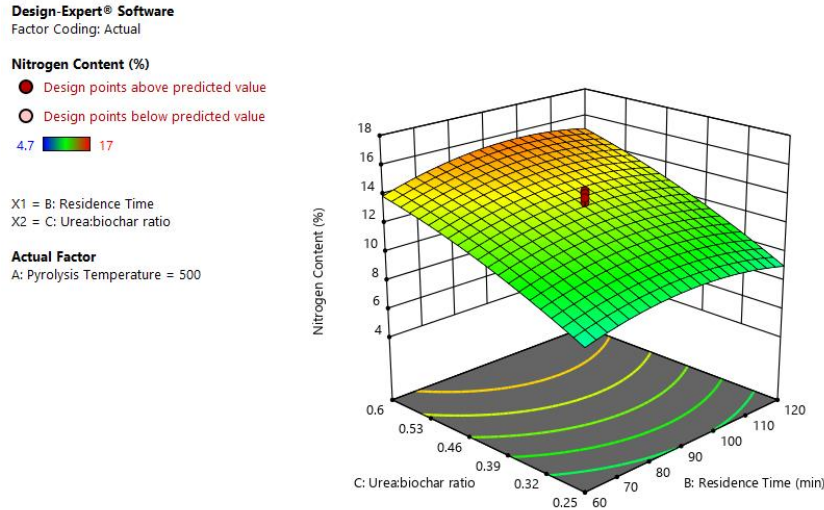


Figure 4.5: Response surface plot of residence time and urea:biochar ratio on nitrogen content

4.2.5 Optimization of Nitrogen Content of UIB Powder

The optimum condition obtained for the UIB was at pyrolysis temperature of 400 °C, residence time of 120 minutes and urea:biochar ratio of 0.6, which predicted 15.89% of nitrogen content. The experimental nitrogen content obtained was 16.07%, which resulted in a low RSE of 1.12% which can be seen from **Table 4.3**. The $RSE \geq 25\%$ is considered a high sampling error and should be taken with caution (Darajeh et al., 2016) This indicated that the optimum condition was capable to produce UIB with the highest nitrogen content, and the correlation model established in this study was satisfactory for predicting the nitrogen content of peppercorn waste-based UIB powder.

Table 4.3: Model validation

Replicate	Pyrolysis temperature (°C)	Residence Time (minutes)	Urea to biochar ratio	Nitrogen Content (%)		RSE (%)	Average Nitrogen content (%)	Average RSE (%)
				Predicted	Experimental		Experimental	
1	400	120	0.6	15.89	15.40	2.99	16.07	1.12
2	400	120	0.6	15.89	16.73	5.31		

4.2.6 pH and EC of Peppercorn Waste-based Biochar and UIB Powder

The pH and EC levels of all the peppercorn derived biochar synthesized and UIB powder in this study are presented in **Table 4.4**. Based on **Table 4.4**, the biochar samples were all alkaline. By increasing the pyrolysis temperature from 400 °C to 600 °C, the pH of the biochar increased from 10.21 to 10.95. In contrast, the pH slightly decreased from 10.30 to 10.21 when the residence time was increased from 60 minutes to 120 minutes, but the change of pH was insignificant. The reduction of the pH could be due to the more acidic functional groups were observed when the residence time increased, as shown in **Figure 4.7**. Similar results were observed by Wang et al. (2020b) which reported that the effect of residence time on the pH of biochar was insignificant as compared to pyrolysis temperature. The study stated that the pH of corn straw, wheat straw, rape straw and peanut shell decreased when the residence time was increased from 60 minutes to 120 minutes. In addition, Dobariya et al. (2022) also observed that the pH of cotton and castor derived biochar decreased from 8.85 and 8.77 to 8.38 and 8.32, respectively when the residence time was increased from 60 minutes to 120 minutes at pyrolysis temperature of 300 °C. Moreover, Zhang et al. (2022b) also found that the extended residence time did not always result in biochar with higher alkalinity. The increment of the pH of the biochar with increasing pyrolysis temperature was possibly due to the increase in metal oxide, carbonates and minerals as well as the reduction in acidic functional groups (Nkomo et al., 2021; Wang et al., 2020b). The pH level of the UIB powder was 9.06. The reduction of the pH level of UIB powder was probably due to the urea impregnated into the biochar. A similar study by Castejón-del Pino et al. (2023) which also observed that the pH level of olive tree prunings derived biochar decreased from 8.32 to 8.05 after urea impregnation. Overall, all the biochar

synthesized in this study are suitable to be used in acidic soil due to their high alkalinity (Wang et al., 2020c).

The EC level of the biochar increased with enhanced pyrolysis temperature. The EC level of biochar increased from 1.82 ms cm⁻¹ to 2.03 ms cm⁻¹ when pyrolysis temperature increased from 400 °C to 600 °C. The increase in EC when pyrolysis temperature increased was due to the loss of volatile matter which led to an increase in the relative concentration of salts within the ash fraction (Gai et al., 2014). The EC level of biochar also increased with increasing residence time from 1.79 ms cm⁻¹ to 1.82 ms cm⁻¹. A study by Wang et al. (2020a) also observed that the EC level of rape straw-based biochar increased with increasing residence time at 500 °C. It is important to note that the high EC of biochar might not be suitable to be utilized for crop production as it might have toxic effects on plants (Song & Guo, 2011). Song and Guo (2011) synthesized poultry litter derived biochar showing EC levels ranging between 22.8 ms cm⁻¹ to 31.0 ms cm⁻¹ which was not favourable for crop production. Kameyama et al. (2017) claimed that EC level of animal manure should not be higher than 5 ms cm⁻¹ to be utilized as a soil amendment. Hence, the EC level less than 5 ms cm⁻¹ was favour for soil amendment. Furthermore, the EC level of the UIB powder increased from 1.82 ms cm⁻¹ to 2.23 ms cm⁻¹. Similar findings were found by Castejón-del Pino et al. (2023) which reported that the EC level of olive tree pruning derived biochar increased from 0.40 ms cm⁻¹ to 0.84 ms cm⁻¹ after urea impregnation. In this study, all the biochar and UIB powder synthesized had a moderate EC level, thus they are suitable to be used as a soil amendment (Kameyama et al., 2017).

Table 4.4: pH and EC level of the peppercorn waste derived biochar and UIB powder.

Synthesis condition	pH level	EC level (ms cm ⁻¹)
400 °C and 60 minutes	10.30	1.79
400 °C and 120 minutes	10.21	1.82
600 °C and 120 minutes	10.92	2.03
UIB powder (400 °C, 120 minutes and 0.6 urea:biochar ratio)	9.06	2.23

4.2.7 Surface Morphology of Peppercorn Waste-based Biochar and UIB Powder

The scanning electron micrographs of the biochar synthesized at different conditions and UIB powder are shown in **Figure 4.6**. All the biochar samples displayed irregular shapes with various sizes of particles. The biochar synthesized at 400 °C and 60 minutes portrayed a slightly lower porosity. Furthermore, the biochar synthesized at 400 °C and 120 minutes and 600 °C and 120 minutes showed more pores on the surface of the biochar. The release of volatile matter during pyrolysis led to the development of pores, thus increasing the pore volume and surface area of the biochar (Méndez et al., 2013). This process was important for microbial activity, retention of nutrients and enhancing water holding capacity (Shaaban et al., 2014). Overall, all the biochar synthesized in this study possessed porous surface which could entrap nutrients in the pores. The UIB powder had a rougher and undulating surface as relative to pristine biochar, as depicted in **Figure 4.6(d)**, which indicated that the urea bound within the pores of the biochar.

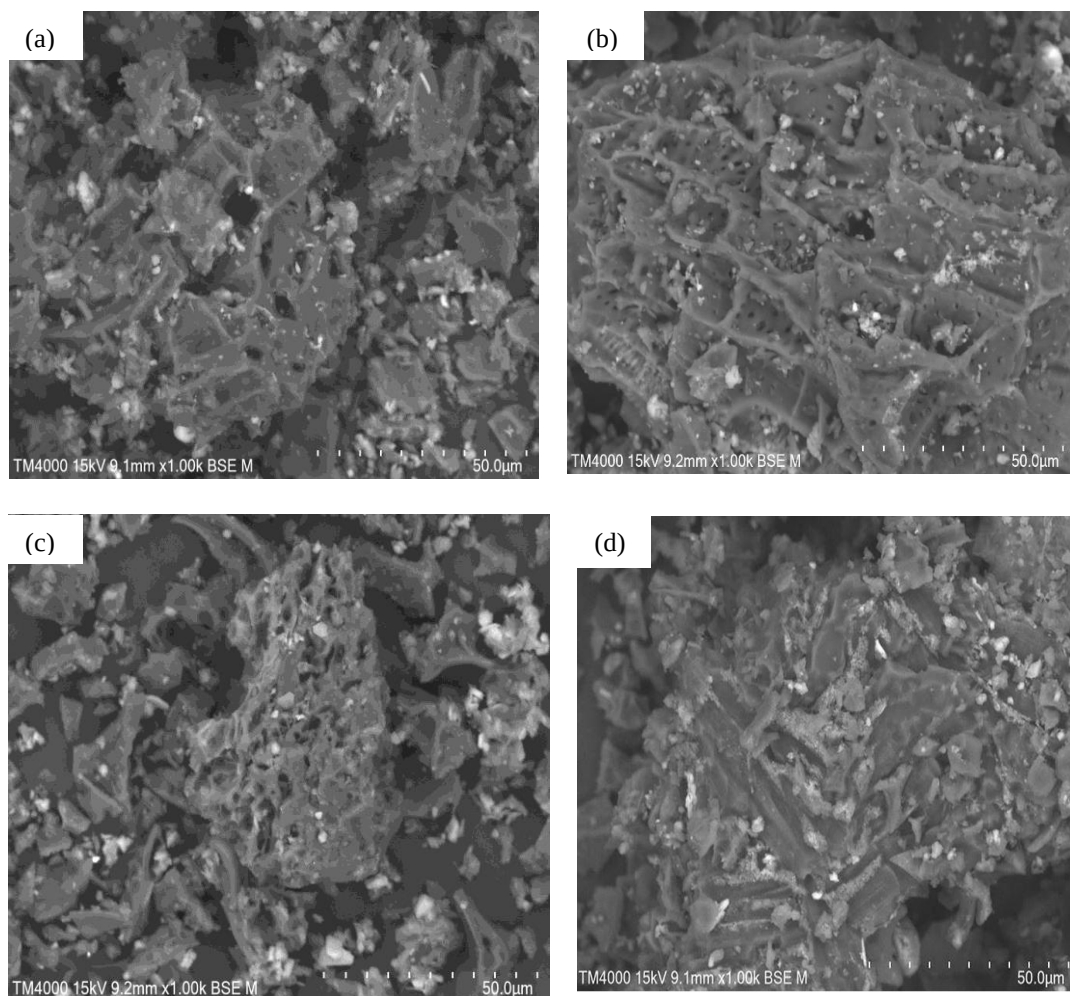


Figure 4.6: Scanning electron micrographs (1000x) of peppercorn waste-based biochar synthesized at (a) 400°C and 60 minutes, (b) 400°C and 120 minutes, (c) 600 °C and 120 minutes and (d) UIB powder (optimum synthesis condition)

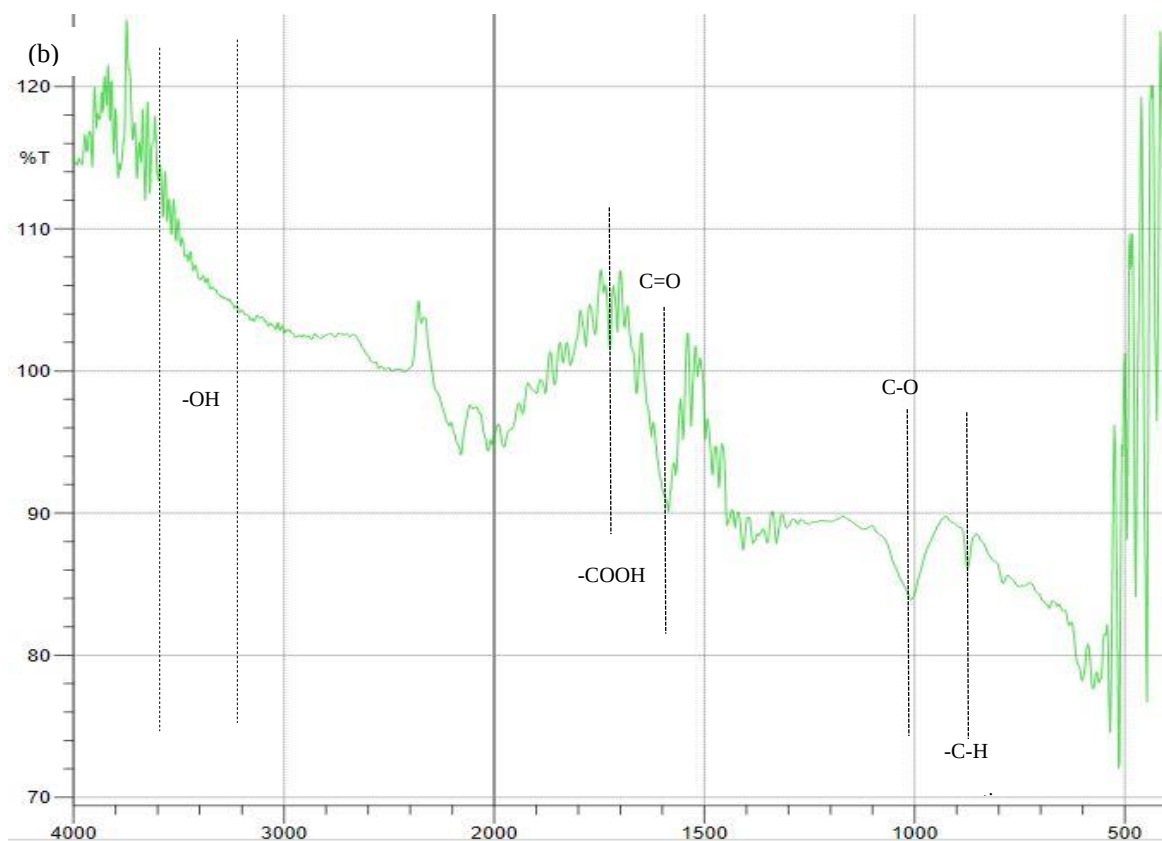
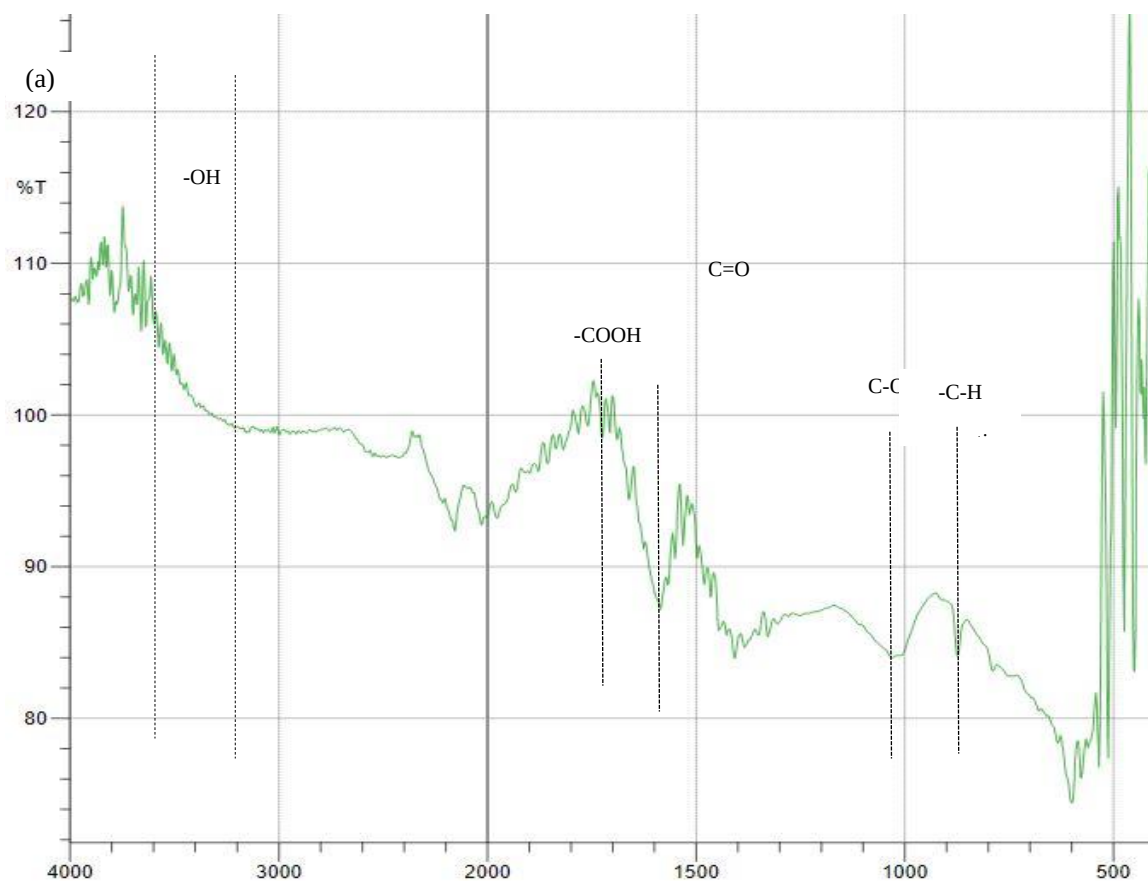
4.2.8 Surface Chemistry of Peppercorn Waste-based Biochar and UIB Powder

The FTIR spectra of peppercorn waste-based biochar synthesized under different pyrolysis conditions are shown in **Figure 4.7**. The broad absorption peak at 3200cm^{-1} - 3700cm^{-1} was due to the -OH stretching (Tang et al., 2019). The weak absorption peak observed at 1707 cm^{-1} was identified as the -COOH group (Nandiyanto et al., 2019). The absorption peak centred at 1585 cm^{-1} was due to stretching of C=O (Kong et al., 2021). The peak observed at 1008 cm^{-1} - 1010 cm^{-1} was due to the stretching of C-O in hemicellulose and

cellulose compound (Gascó et al., 2018). The peak observed at 873 cm^{-1} in the FTIR spectra indicated out-of-plane deformations of aromatic C-H (Antonangelo et al., 2019). Overall, the temperature of pyrolysis had a greater influence on the surface chemistry of the biochar as compared to the residence time. The C-O and C=O peaks decreased when the temperature of pyrolysis was increased from $400\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$, which was probably due to these functional groups were generally cracked to form CO (Kong et al., 2021). Besides, when raising the pyrolysis temperature, the -OH functional group was declined, indicating the loss of -OH group. This was possibly due to the dehydration during pyrolysis (Wang et al., 2021c). This was in accordance with Zhang et al. (2020) which claimed that the -OH peak and C=O peak of crop residue-based biochar also reduced with increasing pyrolysis temperature. The -COOH peak decreased with increasing pyrolysis temperature. Zhang et al. (2022a) also reported that the -OH peak and -COOH peak of bamboo-based biochar diminished when the pyrolysis temperature was elevated. Furthermore, the peak of C-O vanished when the temperature of pyrolysis was increased to $600\text{ }^{\circ}\text{C}$. The decrease in C-O was possibly due to the degradation and dehydration of cellulose and ligneous component (Domingues et al., 2017). However, the residence time showed insignificant change on the surface functional group of the biochar synthesized at 60 minutes and 120 minutes. According to Chandra and Bhattacharya (2019), the surface chemistry of rice straw-based biochar was also insignificantly affected by the residence time. The intensity of the -OH peak reduced slightly with increasing residence time. It was noteworthy that the biochar synthesized at 120 minutes had a slightly higher peak of -COOH, C-O and C=O than at 60 minutes. Past studies have claimed that the surface functional groups affected the hydrophobicity and hydrophilicity of the biochar. In this study, the polar functional group such as -OH, -COOH, C=O and C-O reduced when the temperature of pyrolysis was

elevated, indicating that the hydrophobicity of the biochar was improved when it was synthesized at higher temperature of pyrolysis (Zhao et al., 2017; Tomczyk et al., 2020).

The FTIR spectra of the UIB synthesized at 400 °C, 120 minutes and 6.00 urea:biochar ratio is displayed in **Figure 4.7 (d)**. New functional groups were discovered in the biochar after urea impregnation. The peaks observed at 1151 cm⁻¹, ~1462 cm⁻¹, 3334 cm⁻¹ and 3431 cm⁻¹ were stretching of -CN stretch, amine III and N-H (Vendra Singh et al., 2021; Nandiyanto et al., 2019). The peak of -COOH almost diminished after the urea impregnation. The C-O peak declined and slightly shifted to 1002 cm⁻¹ while the C=O peak shifted to 1587 cm⁻¹. The changes in the peaks and their positions after urea impregnation might be attributed to the reaction of urea with the acidic functional group and C-O. The results were consistent with Zhang et al. (2015) which reported that the peak position of C=O, -COOH in C-O stretching, bonded OH and phenolic -OH were slightly shifted after urea impregnation.



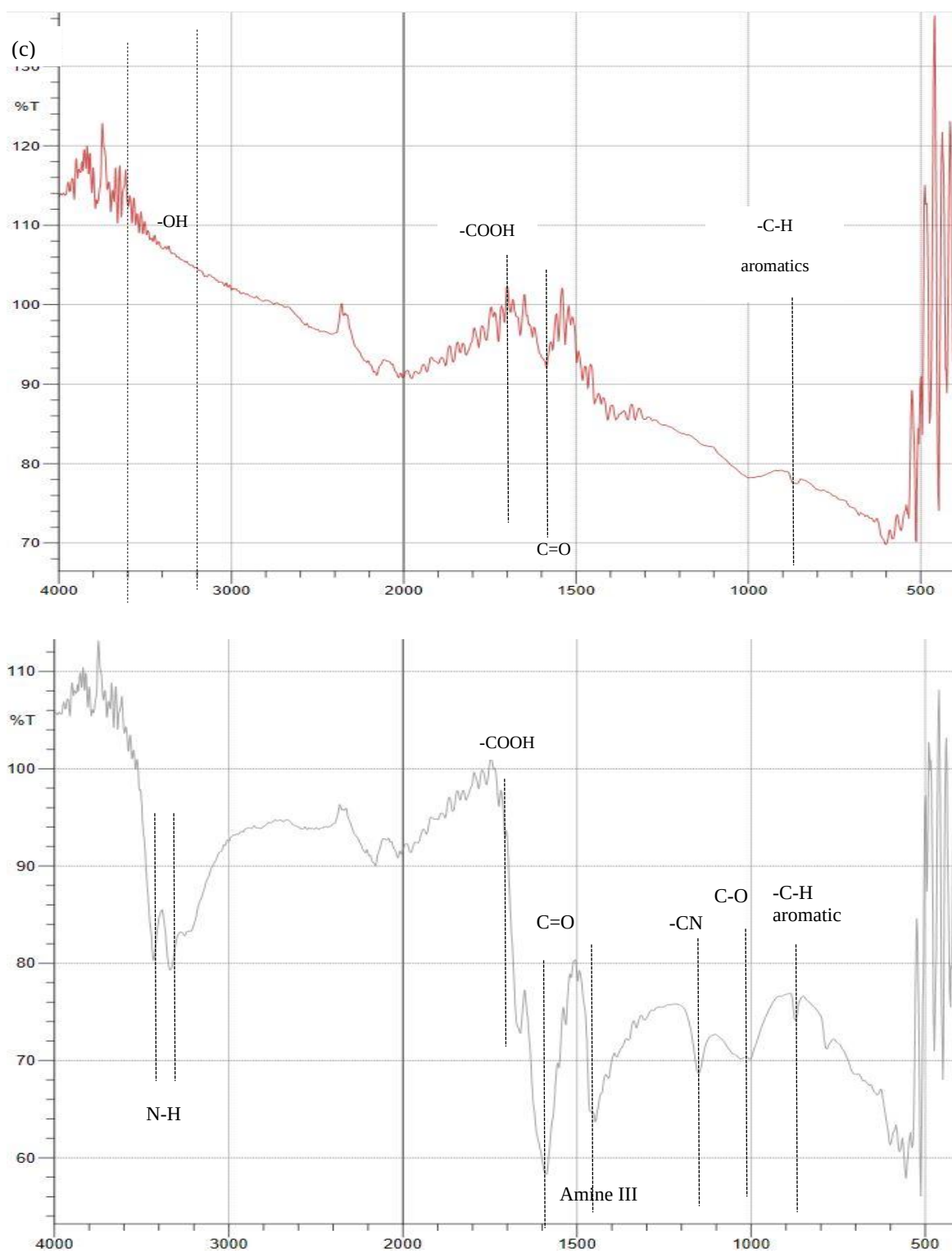


Figure 4.7: FTIR spectra of peppercorn waste-based biochar synthesized at (a) 400°C and 60 minutes, (b) 400°C and 120 minutes, (c) 600 °C and 120 minutes and UIB powder (optimum synthesis condition)

4.2.9 Elemental Composition of Peppercorn Waste-based Biochar and UIB Powder

The elemental composition of the biochar produced at 400 °C and 60 minutes, 400 °C and 120 minutes, 600 °C and 120 minutes and UIB powder are displayed in **Table 4.5**. The findings showed that the pyrolysis temperature significantly influenced the carbon and oxygen content of the biochar as compared to residence time. The carbon content was the major element observed in all synthesized biochar. The oxygen content and potassium content were the second and third major elements present in the biochar. The carbon content of the biochar increased with increasing pyrolysis temperature from 66.12% to 69.06%. The carbon content only slightly increased with increasing residence time. The increase in carbon content at higher pyrolysis temperature was probably due to the formation of stable aromatic hydrocarbons and carbon-hydrogen and carbon-carbon breakage (Das et al., 2021). On the other hand, the oxygen content showed opposite trend. When higher pyrolysis temperature was applied, the oxygen content decreased. This was attributed to the decomposition of the oxygenated bond as well as the release of the low-molecular weight by-product containing oxygen as temperature of pyrolysis increased (Adekanye et al., 2022). In contrast, the oxygen content slightly increased with increasing residence time, but the changes were not significant. Similar findings were observed by Zhang et al. (2022b) which found that the residence time increased the oxygen content of the leaf-based biochar and the changes of oxygen content was insignificant. Other elements such as magnesium, aluminium, silicon, phosphorus, chloride, potassium and calcium were also found in all the biochar synthesized in this study. Magnesium, phosphorus, chloride, potassium and calcium are the macronutrients and micronutrients that are essential for the plant growth. Although silicon is not an essential micronutrient, but it is a beneficial nutrient for plant growth as it can protect the plant from disease, insect and fungi, enhance the salt resistance of plant, facilitate

active immune system of plant as well as able to neutralize the toxicity caused by heavy metals in acid soil (Rao & Susmitha, 2017). The nitrogen content was not found in all the synthesized biochar. Overall, all the synthesized biochar had the potential to be used as a soil amendment to improve soil fertility. On the other hand, the nitrogen content was observed in UIB powder, indicating that urea had been successfully impregnated into the biochar matrix. In addition, after urea impregnation process, the other macronutrients and micronutrients such as phosphorus, potassium, magnesium, calcium and silicon still remained within the biochar. The chlorine element was not observed in UIB powder was probably due to the loss during urea impregnation process.

Biochar is not considered as a fully inert material in soil as it can be mineralized by the soil microbes but at an extremely slow pace. The O/C ratio of the biochar is a crucial parameter as it affects the stability of biochar. Generally, biochar with O/C ratio lower than 0.2 indicates that the biochar has a half-life of greater than 1000. The O/C ratio of biochar ranging between 0.2 to 0.6 is expected to have a half-life of 100 to 1000 years while the O/C ratio greater than 0.6 indicates the half-life is less than 100 years (Tu et al., 2022).

Furthermore, Zhao et al. (2018) claimed that the O/C ratio lower than 0.4 was favourable to be used as a carbon sequestration material to mitigate carbon dioxide emissions in the soil. In this study, the O/C ratio of all the synthesized biochar ranged between 0.280 to 0.354. Hence, the biochar synthesized in this study has the potential to be utilized as a carbon sequestration material in order to prevent climate change. In addition, the O/C ratio also indicated the polarity of the biochar (Abdelaal et al., 2021). In this study, the O/C ratio of the biochar synthesized at 400 °C and 60 minutes as well as 400 °C and 120 minutes was higher as compared to the biochar synthesized at 600 °C and 120 minutes. This illustrated

that the biochar synthesized at lower pyrolysis temperature was more hydrophilic as higher pyrolysis temperature tended to increase the hydrophobicity of the biochar. The changes in the hydrophilicity of the biochar with increased residence time were not significant as the changes of the O/C ratio were insignificant. Abdelaal et al. (2021) also observed that the O/C ratio did not show significant change with increasing residence time.

Table 4.5: Elemental composition of peppercorn waste-based biochar and UIB powder

Pyrolysis conditions	400 °C, 60 minutes	400 °C, 120 minutes	600 °C, 120 minutes	UIB powder
Elemental composition (%)				
Carbon, C	66.121	66.393	69.069	50.032
Oxygen, O	23.071	23.504	19.017	25.523
Nitrogen, N	0	0	0	16.672
Magnesium, Mg	0.785	0.728	0.843	0.632
Aluminium, Al	0.751	0.550	0.828	0.733
Silicon, Si	0.594	0.523	0.670	0.605
Phosphorus, P	0.720	0.765	0.812	0.545
Chloride, Cl	0.618	0.432	0.599	0
Potassium, K	5.310	5.005	5.796	3.216
Calcium, Ca	2.030	2.100	2.366	2.045
O/C ratio	0.348	0.354	0.280	-

4.2.10 Surface Area and Total Pore Volume of Peppercorn Waste-based Biochar and UIB Powder

The surface area and total pore volume are important properties of biochar for soil amendment as they impact the ability of the biochar to retain water and nutrient (Alkharabsheh et al., 2022). As shown in **Table 4.6**, the higher pyrolysis temperature and longer residence time resulted in higher surface area and total pore volume. The pyrolysis temperature had a more significant effect on the surface area and total pore volume of biochar as compared to residence time. The biochar synthesized at 600 °C and 120 minutes had the highest surface area and pore volume which was 6.453 m² g⁻¹ and 0.00626 cc g⁻¹ whereas the lowest surface area and pore volume was observed in the biochar synthesized at 400 °C and 60 minutes which were 1.314 m² g⁻¹ and 0.00371 cc g⁻¹. The surface area and total pore volume increased as the temperature increased which was attributed to the organic matter that had been thermally degraded more completely (Hu et al., 2022). The surface area and total pore volume of the biochar synthesized at 400 °C and 120 minutes were higher than 400 °C and 60 minutes, but the changes of surface area and total pore volume were insignificant. Zhao et al. (2018) also found that the surface area and total pore volume of biochar increased with residence time. The surface area and total pore volume of UIB powder were 0.001 m² g⁻¹ and 3.570 x 10⁻⁷ cc g⁻¹. This indicated that the urea had been recrystallize or bound within the pores of the biochar.

Table 4.6: Surface area and total pore volume of peppercorn-based biochar and UIB powder.

Biochar synthesis conditions	Surface area (m ² g ⁻¹)	Total pore volume (cc g ⁻¹)
400 °C and 60 minutes	1.314	0.00371
400 °C and 120 minutes	2.809	0.00470
600 °C and 120 minutes	6.453	0.00626
UIB powder (400 °C, 120 minutes and 0.6 urea:biochar ratio)	0.001	3.570 x 10 ⁻⁷

4.3 Phase 2: Formulation of Tapioca Starch/PO Encapsulated Biochar-based Fertilizer

In this phase, different formulation of tapioca starch and PO biofilm was investigated by varying the concentration of starch and PO to obtain biofilm with lowest water absorption capacity. Besides, the characteristic of the UIB pellet and EUIB pellet were also studied. The comparison of nitrogen content of synthesized fertilizer and other biochar-based fertilizer were presented.

4.3.1 Water Absorption of Tapioca Starch/PO Biofilm

Figure 4.8 illustrates the water absorption of the biofilm synthesized from different formulations of tapioca starch/PO. Based on **Figure 4.8**, the pure starch biofilm exhibited a higher water absorption capacity as compared to the starch biofilm incorporated with PO. The water absorption capacity of the biofilm incorporated with PO decreased as the PO concentration was increased. The decrease in the biofilm's affinity towards water could be attributed to the hydrogen bonding interaction between the starch network and oil, which

resulted in a decrease in hydrophilic interaction between the hydrogen group and water (Wang et al., 2021a). The hydrogen bonding between tapioca starch and palm oil is illustrated in **Figure 4.9**. This indicated that the hydrophobicity of the tapioca starch biofilm was enhanced. Moreover, the incorporation of hydrophobic PO into the starch biofilm created a longer and tortuous path for water to penetrate into the biofilm which resulted in a low permeation of water into the biofilm (Wang et al., 2022b). Similar observation was reported by Buso-Rios et al. (2020) in which the presence of clove essential oil enhanced the water barrier of sweet potato starch biofilm. Besides, elevating the concentration of the starch from 4 g to 8 g led to a decrease in the water absorption activity of the biofilm from 325.0% to 223.5%. The water absorption of the starch biofilm with the incorporation of PO also decreased with increasing concentration of the starch. This was possibly due to the increment of the thickness of starch biofilm with high concentration of starch, thus resulted in a higher resistance for water to permeate into the biofilm (Halimatul al., 2019).

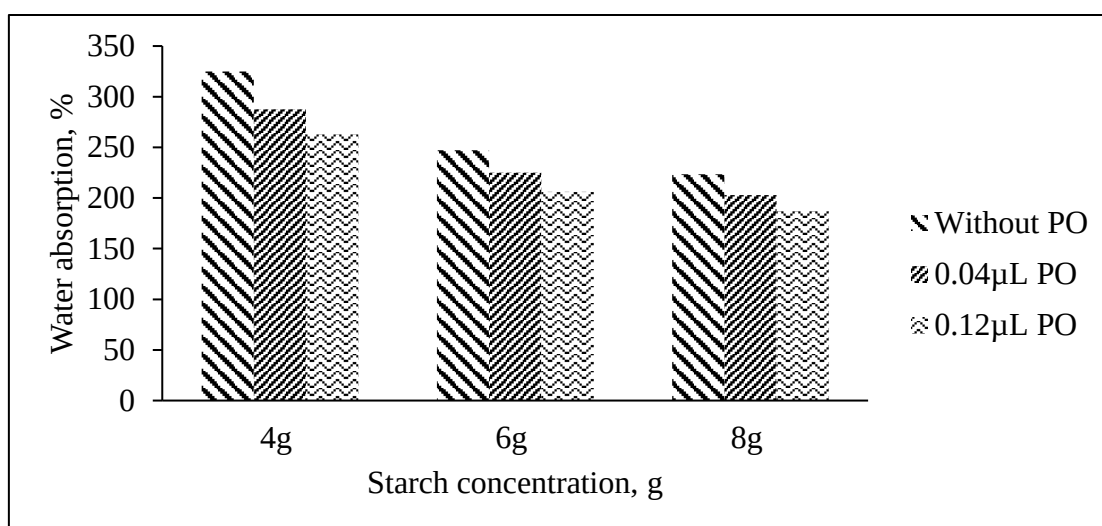


Figure 4.8: Water absorption of biofilm synthesized using different formulation of tapioca starch/palm oil.

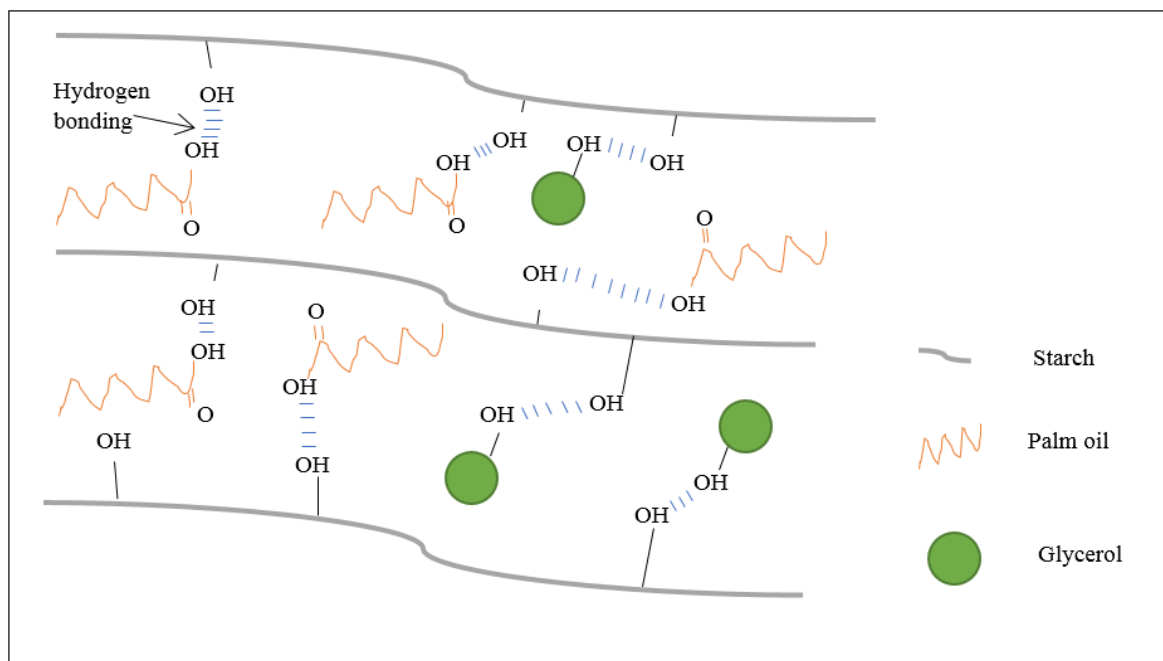


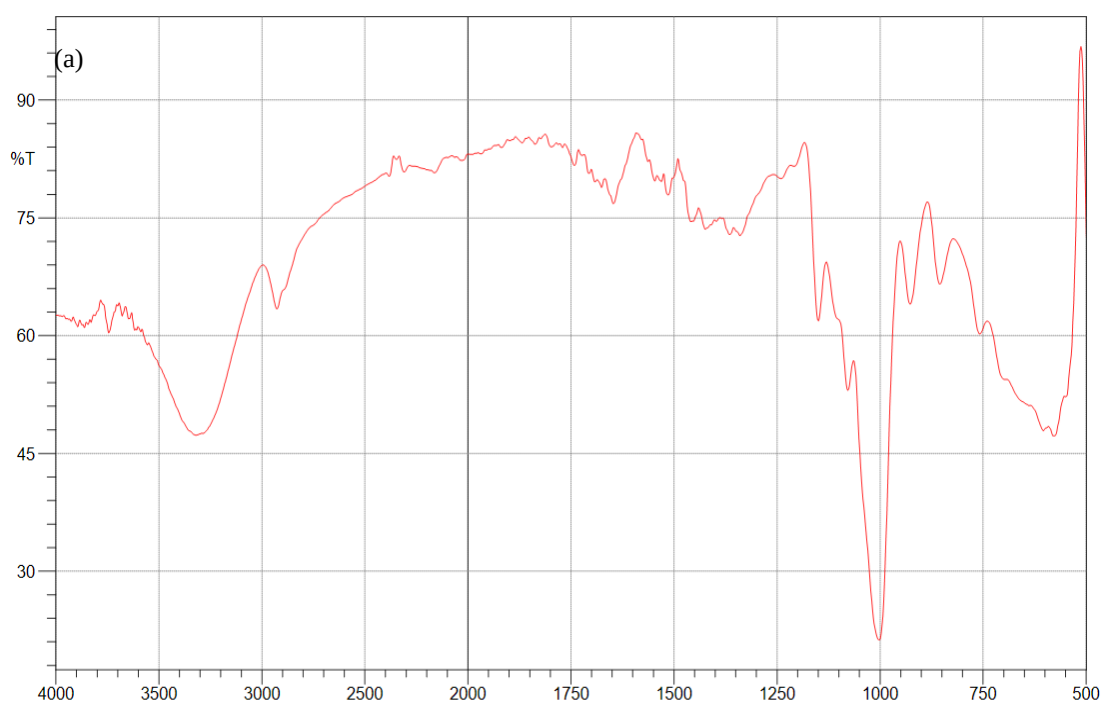
Figure 4.9: Hydrogen bonding interaction between starch and palm oil.

4.3.2 Surface Chemistry of Tapioca Starch and Tapioca Starch/PO Biofilm

Figure 4.10 (a) and (b) shows the FTIR spectra of both tapioca starch biofilm and tapioca starch/PO biofilm. In the tapioca starch biofilm, the peaks at 925 cm^{-1} , 1004 cm^{-1} , 1078 cm^{-1} and 1149 cm^{-1} were the C-O stretching originated from the tapioca starch (Lee et al., 2020). The peak at 1647 cm^{-1} was due O-H bond of water absorbed into the biofilm matrix (Cao et al., 2019). The peak at 2929 cm^{-1} was corresponded to stretching of alkane C-H bond (Nandiyanto et al., 2019; Brandelero et al., 2012) whereas the peak at 3319 cm^{-1} was corresponded to the -OH bond (Nandiyanto et al., 2019).

In contrast, in the tapioca starch/PO biofilm the peaks of C-O stretching at 925 cm^{-1} , 1004 cm^{-1} , 1078 cm^{-1} and 1149 cm^{-1} were also observed. The peak of 1647 cm^{-1} found in the tapioca starch/PO biofilm was slightly less intense as compared to the pristine starch biofilm. Similar findings were found by Kang et al. (2019) which observed that the peak intensity at

1647 cm^{-1} was reduced when clove bud essential oil was added into Job's tears (*Coix lachrymal-jobi L.*) starch biofilm. The reduction of intensity at 1647 cm^{-1} peak was consistent with the water absorption analysis at which the incorporation of PO into the tapioca starch reduced the water absorption into the biofilm. The intensity of the peak of C-H bond stretching slightly increased which shown in **Figure 4.11**. This was attributed to the interaction of the PO and tapioca starch chain (de Souza et al., 2020). Furthermore, with the incorporation of PO, the -OH bond reduced and shifted from 3319 cm^{-1} to 3323 cm^{-1} . This indicated that the hydrogen bond interactions were formed between the oil and the biofilm matrix (Yang et al., 2021).



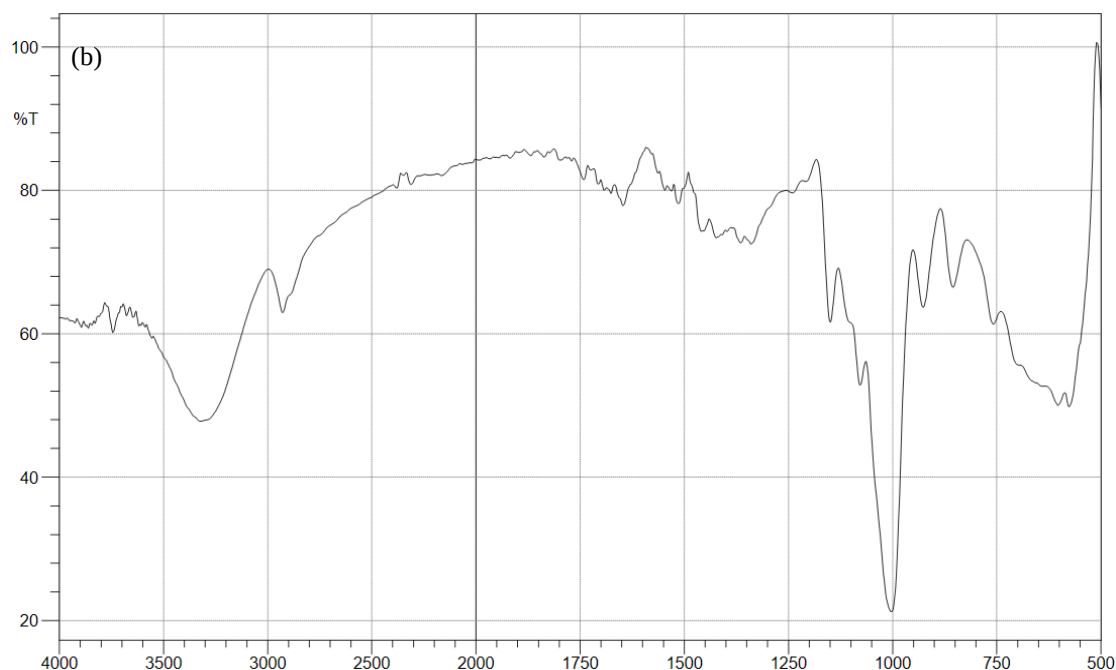


Figure 4.10: FTIR spectra of (a) tapioca starch biofilm and (b) tapioca starch/PO biofilm

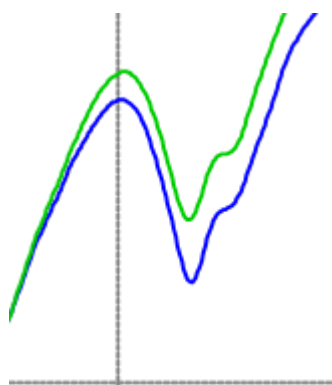


Figure 4.11: FTIR spectra at 2929 cm^{-1} (green) tapioca starch biofilm and (blue) tapioca starch/PO biofilm

4.3.3 pH, EC, Surface Morphology and Surface Chemistry of UIB and EUIB Pellets

The pH level of the UIB and EUIB pellets were 9.12 and 9.20 while the EC level of the UIB pellet and EUIB pellet were 2.15 ms cm^{-1} and 2.07 ms cm^{-1} respectively, as displayed in **Table 4.7**. The pH and EC levels of the EUIB pellet were slightly reduced as

compared to UIB pellet. By comparing the UIB powder in section 4.2.6, the changes in the pH and EC levels were only slightly different from each other. The synthesized UIB and EUIB pellets were still in the alkaline property and the EC level was less than 5 ms cm^{-1} , therefore it can be utilized in acidic soil and are suitable to be used as a soil amendment.

The thickness of EUIB pellet is displayed in **Figure 4.12**. The EUIB pellet showed a biofilm thickness ranging between $341 \text{ }\mu\text{m}$ to $345 \text{ }\mu\text{m}$. Besides, from the top view, the surface of the EUIB pellet was quite smooth with some tiny holes, as illustrated in **Figure 13(a)**. The tapioca starch/PO biofilm covered the surface of the UIB pellet. On the other hand, the UIB pellet had an undulating and coarser surface where all the particles were packed closely after the pelletization process, as illustrated in **Figure 13(b)**. By comparing the surface morphology of UIB and EUIB pellets, the surface of UIB pellets was not covered by the biofilm, thereby the nitrogen release would be fast as the surface of the UIB pellet could directly contact with water.

The FTIR spectra of UIB and EUIB pellets are shown in **Figure 4.14**. Both UIB pellet and EUIB pellet comprised of amine III, and N-H functional groups as shown by the peaks at $\sim 1462 \text{ cm}^{-1}$ and $\sim 3334 \text{ cm}^{-1}$ and $\sim 3431 \text{ cm}^{-1}$, which were also found in the UIB powder. This indicated that urea had retained in the peppercorn biochar matrix after the pelletization and encapsulation process. The differences observed on certain peaks in the EUIB were due to the tapioca starch/PO biofilm. In EUIB, a combination of peaks found in the UIB pellet and tapioca starch/PO biofilm were observed. The additional peaks at 1000 cm^{-1} to 1150 cm^{-1} and 2929 cm^{-1} were from tapioca starch/PO biofilm. The intensity of the peaks at $\sim 3334 \text{ cm}^{-1}$, $\sim 3431 \text{ cm}^{-1}$ (N-H) and $\sim 1462 \text{ cm}^{-1}$ (amine III) was less intense in the EUIB pellet. This might be attributed to the lesser nitrogen content in the EUIB pellet as

relative to the UIB pellet, as presented and discussed in Section 4.3.5 where the nitrogen content of the EUIB pellet was about 9.50% while the UIB pellet was 15.50%.

Table 4.7: pH and EC level of UIB and EUIB pellets

Synthesized Fertilizer	pH	EC (ms cm ⁻¹)
UIB pellet	9.12	2.15
EUIB pellet	9.20	2.07

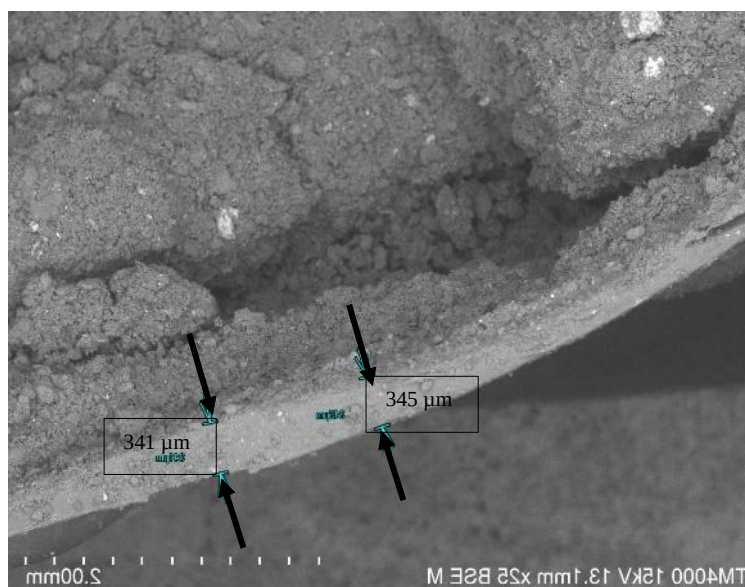


Figure 4.12: Scanning electron micrographs of thickness of the biofilm (cross-section of the EUIB pellet-25x magnification)

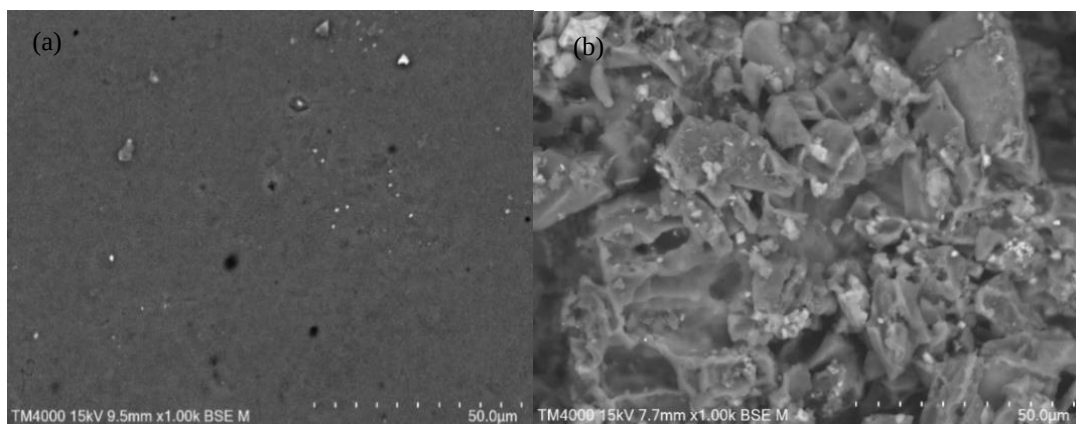
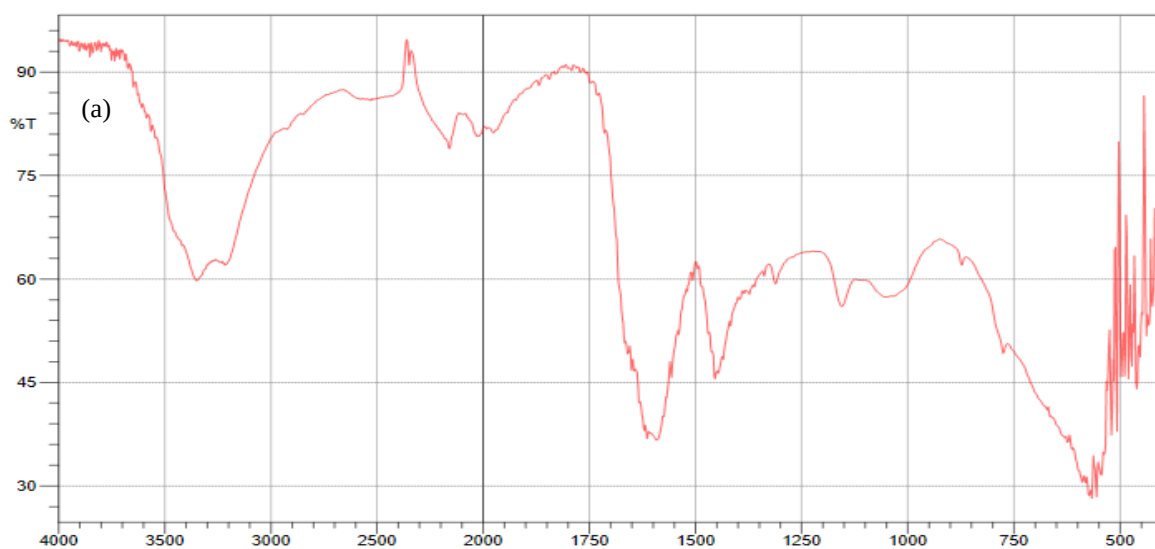


Figure 4.13: Scanning electron micrographs of (1000x magnification) (a) EUIB-top view and (b) UIB pellets



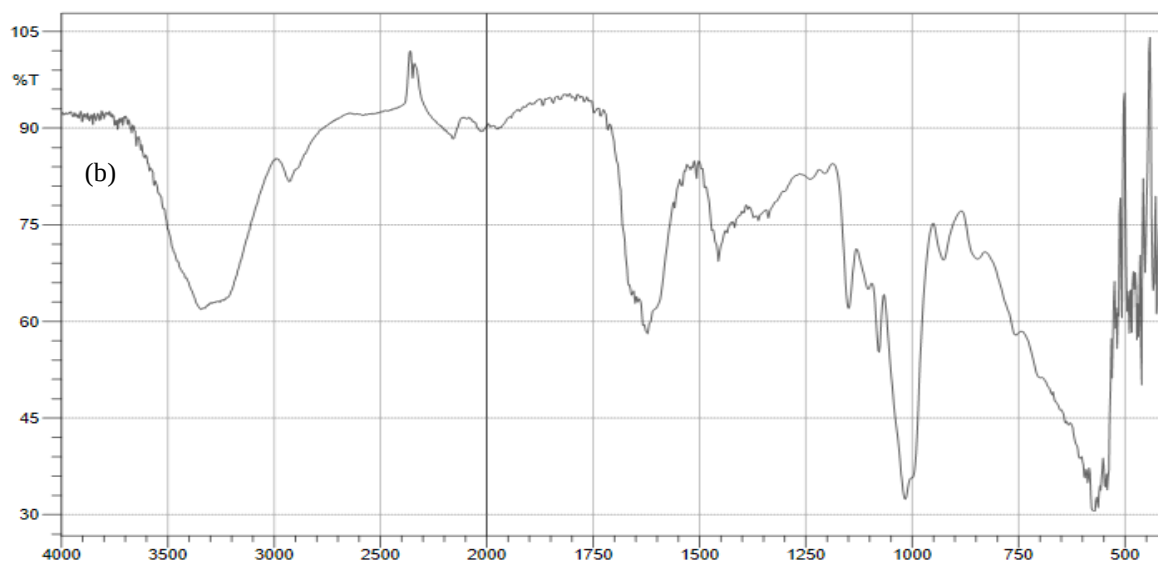


Figure 4.14: FTIR spectra of (a) UIB pellet and (b) EUIB pellet.

4.3.4 Crushing Strength of UIB and EUIB Pellets

The quality and performance of encapsulated/coated fertilizer are greatly influenced by its mechanical properties. When transported, stored or handled under harsh conditions, fertilizer often experiences sudden impacts. Hence, inadequate strength can result in mechanical instability which causes the fertilizer to suffer damage such as disintegration. Based on Beig et al. (2020a), urea prills had crushing strength of 7.08 N. In this study, the UIB pellet was crushed at a crush force of 7.87 N which was slightly better than urea prills. The UIB pellet had lower crushing strength than the EUIB which might be possibly disintegrate into powder if greater force was exerted. Meanwhile, the EUIB exhibited good crushing strength of 81.65 N. The crushing strength was improved by the tapioca starch/PO biofilm and thus it prevented the UIB pellet from being crushed and scattered into pieces or powder during the transporting, storing and handling process. Similar results were observed by Beig et al. (2020b) which found that the crushing strength of biopolymers encapsulated urea fertilizer increased as relative to uncoated urea.

4.3.5 Comparison of Nitrogen Content of Different Biochar-based Fertilizer

The comparison of the nitrogen content of biochar synthesized from various precursors using different synthesis conditions was shown in **Table 4.8**. The condition used to synthesize peppercorn waste derived UIB in this work resulted in a moderately high nitrogen content as compared to some other UIB found in the literature. In contrast, the nitrogen content of UIB pellet and EUIB pellet reduced, which was probably due to the nitrogen loss during the processes of drying, pelletization and encapsulation. Liu et al. (2019a) also claimed that the nitrogen content of urea decreased after encapsulation process. The relatively high nitrogen content obtained by Bakshi et al. (2021) and Norazlina et al. (2019) was possibly due to the phosphoric acid treatment adopted which had enhanced the urea retention property of the biochar. Nonetheless, the downside was that the phosphoric acid treatment would raise the cost of production of the UIB, thereby compromised the economic advantage of the fertilizer. Up to date, the information on the effect of synthesis conditions on UIB and EUIB has been very limited. Hence, more studies should be carried out to explore the various feedstock types and synthesis conditions to produce UIB and EUIB.

Table 4.8: Comparison of nitrogen content of different biochar

Biochar	Pyrolysis condition	Nitrogen content (%)	References
5% phosphoric acid modified urea-impregnated pine derived biochar	500 °C	32.90	Bakshi et al. (2021)
15% phosphoric acid modified urea-impregnated pine derived biochar	500 °C	32.80	
1.5M phosphoric acid modified urea-impregnated rubber wood sawdust derived biochar	-	43.20	Norazlina et al. (2019)
1M phosphoric acid modified urea-impregnated rubber wood sawdust derived biochar	-	42.38	
Urea-impregnated rubber wood sawdust derived biochar	-	40.00	
Urea-impregnated <i>Prosopis juliflora</i> derived biochar	350 °C, 8 hours	29.82	Manikandan & Subramanian (2013)
Urea-impregnated oilseed rape derived biochar	400 °C, 3 hours	11.60	Liu et al. (2019b)

Table 4.8 continued

Urea-impregnated rice straw derived biochar	450 °C	5.80	Vendra Singh et al. (2020)
Urea-impregnated rice husk derived biochar	450 °C	5.40	
Urea-impregnated peppercorn waste derived biochar	400 °C, 2 hours	16.07	This work
Urea-impregnated peppercorn waste derived biochar pellet	400 °C, 2 hours	15.50	This work
Encapsulated urea-impregnated peppercorn waste derived biochar pellet	400 °C, 2 hours	9.50	This work

4.4 Phase 3: Application Efficiency of EUIB Pellet

In this phase, the impact of EUIB pellet on nitrogen release behaviour in water, nitrogen leaching in sand, water retention behaviour in sandy and clayey-textural soils was evaluated. In order to investigate the release mechanism, four kinetic model was utilized. The elemental composition of EUIB pellet before and after nitrogen release in water was investigated. Moreover, the effect of EUIB pellet on the growth performance of the okra plant was also investigated.

4.4.1 Cumulative Release Rate of Nitrogen

Figure 4.15 shows the cumulative nitrogen release curves of pure urea, UIB and EUIB pellets. In the pure urea treatment, the cumulative nitrogen release rate (34.78%) was the highest after 1 minute of incubation in distilled water, as compared to UIB and EUIB pellets. The nitrogen of pure urea was released completely into the distilled water after 15 minutes. For UIB pellet treatment, the cumulative nitrogen release rate (10.77%) was slower than the pure urea treatment, which took 90 minutes to complete the nitrogen release. Maghsoodi et al. (2020) also observed that the urea release rate of UIB derived from rice straw was much slower than pure urea. The cumulative nitrogen release rate in EUIB pellet treatment was the slowest in which only 1.6% of nitrogen was released. The EUIB pellet treatment achieved complete release of nitrogen after 330 minutes. The EUIB pellet demonstrated a better sustained release ability due to the tapioca biofilm which acted as a physical barrier to hinder the water from flowing into the fertilizer's core. Moreover, the incorporation of PO enhanced the hydrophobicity of tapioca starch biofilm as well as creating a tortuous pathway which restricted the amount of water uptake by the tapioca starch biofilm. Therefore, this reduced the release of nitrogen. The slow-release ability of UIB pellet was enhanced as compared to pure urea due to the urea molecules that formed bonding

with the acidic functional groups and C-O of the biochar, thereby it decreased the release of nitrogen. Wang et al. (2021b) claimed that the slow-release of the urea from the synthesized biochar-based fertilizer was due to the urea which connected with the oxygen-containing functional group of the biochar through hydrogen bonding and intermolecular force. Additionally, the urea molecules were also entrapped within the pores of the biochar (Maghsoodi et al., 2020). The integration of tapioca starch/PO biofilm and urea-impregnated biochar-based fertilizer (dual mechanisms) in the EUIB pellet further reduced the nitrogen release as compared to the UIB pellet. The slow/controlled-release mechanism exhibited by EUIB and UIB pellets would retain and provide more nitrogen content in the soil for plant growth. The comparison of nitrogen release behaviour of various slow/controlled-release fertilizer is shown in **Table 4.9**.

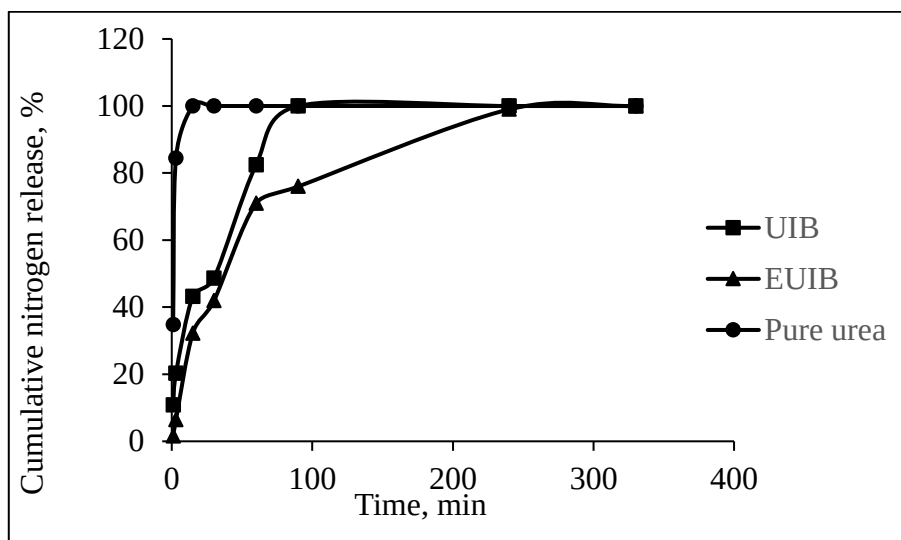


Figure 4.15: Cumulative nitrogen release of pure urea, urea-impregnated biochar (UIB) and encapsulated urea-impregnated biochar (EUIB).

Table 4.9: Comparison of nitrogen release behaviour of various slow/controlled-release fertilizers

Formulation of encapsulating/coating materials	Nitrogen release behaviour	References
Gelatin/potassium iodide coated urea	82% of urea released in 15 minutes	Nezami et al. (2021)
PVA/potassium iodide coated urea	78% of urea released in 15 minutes	
Gum arabic/potassium iodide coated urea	74% of urea released in 15 minutes	
Starch/PVA/molasses coated urea	Urea complete release in 60 minutes and 45 seconds	Beig et al. (2020a)
Starch/PVA/paraffin wax coated urea	Urea complete release in 120 minutes and 45 seconds	
Gelatin/gum arabic/paraffin wax coated urea	Urea complete release in 130 minutes	
Molasses/gelatin/gum arabic coated urea	Urea complete release in 30 minutes and 21 seconds	

Table 4.8 continued

Starch/PVA/acrylic acid (2%, 4%, 6%) coated urea	23.92% of urea released in 9 minutes and urea complete release in 12 minutes (acrylic acid 2%); 72.75% of urea released in 9 minutes and urea complete release in 12 minutes (acrylic acid 4%); 68.58% of urea released in 96 minutes and urea complete release in 9 minutes (acrylic acid 6%)	Zafar et al. (2021)
Starch/PVA/maleic acid (2%, 4%, 6%) coated urea	75.34% of urea released in 9 minutes and urea complete release in 12 minutes (maleic acid 2%); 77.12% of urea released in 9 minutes and urea complete release in 12 minutes (maleic acid 4%); 78.50% of urea released in 9 minutes and urea complete release in 12 minutes (maleic acid 6%)	
Starch/PVA/citric acid (2%, 4%, 6%)) coated urea	62.75% of urea released in 15 minutes and urea complete release in 30 minutes (citric acid 2%); 68.58% of urea released in 9 minutes and urea complete release in 12 minutes (citric acid 4%); 36.91% of urea released in 6 minutes and urea complete release in 9 minutes (citric acid 6%)	

Table 4.8 continued

Urea-impregnated rice straw derived biochar	93.5% of urea release in 260 second	Maghsoodi et al. (2020)
Urea-impregnated rice straw derived hydrochar	95.5% of urea release in 180 second	
Urea-impregnated zeolite	92.0% of urea release in 360 second	
Urea-hydroxyapatite nanohybrids	88.0% of urea release in 460 second	
UIB pellet	Nitrogen complete release in 90 minutes	This study
EUIB pellet	Nitrogen complete release in 330 minutes	

4.4.2 Nitrogen Release Kinetics

The release kinetic of UIB pellet and EUIB pellet obtained from the zero-order release kinetic model, first-order release kinetic model, Higuchi model and Korsmeyer-Peppas model are displayed in **Figures 4.16, 4.17, 4.18 and 4.19**. The parameters such as the release exponent (n), R^2 , standard error and the kinetic rate constant (k) of the zero-order release kinetic model, first-order release kinetic model, Higuchi model and Korsmeyer-Peppas model are summarized in **Table 4.10**. The first-order release kinetic model and zero-order release kinetic model were deemed unsuitable for explaining the nitrogen release mechanism of UIB and EUIB pellets as the R^2 of these models was relatively low as compared to Higuchi model and Korsmeyer-Peppas model. Higuchi model describes the release of nutrient/drug based on fickian diffusion as a square root of time-dependent process while Korsmeyer-peppas model is a semi-empirical model implies that the fractional release of nutrient/drug is exponentially related to the release time (Kaur & Datta, 2014). Although the R^2 of Higuchi model was slightly higher than Korsmeyer-Peppas model for UIB pellet, however the R^2 were very close to each other. Based on the standard error of Korsmeyer-Peppas model and Higuchi model of UIB pellet, the standard error of Korsmeyer-Peppas model was lower than Higuchi model. If based on the R^2 , Higuchi was the best fitting model for UIB pellet whereas if based on combination of R^2 and standard error, Korsmeyer-Peppas model was the best fitting model. Based on the concept of the Higuchi model and Korsmeyer-Peppas model, Higuchi model was better in describing the release of nutrient/drug from solid or porous matrix while Korsmeyer-Peppas model was better in describing the release of nutrient/drug from polymeric system (encapsulated) (Dash et al., 2010). Therefore, in this study the Higuchi model was better in describing the release of nitrogen from UIB pellet. The results obtained in this study were supported by An et al.

(2021b) which stated that the Higuchi model was better in explaining the release of phosphorus from phosphorus enriched biochar. This indicated that the release mechanism of UIB pellet was governed by Fickian diffusion. Based on the n from Korsmeyer-Peppas model, the value of $n < 0.45$ represented Fickian diffusion, whereas $0.45 < n < 0.89$ indicated non-Fickian diffusion (anomalous diffusion). When $n = 0.89$, it suggested case II transport. If $n > 0.89$, it corresponded to super case II transport (Dash et al., 2010). In this study, the Korsmeyer-Peppas model well described the release of nitrogen from EUIB pellet. In the case of EUIB pellet, the n value obtained was 0.7788 which indicated that the nitrogen release from EUIB pellet was governed by non-Fickian diffusion where multiple processes were involved in regulating the release of nitrogen. The release mechanism of the nitrogen from EUIB pellet was dominated by both relaxation and diffusion. This was in accordance with An et al. (2021b) which also observed that the Korsmeyer-Peppas model was best in explaining the phosphorus enriched biochar encapsulated with sodium alginate/bentonite and starch-based hydrogel. Zhang et al. (2023) also found that the Korsmeyer-Peppas model was better describing the sodium alginate and carboxyl methylcellulose encapsulated urea-impregnated biochar.

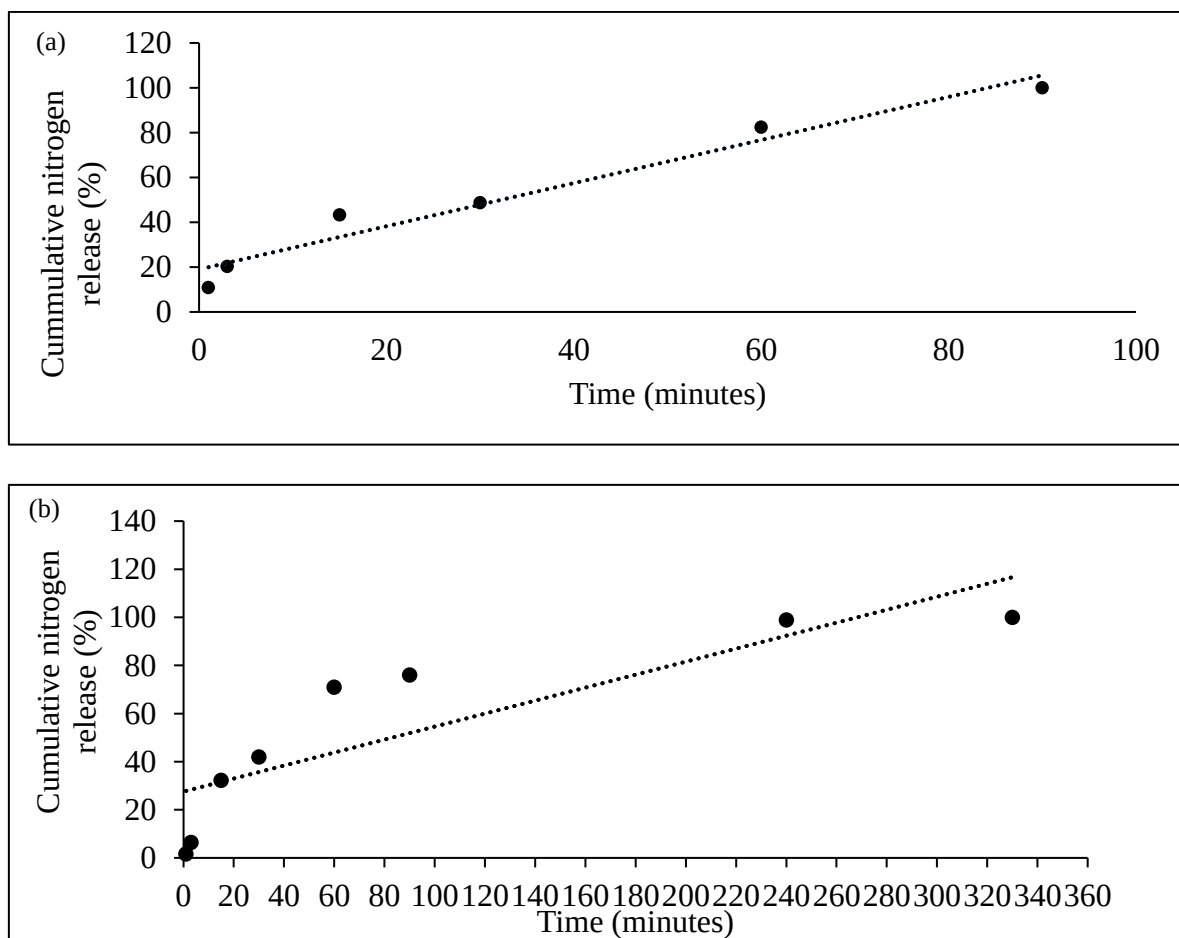


Figure 4.16: Zero order release kinetic of (a) UIB pellet and (b) EUIB pellet

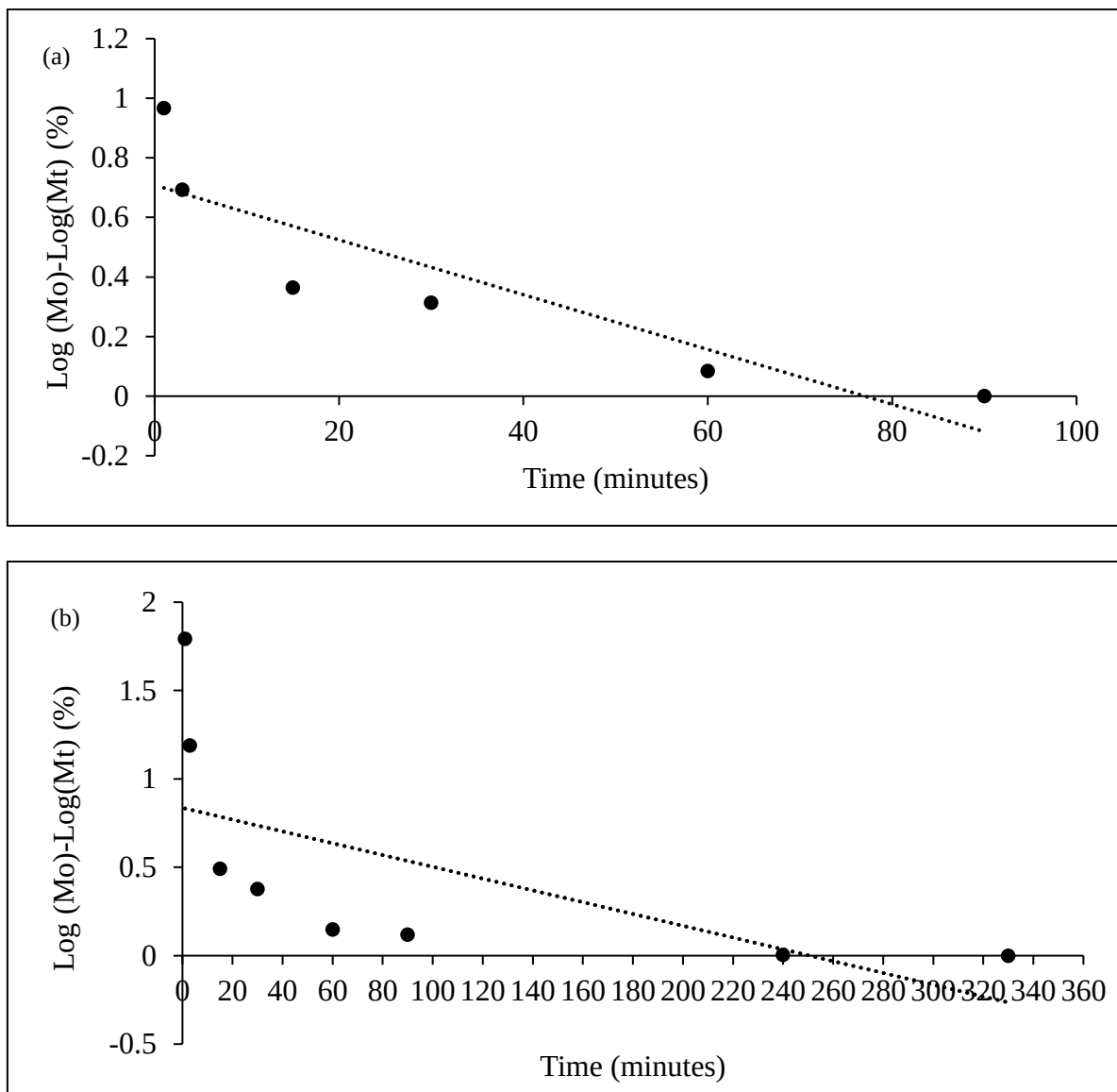


Figure 4.17: First order release kinetic of (a) UIB pellet and (b) EUIB pellet)

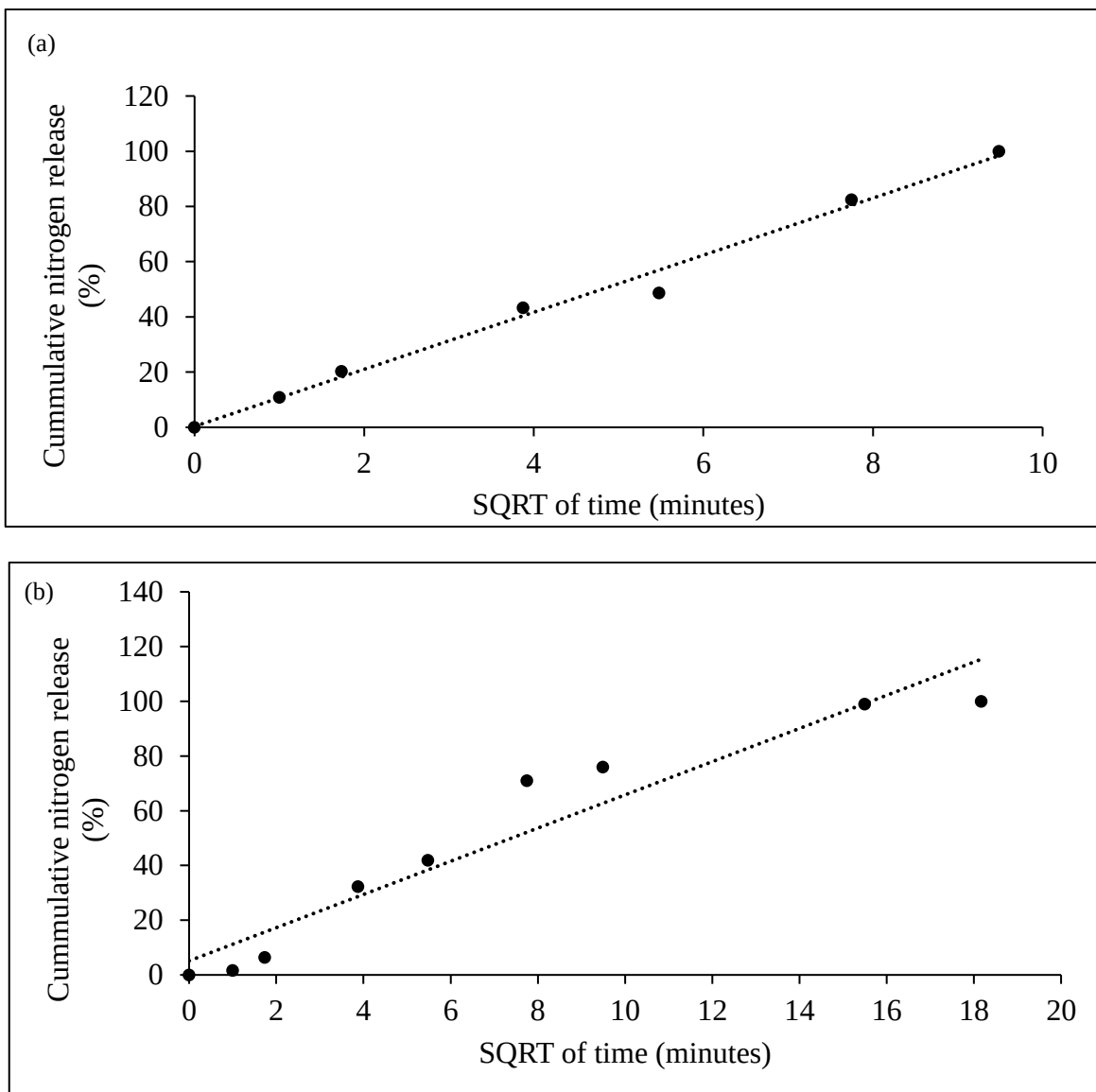


Figure 4.18: Higuchi release kinetic of (a) UIB pellet and (b) EUIB pellet

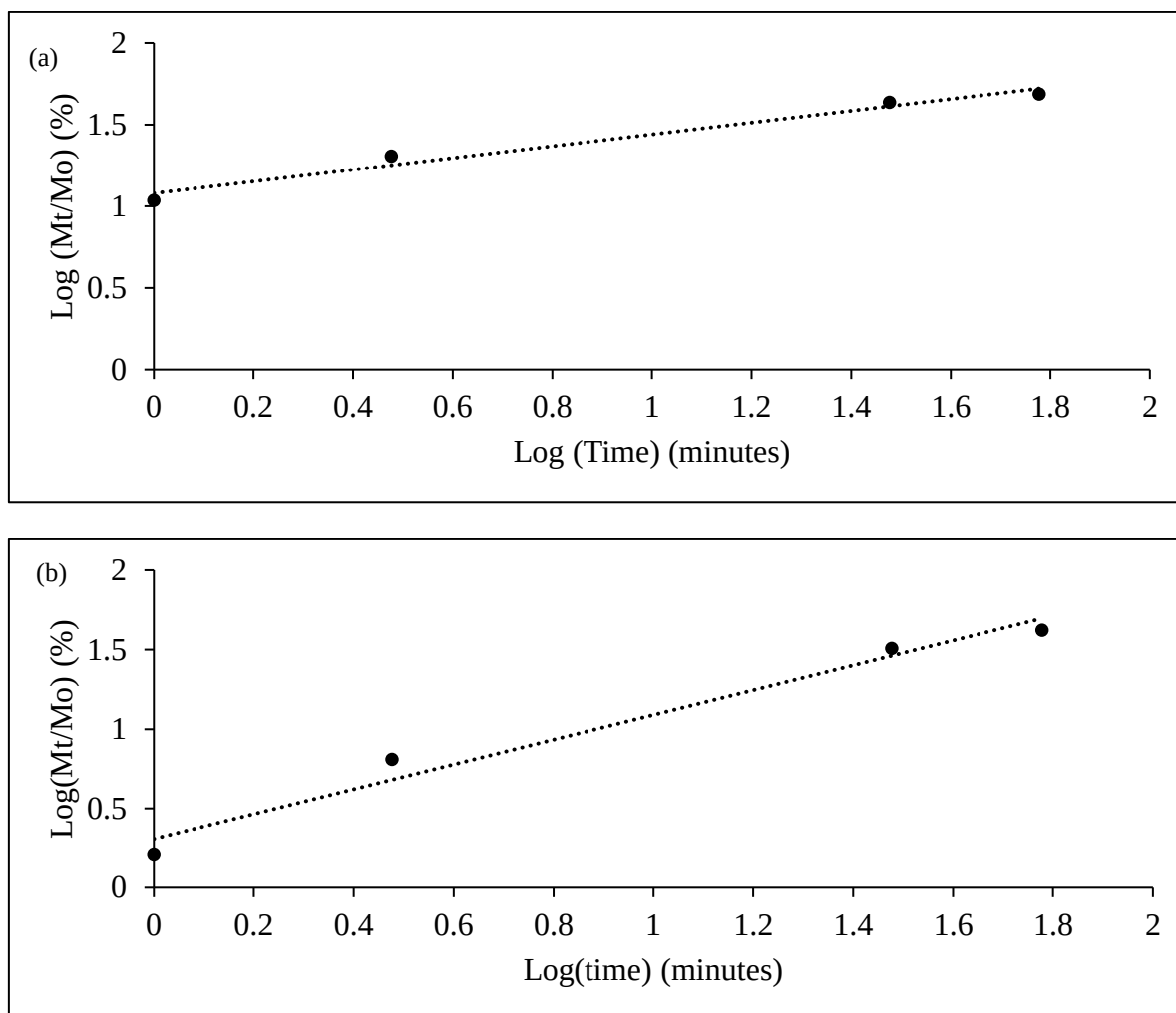


Figure 4.19: Korsmeyer-peppas release kinetic of (a) UIB pellet and (b) EUIB pellet

Table 4.10: Parameters of different kinetic models for urea-impregnated biochar (UIB) and encapsulated urea-impregnated biochar (EUIB)

Kinetic model	Parameters	UIB	EUIB
Zero-order model	R^2	0.9589	0.7293
	k_o (min^{-1})	0.9618	0.2700
	Standard error	14.15	13.70
First-order model	R^2	0.7811	0.4011
	k_t (min^{-1})	0.0212	0.0077
	Standard error	0.14	0.22
Higuchi model	R^2	0.9854	0.9088
	k_H (min^{-1})	10.308	5.9191
	Standard error	14.15	13.70
Korsmeyer-Peppas model	R^2	0.9755	0.9735
	N	0.3615	0.7802
	k_{kp} (min^{-1})	11.9839	2.0361
	Standard error	0.34	0.32

4.4.3 Elemental Composition of UIB and EUIB Pellets Before and After Nitrogen Release Analysis in Water

Table 4.11 and **Table 4.12** respectively show the elemental composition of UIB and EUIB pellets before and after the nitrogen release analysis in water. The urea was distributed evenly within the surface of the biochar after the impregnation process as the nitrogen content found in different spots was rather similar in both UIB and EUIB pellets as tabulated in **Table 4.11**. In EUIB pellet, the nitrogen content was reduced after the encapsulation process. Referring to **Table 4.12**, the nitrogen content could not be observed in the UIB

pellet and EUIB pellet as the nitrogen had been fully released during the nitrogen release analysis in water. Furthermore, some portion of the macronutrients and micronutrients were also released from the UIB and EUIB pellet as showed in **Table 4.12**. The reduction of macronutrients and micronutrients was probably due to their release into the water medium. This indicated that the UIB pellet and EUIB pellet were able to provide some macronutrient and micronutrient such as magnesium, silicon, phosphorus, potassium and calcium into the soil to alleviate the soil fertility issues. However, some of them were still retained in the UIB pellet and EUIB pellet. This was because the magnesium, potassium and calcium were organically bound with the biochar or existed as carbonate and/or oxide form during pyrolysis process, and this form was insoluble in water (Kong, 2014). The phosphorus might exist in the form of insoluble mineral such as apatite while aluminium might be in the oxide form which was insoluble in water (Kong, 2014; Manzoori & Agarwal, 1992). Furthermore, the silicon in the biochar might exist in the form of crystalline, thus reducing the availability of silicon (Nwajiaku et al., 2018).

Table 4.11: Elemental composition of UIB and EUIB pellet before nitrogen release in water.

Sample	UIB pellet		EUIB pellet	
Elemental Composition (%)				
	Spot 1	Spot 2	Spot 1	Spot 2
C	52.178	51.485	54.140	55.888
N	14.137	14.453	10.296	9.492
O	25.263	25.778	24.974	26.542
Mg	0.671	0.677	1.279	0.792

Table 4.11 continued

Al	0.812	0.816	0.845	0.785
Si	0.985	0.855	0.906	0.695
P	0.543	0.715	0.656	0.712
K	3.378	3.177	4.622	3.018
Ca	2.033	2.044	2.282	2.076
Sum	100	100	100	100

Table 4.12: Elemental composition of UIB and EUIB pellet after nitrogen releasing in water.

Sample	UIB pellet		EUIB pellet	
Elemental Composition (%)				
	Spot 1	Spot 2	Spot 1	Spot 2
C	74.440	75.347	76.867	77.046
N	0	0	0	0
O	22.159	21.403	20.376	19.543
Mg	0.291	0.277	0.232	0.493
Al	0.809	0.729	0.689	0.662
Si	0.328	0.435	0.238	0.363
P	0.091	0.108	0.084	0.092
K	0.096	0.102	0.080	0.083
Ca	1.786	1.599	1.434	1.718
Sum	100	100	100	100

4.4.4 Water Retention Behaviour in Clayey and Sandy-Textural Soil

Figure 4.20(a) shows the effect of UIB and EUIB pellets on the water retention ratio in clayey-textural soil whereas **Figure 4.20(b)** illustrates the impact of UIB and EUIB pellets on the water retention ratio in sandy-textural soil. In the clayey-textural soil, the water retention ratio of all treatments conducted was insignificantly different from each other throughout the 30 days of experiment. This was attributed to the clayey-textural soil had a greater capacity to hold water (Finch et al., 2014). However, the water retention ratio of UIB and EUIB pellets treatment was slightly higher than the control treatment after 21 days. The water retention ratio of the control, UIB and EUIB pellets treatment after 30 days was 26.22%, 28.19% and 28.15%, respectively. The sandy-textural soil had lower water and nutrient holding capacity than the clayey-textural soil (Finch et al., 2014). In sandy-textural soil, the water retention ratio was notably higher in the UIB and EUIB pellets treatments as compared to the control treatment. The water retention ratio of the sandy soil that contained UIB pellet and EUIB pellet after 13 days was 35.15 % and 34.00 % respectively. In contrast, the control treatment had a water retention ratio of only 22.07%. The enhancement of water retention ratio of UIB pellet was attributed to the porous structure of the biochar that retained water molecules within its pores (Alghamdi et al., 2020). In EUIB pellet treatment, the tapioca starch/PO biofilm was able to absorb water up to a certain extent as demonstrated in the water absorption analysis, hence it enhanced the water retention performance of the soil. The water retention ratio of UIB pellet treatment was slightly higher than EUIB pellet treatment, which might be due to the incorporation of hydrophobic PO in the tapioca starch biofilm in EUIB pellet which hindered the amount of water flowing through the biofilm. An et al. (2021b) found that sodium alginate and starch-based hydrogel encapsulated phosphorus enriched biochar possessed better water retention in soil than other treatments.

This was due to the low hydrophobicity of the biochar surface. Overall, the EUIB pellet developed in this study is a potential sustainable slow/controlled-release fertilizer with good water retention property. Through the improvement of water retention capacity of the soil, it helps to decrease the need for regular irrigation while simultaneously increasing the quantity of water available for plant growth.

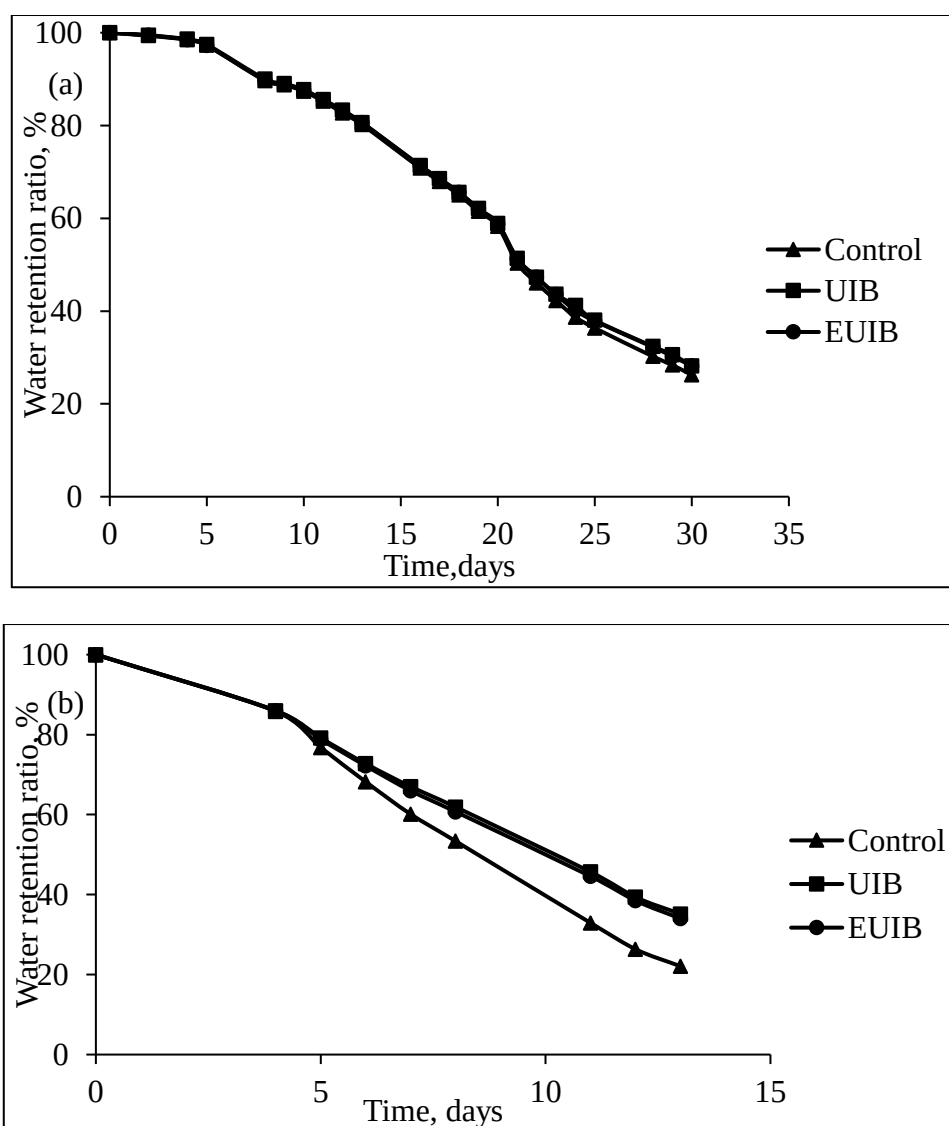


Figure 4.20: Water retention ratio of control, urea-impregnated biochar (UIB) and encapsulated urea-impregnated biochar (EUIB) in (a) clayey-textural soil and (b) sandy-textural soil.

4.4.5 Nitrogen Leaching in Sand

Figure 4.21 and **Table 4.13** shows the nitrogen leaching (mg) and cumulative nitrogen leaching (mg) for pure urea, UIB pellet and EUIB pellet treatment in sand. The cumulative leaching of nitrogen in pure urea treatment was the fastest among the treatments as the leaching of nitrogen was 17.606 mg of N for the first leaching activity and complete leaching was achieved after the second leaching activity (28.991 mg of N). The cumulative leaching of nitrogen of the UIB pellet was much lower than the pure urea, showing 4.592 mg of N and 16.582 mg of N at the first leaching activity and second leaching activity. The UIB pellet leached all the nitrogen after the third leaching activity which was 28.674 mg of N. On the other hand, the cumulative leaching of nitrogen was the slowest for EUIB pellet treatment as relative to UIB pellet and pure urea as the cumulative nitrogen leaching was only 3.00 mg of N and 10.00 mg of N at the first leaching activity and second leaching activity. The complete leaching of the EUIB pellet was achieved after five leaching activities which was 28.650 mg of N. The leaching of nitrogen was slower for UIB pellet and EUIB pellet due to their slow-release property. However, with the assistance of tapioca starch/PO biofilm, the leaching of nitrogen was further reduced in EUIB pellet due to the tapioca starch/PO biofilm acted as a physical barrier to prevent the water from contact directly with the biochar. Similar results were observed by An et al. (2021a) which reported that the phosphorus leaching for cotton straw based encapsulated phosphorus enriched biochar was lesser as compared to unencapsulated phosphorus enriched biochar and conventional fertilizer. Thus, the reduction of nitrogen leaching in EUIB pellet treatment could reduce ground water pollution.

Table 4.13: Amount of mg N leached from UIB and EUIB pellets

	Leaching activity (mg of N)						
Synthesized fertilizer	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th
Pure urea	17.606	11.385	0.000	0.000	0.000	0.000	0.000
UIB pellet	4.592	16.582	7.500	0.000	0.000	0.000	0.000
EUIB pellet	3.000	10.000	6.255	5.420	3.975	0.000	0.000

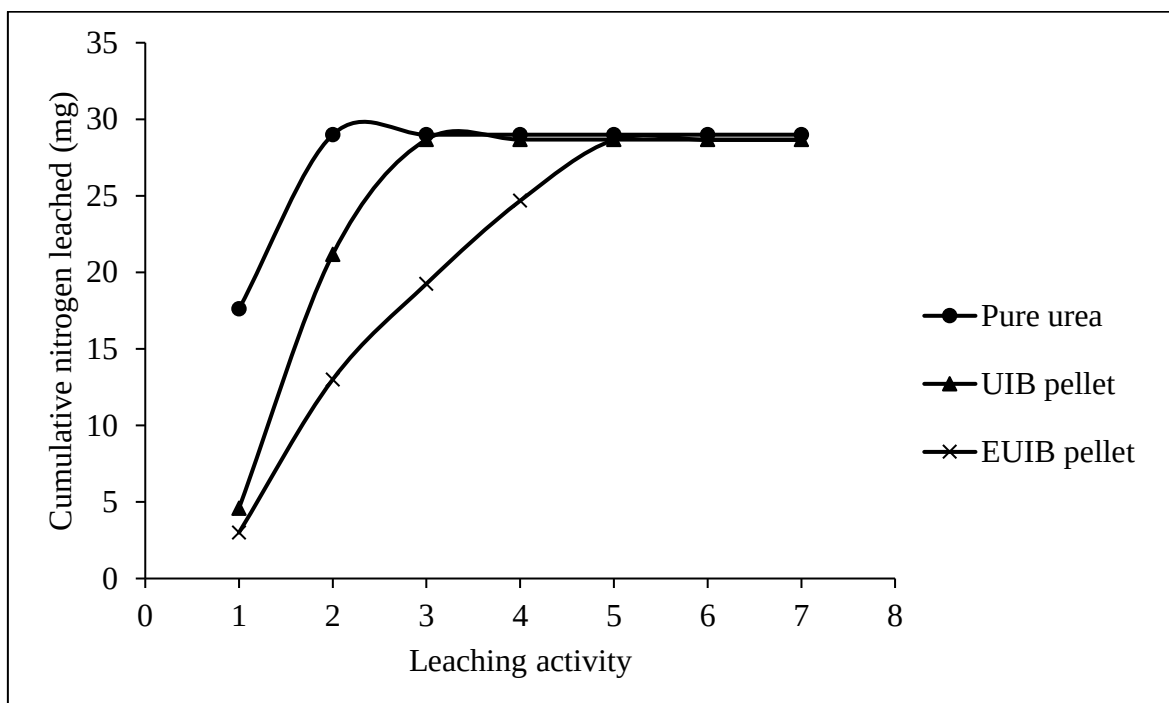


Figure 4.21: Nitrogen leaching and cumulative percentage nitrogen leaching of (a) pure urea, (b) UIB pellet and (c) EUIB pellet.

4.4.6 Plant Growth

The impacts of the UIB, EUIB and pure urea on the growth of the okra plant were evaluated. The okra plant was planted for 30 days. The shoot length, number of leaves, area of leaves, root length as well as wet and dry weight of the okra plant were used to investigate

the growth performance, as displayed in **Table 4.14**. **Figure 4.22** and **Figure 4.23** respectively display the macro diagram of okra potted plant and plant growth after 30 days of incubation. The growth performance of the okra plant with pure urea, UIB pellet and EUIB pellet treatments was enhanced as compared to the control treatment. The length of shoot of UIB pellet treatment was the shortest among the other treatments. Moreover, the dry weight and wet weight of the EUIB pellet, UIB pellet and pure urea treatment were greater than control. However, the dry weight of UIB pellet and pure urea was the same. Besides, the root length, number of leaves, and leaf area of EUIB and UIB pellets treatment were better than pure urea and control treatment. Based on the overall growth performance, the okra plant with EUIB pellet treatment was the best among all the treatments, followed by UIB pellet and pure urea treatments. Although the shoot length was the lowest for UIB pellet treatment, the root length, number of leaves, area of leaves and wet weight were better than pure urea and control treatments. The enhancement in the overall growth performance of the okra plant promoted by the EUIB and UIB pellets was attributed to their slow-release property. Apparently, pure urea was water soluble as the nitrogen was easily lost to the environment which could be seen from the leaching analysis and nitrogen release analysis, thus it was difficult to be utilized by the plants. The okra plant's growth performance of EUIB was better than UIB possibly due to the slow-release property which had been enhanced by the tapioca starch/PO biofilm that released the nitrogen gradually over the period. This was in accordance with the nitrogen release in water and nitrogen leaching in sand. Besides, the nitrogen release rate of EUIB closely matched the demand of growth of the okra plant. An et al. (2021b) also found that the growth performance of pepper in terms of shoot length, root length, size of leaves, dry and wet weight of sodium alginate and starch-based hydrogel encapsulated phosphorus enriched biochar was better than unencapsulated

phosphorus enriched biochar. This was because the slow-release property of the encapsulated biochar-based fertilizer was enhanced by the sodium alginate and starch-based hydrogel based encapsulating material which further reduced the release rate of the nutrient. Moreover, Tarar et al. (2023) also observed that the biochar-based fertilizer enhanced the shoot and root length of the red okra plant as compared to control and conventional fertilizer. This was due to the slow-release property of the biochar-based fertilizer. Laftah & Hashim (2014) also found that the urea loaded hydrogel based slow-release fertilizer enhanced the overall growth performance of the okra plant after 12 weeks as relative to the control. Overall, the EUIB pellet has improved the growth performance of the okra plant.

Table 4.14: Parameters of plant growth for control, pure urea, UIB pellet and EUIB pellet treatments.

Parameters of plant growth						
Sample	Shoot length (cm)	Root length (cm)	Wet weight (g)	Dry weight (g)	Number of leaves	Leaf area (cm²)
Control	10.50	3.50	0.78	0.08	4	5.92
Pure urea	10.80	4.40	0.90	0.12	4	6.40
UIB pellet	10.20	5.00	1.12	0.12	5	6.63
EUIB pellet	11.00	6.10	1.24	0.15	5	7.98



Figure 4.22: Micro diagram of okra potted plant with treatment of (a) control, (b) pure urea, (c) UIB pellet and (d) EUIB pellet

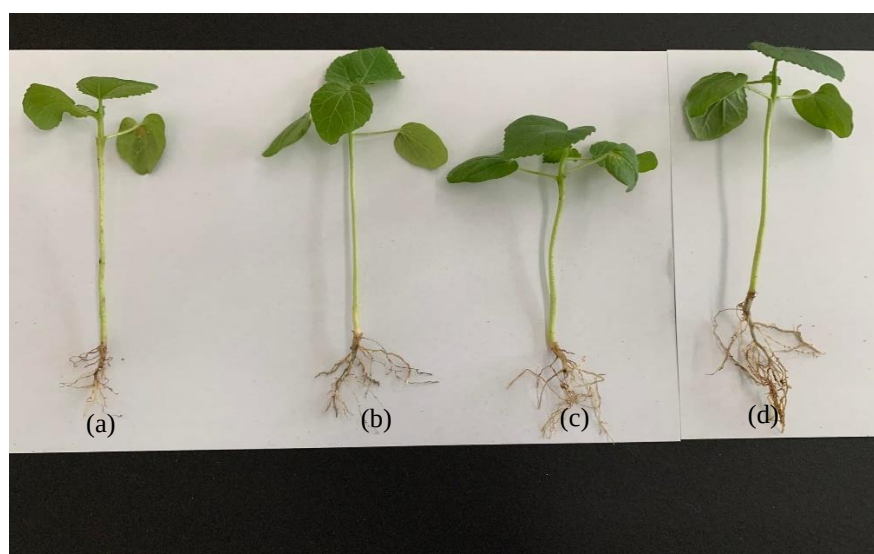


Figure 4.23: Okra plant after 30 days of incubation with treatment of (a) control, (b) pure urea, (c) UIB pellet and (d) EUIB pellet

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The optimum condition obtained for synthesizing UIB powder with high nitrogen content was at 400 °C pyrolysis temperature, 120 minutes residence time and 0.6 urea:biochar ratio, which resulted in 16.07 % of nitrogen content by using central composite rotary design. The tapioca starch/PO biofilm with the lowest water absorption ability was formulated with 8 g of tapioca starch and 0.12 μ L PO. The EUIB pellet had the best crushing strength of 81.65 N as compared to UIB pellet and pure urea. Besides, the UIB pellet and EUIB pellet had a moderate nitrogen content of 15.50% and 9.50%, respectively. The nitrogen release behaviour of EUIB pellet was the slowest in water. The rate of cumulative nitrogen release of EUIB pellet achieved complete release after 330 minutes while UIB pellet and treatment achieved complete release after 90 minutes and 15 minutes, indicating that the encapsulation with tapioca starch/PO biofilm had successfully improved the nitrogen release rate of EUIB. The Korsmeyer-Peppas model was the best model to describe the kinetics of EUIB pellets. Furthermore, the EUIB pellet treatment reduced the nitrogen leaching as compared to UIB pellet and pure urea treatment. The EUIB pellet treatment was able to enhance the water retention ratio of soil. However, the effect of EUIB pellet on water retention ratio was better in sandy-textural soil. Moreover, the EUIB pellet treatment enhanced the leaf area, number of leave, shoot length, root length as well as dry and wet weight of okra plant. Overall, the EUIB pellet formulated in this study has the potential to be used as a green and sustainable fertilizer to enhance the crop yield and reduce the loss of nitrogen due to its controlled-release property. Furthermore, the synthesis of biochar to

formulate EUIB pellet would help to minimize the solid waste generation and disposal by the agriculture industry. The residual biochar after the degradation of the biofilm could be used as a soil amendment or carbon sequestering material in soil. This would contribute towards sustainable agriculture and mitigation of pollution.

5.2 Recommendations

It is recommended other precursors could be utilized to synthesize urea-impregnated biochar-based fertilizer in order to investigate the ability of urea retention property to obtain the highest nitrogen content. It is recommended to extend the study to modify the tapioca starch/PO biofilm to enhance the hydrophobicity of the biofilm. Moreover, it is also recommended that the study of the long-term application effect of the EUIB pellet on various types of plant growth in field trials to be considered in future studies as the demand for nutrient uptake by different plants were varies. Furthermore, the effect of the EUIB pellet on soil properties such as pH level, EC level and CEC can also be studied in the future. In addition, the effect of coating thickness of EUIB on the nitrogen release behaviour in water and nitrogen leaching can be investigated in future studies. Furthermore, the cost analysis of the production of EUIB can be studied to evaluate the economic feasibility of EUIB for practical application by the industry.

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APPENDICES

Appendix A: Journal Publications

1. **Sim, D. H. H.**, Tan, I. A. W., Lim, L. L. P., & Hameed, B. H. (2021). Encapsulated biochar-based sustained release fertilizer for precision agriculture: A review. *Journal of Cleaner Production*, 303, 127018. <https://doi.org/10.1016/J.JCLEPRO.2021.127018>
2. Tan, I. A. W., Tan, M. C., **Sim, D. H. H.**, Lim, L. L. P., & Chin, S. F. (2022). Modelling the effect of wood and maize cob-derived biochar application on soil dynamics and maize growth for sustainable agriculture. *Journal of Sustainability Science and Management*, 17(6), 3–23. <https://doi.org/10.46754/jssm.2022.06.002>
3. **Sim, D. H. H.**, Tan, I. A. W., Lim, L. P., Lau, E. T. & Hameed, B. H. (2024). Synthesis of tapioca starch/palm oil encapsulated urea-impregnated biochar derived from peppercorn waste as a sustainable controlled-release fertilizer. *Waste Management*, 173, 51-61. <https://doi.org/10.1016/j.wasman.2023.11.006>

Appendix B: Calculation

UIB and EUIB pellet amount needed for 600g of sandy-textural soil.

The nitrogen content of UIB and EUIB pellet was 15.50% and 9.50% respectively and the recommended rate of N for Okra plant was 200kg/hectare

1 hectare = 200000 kg of soil

200 kg of N = 200000 g of N

So, 60 mg of N required for 600g of sandy-textural soil.

The amount of distilled water to irrigate the sand column

$$volume = annual\ rainfall\ in\ Malaysia\ (from\ Climatology) \times area\ of\ syringe$$

(1)

Annual rainfall in Malaysia was 3085.55/yr

The volume required = $3.0855m \times 0.013\ m^2 = 0.04\ m^3/yr$ or 40 L/yr. Hence, about 110 mL of distilled water (everyday) was required for sand column leaching experiment